

**I. THE SYNTHESIS AND SOLVOLYSIS OF TRIFLUOROACETATES  
OF CERTAIN CYCLOPROPYLCARBINOLS**

**II. THE SYNTHESIS AND ATTEMPTED THERMAL REARRANGEMENT  
OF CYCLOPROPYLCARBINYL PHENYL ETHER**

By

**James Allen Wrede**

**A THESIS**

**Submitted to the School for Advanced Graduate Studies  
of Michigan State University of Agriculture and  
Applied Science in partial fulfillment of  
the requirements for the degree of**

**DOCTOR OF PHILOSOPHY**

**Department of Chemistry**

**1959**

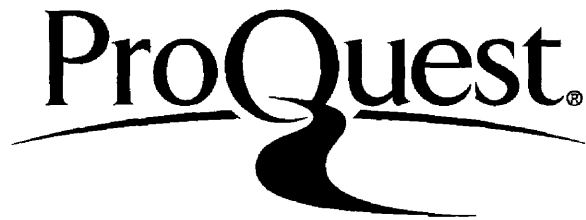
ProQuest Number: 10008635

All rights reserved

INFORMATION TO ALL USERS

The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if material had to be removed, a note will indicate the deletion.



ProQuest 10008635

Published by ProQuest LLC (2016). Copyright of the Dissertation is held by the Author.

All rights reserved.

This work is protected against unauthorized copying under Title 17, United States Code  
Microform Edition © ProQuest LLC.

ProQuest LLC.  
789 East Eisenhower Parkway  
P.O. Box 1346  
Ann Arbor, MI 48106 - 1346

### ACKNOWLEDGMENT

The author wishes to express his sincere thanks and appreciation to Professor Harold Hart for his valued guidance and encouragement throughout the course of the entire investigation.

Appreciation is also extended to the Upjohn Company whose Fellowship Program provided personal financial assistance during part of 1958.

\*\*\*\*\*

## TABLE OF CONTENTS

|                                                                                      | Page |
|--------------------------------------------------------------------------------------|------|
| INTRODUCTION.....                                                                    | 1    |
| PART I                                                                               |      |
| THE SYNTHESIS AND SOLVOLYSIS OF TRIFLUOROACETATES<br>OF CERTAIN CYCLOPROPYLCARBINOLS |      |
| HISTORICAL.....                                                                      | 2    |
| EXPERIMENTAL.....                                                                    | 13   |
| A. Synthesis.....                                                                    | 13   |
| Cyclopropylcarbinol.....                                                             | 13   |
| Cyclopropylmethylecarbinol.....                                                      | 14   |
| Nortricycyl- and methylnortricycylecarbinol.....                                     | 14   |
| Trifluoroacetyl chloride.....                                                        | 15   |
| Cyclopropylcarbonyl trifluoroacetate.....                                            | 15   |
| Nortricycylecarbonyl trifluoroacetate.....                                           | 16   |
| Cyclopropylmethylecarbonyl trifluoroacetate.....                                     | 19   |
| Component 2.....                                                                     | 21   |
| Reaction of cyclopropylmethylecarbinol and Trifluoro-<br>acetic acid.....            | 24   |
| Chromic acid oxidation of 2-Methylcyclobutanol.....                                  | 27   |
| Chromium trioxide in pyridine oxidation of 2-Methylcyclo-<br>butanol.....            | 29   |
| Attempted synthesis of 2-Methylcyclobutanol.....                                     | 31   |
| Methylnortricycylecarbonyl trifluoroacetate.....                                     | 33   |
| Miscellaneous esters of Cyclopropylcarbinol.....                                     | 34   |
| B. Solvolysis Studies.....                                                           | 37   |
| Solvents.....                                                                        | 37   |
| Preliminary Kinetic Studies.....                                                     | 37   |
| Kinetic Procedure.....                                                               | 37   |
| Product Analysis.....                                                                | 38   |
| RESULTS AND DISCUSSION.....                                                          | 43   |



## TABLE OF CONTENTS - Continued

|                                                                              | Page |
|------------------------------------------------------------------------------|------|
| A. The Attempted Structure Proof of 2-Methylcyclobutyl Trifluoroacetate..... | 43   |
| B. The Solvolysis Products.....                                              | 44   |
| C. The Solvolysis Rates.....                                                 | 47   |
| Method of Calculation.....                                                   | 47   |
| Comparison of Solvolysis Rates.....                                          | 49   |
| Cyclopropylmethyl and 2-Methylcyclobutyl trifluoroacetates.....              | 54   |
| Methylnortricyclopentyl trifluoroacetate.....                                | 62   |
| D. The Energetics.....                                                       | 64   |
| E. Conclusions.....                                                          | 68   |

## PART II

### THE SYNTHESIS AND ATTEMPTED THERMAL REARRANGEMENT OF CYCLOPROPYLCARBINYL PHENYL ETHER

|                                                                             |    |
|-----------------------------------------------------------------------------|----|
| INTRODUCTION.....                                                           | 71 |
| EXPERIMENTAL.....                                                           | 73 |
| A. Synthesis of Cyclopropylcarbinyl Phenyl Ether.....                       | 73 |
| Method A: Displacement of the tosylate group by phenoxide ion.....          | 73 |
| Method B: Carbene reaction on allyl phenyl ether.....                       | 74 |
| a. 2,2-Dibromocyclopropylcarbinyl phenyl ether.....                         | 74 |
| b. Reduction of 2,2-dibromocyclopropylcarbinyl phenyl ether.....            | 75 |
| B. Attempted Thermal Rearrangement of Cyclopropylcarbinyl Phenyl Ether..... | 77 |
| RESULTS AND DISCUSSION.....                                                 | 79 |
| SUMMARY.....                                                                | 81 |
| LITERATURE CITED.....                                                       | 83 |
| APPENDIX.....                                                               | 86 |

# LIST OF TABLES

| TABLE                                                                                                                      | Page |
|----------------------------------------------------------------------------------------------------------------------------|------|
| 1. Physical Constants, Yields and Analyses of Several Esters of Cyclopropylcarbinol.....                                   | 36   |
| 2. Specific Rate Constants for the Solvolysis of Cyclopropylcarbinyl Trifluoroacetate in Aqueous Dioxane.....              | 50   |
| 3. Specific Rate Constants for the Solvolysis of Norbornylcarbinyl Trifluoroacetate in Aqueous Dioxane.....                | 51   |
| 4. Specific Rate Constants for the Solvolysis of 2-Methyloxycyclobutyl Trifluoroacetate in Aqueous Dioxane.....            | 52   |
| 5. Specific Rate Constants for the Solvolysis of Cyclopropylmethoxycarbinyl Trifluoroacetate in Aqueous Dioxane at 50° ... | 53   |
| 6. Relative Rates of Several Trifluoroacetates in Aqueous Dioxane.....                                                     | 58   |
| 7. Molar Enthalpies and Entropies of Activation for the Solvolysis of Several Trifluoroacetates in Aqueous Dioxane..       | 66   |
| 8. Comparison of Molar Energy Factors for the Solvolysis of Various Esters of Primary, Secondary and Tertiary Alcohols..   | 67   |
| 9. Solvolysis of 0.1031 Molar Cyclopropylcarbinyl Trifluoroacetate in 50% Dioxane-50% Water at 40.3° C.....                | 86   |
| 10. Solvolysis of 0.01863 Molar Cyclopropylcarbinyl Trifluoroacetate in 50% Dioxane-50% Water at 40.3° C.....              | 87   |
| 11. Solvolysis of 0.07530 Molar Cyclopropylcarbinyl Trifluoroacetate in 60% Dioxane-40% Water at 29.9° C.....              | 88   |
| 12. Solvolysis of 0.1082 Molar Cyclopropylcarbinyl Trifluoroacetate in 60% Dioxane-40% Water at 40.3° C.....               | 89   |
| 13. Solvolysis of 0.05313 Molar Cyclopropylcarbinyl Trifluoroacetate in 60% Dioxane-40% Water at 40.3° C.....              | 90   |

# LIST OF TABLES - Continued

| TABLE                                                                                                         | Page |
|---------------------------------------------------------------------------------------------------------------|------|
| 14. Solvolysis of 0.04516 Molar Cyclopropylcarbonyl Trifluoroacetate in 60% Dioxane-40% Water at 49.8° C..... | 91   |
| 15. Solvolysis of 0.1031 Molar Cyclopropylcarbonyl Trifluoroacetate in 60% Dioxane-40% Water at 50.1° C.....  | 92   |
| 16. Solvolysis of 0.07283 Molar Cyclopropylcarbonyl Trifluoroacetate in 60% Dioxane-40% Water at 59.6° C..... | 93   |
| 17. Solvolysis of 0.03854 Molar Cyclopropylcarbonyl Trifluoroacetate in 60% Dioxane-40% Water at 60.1° C..... | 94   |
| 18. Solvolysis of 0.1032 Molar Cyclopropylcarbonyl Trifluoroacetate in 70% Dioxane-30% Water at 29.9° C.....  | 95   |
| 19. Solvolysis of 0.05084 Molar Cyclopropylcarbonyl Trifluoroacetate in 70% Dioxane-30% Water at 40.3° C..... | 96   |
| 20. Solvolysis of 0.1025 Molar Cyclopropylcarbonyl Trifluoroacetate in 70% Dioxane-30% Water at 40.3° C.....  | 97   |
| 21. Solvolysis of 0.09733 Molar Cyclopropylcarbonyl Trifluoroacetate in 70% Dioxane-30% Water at 50.1° C..... | 98   |
| 22. Solvolysis of 0.1908 Molar Cyclopropylcarbonyl Trifluoroacetate in 70% Dioxane-30% Water at 49.8° C.....  | 99   |
| 23. Solvolysis of 0.05731 Molar Cyclopropylcarbonyl Trifluoroacetate in 70% Dioxane-30% Water at 59.6° C..... | 100  |
| 24. Solvolysis of 0.1126 Molar Cyclopropylcarbonyl Trifluoroacetate in 70% Dioxane-30% Water at 60.1° C.....  | 101  |
| 25. Solvolysis of 0.03807 Molar Cyclopropylcarbonyl Trifluoroacetate in 80% Dioxane-20% Water at 40.0° C..... | 102  |
| 26. Solvolysis of 0.09791 Molar Cyclopropylcarbonyl Trifluoroacetate in 80% Dioxane-20% Water at 50.1° C..... | 103  |
| 27. Solvolysis of 0.08940 Molar Cyclopropylcarbonyl Trifluoroacetate in 80% Dioxane-20% Water at 50.1° C..... | 104  |
| 28. Solvolysis of 0.1025 Molar Cyclopropylcarbonyl Trifluoroacetate in 80% Dioxane-20% Water at 59.6° C.....  | 105  |

LIST OF TABLES - Continued

| TABLE                                                                                                               | Page |
|---------------------------------------------------------------------------------------------------------------------|------|
| 29. Solvolysis of 0.07300 Molar Cyclopropylcarbinyl Trifluoroacetate in 80% Dioxane-20% Water at 59.6°C.....        | 106  |
| 30. Solvolysis of 0.02415 Molar Nortricycylcarbinyl Trifluoroacetate in 60% Dioxane-40% Water at 40.0°C.....        | 107  |
| 31. Solvolysis of 0.05412 Molar Nortricycylcarbinyl Trifluoroacetate in 60% Dioxane-40% Water at 50.0°C.....        | 108  |
| 32. Solvolysis of 0.05486 Molar Nortricycylcarbinyl Trifluoroacetate in 60% Dioxane-40% Water at 59.6°C.....        | 109  |
| 33. Solvolysis of 0.05484 Molar Nortricycylcarbinyl Trifluoroacetate in 60% Dioxane-40% Water at 59.6°C.....        | 110  |
| 34. Solvolysis of 0.06371 Molar Nortricycylcarbinyl Trifluoroacetate in 70% Dioxane-30% Water at 40.1°C.....        | 111  |
| 35. Solvolysis of 0.05713 Molar Nortricycylcarbinyl Trifluoroacetate in 70% Dioxane-30% Water at 50.0°C.....        | 112  |
| 36. Solvolysis of 0.05889 Molar Nortricycylcarbinyl Trifluoroacetate in 70% Dioxane-30% Water at 59.6°C.....        | 113  |
| 37. Solvolysis of 0.06048 Molar Nortricycylcarbinyl Trifluoroacetate in 70% Dioxane-30% Water at 59.6°C.....        | 114  |
| 38. Solvolysis of 0.02402 Molar Nortricycylcarbinyl Trifluoroacetate in 80% Dioxane-20% Water at 40.0°C.....        | 115  |
| 39. Solvolysis of 0.07639 Molar Nortricycylcarbinyl Trifluoroacetate in 80% Dioxane-20% Water at 50.0°C.....        | 116  |
| 40. Solvolysis of 0.07563 Molar Nortricycylcarbinyl Trifluoroacetate in 80% Dioxane-20% Water at 59.6°C.....        | 117  |
| 41. Solvolysis of 0.05477 Molar Mixed Ester from Cyclopropylmethylecarbinol in 60% Dioxane-40% Water at 40.1°C..... | 119  |
| 42. Solvolysis of 0.05493 Molar Mixed Ester from Cyclopropylmethylecarbinol in 60% Dioxane-40% Water at 40.1°C..... | 120  |
| 43. Solvolysis of 0.05108 Molar Mixed Ester from Cyclopropylmethylecarbinol in 60% Dioxane-40% Water at 49.7°C..... | 121  |

# LIST OF TABLES - Continued

| TABLE                                                                                                             | Page |
|-------------------------------------------------------------------------------------------------------------------|------|
| 44. Solvolysis of 0.05233 Molar Mixed Ester from Cyclopropylmethylethanol in 60% Dioxane-40% Water at 60.1°C..... | 122  |
| 45. Solvolysis of 0.04483 Molar Mixed Ester from Cyclopropylmethylethanol in 60% Dioxane-40% Water at 60.1°C..... | 123  |
| 46. Solvolysis of 0.02501 Molar 2-Methylcyclobutyl Trifluoroacetate in 70% Dioxane-30% Water at 40.0°C.....       | 124  |
| 47. Solvolysis of 0.02789 Molar 2-Methylcyclobutyl Trifluoroacetate in 70% Dioxane-30% Water at 49.9°C.....       | 125  |
| 48. Solvolysis of 0.02735 Molar 2-Methylcyclobutyl Trifluoroacetate in 70% Dioxane-30% Water at 49.9°C.....       | 126  |
| 49. Solvolysis of 0.07286 Molar Mixed Ester from Cyclopropylmethylethanol in 70% Dioxane-30% Water at 49.7°C..... | 127  |
| 50. Solvolysis of 0.02759 Molar 2-Methylcyclobutyl Trifluoroacetate in 70% Dioxane-30% Water at 60.0°C.....       | 128  |
| 51. Solvolysis of 0.02684 Molar 2-Methylcyclobutyl Trifluoroacetate in 70% Dioxane-30% Water at 60.0°C.....       | 129  |
| 52. Solvolysis of 0.02501 Molar Cyclopropylmethylethynyl Trifluoroacetate in 60% Dioxane-40% Water at 40.0°C..... | 131  |
| 53. Solvolysis of 0.02526 Molar Cyclopropylmethylethynyl Trifluoroacetate in 60% Dioxane-40% Water at 49.8°C..... | 132  |
| 54. Solvolysis of 0.02718 Molar Cyclopropylmethylethynyl Trifluoroacetate in 60% Dioxane-40% Water at 60.1°C..... | 133  |
| 55. Solvolysis of 0.02887 Molar Cyclopropylmethylethynyl Trifluoroacetate in 70% Dioxane-30% Water at 40.0°C..... | 134  |
| 56. Solvolysis of 0.02553 Molar Cyclopropylmethylethynyl Trifluoroacetate in 70% Dioxane-30% Water at 49.8°C..... | 135  |
| 57. Solvolysis of 0.02631 Molar Cyclopropylmethylethynyl Trifluoroacetate in 70% Dioxane-30% Water at 49.8°C..... | 136  |
| 58. Solvolysis of 0.02737 Molar Cyclopropylmethylethynyl Trifluoroacetate in 70% Dioxane-30% Water at 60.1°C..... | 137  |

# LIST OF TABLES - Continued

| TABLE                                                                                                                                    | Page |
|------------------------------------------------------------------------------------------------------------------------------------------|------|
| 59. Solvolysis of 0.02922 Molar Cyclopropylmethylcarbinyl Trifluoroacetate in 70% Dioxane-30% Water at 60.1°C.....                       | 138  |
| 60. Solvolysis of 0.02604 Molar Cyclopropylmethylcarbinyl Trifluoroacetate in 70% Dioxane-30% Water at 60.1°C.....                       | 139  |
| 61. Solvolysis of 0.02598 Molar Cyclopropylmethylcarbinyl Trifluoroacetate in 80% Dioxane-20% Water at 49.8°C.....                       | 140  |
| 62. Solvolysis of 0.02628 Molar Cyclopropylmethylcarbinyl Trifluoroacetate in 80% Dioxane-20% Water at 49.8°C.....                       | 141  |
| 63. Solvolysis of 0.02782 Molar Cyclopropylmethylcarbinyl Trifluoroacetate in 80% Dioxane-20% Water at 60.1°C.....                       | 142  |
| 64. Solvolysis of 0.02026 Molar Methylnortricycylcarbinyl Trifluoroacetate in 70% Dioxane-30% Water at 49.9°C.....                       | 144  |
| 65. Derived Data from the Solvolysis of 0.02026 Molar Methylnortricycylcarbinyl Trifluoroacetate in 70% Dioxane-30% Water at 49.9°C..... | 145  |
| 66. Solvolysis of 0.02405 Molar Methylnortricycylcarbinyl Trifluoroacetate in 70% Dioxane-30% Water at 49.9°C.....                       | 146  |
| 67. Derived Data from the Solvolysis of 0.02405 Molar Methylnortricycylcarbinyl Trifluoroacetate in 70% Dioxane-30% Water at 49.9°C..... | 147  |
| 68. Solvolysis of 0.02023 Molar Methylnortricycylcarbinyl Trifluoroacetate in 70% Dioxane-30% Water at 49.9°C.....                       | 148  |
| 69. Derived Data from the Solvolysis of 0.02023 Molar Methylnortricycylcarbinyl Trifluoroacetate in 70% Dioxane-30% Water at 49.9°C..... | 149  |
| 70. Solvolysis of 0.02027 Molar Methylnortricycylcarbinyl Trifluoroacetate in 70% Dioxane-30% Water at 49.9°C.....                       | 150  |
| 71. Derived Data from the Solvolysis of 0.02027 Molar Methylnortricycylcarbinyl Trifluoroacetate in 70% Dioxane-30% Water at 49.9°C..... | 151  |

LIST OF TABLES - Continued

| TABLE                                                                                                                                                | Page |
|------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| 72. Solvolysis of 0.02285 Molar Methylnortricyclicylcarbonyl<br>Trifluoroacetate in 80% Dioxane-20% Water at 49.9°C.....                             | 152  |
| 73. Derived Data from the Solvolysis of 0.02026 Molar Methyl-<br>nortricyclicylcarbonyl Trifluoroacetate in 30% Dioxane-<br>20% Water at 49.9°C..... | 153  |
| 74. Solvolysis of 0.05123 Molar n-Butyl Trifluoroacetate in<br>70% Dioxane-30% Water at 45.1°C.....                                                  | 154  |
| 75. Solvolysis of 0.05123 Molar n-Butyl Trifluoroacetate in<br>70% Acetone-29.3% Water at 45.1°C.....                                                | 155  |

## LIST OF FIGURES

| FIGURE                                                                                                                                                                                                           | Page |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| 1. Infrared Spectrum of Cyclopropylcarbonyl Trifluoroacetate..                                                                                                                                                   | 17   |
| 2. Infrared Spectrum of Nortricycylcarbonyl Trifluoroacetate.                                                                                                                                                    | 18   |
| 3. Vapor Chromatograph of Reaction Product in the Preparation of Cyclopropylmethylearbonyl Trifluoroacetate.....                                                                                                 | 20   |
| 4. Infrared Spectrum of Cyclopropylmethylearbonyl Trifluoroacetate.....                                                                                                                                          | 22   |
| 5. Infrared Spectrum of 2-Methylcyclobutyl Trifluoroacetate...                                                                                                                                                   | 23   |
| 6. Infrared Spectrum of 2-Methylcyclobutanol.....                                                                                                                                                                | 25   |
| 7. Infrared Spectrum of Cyclopropylmethylearbonyl.....                                                                                                                                                           | 26   |
| 8. Infrared Spectrum of Chromic Acid Oxidation Product of 2-Methylcyclobutanol.....                                                                                                                              | 28   |
| 9. Infrared Spectrum of Chromium Trioxide in Pyridine Oxidation Product of 2-Methylcyclobutanol.....                                                                                                             | 30   |
| 10. Infrared Spectrum of Methylnortricycylcarbonyl Trifluoroacetate.....                                                                                                                                         | 35   |
| 11. Plot of $\log (R/R_\infty)$ versus $t$ for the Solvolysis of Cyclopropylcarbonyl Trifluoroacetate in 60, 70 and 80% Aqueous Dioxane.....                                                                     | 55   |
| 12. Plot of $\log (R/R_\infty)$ versus $t$ for the Solvolysis of Cyclopropylmethylearbonyl Trifluoroacetate in 60, 70 and 80% Aqueous Dioxane at $50^\circ$ .....                                                | 56   |
| 13. Plot of $\log (R/R_\infty)$ versus $t$ for the Solvolysis of Four Trifluoroacetates in 70% Aqueous Dioxane at $50^\circ$ .....                                                                               | 57   |
| 14. Plot of $\log (R/R_\infty)$ versus $t$ for the Solvolysis of Mixtures Obtained from the Esterification of Cyclopropylmethylearbonyl and Methylnortricycylearbonyl in 70% Aqueous Dioxane at $50^\circ$ ..... | 59   |



# LIST OF FIGURES - Continued

| FIGURE                                                                                                                                           | Page |
|--------------------------------------------------------------------------------------------------------------------------------------------------|------|
| 15. Plot of $\log (R/R_\infty)$ versus $t$ for the Solvolysis of Cyclopropylmethylecarbonyl Trifluoroacetate in 70% Aqueous Dioxane at 50° ..... | 61   |
| 16. Plot of Resistance versus $t$ for the Solvolysis of Methyl-nortricyclylecarbonyl Trifluoroacetate in 70% Aqueous Dioxane at 50° .....        | 63   |
| 17. Infrared Spectrum of 2,2-Dibromocyclopropylcarbonyl Phenyl Ether.....                                                                        | 76   |
| 18. Infrared Spectrum of Cyclopropylcarbonyl Phenyl Ether.....                                                                                   | 78   |
| 19. Plot of $\log k$ versus $1/T$ for the Solvolysis of Cyclopropylcarbonyl Trifluoroacetate in 60% Dioxane-40% Water.....                       | 156  |
| 20. Plot of $\log k$ versus $1/T$ for the Solvolysis of Cyclopropylcarbonyl Trifluoroacetate in 70% Dioxane-30% Water.....                       | 157  |
| 21. Plot of $\log k$ versus $1/T$ for the Solvolysis of Cyclopropylcarbonyl Trifluoroacetate in 80% Dioxane-20% Water.....                       | 158  |
| 22. Plot of $\log k$ versus $1/T$ for the Solvolysis of Nortricyclylcarbonyl Trifluoroacetate in 60% Dioxane-40% Water.....                      | 159  |
| 23. Plot of $\log k$ versus $1/T$ for the Solvolysis of Nortricyclylcarbonyl Trifluoroacetate in 70% Dioxane-30% Water.....                      | 160  |
| 24. Plot of $\log k$ versus $1/T$ for the Solvolysis of Nortricyclylcarbonyl Trifluoroacetate in 80% Dioxane-20% Water.....                      | 161  |
| 25. Plot of $\log k$ versus $1/T$ for the Solvolysis of 2-Methylcyclobutyl Trifluoroacetate in 60% Dioxane-40% Water.....                        | 162  |
| 26. Plot of $\log k$ versus $1/T$ for the Solvolysis of 2-Methylcyclobutyl Trifluoroacetate in 70% Dioxane-30% Water.....                        | 163  |
| 27. Plot of $\log k$ versus $1/T$ for the Solvolysis of Cyclopropylmethylecarbonyl Trifluoroacetate in 60% Dioxane-40% Water....                 | 164  |
| 28. Plot of $\log k$ versus $1/T$ for the Solvolysis of Cyclopropylmethylecarbonyl Trifluoroacetate in 70% Dioxane-30% Water....                 | 165  |
| 29. Plot of $\log k$ versus $1/T$ for the Solvolysis of Cyclopropylmethylecarbonyl Trifluoroacetate in 80% Dioxane-20% Water....                 | 166  |

**PART I**

**THE SYNTHESIS AND SOLVOLYSIS OF TRIFLUOROACETATES  
OF CERTAIN CYCLOPROPYLCARBINOLS**

## INTRODUCTION

Although this thesis is composed of two parts, both are concerned with cyclopropylating systems. Each part will be treated separately for the purpose of clarity. The parts are:

PART I: The Synthesis and Solvolysis of Trifluoroacetates of Certain Cyclopropylating Systems

PART II: The Synthesis and Attempted Thermal Rearrangement of Cyclopropylating Phenyl Ether.

## INTRODUCTION

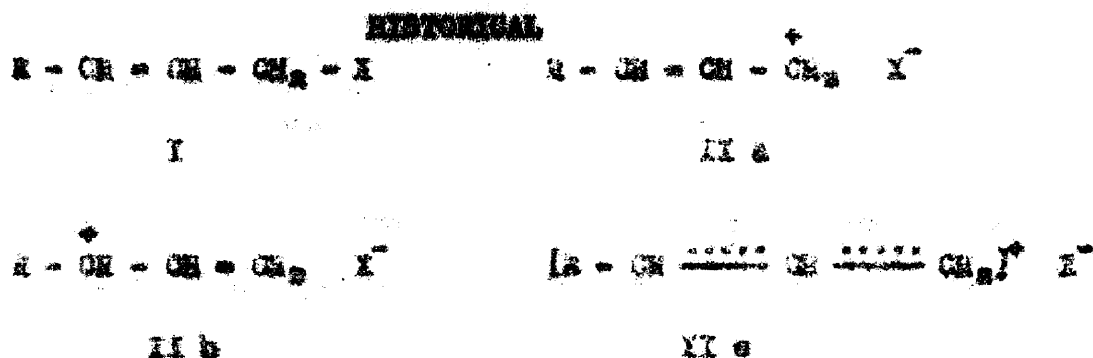
Although this thesis is composed of two parts, both are concerned with cyclopropylcarbiny1 systems. Each part will be treated separately for the purpose of clarity. The parts are:

PART I: The Synthesis and Solvolysis of Trifluoroacetates of Certain Cyclopropylcarbinols.

PART II: The Synthesis and Attempted Thermal Rearrangement of Cyclopropylcarbiny1 Phenyl Ether.

# DISCUSSION

Allylic systems are unusually reactive in solvolytic displacement reactions, presumably because of delocalization of the pi electrons of the double bond in the transition state. Thus, a unimolecular displacement in an allylic system (I) may be facilitated by resonance contributions in the cationic intermediate structures such as II a and II b, which may be summarized as II c.



Analogies have been drawn between the cyclopropane ring and the carbon-carbon double bond (1). On this basis, the cyclopropylcarbinyl system, being comparable with the allylic system, would also be expected to be very reactive in solvolytic displacement reactions, and this is indeed the case. Thus, the rate of solvolysis of cyclopropylcarbinyl chloride (III a) in aqueous ethanol was 20 times faster than p-ethoxyallyl chloride (IV) and cyclopropylcarbinyl bromide (III b) solvolyzed 26 times faster than allyl bromide (V a) (2).

## HISTORICAL

Allylic systems are unusually reactive in solvolytic displacement reactions, presumably because of delocalization of the pi electrons of the double bond in the transition state. Thus, a unimolecular displacement in an allylic system (I) may be facilitated by resonance contributions in the cationic moiety from structures such as II a and II b, which may be summarized as II c.



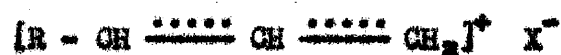
I



II a

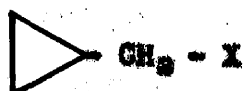


II b



II c

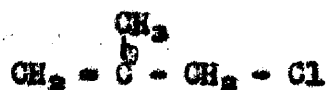
Analogies have been drawn between the cyclopropane ring and the carbon-carbon double bond (1). On this basis, the cyclopropylcarbinyl system, being comparable with the allylic system, would also be expected to be very reactive in solvolytic displacement reactions, and this is indeed the case. Thus, the rate of solvolysis of cyclopropylcarbinyl chloride (III a) in aqueous ethanol was 40 times faster than  $\beta$ -methylallyl chloride (IV) and cyclopropylcarbinyl bromide (III b) solvolyzed 26 times faster than allyl bromide (V a) (2).



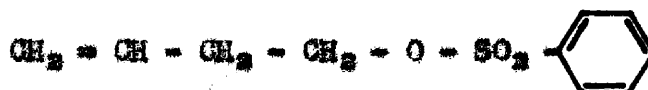
III a, X = Cl

III b, X = Br

III c, X = O-SO<sub>2</sub>-

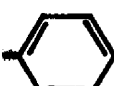


IV



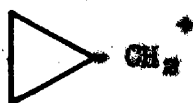
VI a

V a, X = Br

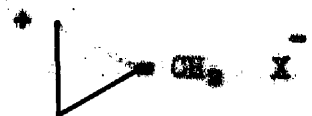
V b, X = O-SO<sub>2</sub>-

Also, the ethanolysis of cyclopropylcarbinyl benzenesulfonate (III c) was 14 times faster than allyl benzenesulfonate (V b) and 1000 times faster than allylcarbinyl benzenesulfonate (VI a) (3).

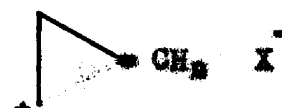
This exceptional reactivity of cyclopropylcarbinyl systems in unimolecular displacement reactions has been attributed to contributing resonance structures such as VII a, VII b and VII c which may be summarized as VII d and VII e (2,3).



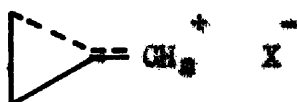
VII a



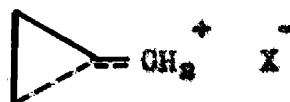
VII b



VII c



VII d



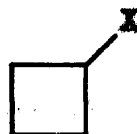
VII e

The products also indicate participation of the cyclopropane ring. In the hydrolysis of cyclopropylcarbinyl chloride and cyclobutyl chloride (VIII a), and in the diazotisation of cyclopropylcarbinylamine (III d) and cyclobutylamine (VIII b), the same ratio of products was obtained; 48% cyclopropylcarbinol (III e), 47% cyclobutanol (VIII c) and 5% allylcarbinol (VI b) (2).



III d, X = NH<sub>2</sub>

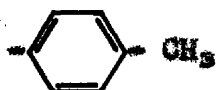
III e, X = OH



VIII a, X = Cl

VIII b, X = NH<sub>2</sub>

VIII c, X = OH

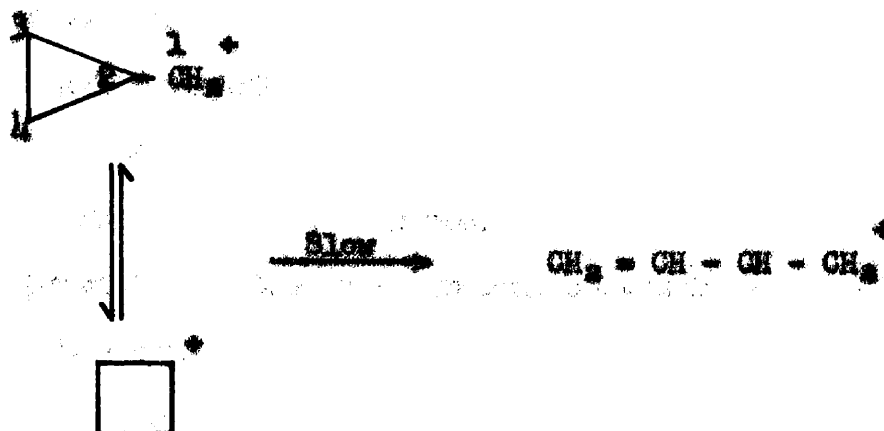
VIII d, X = OSO<sub>2</sub> -  - CH<sub>3</sub>



VI b

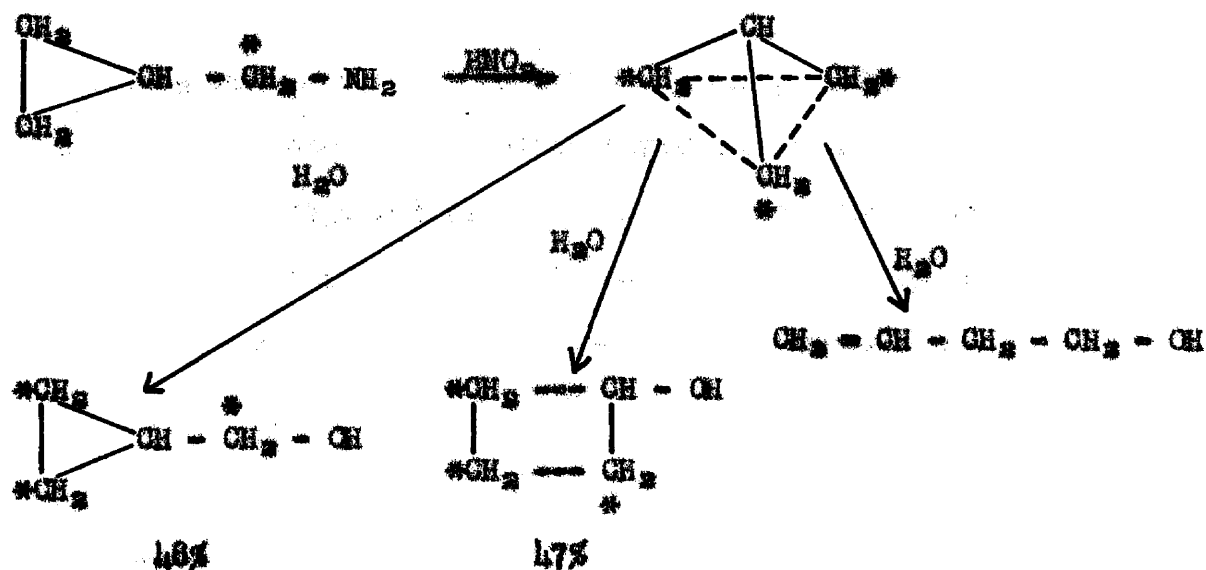
In addition, the acetolysis of cyclopropylcarbinyl chloride (2) and of cyclobutyl p-toluenesulfonate (VIII d) (4) gave the same ratio of products (but different from that just mentioned); cyclopropylcarbinyl and cyclobutyl acetates were formed in a ratio of 2.8 to 1. These results were explained (2) in terms of rapid interconversion of cyclopropylcarbinyl and cyclobutyl cations with a slow and essentially irreversible reaction to allylcarbinyl derivatives.





As a result of such interconversions each of the original carbon atoms 1, 3 and 4 may appear in the side-chain of the cyclopropylcarbinyl compound in the product.

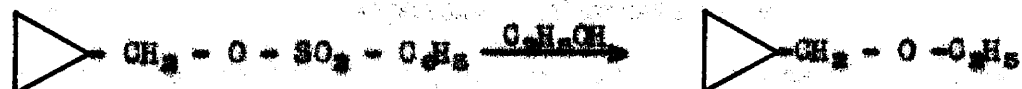
A similar explanation was suggested by Roberts and Mazur (5) to account for the results obtained when cyclopropylcarbinylamine-1- $\text{C}^{14}$  was treated with nitrous acid. In a "non-classical"



carbocation ion of the type shown in the scheme, which has a three-fold axis of symmetry so that the two methylene groups of the cyclopropane

ring become equivalent with the exocyclic methylene group, the  $C^{14}$  should be equally distributed among the starred carbon atoms in each product. This was the case with the cyclobutanol. However, in the cyclopropylcarbinol formed, an excess of  $C^{14}$  (45% rather than 33.3%) over that predicted by the non-classical intermediate was found at the carbinol carbon atom, and only 54% (rather than 66.7%) was found in the ring. This was explained by suggesting that more than one mechanism may be operative.

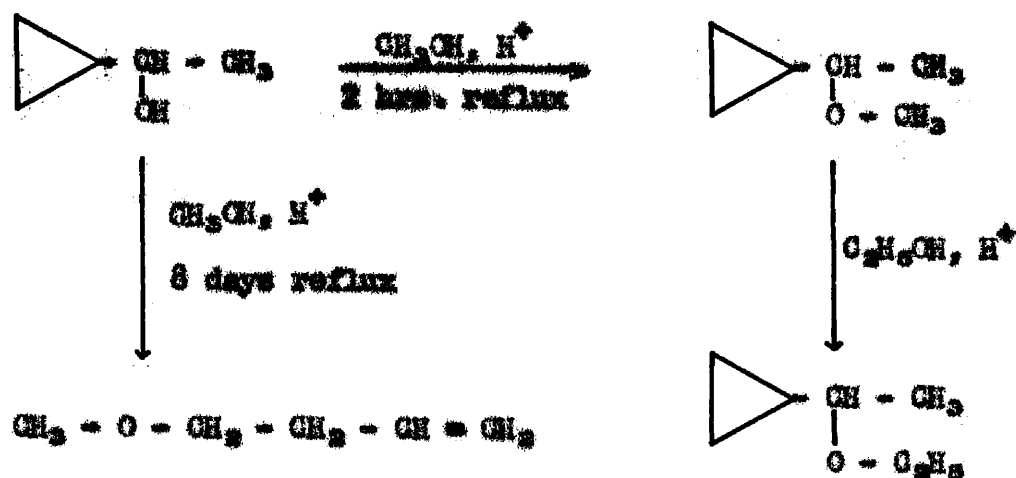
In three instances no rearrangement or ring opening occurred during solvolysis. Cyclopropylcarbinyll benzenesulfonate in absolute ethanol was found to give only cyclopropylcarbinyll ethyl ether in a first order process (3).<sup>1</sup>



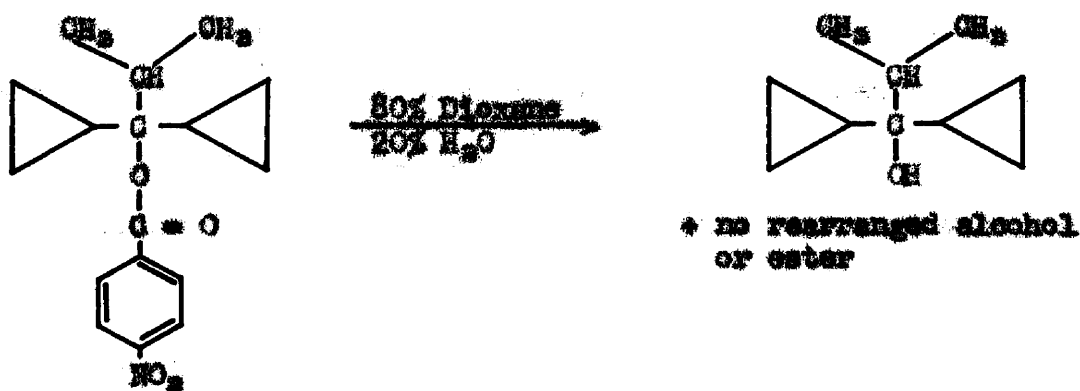
The second instance is the reaction of cyclopropylmethylecarbinol in methanol, in the presence of p-toluenesulfonic acid, to give only cyclopropylmethylecarbinyll methyl ether (11). Also, the methyl ether, under similar conditions, gave only the ethyl ether. Only after eight days at reflux was any allylcarbinyll methyl ether formed.

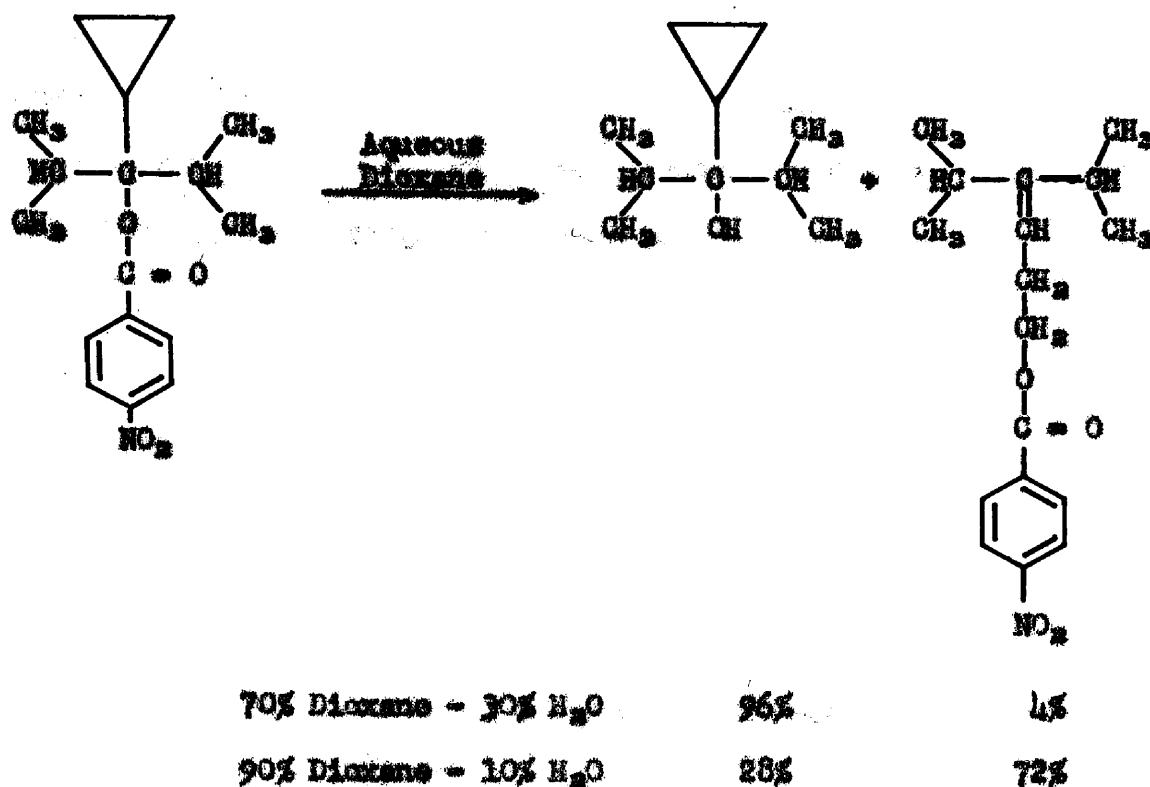
---

<sup>1</sup>It should be noted, however, that cyclopropylcarbinyll benzenesulfonate in chloroform was reported to rearrange rapidly to allylcarbinyll benzenesulfonate and a small amount of the cyclobutyl isomer.



Finally, Hart and Sandri (12) have recently reported the solvolysis of several *p*-nitrobenzoates of tertiary alcohols and one secondary alcohol containing the cyclopropylcarbonyl group. The rates of solvolysis of these esters in aqueous dioxane followed first order kinetics, and were the fastest recorded for aliphatic *p*-nitrobenzoates. No rearranged alcohols were observed in the solvolysis products. In some instances, however, solvolysis to alcohol and *p*-nitrobenzoic acid was incomplete. In these cases, another product, an allylcarbonyl ester, was formed, but these esters were not solvolyzed under the reaction conditions.

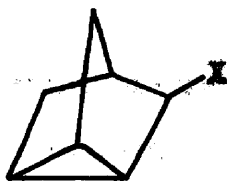




One cyclopropyl group on the carbinol carbon atom was superior to an isopropyl or *t*-butyl group in facilitating solvolysis. A second cyclopropyl group caused a rate increase nearly equal to that of the first. The results were interpreted in terms of a mechanism involving ionization to ion-pairs, from which rearranged ester could be formed via internal return. The solvolysis products could be formed from either the ion-pair or from dissociated ions. This interpretation is similar to that of Kosower and Winstein (13) in the methanolyses of 3,5-cyclocholestan-6-yl trichloroacetate.

The inclusion of the three membered ring in a cage structure may limit its ability to participate in the solvolysis reaction. For example, the solvolysis of 3-chloronortricyclane (IXa), a cyclopropyl-carbinyl derivative with rather special geometric limitations, in

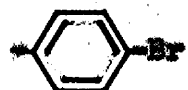
aqueous ethanol is reported to be 50 to 100 times slower than cyclopropylcarbinyl chloride, and approximately the same as cyclopentyl chloride (6,7). A suggested reason for



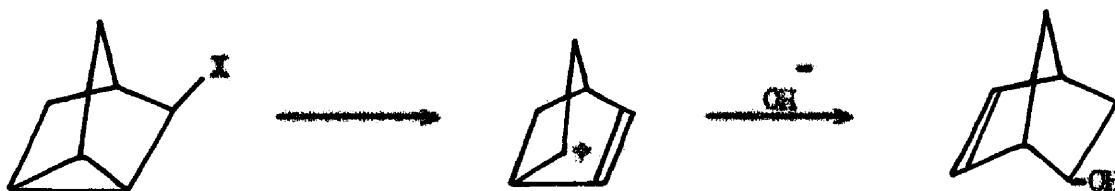
IX a, X = Cl

IX b, X = Br

IX c, X = OH

IX d, X = O - SO<sub>2</sub> -  - Br

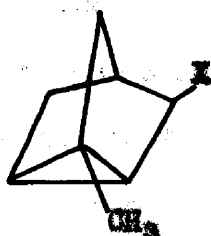
the low reactivity of the 3-halonorbornene was steric inhibition of resonance. The only product reported in the solvolysis of the chloride (IX a) or the bromide (IX b) was 3-hydroxynorbornene (IX c) (8). By analogy with other cyclopropylcarbinyl systems, rearrangement according to the following scheme could have accompanied solvolysis if participation by the cyclopropane ring had occurred.



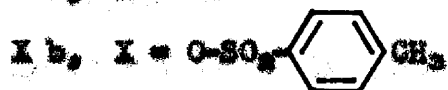
Winstein (9), however, observed that the acetolysis of the p-bromobenzenesulfonate (IX d) was about 200 times faster than that of cyclohexyl p-bromobenzenesulfonate and concluded that the system had

considerable reactivity. It should be noted that the conclusions concerning the reactivity of the 3-norbornyl derivatives depended on whether they were compared with cyclopentyl or with cyclohexyl systems.

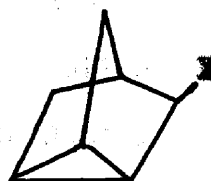
In another study (10), two 1-methyl-3-norbornyl derivatives (I a, I b) were found to solvolyse up to 200 times more rapidly than did the corresponding methyl-free 3-norbornyl derivatives (IX a, IX c).



I a, X = Cl

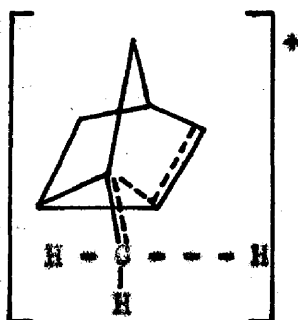


I b, X = O-SO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-CH<sub>3</sub>



IX c, X = O-SO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-CH<sub>3</sub>

The rate enhancing effect of the methyl group was attributed to assistance of homoallylic participation, which might be pictured as follows:



There are some aspects of the previous work on primary and secondary cyclopropylcarbonyl systems, that are not entirely satisfactory. Because of purification difficulties, the kinetic work on cyclopropylcarbonyl chloride, bromide and benzenesulfonate was not done on pure (less than

90% pure) compounds. Also, in the conversion of cyclopropylmethylcarbinol to cyclopropylmethylcarbinyl methyl ether in methanol, in the presence of *p*-toluenesulfonic acid, it was not established that the reaction was kinetically first order. One purpose of the present investigation was to prepare pure, stable cyclopropylcarbinyl derivatives whose solvolyses could be studied.

Also, the only studies on cyclopropylcarbinyl analogs in nortricyclene compounds have been on 3-substituted derivatives, where participation of the three-membered ring may be limited for geometric reasons. It was therefore decided to study the solvolyses of 1-substituted nortricyclene derivatives in which this geometric limitation was not present.

In an attempt to find an ester suitable for solvolysis studies the *p*-nitrobenzoate, the 2,4-dinitrobenzoate and the mono-, di-, and tri-chloroacetates of cyclopropylcarbinol were prepared. These compounds were found to be stable and could be readily purified, but their solvolysis was too slow for convenient study. Finally, the trifluoroacetate of cyclopropylcarbinol was prepared and found to be satisfactory for kinetic studies.

The solvolysis of the trifluoroacetates of several primary, secondary and tertiary alcohols has recently been reported (14,15,16). The esters of the primary and secondary alcohols were reported to solvolyse by acyl-oxygen cleavage, while the esters of the tertiary alcohols solvolyzed by alkyl-oxygen cleavage. Because of the solvolytic

reactivity of cyclopropylcarbiny1 systems it was anticipated that the trifluoroacetates of the cyclopropylcarbinols would solvolyze by alkyl-oxygen cleavage.

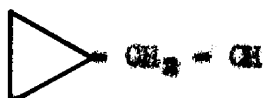


## EXPERIMENTAL

## EXPERIMENTAL<sup>1</sup>

### A. Synthesis

#### Cyclopropylcarbinol



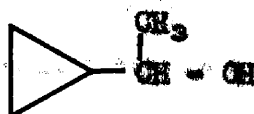
In a dry, 5-l. three-necked flask equipped with a Hershberg stirrer, a dropping funnel and a reflux condenser was placed 800 ml. of anhydrous ether and 80.0 g. (2.1 moles) of lithium aluminum hydride. After the mixture was stirred for one hour it was cooled in an ice bath and a solution of 160 g. (1.86 moles) of cyclopropanecarboxylic acid (40) in 300 ml. of anhydrous ether was added dropwise (one and one-half hours) with stirring. The mixture was stirred for an additional hour at room temperature, then was cooled (ice bath) and the excess lithium aluminum hydride decomposed (17) cautiously with successive portions of 80 ml. of water, 80 ml. of 15% sodium hydroxide and 240 ml. of water. The solution was stirred one hour at room temperature, filtered, and the aluminum salts washed two times with 100-ml. portions of ether. The ether solution was dried over Drierite, filtered, and the solvent removed. Distillation of the residue through a thirteen-inch Fenske column yielded 113 g. (85%) of cyclopropylcarbinol, b.p. 123.5-124.0°,  $n_D^{25}$  1.4301.

---

<sup>1</sup>Analyses in this thesis were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

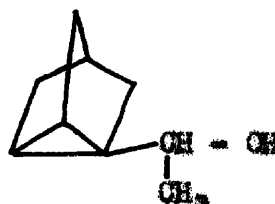
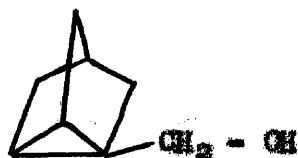
The alcohol gave a single peak (Anal., 14 min.) in the vapor chromatograph.<sup>1</sup>

Cyclopropylmethylecarbinol



Cyclopropyl methyl ketone (supplied by the Aldrich Chemical Co., Milwaukee, Wisconsin) was reduced to cyclopropylmethylecarbinol using a procedure analogous to that for cyclopropylcarbinol. The yield of alcohol was 87%, b.p. 122.0-122.5°,  $n_D^{20}$  1.4311. The alcohol gave a single peak (Anal., 13 min.) in the vapor chromatograph.

Northtricycyl- and methylnorthtricycylecarbinol



These alcohols were prepared by Robert A. Martin (48). The physical constants for northtricycylecarbinol were b.p. 52-54° at 0.8 mm.,

<sup>1</sup>A Perkin-Elmer Model 154 Vapor Fractionator was used for analysis or purification of products, with three different columns: a two-meter one-fourth inch analytical column (abbreviated, Anal.) containing Perkin-Elmer packing type "A" (didecyl phthalate on firebrick), a three-meter one-inch preparative column with the same packing (abbreviated, Prep. A), and a similar preparative column with packing of type "O" (silicone; abbreviated, Prep. O). The usual operating conditions, unless otherwise specified, were a temperature of  $94 \pm 1^\circ$  and a pressure of 10 p.s.i. of oil pumped nitrogen through the column. The type of column and the time of appearance, in minutes, of the maximum conductance are listed.

$n_D^{25}$  1.4942. The physical constants for methyltricycetylcyclitol were b.p. 63-64° at 1.0 mm.,  $n_D^{25}$  1.4837.

### Trifluoroacetyl chloride

Trifluoroacetic acid (34.5 g., 0.3 mole) and benzoyl chloride (84 g., 0.6 mole) were mixed in a 200-ml. round-bottomed flask, and the flask immediately connected to a twelve-inch Vigreux column. The top of the column was attached to a 100-ml. round-bottomed flask, filled with 90 ml. of anhydrous ether, so that any gas produced would have to bubble through the ether. A dry ice-isopropyl alcohol bath was used to cool the ether. The reaction flask was heated gently (maximum of 35°) and the trifluoroacetyl chloride collected in the cooled ether. After heating for four hours the ether solution was removed and stoppered, and allowed to warm almost to room temperature.

### Cyclopropylcarbonyl trifluoroacetate



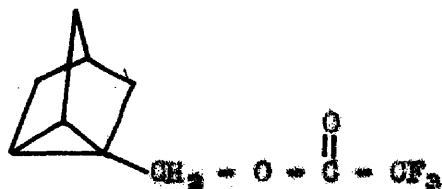
A 300-ml. three-necked flask fitted with a Hershberg stirrer, a reflux condenser and a dropping funnel was charged with 50 ml. of anhydrous ether and 2.40 g. (0.1 mole) of sodium hydride. A solution of 7.20 g. (0.1 mole) of cyclopropylcarbinol in 50 ml. of anhydrous ether was added dropwise in thirty minutes. After addition was complete the mixture was refluxed and stirred for five or six hours.

The suspension of the sodium salt of the alcohol was cooled in an ice bath and a solution of trifluoroacetyl chloride in ether, prepared as previously described, added over a period of fifteen minutes. After the mixture was stirred for fifteen minutes it was filtered and then extracted three times with 25-ml. portions of ice-cold 10% sodium bicarbonate and once with ice-cold water. After drying over Drierite and removing the solvent, the residue was distilled through a Claisen head and the fraction boiling from 105-109° was collected. Fractionation through a semi-micro Vigreux column gave 13.4 g. (80%) of cyclopropylcarbinyl trifluoroacetate, b.p. 106.5-107.5°,  $n_D^{25}$  1.3515. The ester gave a single peak (Anal., 9 min.) in the vapor chromatograph. The infrared spectrum of the ester is given in Figure 1.

Anal. Calc'd for  $C_6H_7F_3O_2$ : C, 42.87; H, 4.20

Found: C, 43.27, 43.31; H, 4.51, 4.47

Nortricyclylcarbinyl trifluoroacetate



This ester was prepared from 5.00 g. (0.04 mole) of nortricyclylcarbinol in a manner similar to that for cyclopropylcarbinyl trifluoroacetate. Distillation gave 7.44 g. (85%) of nortricyclylcarbinyl trifluoroacetate, b.p. 64.5-65.1° at 12 mm.,  $n_D^{25}$  1.4110-1.4114.

Anal. Calc'd for  $C_{10}H_{11}F_3O_2$ : C, 54.54; H, 5.04

Found: C, 54.63; H, 5.15

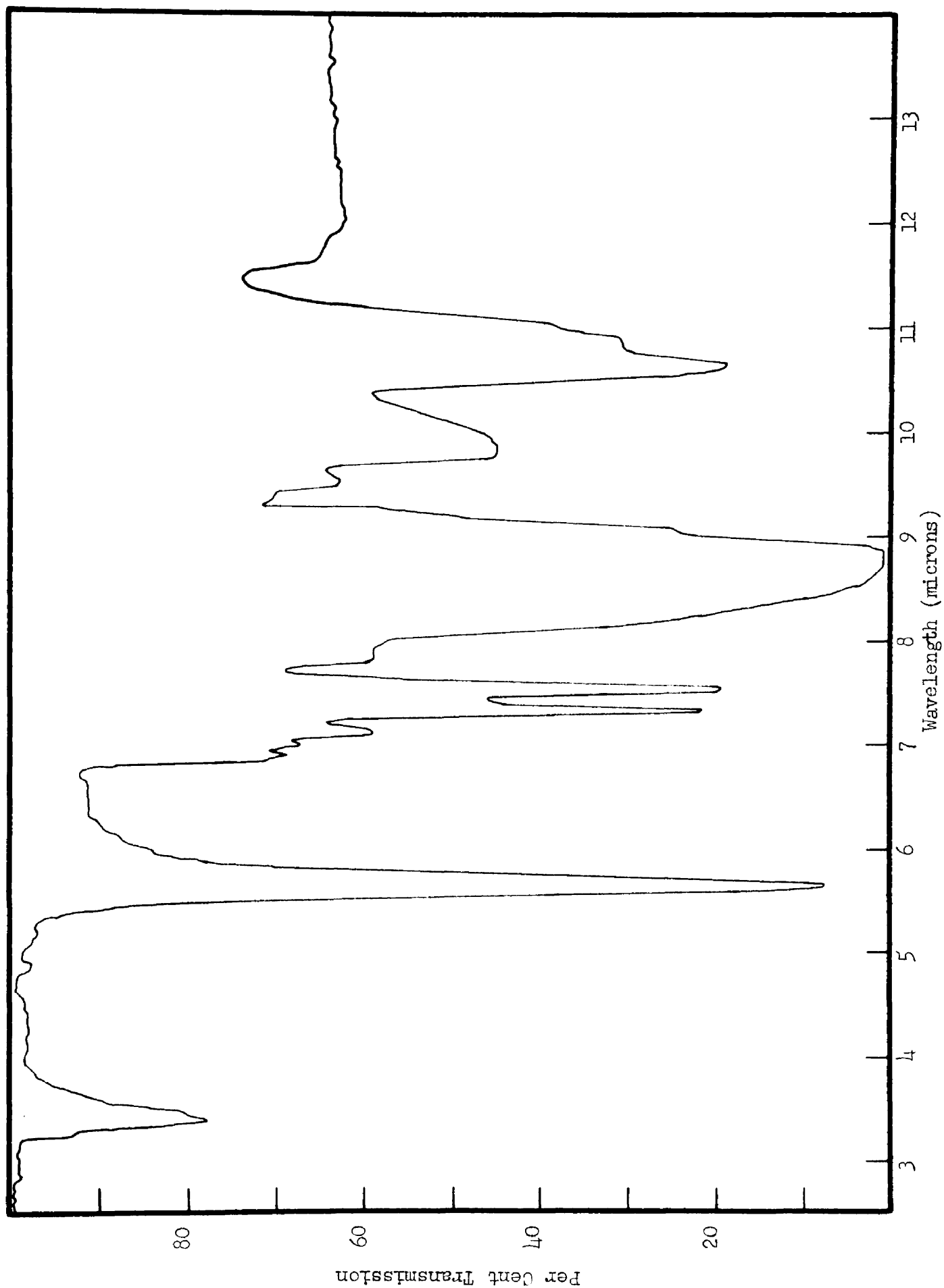


Figure 1. Infrared Spectrum of Cyclopropylcarbonyl Trifluoroacetate ( $\text{CCl}_4$  solution).

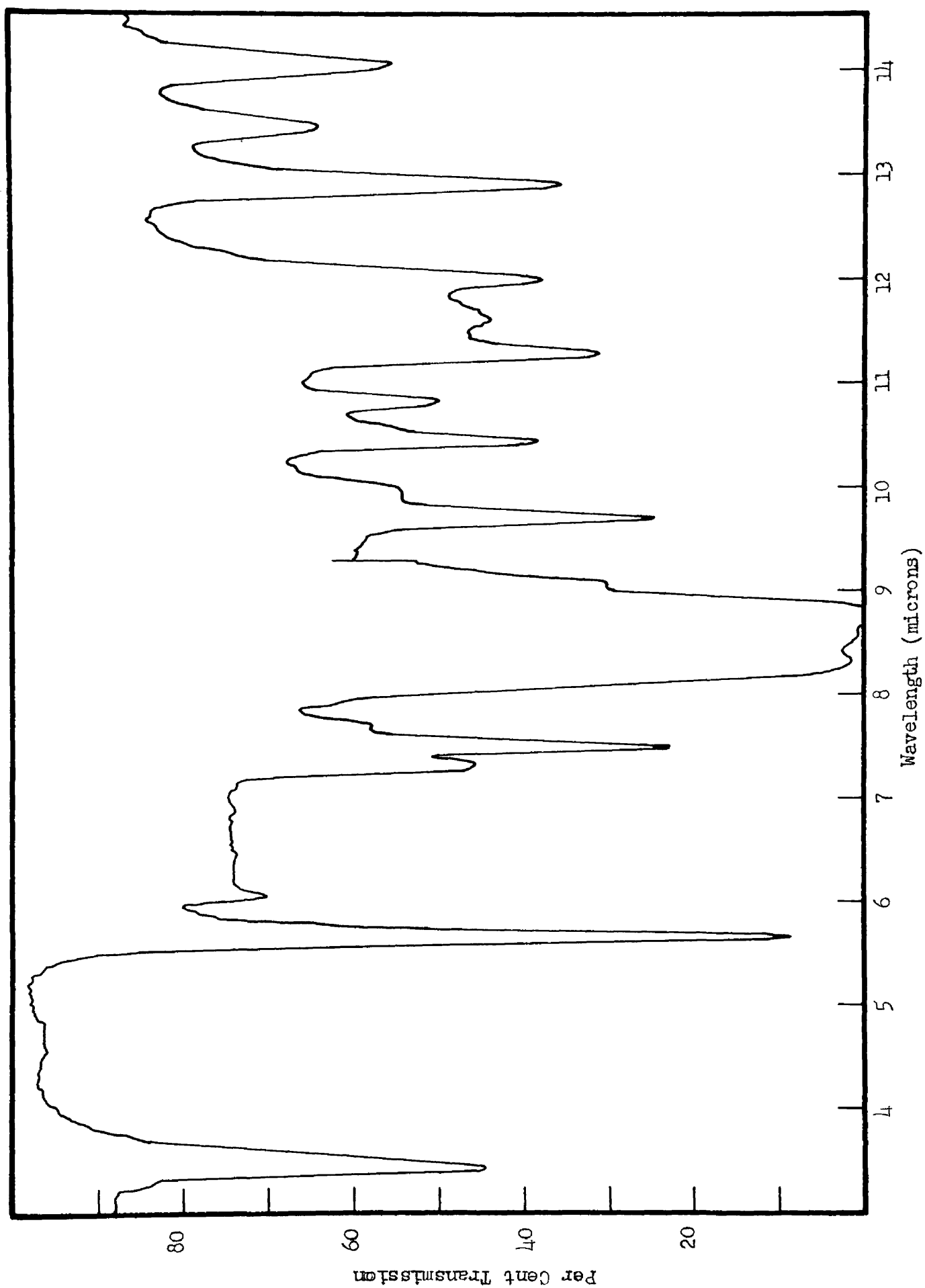
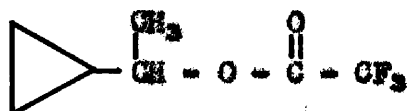


Figure 2. Infrared Spectrum of Nortricyclylcarbonyl Trifluoroacetate ( $\text{CS}_2$  solution).

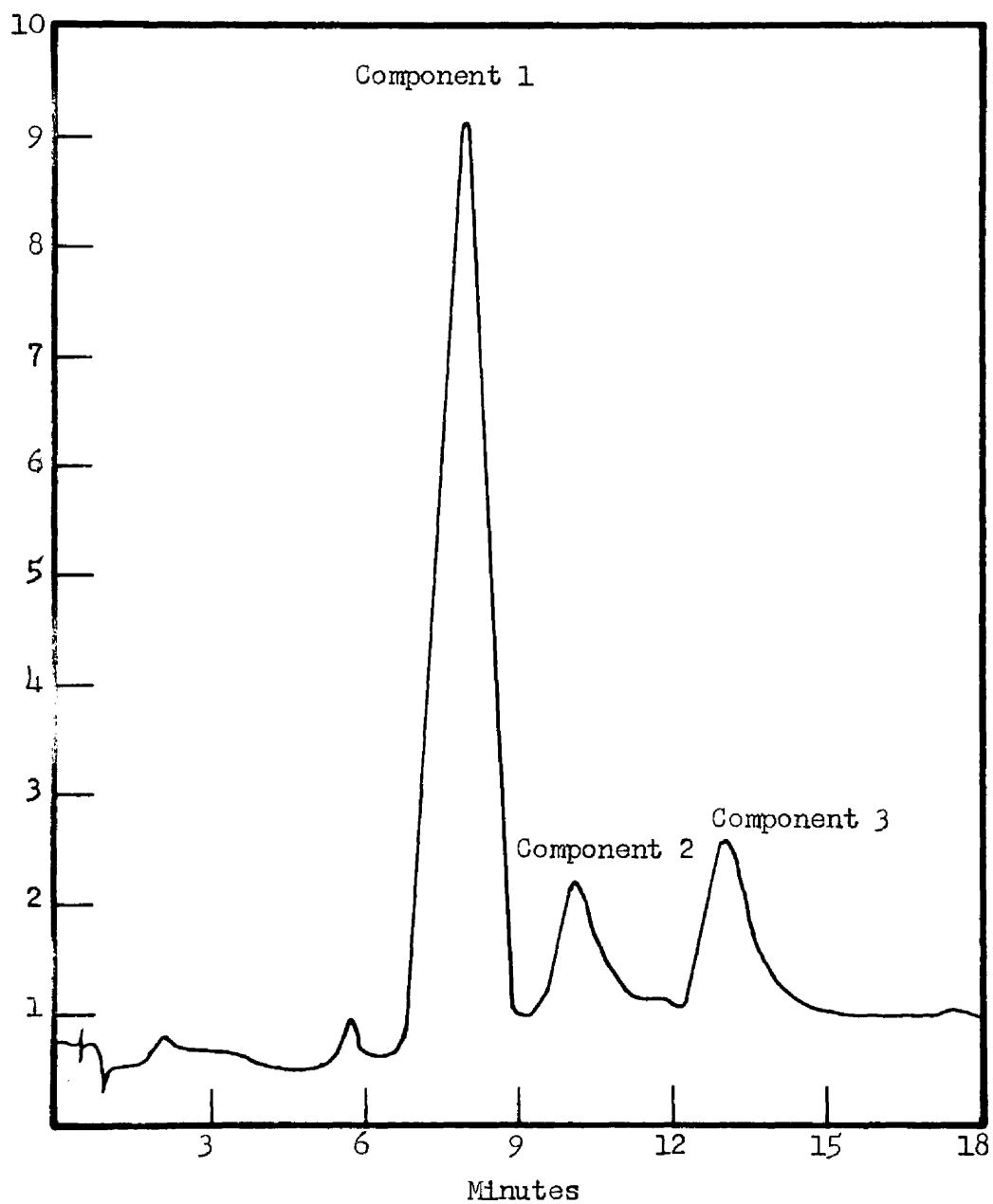
Cyclopropylmethylearbiny1 trifluoroacetate

A suspension of sodium cyclopropylmethylearbiny1ate was prepared, as previously described, from 8.60 g. (0.1 mole) of cyclopropylmethylearbiny1 (that gave a single peak in the vapor chromatograph) and 2.40 g. (0.1 mole) of sodium hydride in 100 ml. of anhydrous ether. A solution of trifluoroacetyl chloride, prepared as previously described, was added in ten minutes to the alcoholate solution cooled in an ice bath. The solution was stirred two hours at room temperature, filtered, washed three times with 25-ml. portions of ice-cold sodium bicarbonate and once with ice-cold water, and dried over Drierite. After removing the solvent the residue was distilled through a Claisen head and the fraction boiling 55-65° at 80-95 mm. was collected. Fractionation through a semi-micro Vigreux column gave fractions with b.p. 58-60° at 80-90 mm. and  $n_D^{25}$  1.3583-1.3601. The vapor chromatograph (Figure 3) had three main peaks (Anal., 8 min., 10 min. and 13 min.). These will be referred to as Components, 1, 2 and 3, respectively. In another preparation of cyclopropylmethylearbiny1 trifluoroacetate, using a larger excess of trifluoroacetyl chloride, vapor chromatography indicated that less of Component 1 and more of Component 2 was formed.

Attempts to separate Components 1, 2 and 3 by fractionation were unsuccessful. They could be separated by two passes through the vapor chromatograph (Prep. A, 31 min., 41 min. and 53 min.). Separate



Figure 3. Vapor Chromatograph of Reaction Product in the Preparation of Cyclopropylmethylcarbonyl Trifluoroacetate (Analytical Column).



distillation of these fractionator fractions gave the three components with an estimated purity of at least 98%, as indicated by vapor chromatography. Component 3 was shown to be cyclopropylmethylecarbinol by comparison of physical constants and infrared spectra, and by vapor chromatography.

Component 1 had b.p.  $57-58^{\circ}$  at 80 mm. and  $n_D^{25}$  1.3576-1.3579. The infrared spectrum (Figure 4) indicated that it was an ester. There is an absorption band at  $3.23\mu$  and there is also a band at  $1.65\mu$  in the near infrared spectrum. These bands are consistent with the presence of a cyclopropane ring (18,21a).

The ester (0.50 g.) was hydrolyzed by shaking with 1 ml. of 6 N sodium hydroxide. The base solution was extracted with carbon tetrachloride and the extracts were dried over sodium sulfate. After filtering, an infrared spectrum was obtained that was identical with that of pure cyclopropylmethylecarbinol. A phenylurethane was obtained from the carbon tetrachloride solution, m.p.  $69-70^{\circ}$  (reported m.p.  $69.6-70.5^{\circ}$ ) (19) after recrystallization from petroleum ether. Thus it appears that this ester is cyclopropylmethylecarbonyl trifluoroacetate.

Anal. Calcd. for  $C_7H_9F_3O_2$ : C, 46.16; H, 4.98

Found: C, 46.51, 46.54; H, 5.23, 5.30

#### Component 2

The second component had b.p.  $68-69^{\circ}$  at 90 mm.,  $n_D^{25}$  1.3589-1.3592. The infrared spectrum (Figure 5) indicated that it was an ester.

Anal. Calcd. for  $C_7H_9F_3O_2$ : C, 46.16; H, 4.98

Found: C, 45.94; H, 5.12

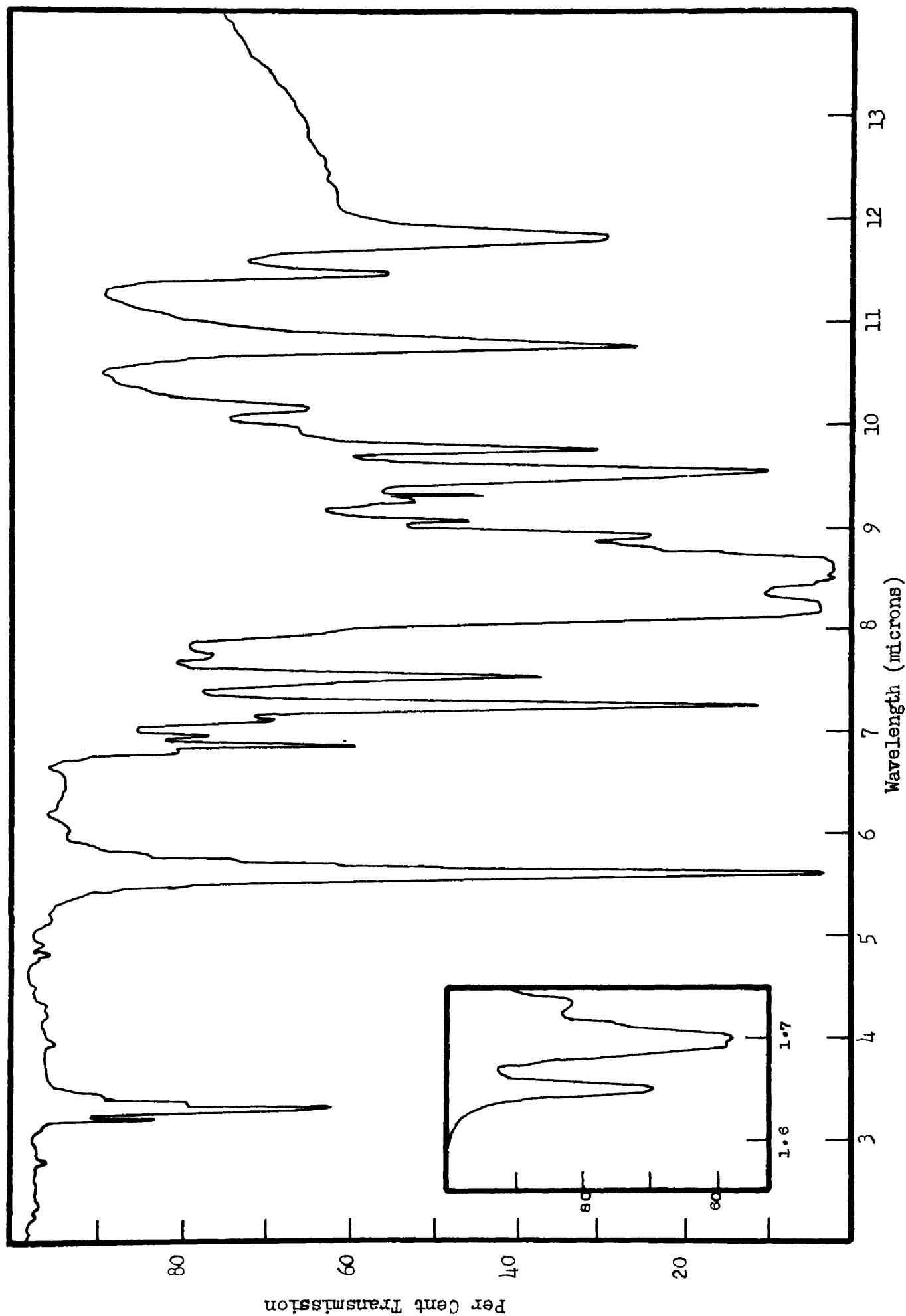


Figure 4. Infrared Spectrum of Cyclopropylmethylcarbonyl Trifluoroacetate ( $\text{CCl}_4$  solution).

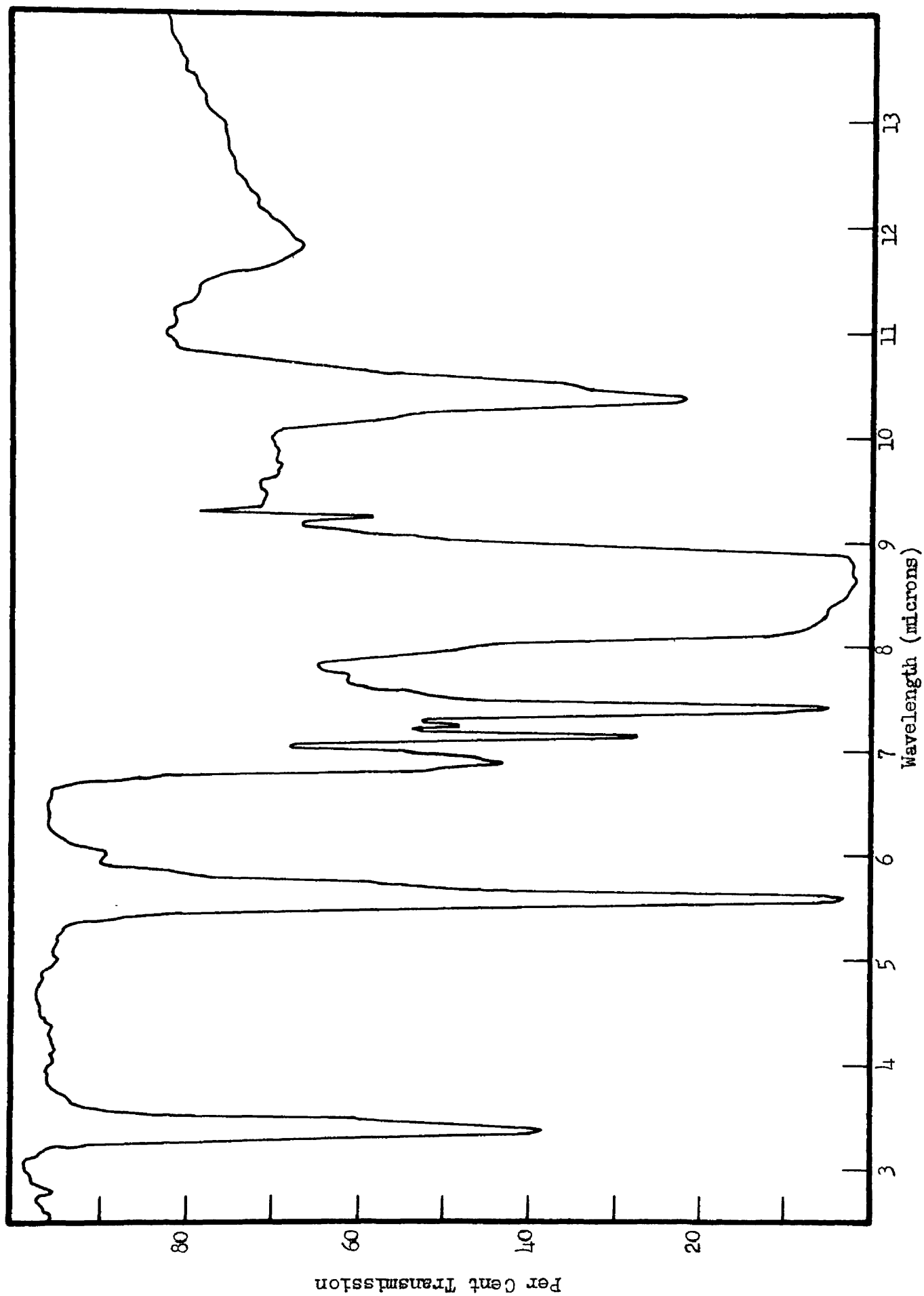


Figure 5. Infrared Spectrum of 2-Methylcyclobutyl Trifluoroacetate ( $\text{CCl}_4$  solution).

There were no bands near  $1.64\ \mu$  in the near infrared spectrum or near  $3.23\ \mu$  in the infrared spectrum.

Base catalyzed hydrolysis of 0.26 g. of this ester by the same procedure as previously described gave an alcohol with an infrared spectrum (Figure 6) different from that of cyclopropylmethylecarbinol. The infrared spectrum of cyclopropylmethylecarbinol (Figure 7) is included for comparison. The carbon tetrachloride solution did not decolorize bromine in carbon tetrachloride. The phenylurethane of the alcohol, recrystallized from petroleum ether, melted at  $39-41^\circ$ .

Anal. Calc'd. for  $C_{12}H_{18}NO_2$ : C, 70.22; H, 7.37; N, 6.92

Found: C, 70.04; H, 7.37; N, 6.85.

Several recrystallizations from hexane, carbon tetrachloride, or methanol did not sharpen the melting point. An attempt was made to prepare the 3,5-dinitrobenzoate, but no product melting above room temperature could be obtained. The infrared spectra of the ester (Component 2) and of the alcohol both contained an absorption peak at about  $10.4\ \mu$ , which may be ascribed to the cyclobutane ring (21b).

The alcohol portion of this ester is probably 2-methylcyclobutanol. Data indicating the structure of this alcohol are discussed in the section on results. Nevertheless, Component 2 will be referred to as 2-methylcyclobutyl trifluoroacetate in the remainder of this thesis.

#### Reaction of Cyclopropylmethylecarbinol and Trifluoroacetic Acid

Cyclopropylmethylecarbinol (17.2 g., 0.20 mole) and trifluoroacetic acid (25.0 g., 0.22 mole) were mixed in a 50-ml. round-bottomed flask,

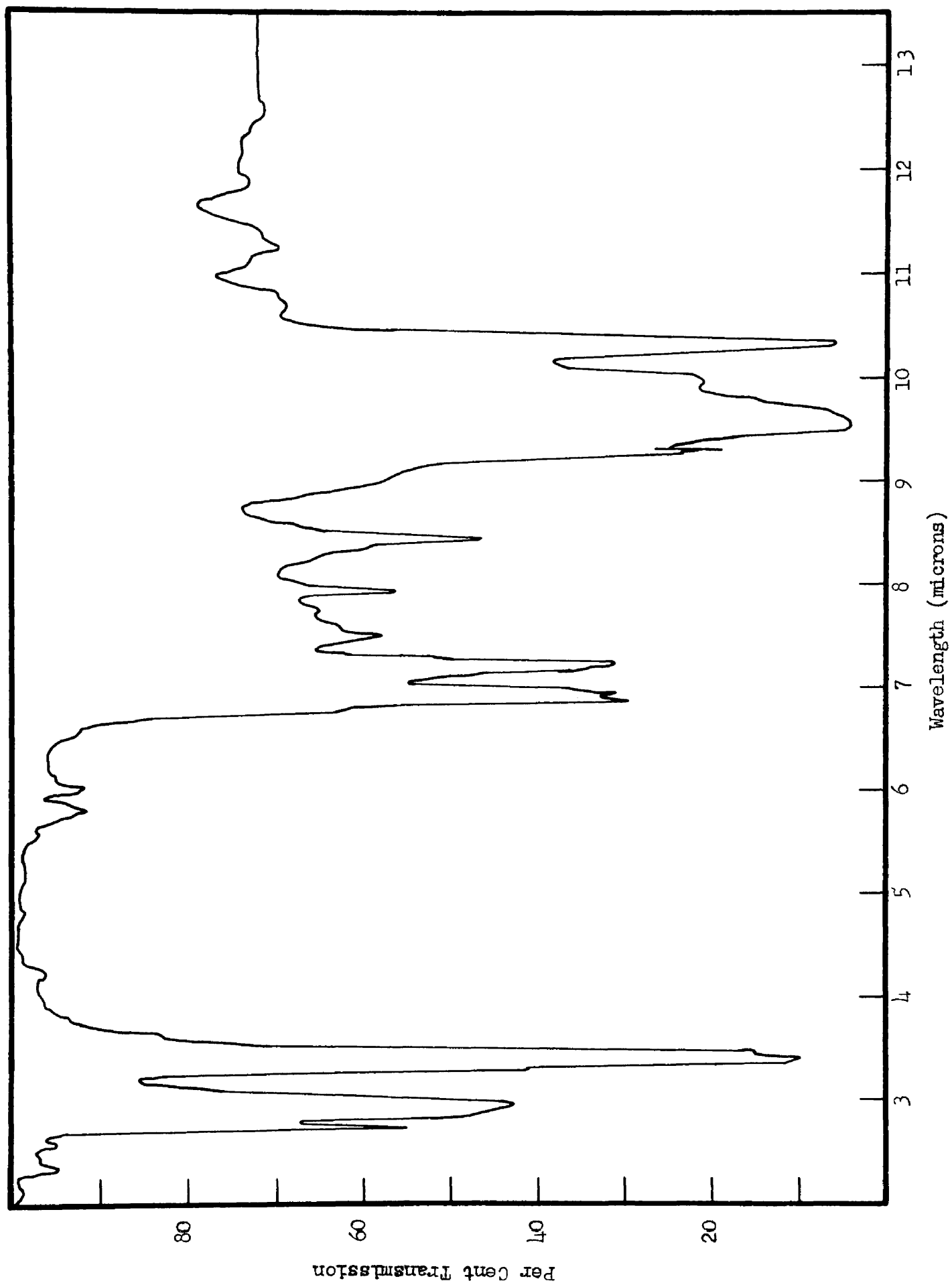


Figure 6. Infrared Spectrum of 2-Methylcyclobutanol ( $\text{CCl}_4$  solution).

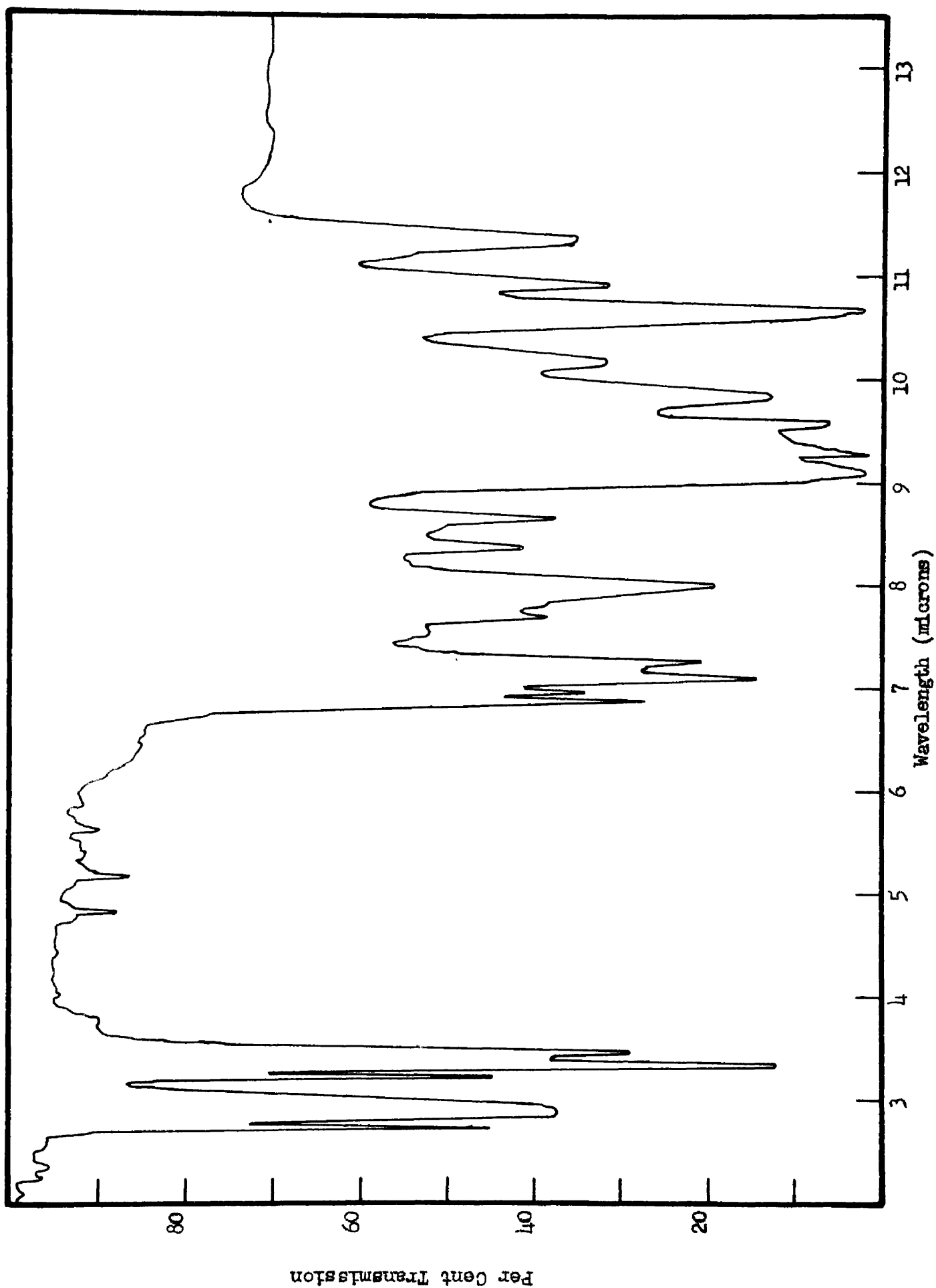


Figure 7. Infrared Spectrum of Cyclopropylmethylcarbinol ( $\text{CCl}_4$  solution).

and the mixture became warm. After refluxing the solution for one-half hour it had become dark red, and refluxing was stopped. The solution was then allowed to remain at room temperature for 20 hours. After diluting with 50 ml. of ether the solution was extracted with ice-cold 10% sodium bicarbonate until the aqueous layer was neutral, and then it was washed once with water. The organic layer was dried over magnesium sulfate and distilled, b.p.  $104-122^{\circ}$ ,  $n_D^{25}$  1.3639-1.3649. Infrared analysis of this product indicated that it was primarily (about 90%) 2-methylcyclobutyl trifluoroacetate. The yield was about 40%.

#### Chromic acid oxidation of 2-Methylcyclobutanol (20)

In a 10-ml. Claisen flask, fitted with a 15-cm. piece of glass tubing (serving as condenser and addition tube) inserted to the bottom of the neck of the flask, was placed 0.50 g. of 2-methylcyclobutanol. The alcohol was heated almost to reflux. The oxidizing solution, prepared by dissolving 1.15 g. of sodium dichromate dihydrate in 1.5 ml. of water and slowly adding 1.0 ml. of concentrated sulfuric acid with swirling, was added dropwise through the glass tubing at such a rate that the oxidized material and water distilled slowly. After all of the oxidizing agent had been added (20 minutes) suction was applied to distill over as much of the organic components as possible. The water layer was saturated with potassium carbonate and the organic layer separated with a medicine dropper. The crude organic layer weighed 0.32 g. After drying over Drierite an infrared spectrum was obtained that had two peaks in the carbonyl region (Figure 8). This oxidation



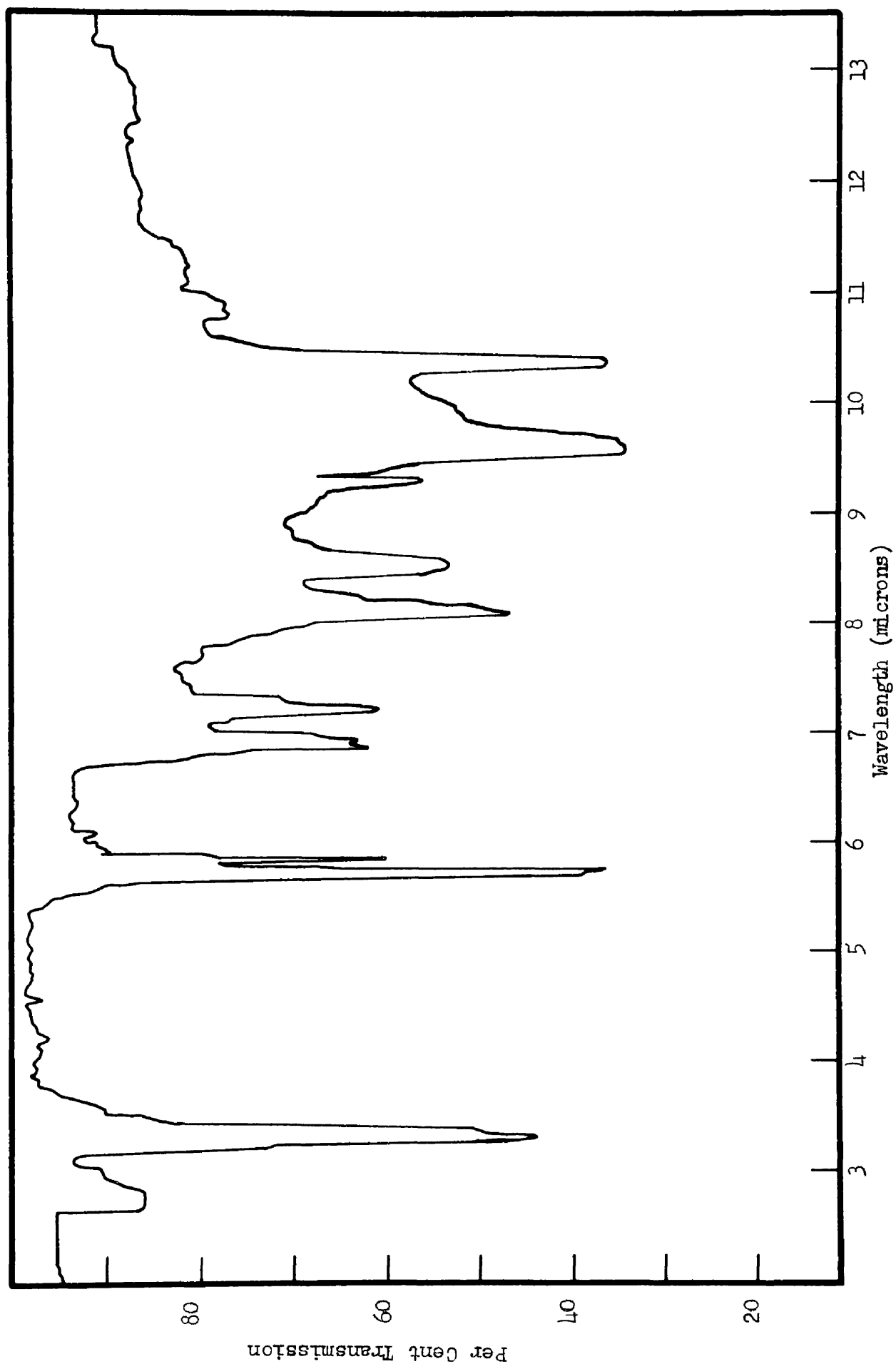


Figure 8. Infrared Spectrum of Chromic Acid Oxidation Product of 2-Methylcyclobutanol ( $\text{CCl}_4$  solution).

procedure was separately shown to yield cyclopropylmethyl ketone from the corresponding alcohol.

The carbon tetrachloride infrared solution was extracted with 8% sodium hydroxide. The basic solution was acidified with concentrated hydrochloric acid and extracted with carbon tetrachloride. After drying these carbon tetrachloride solutions over Drierite, the infrared spectrum showed no separation of the original carbonyl absorption peaks.

The carbon tetrachloride solutions did not give a Fuchsin-Aldehyde test, although isovaleraldehyde, under similar conditions, gave a positive test.

#### Chromium trioxide in pyridine oxidation of 2-Methylcyclobutanol (22,23)

To 17 ml. of pyridine, which had been dried over magnesium sulfate and distilled, was added slowly 1.60 g. (0.016 mole) of chromium trioxide. To this yellow complex was added dropwise with swirling over a period of twenty minutes a solution of 0.50 g. of 2-methylcyclobutanol in 8 ml. of pyridine. Within one hour the mixture was brown, and in two hours it was a very dark brown. The solution was swirled frequently for 16 hours and then 20 ml. of water added and mixed thoroughly. The aqueous solution was extracted three times with 25-ml. portions of 20% hydrochloric acid. After drying over sodium sulfate and removing the solvent the infrared spectrum (Figure 9) on the crude residue had a strong carbonyl peak at  $5.75\mu$ , another peak at  $5.86\mu$ , and a smaller peak at  $5.61\mu$ .

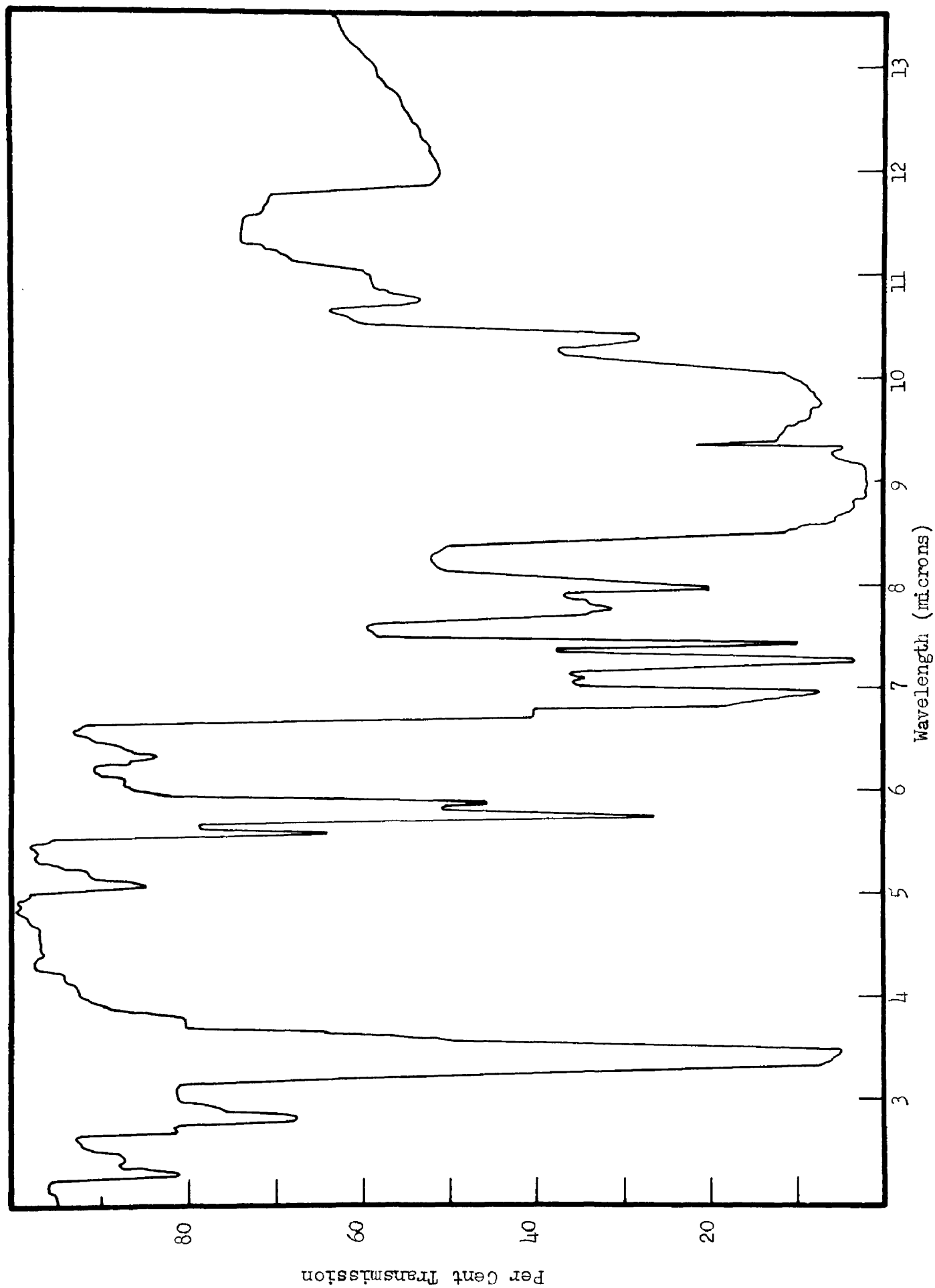
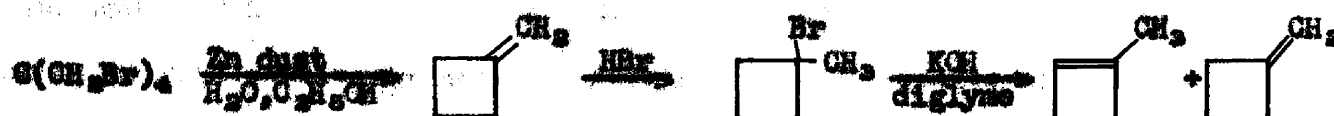


Figure 9. Infrared Spectrum of Chromium Trioxide in Pyridine Oxidation Product of 2-Methylcyclobutanol ( $\text{CCl}_4$  solution).

### Attempted Synthesis of 2-Methylcyclobutanol

Methylcyclobutene was prepared by the method of Shand, etc. (41) according to the following reaction sequence.



The olefin mixture was fractionated through a 45 cm. tantalum wire spiral column. The fractions, b.p. 37-39°, were collected and used as methylcyclobutene (reported b.p. 37.1°). The remaining fractions, b.p. 39-42°, should be mainly methylenecyclobutane (reported b.p. 41.7°).

The diborane generator was set up as follows (45). A 300-ml. 3-necked round-bottomed flask was fitted with a nitrogen inlet, exits to a mercury safety release valve (with any exit gases then bubbling through water) and to the reaction flask containing the olefin, and a pressure equalized dropping funnel, containing 3.7 g. (0.1 mole) of recrystallized sodium borohydride (46) in 100 ml. of anhydrous diglyme. In the flask was placed 22.8 g. (0.16 mole) of freshly distilled (b.p. 122-126°) boron trifluoride-ethyl etherate in 50 ml. of diglyme.

In a 250-ml. 3-necked flask fitted with a spiral condenser connected to a water bath bubbler, and an inlet from the diborane generator so that any gas bubbled thru the solution in the flask, was placed 14.2 g. (0.21 mole) of the previously mentioned 1-methylcyclobutene in 50 ml. of anhydrous tetrahydrofuran. The flask containing the olefin was cooled in an ice-salt bath, and both flasks were stirred with magnetic stirrers. The system was flushed well with dry nitrogen.

The sodium borohydride solution was added to the boron trifluoride-ethyl etherate solution over a period of one hour to generate diborane (42). After stirring an additional hour the exit to the olefin reaction flask was disconnected and the excess diborane in the generating flask was hydrolyzed cautiously with the addition of small pieces of ice.

The olefin reaction flask was equipped with a dropping funnel and 45 ml. of 3 M sodium hydroxide was added as fast as foaming permitted. Then 25 ml. of 30% hydrogen peroxide was added over a period of one hour. The ice-salt bath was removed and stirring continued for another hour. After filtering the white solid obtained and washing it with ether, the two layers were separated and the aqueous layer extracted once with ether, and the combined organic solutions dried over magnesium sulfate.

Distillation appeared to give two main fractions. The first fraction (6.0 g.), b.p. 130-132.5°,  $n_D^{25}$  1.4301-1.4305 gave a phenylurethane, m.p. 77.3-78.0° after several recrystallizations from hexane.

Anal. Calc'd. for  $C_{12}H_{12}NO_2$ : C, 70.22; H, 7.37; N, 6.93

Found: C, 70.28; H, 7.40; N, 6.88

The 3,5-dinitrobenzoate of this fraction, after several recrystallizations from 95% ethanol, had m.p. 97.5-98.5°.

Anal. Calc'd. for  $C_{12}H_{12}N_2O_6$ : C, 51.43; H, 4.32; N, 10.00

Found: C, 51.45; H, 4.41; N, 9.99

The second fraction, b.p. 136-139°,  $n_D^{25}$  1.4401-1.4412 gave a phenylurethane, m.p. 111-112°. The yield of this fraction was 3.0 g.

Anal. Calc'd. for  $C_{12}H_{12}NO_2$ : C, 70.22; H, 7.37; N, 6.93

Found: C, 70.20; H, 7.24; N, 6.87

and a 3,5-dinitrobenzoate, m.p. 98-99°. A mixed melting

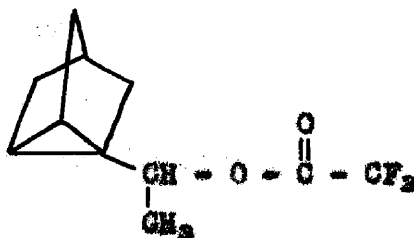
Anal. Calc'd. for  $C_{12}H_{12}N_2O_6$ : C, 51.43; H, 4.32; N, 10.00

Found: C, 51.44; H, 4.41; N, 9.95

point of the 3,5-dinitrobenzoates was 72-81°. The reported melting point of the phenylurethane of cyclobutylcarbinol is 65.0-66.5° and of the 3,5-dinitrobenzoate is 98.5-99.5° (47). The reported melting point of the phenylurethane of 1-methylcyclobutanol is 139.9° (41). Neither of the alcohols obtained in this synthesis correspond to these cyclobutane derivatives.

The infrared spectrum of neither of the alcohols obtained in this reaction is similar to that of the alcohol obtained from rearrangement in this thesis. Lucas tests on these fractions indicate that the lower boiling alcohol is tertiary and that the higher boiling alcohol is primary. A Lucas test on the purported 2-methylcyclobutanol indicated that it is a secondary alcohol.

Methylnortricycylcarbinyl trifluoroacetate



This ester was prepared by a method analogous to that for cyclopropylcarbinyl trifluoroacetate. Methylnortricycylcarbinol (6.80 g., 0.049 mole) in 25 ml. of anhydrous ether was added to 1.2 g. (0.05 mole)

of sodium hydride in 25 ml. of ether. A solution of trifluoroacetyl chloride in 90 ml. of ether, prepared from 20 g. of trifluoroacetic acid and 40 g. of benzoyl chloride and heated below  $30^{\circ}$  for two hours, was added in twenty-five minutes. Distillation of the crude product gave 6.4 g., b.p.  $82-83^{\circ}$  at 13 mm.,  $n_D^{25}$  1.4506. Solvolysis studies indicated the presence of more than one component. The esterification product was fractionated through a fifteen-inch vacuum-jacketed Vigreux column, b.p.  $80.5-83.1^{\circ}$  at 12 mm.,  $n_D^{25}$  1.4448-1.4560. A center fraction was sent out for analysis. Figure 10 is the infrared spectrum of this fraction.

Anal. Calc'd. for  $C_{11}H_{12}F_3O_2$ : C, 56.40; H, 5.59

Found: C, 60.84, 60.95; H, 6.61, 6.71

Attempts to purify the ester by vapor chromatography were unsuccessful. No conductance peaks were observed on the recorder and no ester could be obtained from the exit of the vapor chromatograph.

#### Miscellaneous esters of Cyclopropylcarbinol

Several esters of cyclopropylcarbinol were prepared in an attempt to find a compound suitable for kinetic studies. These esters were prepared, with procedures analogous to that for cyclopropylcarbonyl trifluoroacetate, from the appropriate acid chloride and sodium cyclopropylcarbinolate. The liquid esters were fractionated and the solid esters were recrystallized from petroleum ether (b.p.  $30-60^{\circ}$ ) or from absolute ethanol. Physical constants, yields and analyses are given in Table I.

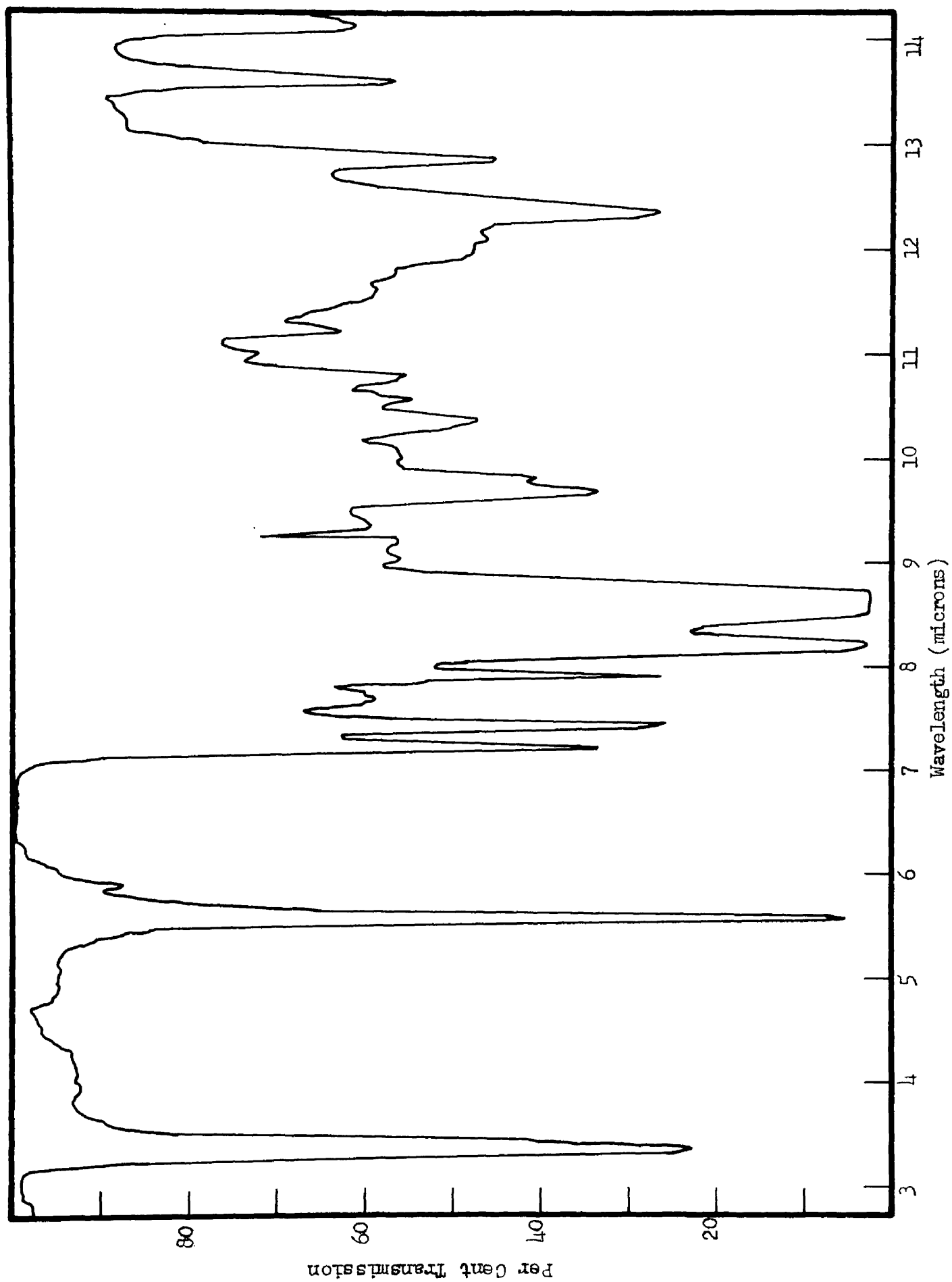


Figure 10. Infrared Spectrum of Methylnortricyclylcarbonyl Trifluoroacetate ( $\text{CS}_2$  solution).



TABLE 1

## PHYSICAL CONSTANTS, YIELDS AND ANALYSES OF SEVERAL ESTERS OF CYCLOHEPTACARBOXYLIC ACID

| Acid               | Melting Point | Boiling Point    | $n_D^{20}$ | Yield | Percent Carbon |       | Percent Hydrogen |       | Percent Chlorine |       | Percent Nitrogen |       |
|--------------------|---------------|------------------|------------|-------|----------------|-------|------------------|-------|------------------|-------|------------------|-------|
|                    |               |                  |            |       | Calcd.         | Found | Calcd.           | Found | Calcd.           | Found | Calcd.           | Found |
| Chlorosuccinic     |               | 81-82° at 13 mm. | 1.4510     | 39    | 48.50          | 48.22 | 6.10             | 6.34  | 23.86            | 24.02 |                  |       |
| Dichlorosuccinic   |               | 87-88° at 13 mm. | 1.4602     | 72    | 39.37          | 39.25 | 4.40             | 4.49  | 36.74            | 36.84 |                  |       |
| Trichlorosuccinic  |               | 67-69° at 4 mm.  | 1.4680     | 63    | 33.13          | 32.86 | 3.25             | 3.48  | 48.91            | 49.11 |                  |       |
| p-Nitrobenzoic     | 54.2-55.0     |                  |            | 95    | 59.72          | 59.79 | 5.01             | 5.07  |                  |       | 6.33             | 6.35  |
| 2,4-Dinitrobenzoic | 55-56         |                  |            | 77    | 49.63          | 49.48 | 3.79             | 3.89  |                  |       | 10.53            | 10.54 |

## B. Solvolysis Studies

### Solvents

Dioxane was purified by the method of Fieser (24). Conductance water supplied by Dr. James L. Dye was employed for making up solvent mixtures. The resistance of the conductance water and of the solvent mixtures was so high that it could not be measured with the conductance bridge that was used.

Methanol was purified by distillation over magnesium methoxide.

The kinetic studies and product analyses were carried out in water-dioxane solvents of several weight per cent compositions. Product analysis for three of the esters was also carried out in methanolic dioxane or in absolute methanol.

### Preliminary Kinetic Studies

Several esters of cyclopropylcarbinol were prepared and the kinetic analyses of Hart and Sandri (12) by titration of the liberated acid with standard base was attempted. The nitrobenzoates and the mono- and dichloroacetates showed no appreciable solvolysis in 90 or 70% dioxane at 70° after sixty hours. With the trichloro- and trifluoroacetates the phenolphthalein end point faded, so that definite values could not be obtained.

### Kinetic Procedure

The reaction was followed by noting the increase in conductance of approximately 0.025-0.050 molar solutions of ester in the particular

solvent, this increase being due to the liberated trifluoroacetic acid. This method was used previously for esters of trifluoroacetic acid by Hunt and Moffat (14,15,16). An Industrial Conductivity Bridge, model RG-1B, was used to follow the change in conductance. Kinetic runs were performed in either of two conductance cells (platinized platinum electrodes) that had cell constants of 0.1808 and 0.1460 and volumes of approximately 25 ml. The cells were placed in a constant temperature bath maintained at  $\pm 0.1^\circ$  of the desired temperature.

The aqueous dioxane was equilibrated in the constant temperature bath before each run. Approximately 0.0006 mole of the ester was accurately weighed into the dry conductance cell and the cell equilibrated in the constant temperature bath. At zero time, a 25-ml. aliquot of the equilibrated solvent was pipetted into the conductance cell containing the ester and the solution was thoroughly mixed. At various time intervals the resistance of the solution was determined with the conductance bridge. The infinity resistance value was obtained by allowing the cell to remain in the bath until the resistance reading remained constant over a period of several hours. Usually 15 to 25 points were taken for each run.

Tables containing the results of the kinetic experiments are given in the Appendix which appears at the end of this thesis.

### Product Analysis

(a) Solvolysis of cyclopropylcarbinyl trifluoroacetate in 70% dioxane-30% water at  $60^\circ$ .

Cyclopropylcarbinyl trifluoroacetate (8.4 g., 0.050 mole) was dissolved in 100 ml. of 70% dioxane-30% water and maintained at 60° for 60 hours. After cooling, the solution was saturated with sodium hydroxide and the two layers that appeared were separated. The dioxane layer was again treated with sodium hydroxide and the layers separated. The dioxane solution was then dried over Drierite, filtered and distilled until about 5 ml. remained. An infrared spectrum on this crude residue had no carbonyl or carbon-carbon double bond peaks but did have peaks ascribable to an alcohol and a cyclopropane ring (at 3.24  $\mu$ ). Vapor chromatography indicated that only dioxane and cyclopropylcarbinol (Anal., 13 min.) were present.

(b) Solvolysis of cyclopropylcarbinyl trifluoroacetate in 70% dioxane-30% methanol at reflux.

Cyclopropylcarbinyl trifluoroacetate (8.4 g., 0.05 mole) was dissolved in 200 ml. of 70% dioxane-30% methanol and refluxed for 48 hours. After cooling, the solution was fractionated through a 13-inch Fenske column. The infrared spectrum of the first fraction had a carbonyl absorption peak at about 5.6  $\mu$ , similar to the carbonyl absorption of all of the trifluoroacetates. Vapor chromatography on this fraction had a conductance peak (Anal., 2.5 min.) analagous to that of authentic methyl trifluoroacetate (14). The later fractions, containing mostly dioxane, also had present cyclopropylcarbinol (Anal., 13 min.) and the original ester (Anal., 9 min.) as indicated by vapor chromatography and infrared.

(c) Attempted solvolysis of cyclopropylmethylecarbonyl trifluoroacetate in water at 50°.

Cyclopropylmethylecarbonyl trifluoroacetate (3.00 g., 0.016 mole) was heated with 10 ml. of water at 50° for twenty-four hours. As the ester was insoluble in the water, the mixture was swirled frequently. After cooling, the solution was extracted three times with 15 ml.-portions of ether and the combined ether extracts dried over sodium sulfate. After removing the solvent, infrared analysis and vapor chromatography indicated that very little solvolysis had occurred and that more of 2-methylcyclobutyl trifluoroacetate was present than was in the starting ester.

(d) Solvolysis of cyclopropylmethylecarbonyl trifluoroacetate in 60% acetone-40% water (by volume) at reflux.

Cyclopropylmethylecarbonyl trifluoroacetate (3.0 g., 0.016 mole) was dissolved in 15.0 ml. of acetone and 10.0 ml. of water was added. The solution was heated at reflux for eighteen hours, and then distilled until most of the acetone was removed. After cooling, the aqueous solution was extracted three times with 20 ml.-portions of ether and dried over magnesium sulfate. Most of the ether was removed and the residue put through the vapor chromatograph (Prep. O, 50°, 5 p.s.i. of nitrogen). Four fractions were collected. Infrared analysis indicated that fraction one (Prep. O, 10 min.) was diethyl ether.

The infrared spectrum of fraction two (Prep. O, 39-57 min.) contained absorption peaks characteristic of an alcohol, the cyclopropane ring,

the trifluoroacetate carbonyl and the carbon-carbon double bond. The infrared spectra of fraction three (Prep. C, 66-100 min.) and of fraction four (Prep. C, 110-140 min.) were almost identical and were very similar to the spectrum of 2-methylcyclobutanol. No bands characteristic of cyclopropylmethylcarbinol or its trifluoroacetate were present in the spectra of these last two fractions.

(e) Solvolysis of cyclopropylmethylcarbinyl trifluoroacetate in methanolic dioxane and in methanol at reflux.

This ester (15.0 g., 0.08 mole, with an estimated impurity of less than 10% of 2-methylcyclobutyl trifluoroacetate) was mixed with 100 ml. of 70% dioxane-30% methanol and refluxed for 24 hours. After fractionation through a 45 cm. tantalum wire spiral column, index of refraction and infrared analysis indicated that the products were mainly methyl trifluoroacetate and 2-methylcyclobutanol, plus some ester which appeared to be mainly the rearranged ester. No cyclopropylmethylcarbinyl methyl ether was observed, which should have been formed if alkyl-oxygen fission had occurred.

After refluxing 10.0 g. (0.06 mole) of approximately 90% pure cyclopropylmethylcarbinyl trifluoroacetate in 50% dioxane-50% methanol for 12 hours and then fractionating the solution through the wire spiral column, infrared analysis showed that the main products were methyl trifluoroacetate, 2-methylcyclobutanol and some rearranged ester. But a small amount of cyclopropylmethylcarbinyl methyl ether was also shown to be a product by comparison with the infrared spectrum of an authentic sample (11).

The ester (5.0 g., 0.03 mole) was also refluxed for 12 hours in absolute methanol and then fractionated. Analysis of these fractions showed that methyl trifluoroacetate and cyclopropylmethylcarbonyl methyl ether were the main products and were formed in approximately equal amounts. 2-Methylcyclobutanol was also identified.

(f) Solvolysis of 2-methylcyclobutyl trifluoroacetate in methanol at reflux.

This ester (3.2 g., 0.02 mole, 99% pure) was refluxed for 12 hours with methanol and then fractionated. Methyl trifluoroacetate (2.18 g., 95% yield) and 2-methylcyclobutanol were the only detectable products of solvolysis.

## RESULTS AND DISCUSSION

## A. The Attempted Structure Proof of 2-Ethylcyclobutyl Trifluoroacetate

This ester, obtained from the reaction of cyclopropylmethylcyclobutanol with trifluoroacetyl chloride or trifluoroacetic acid, had the same analysis as cyclopropylmethylcyclobutyl trifluoroacetate, but different infrared and near infrared absorption spectra. The absence of bands at  $1.65 \mu$  and at  $3.23 \mu$  indicated that it did not contain a cyclopropane ring. Hydrolysis with base gave an alcohol whose boiling point ( $130-131^\circ$ ) and infrared spectrum were different from those of cyclopropylmethylcyclobutanol (b.p.  $122^\circ$ ). A Lucas test indicated that it was a secondary alcohol. There was no carbon-carbon double bond absorption peak in the infrared spectra of the ester or the alcohol. Both of these spectra did have absorption peaks at about  $10.4 \mu$ , which may be ascribed to the cyclobutane ring (21b). The alcohol did not decolorize bromine in carbon tetrachloride, and gave a different phenylurethane (m.p.  $39-41^\circ$ ) than cyclopropylmethylcyclobutanol (m.p.  $69-70^\circ$ ). An attempt to prepare the 3,5-dinitrobenzoate gave a solid which melted below room temperature.

A search of the literature did not disclose any  $C_8H_{16}O$  alcohol corresponding to the alcohol obtained from rearrangement in this thesis. The alcohol is probably 2-ethylcyclobutanol, which could have several isomers, and this would account for the difficulty in preparing sharp melting derivatives.



## RESULTS AND DISCUSSION

### 1. The Attempted Structure Proof of 2-Methylcyclobutyl Trifluoroacetate

This ester, obtained from the reaction of cyclopropylmethylcarbinol with trifluoroacetyl chloride or trifluoroacetic acid, had the same analysis as cyclopropylmethylcarbonyl trifluoroacetate, but different infrared and near infrared absorption spectra. The absence of bands at  $1.65\mu$  and at  $3.23\mu$  indicated that the ester did not contain a cyclopropane ring. Hydrolysis with base gave an alcohol whose boiling point ( $130-131^\circ$ ) and infrared spectrum were different from those of cyclopropylmethylcarbinol (b.p.  $122^\circ$ ). A Lucas test indicated that it was a secondary alcohol. There was no carbon-carbon double bond absorption peak in the infrared spectra of the ester or the alcohol. Both of these spectra did have absorption peaks at about  $10.4\mu$ , which may be ascribed to the cyclobutane ring (21b). The alcohol did not decolorize bromine in carbon tetrachloride, and gave a different phenylurethane (m.p.  $39-41^\circ$ ) than cyclopropylmethylcarbinol (m.p.  $69-70^\circ$ ). An attempt to prepare the 3,5-dinitrobenzoate gave a solid which melted below room temperature.

A search of the literature did not disclose any  $C_6H_{10}O$  alcohol corresponding to the alcohol obtained from rearrangement in this thesis. The alcohol is probably 2-methylcyclobutanol, which could have geometrical isomers, and this would account for the difficulty in preparing sharp melting derivatives.

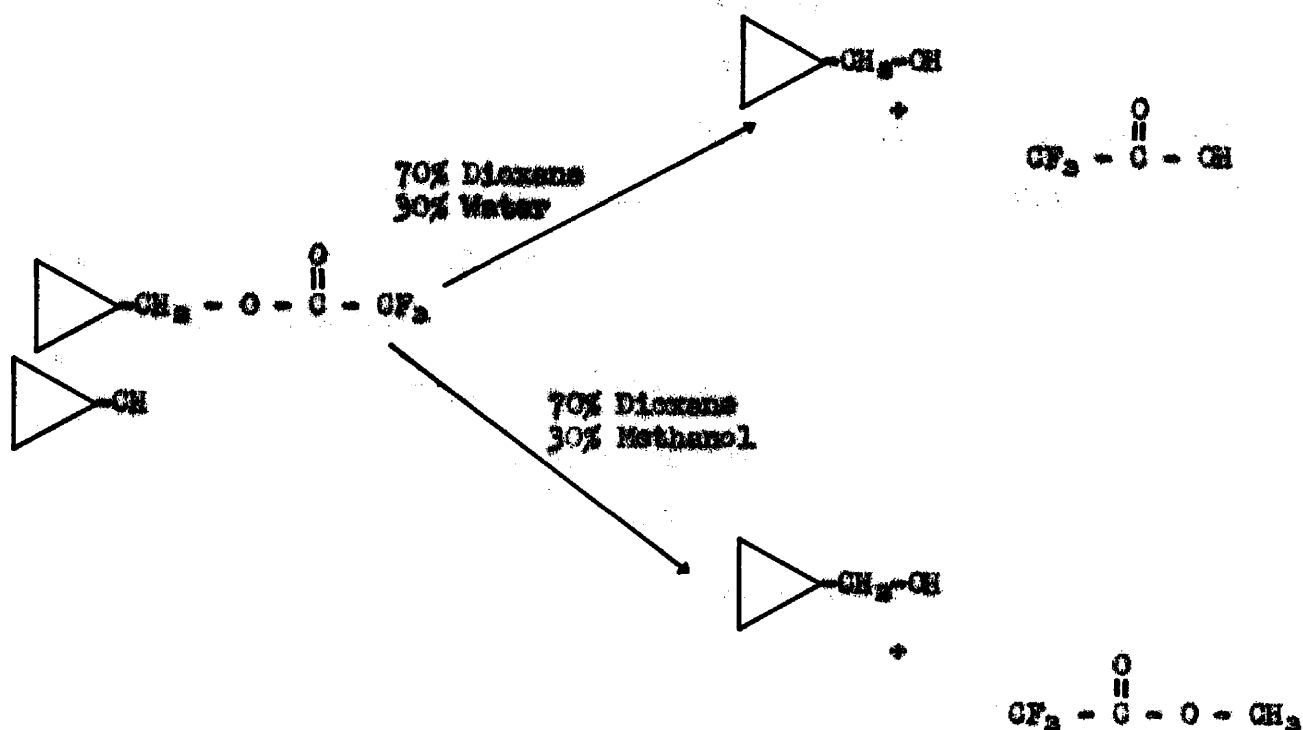
Two attempts to oxidize the alcohol to a cyclobutanone, which has a characteristic infrared carbonyl absorption at about  $5.6\mu$  (21a), were inconclusive. Both oxidations gave product with more than one carbonyl peak, and in only one case was there an absorption peak at about  $5.6\mu$ . Further oxidation of cyclobutanone derivatives with cleavage of the cyclobutane ring is not uncommon (20).

An attempt was made to synthesize 2-methylcyclobutanol from 1-methylcyclobutene, that probably had an impurity of some methylenecyclobutene. Using a new synthesis of alcohols (43,44) that is reported to give anti-Markownikoff hydration of olefins, two alcohols were obtained, neither of which corresponded to the alcohol obtained from rearrangement in this thesis. Lucas tests indicated that the synthetic alcohols were primary and tertiary, while the alcohol obtained from the rearrangement of cyclopropylmethylcarbonyl trifluoroacetate was a secondary alcohol. The primary and tertiary alcohols did not correspond to the known cyclobutylcarbinol and 1-methylcyclobutanol. Either the starting olefin did not have the expected structure, or this synthesis of alcohols does not proceed in the normal fashion on cyclobutene derivatives.

### B. The Solvolysis Products

Solvolysis of cyclopropylcarbonyl trifluoroacetate in 70% dioxane-30% water at  $60^\circ$  gave cyclopropylcarbinol, identified by vapor chromatography and by its infrared spectrum. There was no evidence of olefin formation. When the water was replaced with methanol, the only

observed products were methyl trifluoroacetate and cyclopropylcarbinol, again identified by vapor chromatography and infrared analysis. Formation of the ester demonstrates that solvolysis of cyclopropylcarbinyl trifluoroacetate proceeded by acyl-oxygen fission; this criterion has been used in numerous other cases (29a).

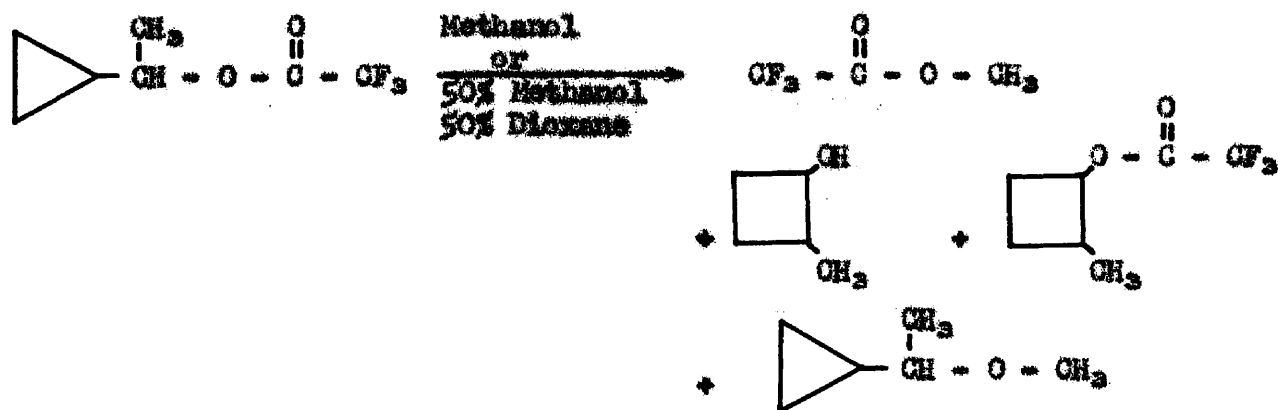


Refluxing 2-methylcyclobutyl trifluoroacetate in methanol gave only methyl trifluoroacetate and 2-methylcyclobutanol.

Although cyclopropylmethylcarbinyl trifluoroacetate is not very soluble in water, an attempt was made to solvolyze this ester in water. Very little solvolysis occurred at 50° during 24 hours, but vapor chromatography on the product indicated that more 2-methylcyclobutyl trifluoroacetate was present than was in the starting ester. Also, the

main product obtained from mixing cyclopropylmethylearbinal and trifluoroacetic acid was 2-methylcyclobutyl trifluoroacetate. Cyclopropylmethylearbinyll trifluoroacetate was also solvolysed in 60% acetone-40% water (by volume) at reflux. Vapor chromatography and infrared analysis indicated that the products were probably cyclopropylmethylearbinal, an unsaturated ester of trifluoroacetic acid, 2-methylcyclobutyl trifluoroacetate and 2-methylcyclobutanol.

In methanol or 50% methanolic dioxane at reflux, the products of solvolysis were methyl trifluoroacetate, cyclopropylmethylearbinyll methyl ether, 2-methylcyclobutyl trifluoroacetate, and 2-methylcyclobutanol. More of the ether was formed in methanol than was formed in the methanolic dioxane. No ether formation was observed after refluxing in 70% methanolic dioxane. The formation of cyclopropylmethylearbinyll methyl ether demonstrates that the solvolysis of cyclopropylmethylearbinyll trifluoroacetate proceeded via alkyl-oxygen fission.



The 2-methylcyclobutyl trifluoroacetate presumably would arise via internal return, and this would in turn produce the methyl trifluoroacetate and the 2-methylcyclobutanol. A more complete description of

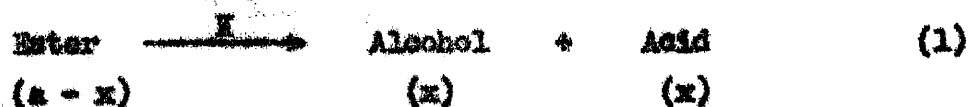
the probable mechanism of solvolysis of cyclopropylmethylcarbonyl trifluoroacetate will be given in the section on conclusions.

### C. The Solvolysis Rates

The rate of solvolysis of the trifluoroacetates was measured in several weight per cent dioxane-water solutions at several temperatures. The reactions were followed by noting the decrease in resistance due to the liberation of trifluoroacetic acid and were usually followed to 50-60% completion.

#### Method of Calculation

The kinetic treatment is analogous to that found in Frost and Pearson (25). The solvolysis reaction may be expressed by the general equation



where

$a$  = initial ester concentration in moles/liter

$x$  = alcohol or acid concentration at time  $t$

$a - x$  = ester concentration at time  $t$ .

For a first-order or pseudo first-order reaction the integrated form of the rate expression is

$$\ln (a/a-x) = kt. \quad (2)$$

The measured quantities were

$R$  = resistance (ohms) of the solution at time  $t$

and

$R_{\infty}$  = resistance (ohms) of the solution after it had remained constant over a period of several hours.

Since concentration is directly proportional to conductance which in turn is inversely proportional to resistance, then

$(a-x)$  is proportional to  $(1/R_{\infty} - 1/R)$

and

$(a)$  is proportional to  $(1/R_{\infty} - 1/R_0)$

where

$R_0$  = resistance (ohms) of the solvent and ester at time zero.

Then, substituting into equation (2)

$$\ln(a/a-x) = \ln\left(\frac{1/R_{\infty} - 1/R_0}{1/R_{\infty} - 1/R}\right) = \ln\left(\frac{R}{R-R_{\infty}}\right)\left(\frac{R_0-R_{\infty}}{R_0}\right) = kt \quad (3)$$

After converting to base 10 logarithms and separating terms, the expression becomes

$$\log (R/R-R_{\infty}) = (k/2.3) t + \log (R_0/R_0-R_{\infty}) \quad (4)$$

From equation (4) it is seen that a plot of  $\log (R/R-R_{\infty})$  versus  $t$  for a first order reaction should give a straight line, the slope of which is equal to  $(k/2.3)$  and whose intercept is  $\log (R_0/R_0-R_{\infty})$ . The slopes of all lines obtained in this thesis were calculated by the method of least squares (26a,27).

Some non-linearity of the plots of  $\log (R/R-R_{\infty})$  versus  $t$  might be expected due to curvature of the plot of specific conductance versus

acid concentration. Corrections for this curvature were considered to be unnecessary because the concentration of the liberated acid was small and because the inherent errors in such a correction are fairly large. Also, the plots of  $\log (R/R_0)$  versus  $t$  were observed to be linear.

### Comparison of Solvolysis Rates

The values of the solvolysis rate constants for the esters under various conditions are listed in Tables 2, 3, 4 and 5. The value of the specific rate constant is the arithmetic mean of all rate constants obtained for each set of conditions. Where more than one determination was made for a given solvent and temperature the standard deviation (26b) from each mean value is also given. All of the kinetic data are given in Tables 9 to 75 in the Appendix.

For a comparison of the rate constants reported in this thesis with those reported by Moffat and Hunt (14,15,16), *n*-butyl trifluoroacetate was prepared and solvolyzed in 70% acetone-30% water (by volume, the solvent used by Moffat and Hunt) and in 70% dioxane-30% water (by weight, a solvent used in the kinetic studies in this thesis). A value of the specific rate constant of  $6.1 \times 10^{-5} \text{ sec}^{-1}$  at  $45^\circ$  in aqueous acetone was obtained, compared with the reported value of  $5.5 \times 10^{-5} \text{ sec}^{-1}$ . The rate constant for this ester in the aqueous dioxane solvent at  $45^\circ$  was  $4.7 \times 10^{-5} \text{ sec}^{-1}$ . Thus, cyclopropylcarbonyltrifluoroacetate ( $k = 7.1 \times 10^{-5} \text{ sec}^{-1}$  at  $45^\circ$ ) and *n*-butyl trifluoroacetate both solvolyze at about the same rate.

TABLE 2  
SPECIFIC RATE CONSTANTS FOR THE SOLVOLYSIS OF CYCLOPROPYLOXYMETHYL  
TRIFLUOROMETHANE IN AQUEOUS DIOXANE

| °C. | $10^5 k, \text{ sec}^{-1}$<br>Weight Per Cent Dioxane |                |                 |                 |
|-----|-------------------------------------------------------|----------------|-----------------|-----------------|
|     | 50                                                    | 60             | 70              | 80              |
| 30  |                                                       | 18.8           | 3.56            |                 |
| 40  | $45.0 \pm 0.2$                                        | $29.8 \pm 0.5$ | $5.64 \pm 0.04$ | 2.32            |
| 50  |                                                       | $45.3 \pm 2.3$ | $9.25 \pm 0.2$  | $4.00 \pm 0.04$ |
| 60  |                                                       | $66.7 \pm 1.5$ | $13.5 \pm 0.8$  | $6.10 \pm 0.2$  |



TABLE 3

SPECIFIC RATE CONSTANTS FOR THE SOLVOLYSIS OF NORTRECTOLYL CARBITYL  
TRIFLUOROACETATE IN AQUEOUS DIOXANE

| °C | $10^5 k, \text{sec}^{-1}$<br>Weight Per Cent Dioxane |                 |       |
|----|------------------------------------------------------|-----------------|-------|
|    | 60                                                   | 70              | 80    |
| 40 | 3.95                                                 | 1.33            | 0.631 |
| 50 | 6.32                                                 | 2.41            | 1.09  |
| 60 | $11.5 \pm 0.7$                                       | $4.00 \pm 0.24$ | 2.16  |

TABLE 1

SPECIFIC RATE CONSTANTS FOR THE SOLVOLYSIS OF 2-METHYLOCTYL BUTYL  
TRIFLUOROACETATE IN AQUEOUS DIOXANE

| °C | $10^4 k_2 \text{ sec}^{-1}$<br>Weight Per Cent Dioxane |                 |
|----|--------------------------------------------------------|-----------------|
|    | 60                                                     | 70              |
| 40 | $17.8 \pm 1.8$                                         | 4.41            |
| 50 | 30.2                                                   | $6.83 \pm 0.07$ |
| 60 | $44.7 \pm 3.3$                                         | $10.1 \pm 0.1$  |

TABLE 5

SPECIFIC RATE CONSTANTS FOR THE SOLVOLYSIS OF CYCLOPROPYLMETHYL-  
GAMMAYL TRIFLUOROACETATE IN AQUEOUS DIOXANE

| °C | 10 <sup>4</sup> k, sec <sup>-1</sup><br>Weight Per Cent Dioxane |             |       |
|----|-----------------------------------------------------------------|-------------|-------|
|    | 60                                                              | 70          | 80    |
| 40 | 16.6                                                            | 1.72        | 0.608 |
| 50 | 44.4                                                            | 4.71 ± 0.03 | 1.96  |
| 60 | 106                                                             | 12.5 ± 0.4  | 6.81  |

Typical plots of the data are shown in Figures 11, 12 and 13.

In these graphs the data for cyclopropylcarbiny1 (Figure 11) and cyclopropylmethylcarbiny1 (Figure 12) trifluoroacetates in 60, 70 and 80% aqueous dioxane are compared. Figure 13 is a plot of the data for four of the esters under the same conditions.

Some of the solvolysis data are compared in Table 6. It is evident from this table that the trifluoroacetates of cyclopropylcarbinol, nortricyclohexylcarbinol and 2-methylcyclobutanol all solvolyse at about the same rate, while the trifluoroacetates of cyclopropylmethylcarbinol and methylnortricyclohexylcarbinol solvolyse somewhat faster.

#### Cyclopropylmethylcarbiny1 and 2-Methylcyclobutyl trifluoroacetates

In the preparation of cyclopropylmethylcarbiny1 trifluoroacetate two esters were obtained. A typical plot of the kinetic data obtained from the mixture of these two esters, as obtained from the esterification of cyclopropylmethylcarbinol, is shown in Figure 14 (curve A). The esters were separated using vapor chromatography, and kinetic data on the separate esters were also obtained.

An attempt was made to analyze the kinetic data of the esterification mixture into the individual solvolysis rate constants. Satisfactory rate constants were obtained only for the slower solvolysing ester, 2-methylcyclobutyl trifluoroacetate. The latter portion of the plots of  $\log (R/R_\infty)$  versus  $t$  were linear (see Figure 14) and from the slope of this portion of the graphs, which represents the solvolysis of the slow ester, rate constants for the solvolysis of 2-methylcyclobutyl

Figure 11. Plot of  $\log (R/R_{\infty})$  versus  $t$  for the Solvolysis of Cyclopropylcarbinyl Trifluoroacetate in 60, 70 and 80% Aqueous Dioxane at  $50^{\circ}$ . Data from Tables 11, 21 and 26.

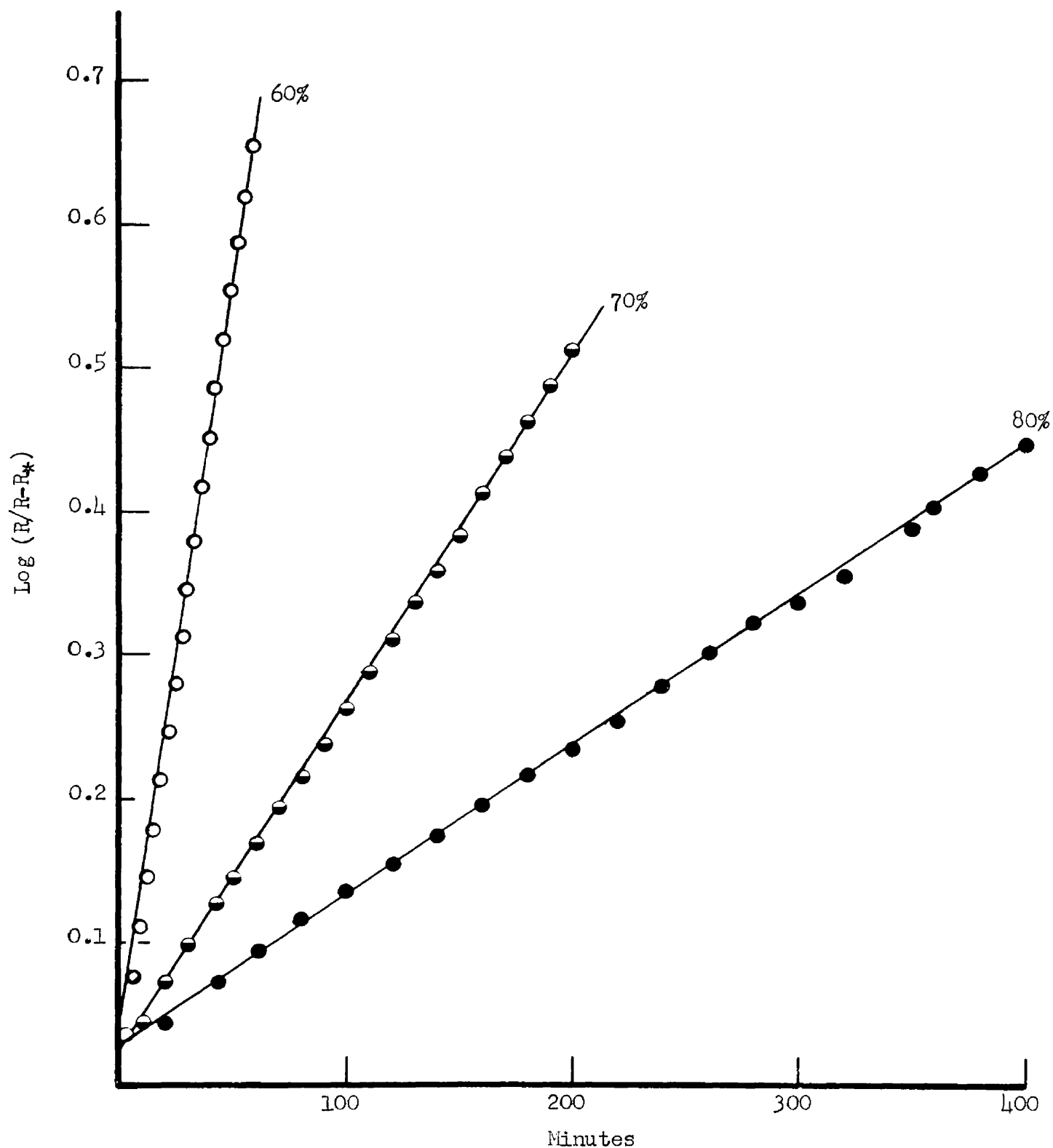


Figure 12. Plot of  $\log (R/R-R_*)$  versus  $t$  for the Solvolysis of Cyclopropylmethylcarbiny Trifluoroacetate in 60, 70 and 80% Aqueous Dioxane at  $50^\circ$ . Data from Tables 53, 56 and 62.

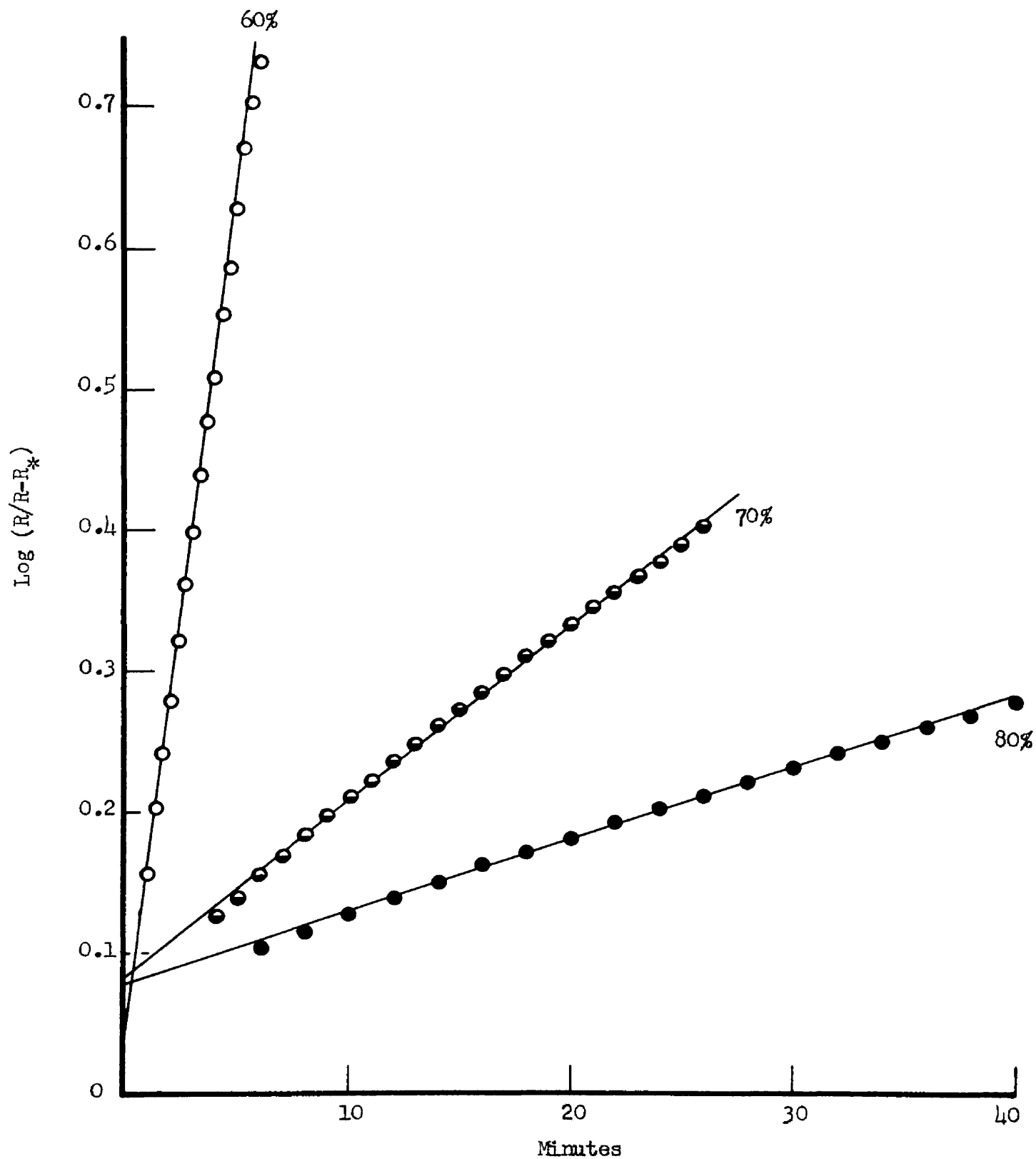


Figure 13. Plot of  $\log (R/R-R_*)$  versus  $t$  for the Solvolysis of Four Trifluoroacetates in 70% Aqueous Dioxane at  $50^\circ$ . Data from Tables 22, 35, 47 and 57.

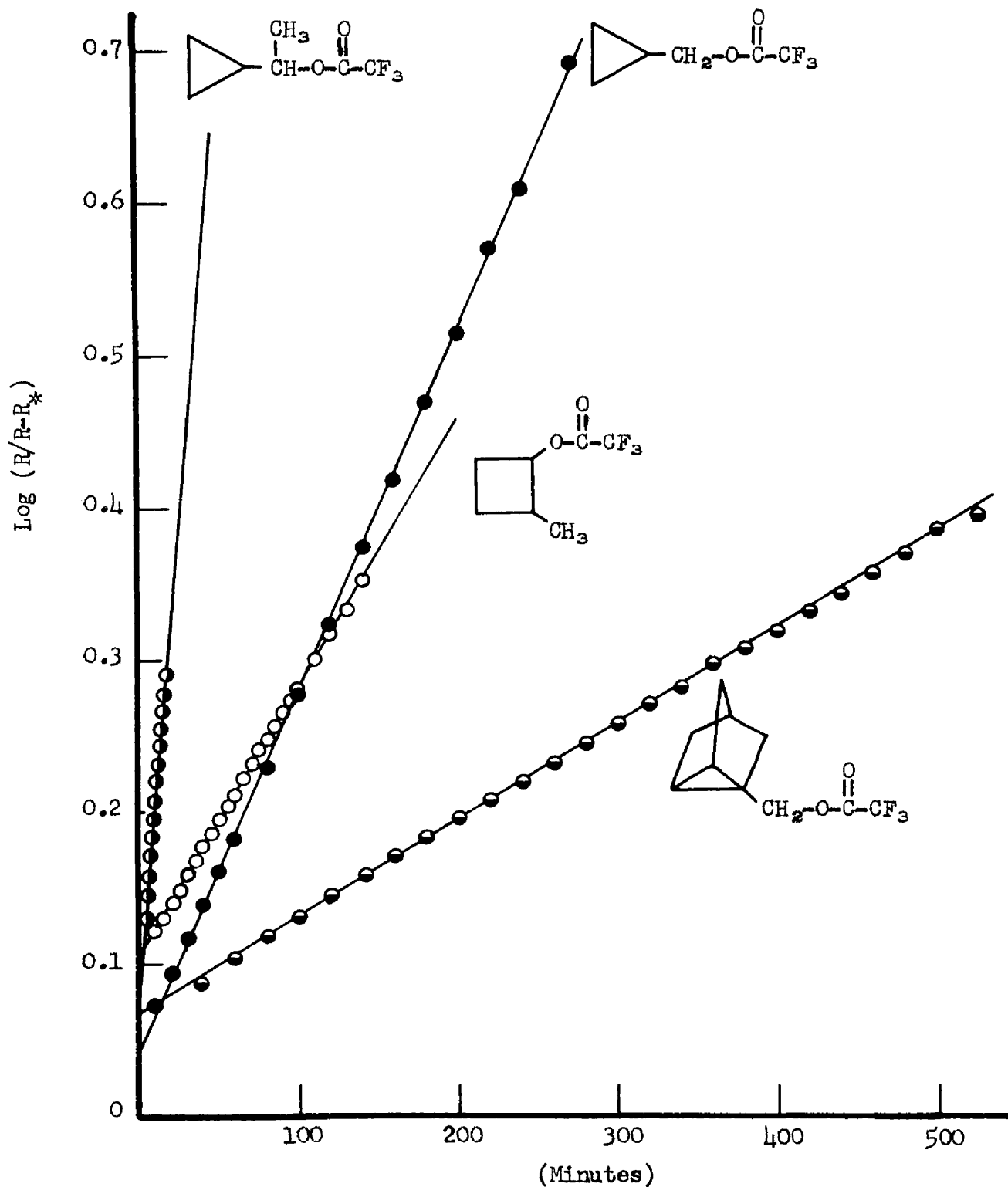


TABLE 6

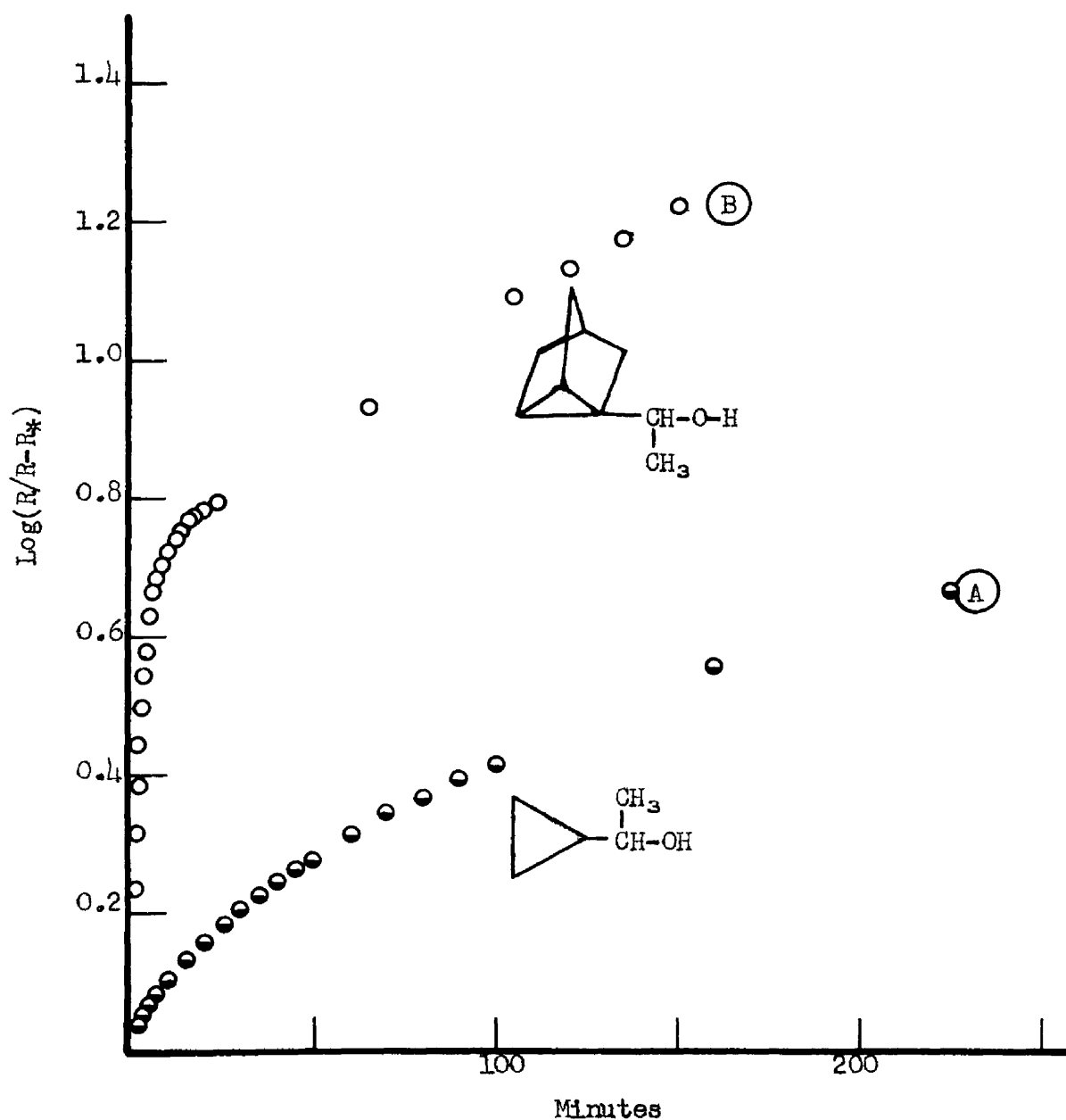
RELATIVE RATES OF SOLVOLYSIS OF SEVERAL TRIFLUOROACETATES IN AQUEOUS DIMETHYL<sup>a</sup>

| Trifluoroacetate                  | Weight Per Cent Dimethyl                         |                                                   |                                                   |                                                    |
|-----------------------------------|--------------------------------------------------|---------------------------------------------------|---------------------------------------------------|----------------------------------------------------|
|                                   | 45°                                              | 50°                                               | 60°                                               | 60°                                                |
| Methylmercaptomethyl-<br>carbonyl |                                                  | 364                                               |                                                   |                                                    |
| Cyclopropylmethyl-<br>carbonyl    |                                                  | 19.5                                              | 31.2                                              | 42.0                                               |
| n-Butyl                           | 0.67                                             |                                                   |                                                   | 92.2                                               |
| Cyclopropylmethyl-<br>carbonyl    | 1.0<br>( $7.1 \times 10^{-6} \text{ sec}^{-1}$ ) | 3.84                                              | 3.38                                              | 7.55                                               |
| 2-Methylcyclobutyl                |                                                  | 2.83                                              | 2.52                                              | 4.50                                               |
| Methylcyclobutyl                  |                                                  |                                                   |                                                   | 3.88                                               |
| Methylcyclobutyl                  |                                                  | 1.00<br>( $2.4 \times 10^{-6} \text{ sec}^{-1}$ ) | 1.00<br>( $4.0 \times 10^{-6} \text{ sec}^{-1}$ ) | 1.00<br>( $3.95 \times 10^{-6} \text{ sec}^{-1}$ ) |
|                                   |                                                  |                                                   |                                                   | 1.00<br>( $11.5 \times 10^{-6} \text{ sec}^{-1}$ ) |

<sup>a</sup>Values in parentheses are the absolute rate constants.



Figure 14. Plot of  $\log(R/R_\infty)$  versus  $t$  for the Solvolysis of Mixtures Obtained from the Esterification of Cyclopropylmethylcarbinol and Methyl-nortricyclylcarbinol in 70% Aqueous Dioxane at  $50^\circ$ . Data from Tables 49 and 64.

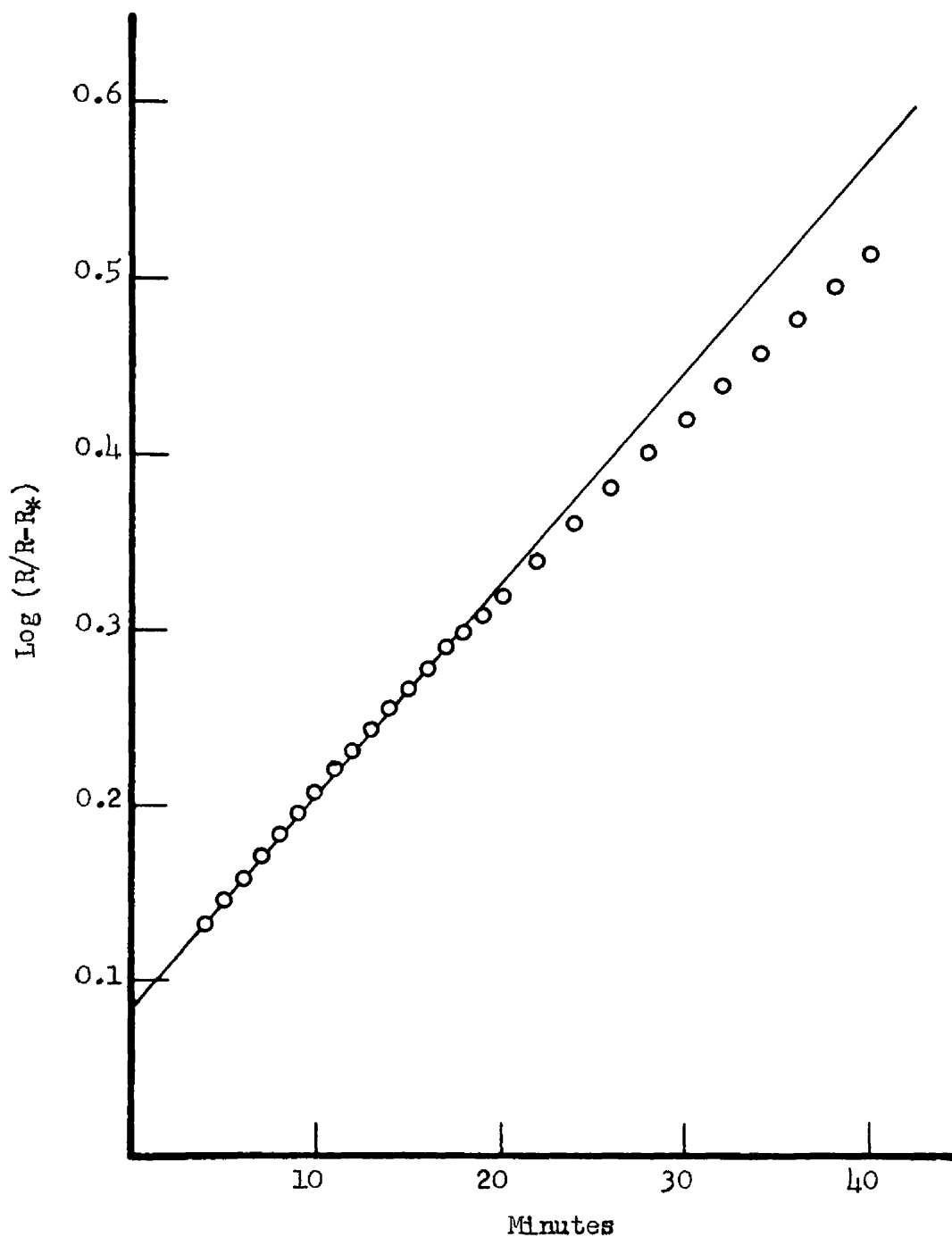


trifluoroacetate (which agreed within 10% with those obtained from studies on the pure ester) were calculated. Rate constants for this ester in 60% aqueous dioxane (Table 4) were all obtained in this manner, whereas those in 70% dioxane were obtained on the pure ester.

Rate constants for the solvolysis of cyclopropylmethylecarbonyl trifluoroacetate (the initial portion of the data) calculated from the kinetic data of the esterification mixture were about 50-100% slower than those obtained with the pure ester. The method used for these rate calculations was the same as that given later for methylnortriptylcarbonyl trifluoroacetate. The rate constants reported for cyclopropylmethylecarbonyl trifluoroacetate (Table 5) are those obtained on the pure ester.

Even when pure (at least 98%) cyclopropylmethylecarbonyl trifluoroacetate was solvolyzed, the plotted data (see Figure 15) frequently had a slight curvature. This curvature was most evident in the higher per cent dioxane solvents and at the lower temperatures; it was not observed in the lower per cent dioxane solvents at the higher temperatures. In all cases, the reported rate constants are only from that portion of the data that gave the initial straight line. A minimum of about 35-40% of the reaction (in 80% dioxane at 40°) and a maximum of about 90% of the reaction (in 60% dioxane at 60°) was used in calculating the reported rate constants. This curvature of the kinetic data for this ester is probably due to internal return of the cyclopropylmethylecarbonyl trifluoroacetate to 2-methylcyclobutyl trifluoroacetate which then solvolyzes at a measurable, but slower, rate than the original ester.

Figure 15. Plot of  $\log(R/R_{\infty})$  versus  $t$  for the Solvolysis of Cyclopropylmethylcarbinyl Trifluoroacetate in 70% Aqueous Dioxane at  $50^{\circ}$ . Data from Table 57.

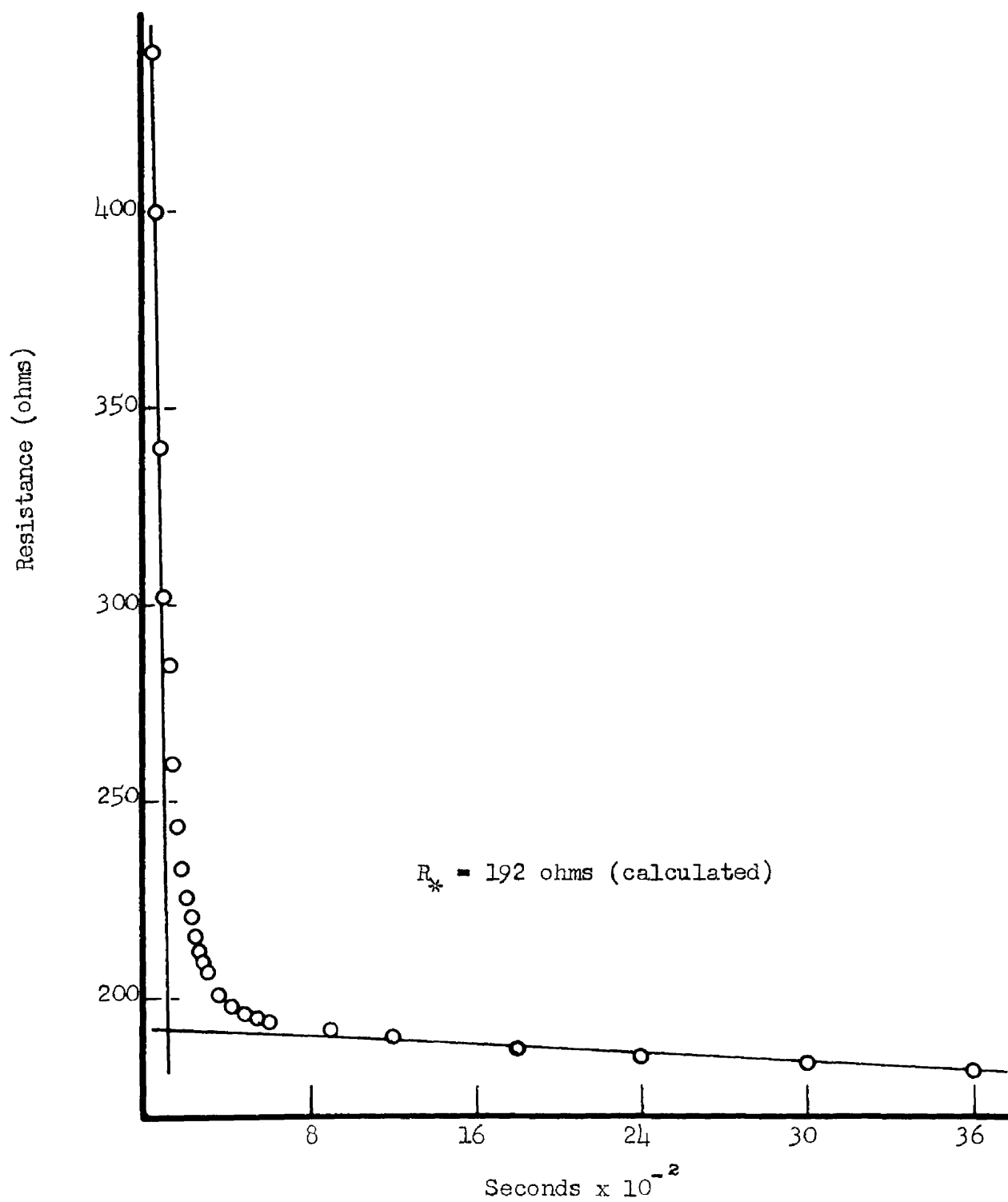


### Methylnortriacycliccarbonyl trifluoroacetate

Kinetic analysis of the distilled reaction mixture from the preparation of methylnortriacycliccarbonyl trifluoroacetate also gave curved plots (see Figure 14, curve B). The kinetic plots for this ester had much sharper breaks than those for cyclopropylmethylecarbonyl trifluoroacetate. The product could not be purified by fractionation or by vapor chromatography. A carbon and hydrogen analysis on a sample did not agree with the calculated values.

By analogy with kinetic studies on the esterification mixture of cyclopropylmethylecarbonyl, the faster solvolysing ester in this case is probably methylnortriacycliccarbonyl trifluoroacetate. Rate constants for the initial portion of the data were calculated in the following manner. From a plot of resistance versus time (see Figure 16) a calculated  $R_{\infty}$  was obtained by extrapolating the two approximately straight lines to their intersection. The resistance at this point was taken as the  $R_{\infty}$  value for the solvolysis of the faster solvolysing ester. Using this value of  $R_{\infty}$ , plots of  $\log(R/R_{\infty})$  versus  $t$  were made which were straight lines for the first part of the kinetic data. From the slope of these lines some rate constants for the solvolysis of methylnortriacycliccarbonyl trifluoroacetate were obtained. At  $50^{\circ}$  in 70% dioxane-30% water,  $k = 8.8 \times 10^{-3} \pm 0.3 \text{ sec.}^{-1}$  (four runs). Also at  $50^{\circ}$ , in 80% dioxane-20% water,  $k = 3.5 \times 10^{-4} \text{ sec.}^{-1}$  (one run). No attempt was made to analyze the slopes of the latter portion of the curves.

Figure 16. Plot of Resistance versus  $t$  for the Solvolysis of Methylnortricycylcarbinyl Trifluoroacetate in 70% Aqueous Dioxane at  $50^\circ$ . Data from Table 68.



### D. The Energetics

The Arrhenius activation energy,  $E_a$ , was calculated in the usual manner from

$$\log k = - (E_a/2.3 R)(1/T) + Z \quad (5)$$

Plots of  $\log k$  versus  $1/T$  for the esters in various solvents appear in Figures 19 to 29 in the Appendix. After obtaining the slope by the method of least squares the activation energy was calculated from

$$E_a = 2.3 R (-\text{slope})$$

where  $R = 1.987$  calories degree<sup>-1</sup> mole<sup>-1</sup>.

The enthalpy of activation,  $\Delta H^\ddagger$ , was calculated from the following equation.

$$\Delta H^\ddagger = E_a - RT \quad (6)$$

The entropy of activation,  $\Delta S^\ddagger$ , was calculated from the Eyring equation (28).

$$k = \frac{k_B T}{h} e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT} \quad (7)$$

or

$$\Delta S^\ddagger = 2.3 R \log \left( \frac{k h}{k_B T} \right) + \frac{\Delta H^\ddagger}{T} \quad (8)$$

where  $h$  = Planck's constant,  $6.623 \times 10^{-27}$  erg second

$k_B$  = Boltzmann constant,  $1.380 \times 10^{-16}$  erg degree<sup>-1</sup> molecule<sup>-1</sup>.

Values of  $\Delta H^*$  and  $\Delta S^*$  for the various reactions are listed in Table 7. The  $\Delta S^*$  values are the arithmetic mean of all of the  $\Delta S^*$  values calculated from equation (8) for each K obtained for a given ester in each solvent. The standard deviation from each mean value is also given.

Of particular interest are the similarities of the entropies and enthalpies of activation for the trifluoroacetates of cyclopropylcarbinol, norcycopylcarbinol, and 2-methylcyclobutanol as compared to the same energy factors for cyclopropylmethylcarbonyl trifluoroacetate.

A comparison of these energy factors with those obtained in other studies is given in Table 8. The trifluoroacetates of the primary alcohols and all of the secondary aliphatic alcohols except that of cyclopropylmethylcarbinol have relatively small enthalpies and large, negative entropies. In these cases the rate of solvolysis is controlled by the high orientation requirements of solvent molecules about the trifluoroacetate carbonyl group.

The entropies and enthalpies of activation for the solvolysis of cyclopropylmethylcarbonyl trifluoroacetate are similar to those for esters of tertiary alcohols studied by Moffat and Hunt (15) and by Hart and Sandri (12). The enthalpies are large while the entropies are relatively small, but still negative. This indicates that the rate controlling factor in these cases is the cleavage of the alkyl-oxygen bond (which would have a relatively large energy requirement).

TABLE 7

MOLAR ENTHALPIES AND ENTROPIES OF ACTIVATION FOR THE SOLVOLYSIS  
OF SEVERAL TRIFLUOROACETATES IN AQUEOUS DIOXANE

|                                | Weight Per Cent Dioxane      |                             |                              |                             |                              |                             |
|--------------------------------|------------------------------|-----------------------------|------------------------------|-----------------------------|------------------------------|-----------------------------|
|                                | 60                           |                             | 70                           |                             | 80                           |                             |
|                                | $\Delta H^\ddagger$<br>Kcal. | $\Delta S^\ddagger$<br>e.u. | $\Delta H^\ddagger$<br>Kcal. | $\Delta S^\ddagger$<br>e.u. | $\Delta H^\ddagger$<br>Kcal. | $\Delta S^\ddagger$<br>e.u. |
| Trifluoroacetate               |                              |                             |                              |                             |                              |                             |
| Cyclopropyl-<br>carbonyl       | 7.89                         | -49.6 $\pm$ 0.1             | 8.33                         | -51.4 $\pm$ 0.1             | 9.18                         | -50.5 $\pm$ 0.1             |
| Isopropyl-<br>carbonyl         | 10.8                         | -44.2 $\pm$ 0.2             | 11.0                         | -45.7 $\pm$ 0.1             | 12.3                         | -43.1 $\pm$ 0.1             |
| 2-Methylcyclo-<br>butyl        | 9.61                         | -45.2 $\pm$ 0.1             | 8.23                         | -52.3 $\pm$ 0.1             |                              |                             |
| Methylcyclopropyl-<br>carbonyl | 18.5                         | -12.3 $\pm$ 0.1             | 19.7                         | -13.0 $\pm$ 0.1             | 24.2                         | -0.56 $\pm$ 0.08            |



TABLE 8

COMPARISON OF MOLAR ENERGY FACTORS FOR THE SOLVOLYSIS OF VARIOUS  
ESTERS OF PRIMARY, SECONDARY AND TERTIARY ALCOHOLS

| Type of<br>Alcohol | Solvent                               |                                         |                             |                            |
|--------------------|---------------------------------------|-----------------------------------------|-----------------------------|----------------------------|
|                    | 70% Aqueous Dioxane                   |                                         | 70% Aqueous Acetone         |                            |
|                    | $\Delta H^\ddagger$ (kcal.)           | $\Delta S^\ddagger$ (e.u.)              | $\Delta H^\ddagger$ (kcal.) | $\Delta S^\ddagger$ (e.u.) |
| Primary            | 8.3 to 11.0 <sup>a</sup>              | -45.7 to -51.4 <sup>a</sup>             | 8.3 <sup>b</sup>            |                            |
| Secondary          | 8.2 <sup>c</sup><br>20.7 <sup>d</sup> | -52.3 <sup>e</sup><br>-9.7 <sup>d</sup> | 10.3 <sup>e</sup>           | -51.7 <sup>e</sup>         |
| Tertiary           | 19.7 <sup>f</sup>                     | -13.0 <sup>f</sup>                      | 24.4 <sup>g</sup>           | -4.25 <sup>g</sup>         |

<sup>a</sup>This thesis, cyclopropylcarbinyl and nortricycylcarbinyl trifluoroacetates

<sup>b</sup>Reference 14, n-butyl trifluoroacetate

<sup>c</sup>This thesis, 2-methylcyclobutyl trifluoroacetate

<sup>d</sup>This thesis, cyclopropylmethylecarbinyl trifluoroacetate

<sup>e</sup>Reference 16, methylpropylcarbinyl trifluoroacetate

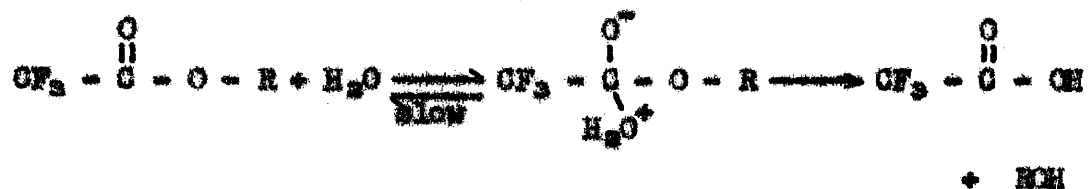
<sup>f</sup>Reference 12, diisopropylcyclopropylcarbinyl p-nitrobenzoate

<sup>g</sup>Reference 15, t-butyl trifluoroacetate

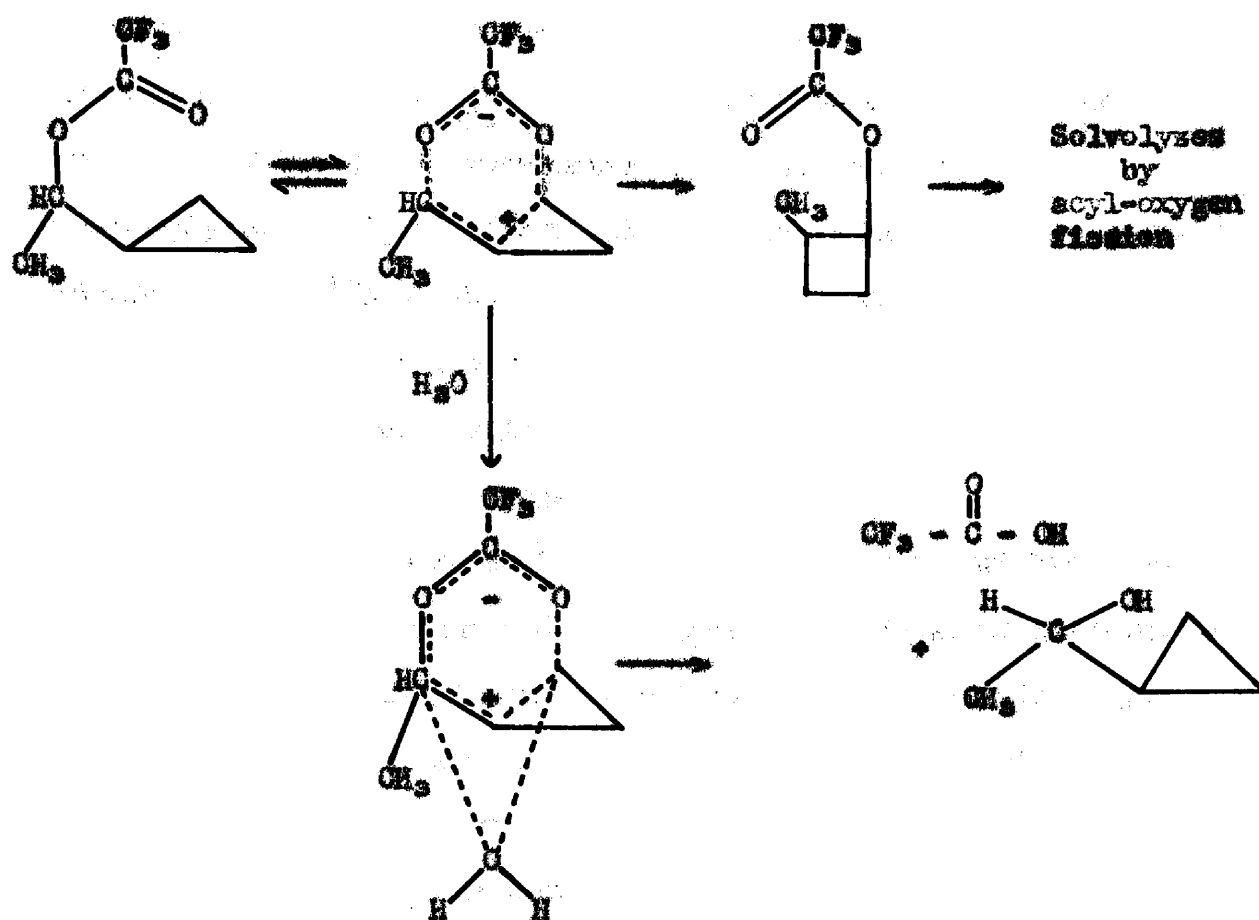
### E. Conclusions

It is apparent from the experimental results that the solvolyses of the trifluoroacetates reported in this thesis proceed by two different mechanisms.

The rates, enthalpies and entropies of activation, and the products from methanolysis are all consistent with the following mechanism (29b, 30) for the solvolyses of the trifluoroacetates of cyclopropylcarbinol, nortricycylcarbinol and 2-methylcyclobutanol.

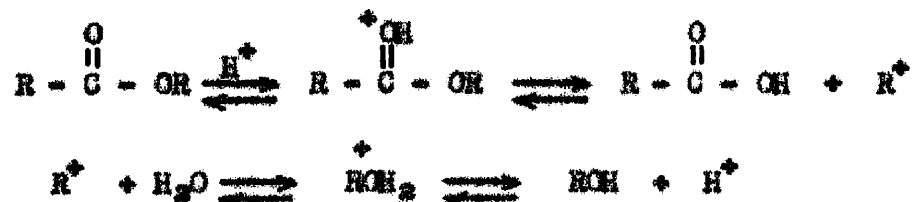


Cyclopropylmethylecarbonyl trifluoroacetate solvolyses with alkyl-oxygen fission and with simultaneous rearrangement. This was demonstrated by solvolysing this ester in methanol and showing that two of the products were cyclopropylmethylecarbonyl methyl ether and 2-methylcyclobutyl trifluoroacetate. By analogy with the work of Hart and Sandri (12) the mechanism of the solvolysis of this ester probably proceeds through an ion-pair intermediate, as summarized by the following scheme:



The proof of structure of the rearranged alcohol and measurement of the amount of rearrangement would place this postulated mechanism on a sounder basis.

In discussing the mechanism of the acid-catalyzed hydrolysis of esters of tertiary alcohols (as given below), Hine (30) has stated



that, "in order for this cleavage to occur without acid catalysis, the

carbonium ion to be formed should be more stable or the anion to be formed should be less basic, or both." From this, and considering the solvolyses of the trifluoroacetates of cyclopropylcarbinol and cyclopropylmethylcarbinol, it is evident that the stability of the secondary carbonium ion (  $\triangle^+ \text{CH-CH}_3$  ) that is formed is sufficiently greater than the stability of the primary carbonium ion (  $\triangle^+ \text{CH}_2$  , that would be formed if alkyl-oxygen fission had occurred) to allow for the observed duality of mechanisms for these two esters.

It should also be noted that the secondary-alkyl trifluoroacetates studied by Moffat and Hunt (16) solvolyzed by acyl-oxygen fission. For cyclopropylmethylcarbonyl trifluoroacetate to solvolyse via alkyl-oxygen fission, the cyclopropane ring must be aiding in stabilizing the carbonium ion that is formed.

By analogy, methylnortricycylcarbonyl trifluoroacetate probably solvolyzes by the same mechanism as the trifluoroacetate of cyclopropylmethylcarbinol. The faster rate of solvolysis of the ester of methylnortricycylcarbinol may be ascribed to a greater release of steric strain or to an enhanced stability of the carbonium ion formed in this case in contrast to the trifluoroacetate of cyclopropylmethylcarbinol.

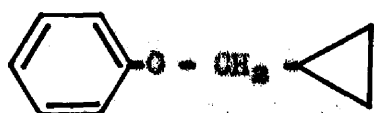
**PART II**

**THE SYNTHESIS AND ATTEMPTED THERMAL REARRANGEMENT  
OF CYCLOPROPYLCARBENYL PHENYL ETHER**

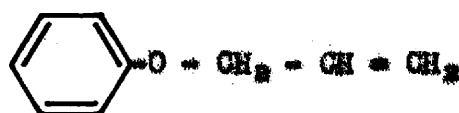
## INTRODUCTION

## INTRODUCTION

This part of the thesis is concerned with the synthesis and attempted thermal rearrangement of cyclopropylcarbinyl phenyl ether (I). In this ether the cyclopropane ring is in a position analogous to that of the carbon-carbon double bond in allyl phenyl ether (II).



(I)



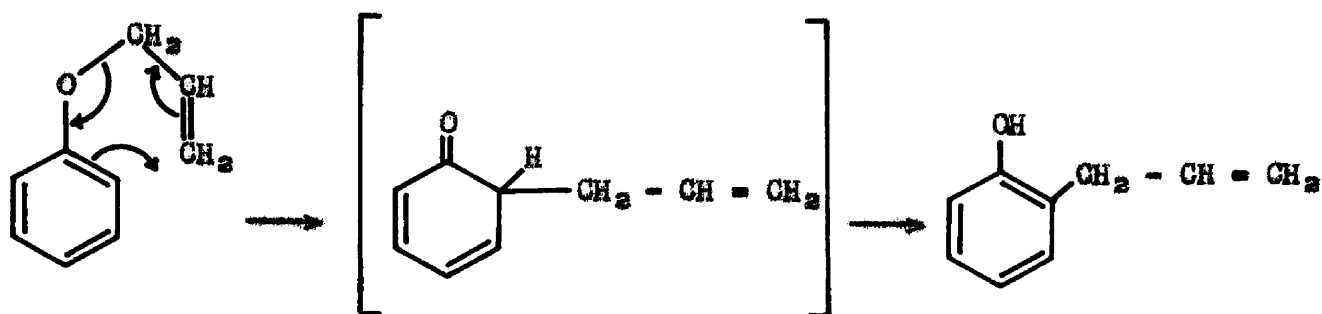
(II)

The Claisen rearrangement of allyl phenyl ethers has been extensively studied and two reviews have been written (32,33). Recent work has been concerned with the p-Claisen rearrangement (34).

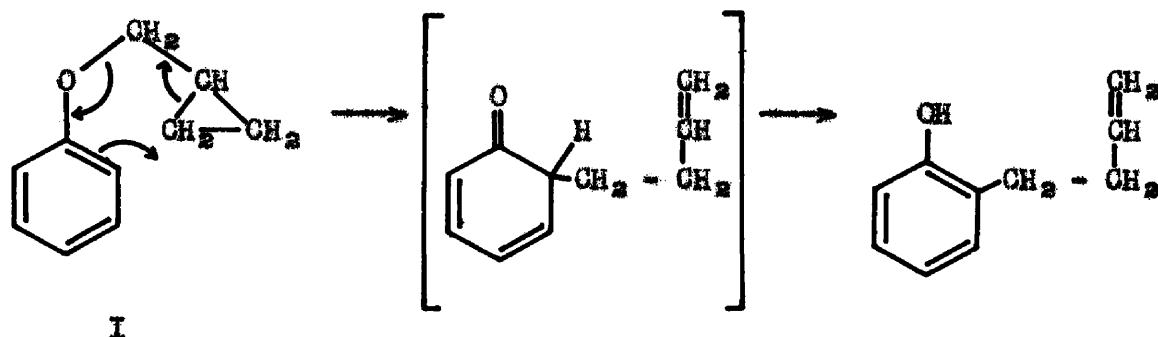
The structural arrangement of atoms necessary for the Claisen rearrangement is



The double bond on the right may be an aliphatic double bond, as in an enol ether or a vinyl ether, or part of an aromatic ring, as in the phenyl ethers (33). The rearrangement is best represented by a concerted cyclic mechanism, with the formation of a dienone intermediate which then enolizes to give the final product.



The similarities between the cyclopropane ring and the carbon-carbon double bond are well recognized (1). It was of interest, therefore, to determine whether cyclopropylcarbinyl phenyl ether (I) would undergo the Claisen rearrangement. A plausible mechanism analogous to that already demonstrated for allyl phenyl ether, and in agreement with the current concept of the cyclopropane ring, can be envisioned.



A partial increase in the positive character of the  $\alpha$ -carbon atom of the allyl group in the Claisen rearrangement has been postulated (34). Thus, in accord with the postulated resonance structures ascribed to the cyclopropylcarbinyl system in unimolecular displacements, it was further expected that cyclopropylcarbinyl phenyl ether would undergo a Claisen rearrangement.

This part of the thesis is concerned with the synthesis and attempted thermal rearrangement of cyclopropylcarbinyl phenyl ether.



## EXPERIMENTAL

## A. Synthesis of Cyclopropylmethyl Phenyl Ether

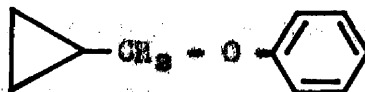
Method A. Displacement of the tosylate group by phenoxide ion (1).

A 300-ml. three-necked flask, fitted with a Hareberg stirrer, reflux condenser, thermometer ~~XXXXXXXXXX~~ funnel was charged with 25.4 ml. of 2,4,6-collidine and 7.2 g. (0.1 mole) of cyclopropylmethyl and cooled to  $-3^{\circ}$  in an ice-salt bath. p-Toluenesulfonyl chloride (16.0 g., 0.1 mole) in 50 ml. of methylene chloride was added in forty-five minutes, the temperature remaining below  $3^{\circ}$ . An additional 25 ml. of methylene chloride was added and stirring continued at about  $0^{\circ}$  for two hours. The collidine was neutralized with 25 ml. of 15 N sulfuric acid, the temperature remaining below  $15^{\circ}$ . The layers were separated and the aqueous layer extracted once with 25 ml. of methylene chloride. The combined methylene chloride solution was extracted three times with 20 ml. portions of ice-cold 2.5 N sulfuric acid and dried over potassium carbonate.

The solvent was removed at reduced pressure with no heat applied. The residue was a reddish oil. The red oil was dissolved in 50 ml. of anhydrous ether and added (30 minutes) to a suspension of sodium

## EXPERIMENTAL

## A. Synthesis of Cyclopropylcarbonyl Phenyl Ether

Method A. Displacement of the tosylate group by phenoxide ion (3).

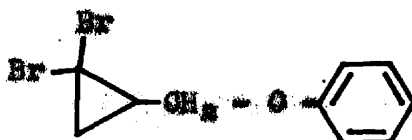
A 300-ml. three-necked flask, fitted with a Hersehberg stirrer, reflux condenser, thermometer and a dropping funnel was charged with 26.4 ml. of 2,4,6-collidine and 7.2 g. (0.1 mole) of cyclopropylcarbinol and cooled to  $-3^{\circ}$  in an ice-salt bath. p-Toluenesulfonyl chloride (19.0 g., 0.1 mole) in 50 ml. of methylene chloride was added in forty-five minutes, the temperature remaining below  $3^{\circ}$ . An additional 25 ml. of methylene chloride was added and stirring continued at about  $0^{\circ}$  for two hours. The collidine was neutralized with 25 ml. of 10 N sulfuric acid, the temperature remaining below  $15^{\circ}$ . The layers were separated and the aqueous layer extracted once with 25 ml. of methylene chloride. The combined methylene chloride solution was extracted three times with 20 ml.-portions of ice-cold 2.5 N sulfuric acid and dried over potassium carbonate.

The solvent was removed at reduced pressure with no heat applied. The residue was a reddish oil. The red oil was dissolved in 50 ml. of anhydrous ether and added (30 minutes) to a suspension of sodium

phenoxide, prepared from 250 g. of phenol and 34.5 g. (1.5 mole) of sodium in 200 ml. of ether, in a 1-l. three-necked flask fitted with a Hershberg stirrer, reflux condenser, thermometer and dropping funnel and cooled in an ice bath. The solution was then stirred at room temperature for five days. The solution was filtered and washed six times with 10% sodium hydroxide and twice with water. After removing the solvent distillation yielded 1.0 g. of cyclopropylcarbonyl phenyl ether, b.p. 45-48° at 2 mm.,  $n_D^{25}$  1.5189. It gave a negative ferric chloride test. This product was not analyzed, but it did have similar physical constants and an identical infrared spectrum with the same product prepared by a different method.

Method B. Carbene reaction on allyl phenyl ether (35).

(a) 2,2-Dibromocyclopropylcarbonyl phenyl ether (35).



Potassium tertiary butoxide (0.5 mole) was prepared from excess anhydrous tertiary butyl alcohol and 20 g. (0.5 mole) of potassium in a 2-l., three-necked flask fitted with a Hershberg stirrer, reflux condenser, thermometer and a dropping funnel. The excess tertiary butyl alcohol was removed by distillation and the potassium tertiary butoxide dried at about 100° at 1 mm. for four hours. After cooling in an ice bath and breaking up the potassium tertiary butoxide with a glass rod and with the stirrer, the white powder was covered with 165 g. (1.2 moles)

of allyl phenyl ether and 100 ml. of anhydrous pentane. Bromoform (126.5 g., 0.5 mole) was added with stirring in one hour. The mixture immediately turned orange-red and later became brown. Stirring was continued an additional five hours at room temperature, during which time an additional 200 ml. of pentane was added. After pouring into 200 ml. of water the organic layer was separated, the aqueous layer extracted once with 75 ml. of pentane and the combined pentane solutions dried over magnesium sulfate. Distillation gave recovered allyl phenyl ether (133 g.) and 41.2 g. of material, b.p. 119-126° at 1 mm. which solidified at room temperature. After several recrystallizations from ethanol the product (31.5 g., 21%) had a melting point of 53-54°.

Anal. Calc'd. for  $C_{10}H_{10}Br_2O$ : C, 39.23; H, 3.27; Br, 52.32

Found: C, 39.21, 39.06; H, 3.38, 3.31; Br, 52.43, 52.47

(b) Reduction of 2,2-dibromocyclopropylcarbonyl phenyl ether (36).

A 1-l. three-necked flask was fitted with an efficient reflux condenser, Hershberg stirrer and a dropping funnel and was charged with 100 ml. of 95% ethanol, 60 g. of Raney nickel alloy and 10.0 g (0.033 mole) of 2,2-dibromocyclopropylcarbonyl phenyl ether. This mixture was treated with 600 ml. of 10% sodium hydroxide (one hour). Addition was slow at first because there was an induction period before the base began reacting with the Raney-nickel alloy. The solution was refluxed an additional two hours, filtered, and the filtrate washed with 100 ml. of 10% sodium hydroxide and then with 400 ml. of pentane. The aqueous layer was poured into 400 ml. of concentrated hydrochloric acid and then

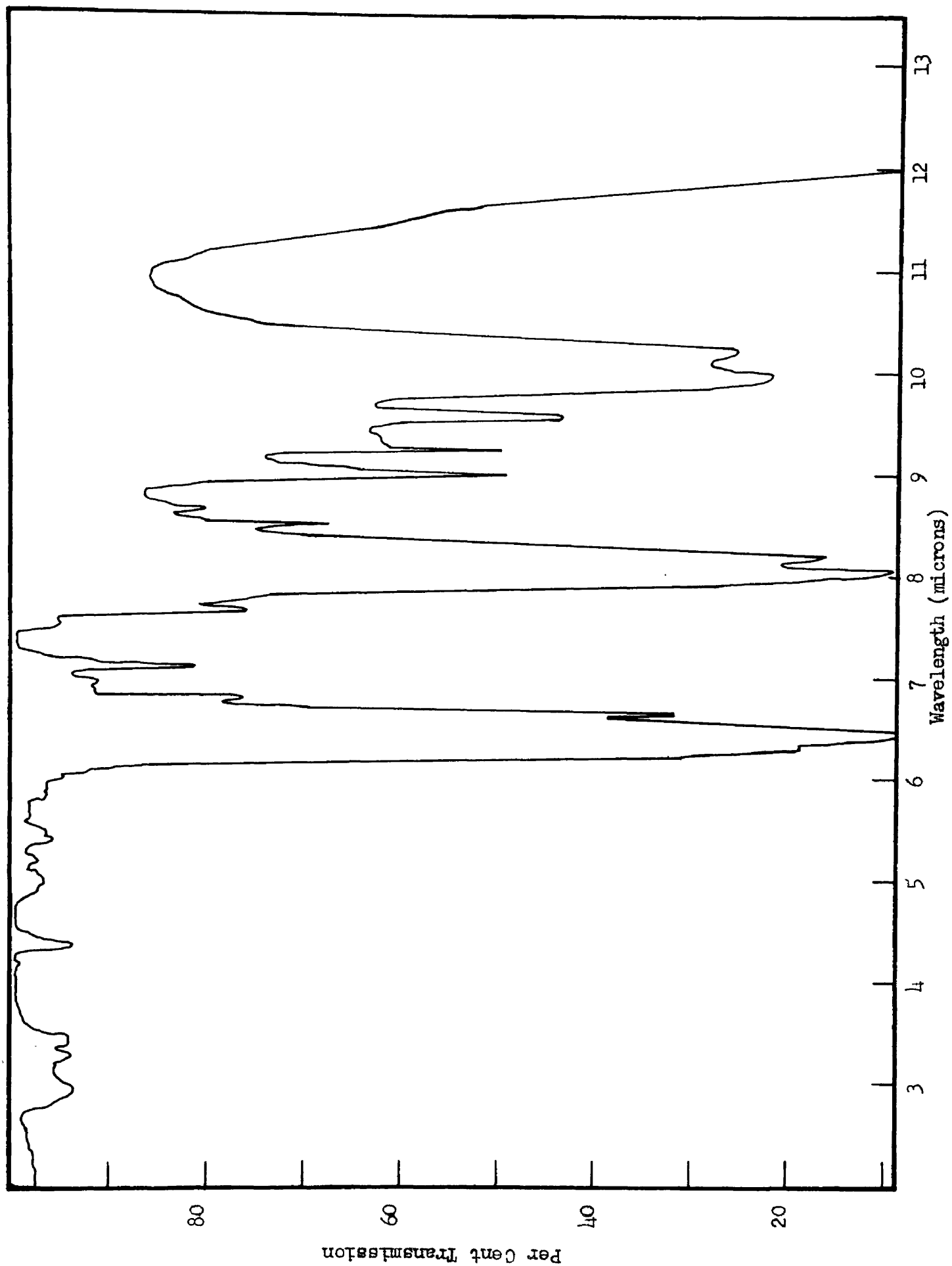


Figure 17. Infrared Spectrum of 2,2-Dibromocyclopropylcarbonyl Phenyl Ether ( $\text{CCl}_4$  solution).

extracted two times with 100 ml.-portions of pentane. After drying the combined pentane solutions over sodium sulfate and removing the solvent the product (3.0 g., 62%) distilled at  $43-55^{\circ}$  at 2 mm.

The product from several reductions were combined and fractionated to give cyclopropylcarbiny1 phenyl ether, b.p.  $51-53^{\circ}$  at 2 mm.,  $n_D^{25}$  1.5191-1.5199. It gave a negative ferric chloride test.

Anal. Calc'd. for  $C_{10}H_{12}O$ : C, 81.04; H, 8.17

Found: C, 81.11, 81.16; H, 8.29, 8.34

#### B. Attempted Thermal Rearrangement of Cyclopropylcarbiny1 Phenyl Ether

One ml. of cyclopropylcarbiny1 phenyl ether was refluxed ( $214^{\circ}$ ) at atmospheric pressure for six hours. After cooling, an infra red spectrum was obtained that was unchanged from that of the starting ether. Refluxing this solution for an additional twelve hours also did not change the infra red spectrum.

A one-ml. portion of the ether was heated in a sealed tube, whose volume was approximately 11 ml., at  $300 \pm 4^{\circ}$  for ten hours. The infra red spectrum of this material was identical with that of the starting ether. Both after refluxing for eighteen hours and after heating in a sealed tube the final material gave a negative ferric chloride test for phenols.

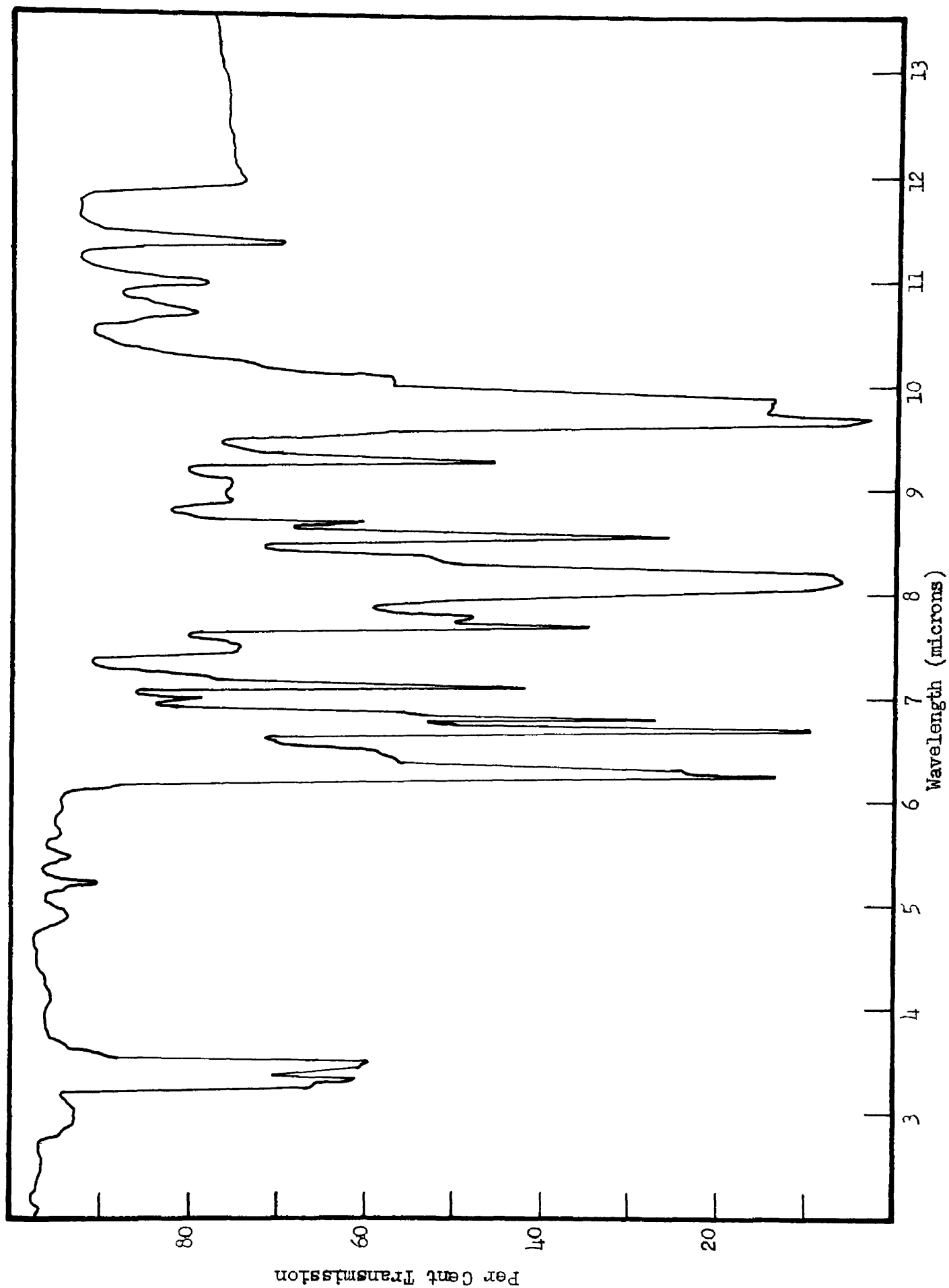


Figure 18. Infrared Spectrum of Cyclopropylcarbonyl Phenyl Ether ( $\text{CCl}_4$  solution).

## RESULTS AND DISCUSSION

10

11

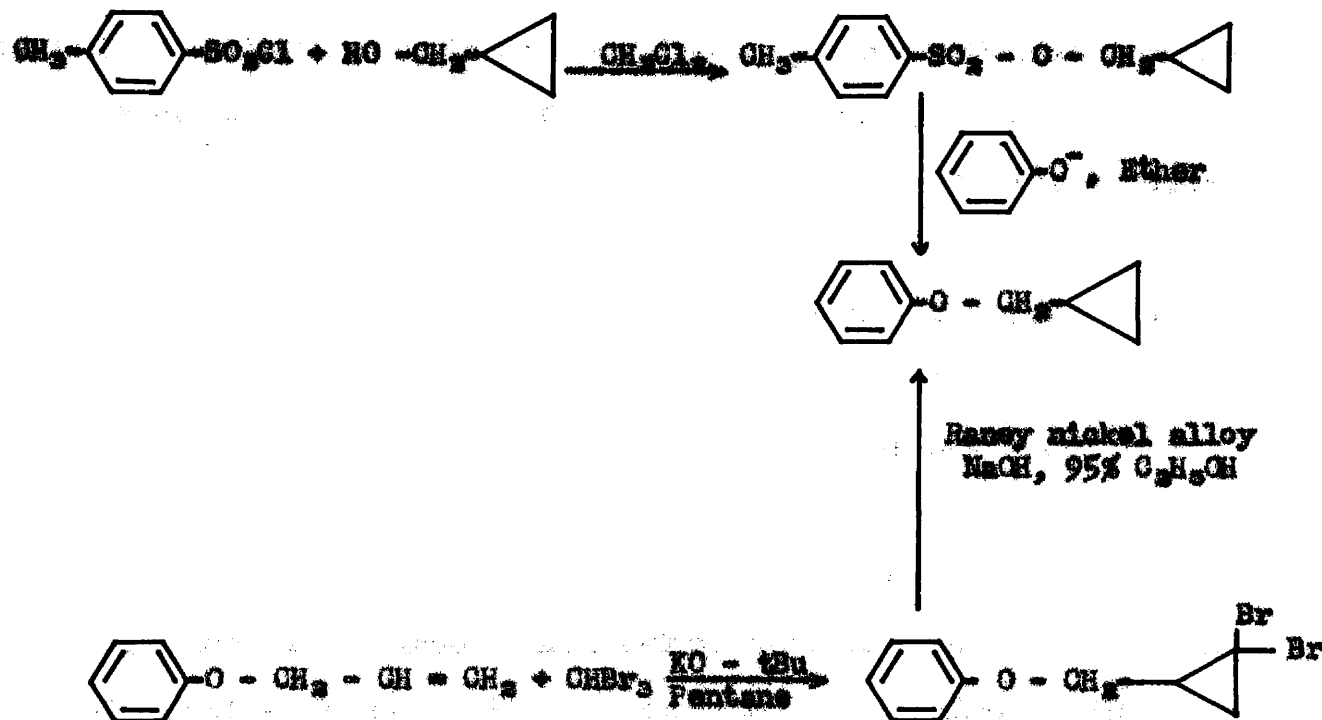
12

13



## RESULTS AND DISCUSSION

Cyclopropylcarbonyl phenyl ether was prepared by two independent methods, as outlined in the following scheme.



Bergstrom and Siegel (3) have shown that the benzenesulfonate of cyclopropylcarbinol in ethanol gives unrearranged cyclopropylcarbonyl ethyl ether. The tosylate derivative was used in the present work because it would be more stable than the benzenesulfonate. Also, the phenoxide ion should be a stronger nucleophilic reagent than ethyl alcohol and this should accord a more  $\text{S}_{\text{N}}2$  type reaction involving a smaller possibility for rearrangement.

Dihalocarbenes have been postulated as intermediates in the hydrolysis of haloforms with potassium *t*-butoxide (35,37,38). The intermediate dihalocarbene will add to olefins to give dihalocyclopropane derivatives. After dehalogenation (36) of the dihalocyclopropane compound obtained in this thesis, the product had similar physical properties and an identical infrared spectrum with that obtained by the first synthetic method. The second method was used to prepare a sufficient quantity of cyclopropylcarbinyl phenyl ether for the attempted rearrangement.

The Claisen rearrangement is a thermal reaction. The normal conditions used are temperatures of 200-240°C., with reaction periods of two to five hours. Occasionally a solvent such as diphenyl ether or *N,N*-diethylaniline has been used (33). The rate of rearrangement is not greatly affected by acetic acid or dimethylaniline (39).

Three attempts to cause a Claisen-type rearrangement of cyclopropylcarbinyl phenyl ether were made. The ether was first refluxed (214°C) for six hours and then for 18 hours. In the third attempt the ether was heated in a sealed tube at about 300°C., for ten hours. In all cases the infrared spectrum of the heated material was identical with the starting material and no positive ferric chloride test for phenols was observed.

It thus appears that despite a plausible mechanism, cyclopropylcarbinyl phenyl ether will not undergo a thermal Claisen-type rearrangement, and that in this particular case, the cyclopropane ring is not analogous to the carbon-carbon double bond.

## SUMMARY

1. The trifluoroacetates of cyclopropylcarbinal, neopentylcarbinal and cyclopropylmethylcarbinal were prepared and purified by conventional methods. A rearranged ester which is probably 2-methylcyclobutyl trifluoroacetate was also formed during the synthesis of cyclopropylmethylcarbonyl trifluoroacetate.

2. The rates of solvolysis of these esters were followed conductimetrically in several aqueous ~~alcoholic~~ solvents at several temperatures. Cyclopropylcarbonyl, neopentylcarbonyl and 2-methylcyclobutyl trifluoroacetates solvolyzed by acyl-oxygen fission. Thus, cyclopropylcarbonyl trifluoroacetate solvolyzed in methanolic diamine to give methyl trifluoroacetate and cyclopropylcarbinal. Also, 2-methylcyclobutyl trifluoroacetate in methanol gave only methyl trifluoroacetate and 2-methylcyclobutanol. The other ester, cyclopropylmethylcarbonyl trifluoroacetate, solvolyzed via alkyl-oxygen fission, as evidenced by solvolysis in methanol or 50% methanolic diamine to yield cyclopropylmethylcarbonyl methyl ether. The solvolysis appears to proceed with extensive rearrangement as a large percentage of methyl trifluoroacetate (presumably arising from rearranged ester) and 2-methylcyclobutanol were also observed in these solvolyses. The rates, solvent effects and entropies and enthalpies of activation for all of the esters are consistent with the mechanistic postulation (bond cleavage) mentioned above.

### SUMMARY

1. The trifluoroacetates of cyclopropylcarbinol, nortricycylcarbinol and cyclopropylmethylecarbinol were prepared and purified by conventional methods. A rearranged ester which is probably 2-methylcyclobutyl trifluoroacetate was also formed during the synthesis of cyclopropylmethylecarbiny l trifluoroacetate.

2. The rates of solvolysis of these esters were followed conductrimetrically in several aqueous dioxane solvents at several temperatures. Cyclopropylcarbiny l, nortricycylcarbiny l and 2-methylcyclobutyl trifluoroacetates solvolyzed by acyl-oxygen fission. Thus, cyclopropylcarbiny l trifluoroacetate solvolyzed in methanolic dioxane to give methyl trifluoroacetate and cyclopropylcarbinol. Also, 2-methylcyclobutyl trifluoroacetate in methanol gave only methyl trifluoroacetate and 2-methylcyclobutanol. The other ester, cyclopropylmethylecarbiny l trifluoroacetate, solvolyzed via alkyl-oxygen fission, as evidenced by solvolysis in methanol or 50% methanolic dioxane to yield cyclopropylmethylecarbiny l methyl ether. The solvolysis appears to proceed with extensive rearrangement as a large percentage of methyl trifluoroacetate (presumably arising from rearranged ester) and 2-methylcyclobutanol were also observed in these solvolyses. The rates, solvent effects and entropies and enthalpies of activation for all of the esters are consistent with the mechanistic postulates (bond cleavages) mentioned above.

3. Methylnortricyclohexylcarbinyl trifluoroacetate was also prepared but could not be purified. A few kinetic studies on the impure ester indicated that it solvolyzed by alkyl-oxygen fission, and that it was very reactive.

4. Cyclopropylcarbinyl phenyl ether was prepared by two independent methods and its thermal rearrangement was attempted. No rearrangement was observed.

## REFERENCES

1. For a review, see E. E. Regehr, "Advanced Organic Chemistry," Prentice-Hall, New York, 1954, pp. 218-222.
2. J. D. Roberts and R. E. Koser, *J. Am. Chem. Soc.*, **73**, 2509 (1951).
3. O. R. Bergstrom and E. E. Regehr, *J. Am. Chem. Soc.*, **74**, 115 (1952).
4. J. D. Roberts and V. G. Chambers, *J. Am. Chem. Soc.*, **73**, 928 (1951).
5. J. D. Roberts and R. E. Koser, *J. Am. Chem. Soc.*, **73**, 3422 (1951).
6. J. D. Roberts, W. Bennett and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3389 (1950).  
LITERATURE CITED
7. J. D. Roberts and W. Bennett, *J. Am. Chem. Soc.*, **76**, 1483 (1954).
8. J. D. Roberts, E. E. Trumbull, Jr., W. Bennett and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3386 (1950).
9. S. Winstein, H. H. Welbourn and K. Schreiber, *J. Am. Chem. Soc.*, **72**, 5795 (1950).
10. P. von R. Schleyer and R. E. O'Banner, Abstract of Papers, 124th Meeting of the American Chemical Society, Chicago, p. 7-19.
11. R. E. Pearson and S. H. Langer, *J. Am. Chem. Soc.*, **75**, 1065 (1953).
12. H. Hart and J. H. Seidel, *J. Am. Chem. Soc.*, **81**, 380 (1959).
13. E. H. Koser and S. Winstein, *J. Am. Chem. Soc.*, **78**, 1317 (1956).
14. A. Moffat and E. Hart, *J. Am. Chem. Soc.*, **79**, 54 (1957).
15. A. Moffat and E. Hart, *J. Am. Chem. Soc.*, **80**, 2905 (1958).
16. A. Moffat and E. Hart, *J. Am. Chem. Soc.*, **81**, 2082 (1959).
17. E. I. Gaylor, "Kinetics With Complex Metal Hydrides," International Publications, New York, 1955, p. 1011.
18. W. S. Washburn and J. H. Kinsley, *J. Am. Chem. Soc.*, **80**, 524 (1958).

## REFERENCES

1. For a review, see E. E. Royals, "Advanced Organic Chemistry," Prentice-Hall, New York, 1954, pp. 210-222.
2. J. D. Roberts and R. H. Masur, *J. Am. Chem. Soc.*, 73, 2509 (1951).
3. G. G. Bergstrom and S. Siegel, *J. Am. Chem. Soc.*, 74, 145 (1952).
4. J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, 73, 5084 (1951).
5. J. D. Roberts and R. H. Masur, *J. Am. Chem. Soc.*, 73, 3452 (1951).
6. J. D. Roberts, W. Bennett and R. Armstrong, *J. Am. Chem. Soc.*, 72, 3329 (1950).
7. J. D. Roberts and W. Bennett, *J. Am. Chem. Soc.*, 76, 4623 (1954).
8. J. D. Roberts, E. R. Turnbull, Jr., W. Bennett and R. Armstrong, *J. Am. Chem. Soc.*, 72, 3115 (1950).
9. S. Winstein, H. M. Walborsky and K. Schreiber, *J. Am. Chem. Soc.*, 72, 5795 (1950).
10. P. von. R. Schleyer and R. E. O'Connor, Abstract of Papers, 134th Meeting of the American Chemical Society, Chicago, p. P-39.
11. R. G. Pearson and S. H. Langer, *J. Am. Chem. Soc.*, 75, 1065 (1953).
12. H. Hart and J. M. Sandri, *J. Am. Chem. Soc.*, 81, 320 (1959).
13. E. M. Kosower and S. Winstein, *J. Am. Chem. Soc.*, 78, 4347 (1956).
14. A. Moffat and H. Hunt, *J. Am. Chem. Soc.*, 79, 54 (1957).
15. A. Moffat and H. Hunt, *J. Am. Chem. Soc.*, 80, 2985 (1958).
16. A. Moffat and H. Hunt, *J. Am. Chem. Soc.*, 81, 2082 (1959).
17. E. L. Gaylord, "Reductions With Complex Metal Hydrides," Interscience Publishers, New York, 1956, p. 1011.
18. W. H. Washburn and J. H. Mahoney, *J. Am. Chem. Soc.*, 80, 504 (1958).

19. R. Von Volkmann, K. W. Grossman, J. B. Daxler and G. E. Boord, J. Am. Chem. Soc., 71, 3595 (1949).
20. N. J. Denjanow and M. Boyarsko, Ber., 41, 43 (1908).
21. L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Second Edition, John Wiley and Sons, New York, 1958, (a) p. 149, (b) p. 30.
22. M. Avram, C. D. Nenitzescu and M. Marin, Chem. Ber., 90, 1430 (1957).
23. G. I. Posa, G. E. Arth, R. E. Beyler and L. H. Sarett, J. Am. Chem. Soc., 75, 422 (1953).
24. L. F. Fieser, "Experiments in Organic Chemistry," Third Edition, D. C. Heath, Boston, 1941, p. 284.
25. A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, New York, 1956, p. 28-29, 35-37.
26. F. Daniels, J. H. Mathews, et al., "Experimental Physical Chemistry," Fourth Edition, McGraw-Hill Book Co., New York, 1949, (a) p. 370, (b) p. 356.
27. A. G. Worthing and J. Gaffner, "Treatment of Experimental Data," John Wiley and Sons, New York, 1943.
28. S. Glasstone, K. J. Laidler and H. Eyring, "Theory of Rate Processes," McGraw-Hill Book Co., New York, 1940, p. 196.
29. C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, New York, 1953, (a) p. 763-764, (b) p. 752-752.
30. J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, 1956, Chap. 12.
31. A. Streitwieser, Jr., Chem. Revs., 56, 571 (1956).
32. D. S. Tarbell, Chem. Revs., 27, 495 (1940).
33. D. S. Tarbell, Organic Reactions, Vol. II, John Wiley and Sons, New York, 1944, p. 1.
34. E. Müller, "Neuere Anschauungen der Organischen Chemie," Springer-Verlag, Berlin, 1957, p. 404-406.



35. W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, 76, 6162 (1954).
36. H. Hart, *J. Am. Chem. Soc.*, 71, 1966 (1949).
37. P. S. Skell and A. V. Garner, *J. Am. Chem. Soc.*, 78, 3409, 5130 (1956).
38. W. von E. Doering and P. LaFlamme, *J. Am. Chem. Soc.*, 78, 5447 (1956).
39. D. S. Tarbell and J. F. Kincaid, *J. Am. Chem. Soc.*, 62, 728 (1940).
40. *Organic Syntheses, Collective Volume III*, John Wiley and Sons, New York, 1955, p. 221.
41. W. Shand, Jr., V. Shomaker and J. R. Fischer, *J. Am. Chem. Soc.*, 66, 636 (1944).
42. H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, 81, 247 (1959).
43. H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, 22, 1135 (1957).
44. H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, 78, 5694 (1956).
45. H. C. Brown and P. A. Tierney, *J. Am. Chem. Soc.*, 80, 1557 (1958).
46. H. C. Brown, *J. Am. Chem. Soc.*, 77, 6209 (1955).
47. B. A. Behn, *J. Org. Chem.*, 24, 728 (1959).
48. H. Hart and R. A. Martin, *J. Org. Chem.*, in press.

# TABLE 3

MEAN VALUES OF 0.1001 MOLES CYCLOPENTYLAMINE, TERTIARYAMINE,  
IN 50% DIETHYL-50% WATER AT 10.0°C.

| $\lambda$<br>mic. | $\lambda$<br>mic. | $\log \frac{1}{1-\alpha}$ |
|-------------------|-------------------|---------------------------|
| 3                 | 102.0             | 0.0000                    |
| 4                 | 88.0              | 0.0000                    |
| 5                 | 78.0              | 0.0000                    |
| 6                 | 70.0              | 0.0000                    |
| 7                 | 63.0              | 0.0000                    |
| 8                 | 57.0              | 0.0000                    |
| 9                 | 52.0              | 0.0000                    |
| 10                | 47.0              | 0.0000                    |
| 11                | 43.0              | 0.0000                    |
| 12                | 40.0              | 0.0000                    |
| 13                | 37.0              | 0.0000                    |
| 14                | 35.0              | 0.0000                    |
| 15                | 33.0              | 0.0000                    |
| 16                | 31.0              | 0.0000                    |
| 17                | 29.0              | 0.0000                    |
| 18                | 27.0              | 0.0000                    |
| 19                | 25.0              | 0.0000                    |
| 20                | 23.0              | 0.0000                    |
| 21                | 21.0              | 0.0000                    |
| 22                | 19.0              | 0.0000                    |
| 23                | 17.0              | 0.0000                    |
| 24                | 15.0              | 0.0000                    |
| 25                | 13.0              | 0.0000                    |
| 26                | 11.0              | 0.0000                    |
| 27                | 9.0               | 0.0000                    |
| 28                | 7.0               | 0.0000                    |
| 29                | 5.0               | 0.0000                    |
| 30                | 3.0               | 0.0000                    |

$$\begin{aligned} \epsilon_{\lambda} &= 22.1 \text{ cm}^2/\text{mole} \\ \epsilon &= 2.21 \times 10^{-4} \text{ cm}^2/\text{mole} \\ \epsilon &= 1.52 \times 10^{-4} \text{ cm}^2/\text{mole} \end{aligned}$$

TABLE 9

SOLVOLYSIS OF 0.1031 MOLAR CYCLOPROPYLCARBENYL TRIFLUOROACETATE  
IN 50% DIOXANE-50% WATER AT 40.3°C.

| $t$<br>min. | $R$<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-------------|-------------|---------------------------------|
| 3           | 118.0       | 0.0903                          |
| 6           | 88.0        | 0.1281                          |
| 9           | 74.0        | 0.1575                          |
| 12          | 59.0        | 0.2038                          |
| 15          | 52.0        | 0.2403                          |
| 18          | 47.0        | 0.2760                          |
| 21          | 43.4        | 0.3092                          |
| 24          | 40.3        | 0.3442                          |
| 27          | 37.8        | 0.3817                          |
| 30          | 35.9        | 0.4151                          |
| 33          | 34.2        | 0.4512                          |
| 36          | 32.8        | 0.4861                          |
| 39          | 31.8        | 0.5156                          |
| 42          | 30.8        | 0.5490                          |
| 45          | 29.8        | 0.5877                          |
| 48          | 28.9        | 0.6281                          |
| 51          | 28.3        | 0.6594                          |
| 54          | 27.7        | 0.6943                          |
| 57          | 27.1        | 0.7326                          |
| 60          | 26.7        | 0.7637                          |

$$R_{\infty} = 22.1 \text{ ohms}$$

$$k = 2.71 \times 10^{-2} \text{ min.}^{-1}$$

$$k = 4.52 \times 10^{-4} \text{ sec.}^{-1}$$

TABLE 10

SOLVOLYSIS OF 0.04863 Molar CYCLOPROPYLCARBONYL TRIFLUOROACETATE  
IN 50% DIOXANE-50% WATER AT 40.3°C.

| t<br>min. | R<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-----------|-----------|---------------------------------|
| 3         | 405       | 0.0416                          |
| 6         | 230       | 0.0763                          |
| 9         | 165       | 0.1102                          |
| 12        | 131.0     | 0.1443                          |
| 15        | 110.0     | 0.1781                          |
| 18        | 95.5      | 0.2122                          |
| 21        | 85.5      | 0.2453                          |
| 24        | 77.5      | 0.2808                          |
| 27        | 71.5      | 0.3151                          |
| 30        | 67.0      | 0.3475                          |
| 33        | 62.5      | 0.3867                          |
| 36        | 59.5      | 0.4204                          |
| 39        | 57.0      | 0.4527                          |
| 42        | 54.7      | 0.4876                          |
| 45        | 52.5      | 0.5270                          |
| 48        | 50.5      | 0.5697                          |
| 51        | 49.5      | 0.5943                          |
| 54        | 48.0      | 0.6359                          |
| 57        | 46.8      | 0.6746                          |
| 60        | 45.9      | 0.7076                          |

$$R_{\infty} = 36.9 \text{ ohms}$$

$$k = 2.69 \times 10^{-2} \text{ min.}^{-1}$$

$$k = 4.48 \times 10^{-2} \text{ sec.}^{-1}$$

TABLE 11

SOLVOLYSES OF 0.07530 MOLAR CYCLOHEXYLCARBIMIDE TRIFLUOROACETATE  
IN 60% DIOXANE-40% WATER AT 29.9°C.

| $t$<br>min. | $R$<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-------------|-------------|---------------------------------|
| 5           | 570         | 0.0279                          |
| 10          | 320         | 0.0550                          |
| 15          | 230         | 0.0785                          |
| 20          | 182         | 0.1017                          |
| 25          | 152         | 0.1248                          |
| 30          | 128.0       | 0.1463                          |
| 35          | 117.0       | 0.1706                          |
| 40          | 108.5       | 0.1940                          |
| 45          | 98.5        | 0.2175                          |
| 50          | 89.0        | 0.2418                          |
| 55          | 82.5        | 0.2681                          |
| 60          | 78.0        | 0.2900                          |
| 65          | 73.5        | 0.3160                          |
| 70          | 70.0        | 0.3399                          |
| 76          | 66.5        | 0.3679                          |
| 81          | 63.0        | 0.4011                          |
| 85          | 62.0        | 0.4121                          |
| 92          | 58.5        | 0.4551                          |
| 100         | 56.0        | 0.4929                          |
| 105         | 54.5        | 0.5189                          |
| 110         | 53.0        | 0.5481                          |

$$R_{\infty} = 38.0 \text{ ohms}$$

$$k = 1.13 \times 10^{-2} \text{ min.}^{-1}$$

$$k = 1.88 \times 10^{-4} \text{ sec.}^{-1}$$

TABLE 12

SOLVOLYSIS OF 0.1082 MNEAR CYCLOPROPYLCARBINYL TRIFLUOROACETATE  
IN 60% DIOXANE-40% WATER AT 40.3° C.

| t<br>min. | R<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-----------|-----------|---------------------------------|
| 2         | 445       | 0.0230                          |
| 3         | 330       | 0.0314                          |
| 6         | 195       | 0.0546                          |
| 10        | 130.0     | 0.0846                          |
| 15        | 94.5      | 0.1206                          |
| 20        | 75.0      | 0.1584                          |
| 25        | 63.0      | 0.1962                          |
| 30        | 55.0      | 0.2338                          |
| 35        | 49.0      | 0.2735                          |
| 40        | 45.0      | 0.3088                          |
| 45        | 41.2      | 0.3524                          |
| 50        | 38.2      | 0.3974                          |
| 55        | 36.1      | 0.4370                          |
| 60        | 34.2      | 0.4810                          |
| 65        | 32.8      | 0.5202                          |

$$R_{\infty} = 22.9 \text{ ohms}$$

$$k = 1.81 \times 10^{-3} \text{ min.}^{-1}$$

$$k = 3.01 \times 10^{-4} \text{ sec.}^{-1}$$

TABLE 13

SOLVOLYSIS OF 0.05313 MOLAR CYCLOPROPYLCARBINYL TRIFLUOROACETATE  
IN 60% DIOXANE-40% WATER AT 40.3°C.

| t<br>min. | R<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-----------|-----------|---------------------------------|
| 3         | 750       | 0.0260                          |
| 5         | 470       | 0.0438                          |
| 7         | 347       | 0.0603                          |
| 10        | 255       | 0.0842                          |
| 15        | 193       | 0.1153                          |
| 20        | 148.0     | 0.1575                          |
| 25        | 124.5     | 0.1942                          |
| 30        | 108.0     | 0.2332                          |
| 35        | 95.0      | 0.2778                          |
| 40        | 89.0      | 0.3049                          |
| 45        | 82.0      | 0.3444                          |
| 50        | 77.0      | 0.3800                          |
| 55        | 72.5      | 0.4195                          |
| 60        | 68.5      | 0.4629                          |
| 65        | 65.0      | 0.5097                          |
| 70        | 63.0      | 0.5417                          |
| 75        | 61.0      | 0.5785                          |
| 80        | 59.0      | 0.6216                          |

$R_{\infty} = 44.9$  ohms  
 $k = 1.77 \times 10^{-3} \text{ min.}^{-1}$   
 $k = 2.94 \times 10^{-4} \text{ sec.}^{-1}$

TABLE 1A

SOLVOLYSIS OF 0.04516 MOLAR CYCLOPROPYLAMMONIUM TRIFLUOROACETATE  
IN 60% DIOXANE-40% WATER AT 49.6°C.

| $t$<br>min. | $R$<br>ohms | $\log \frac{R}{R - R_0}$ |
|-------------|-------------|--------------------------|
| 3           | 615         | 0.0354                   |
| 6           | 303         | 0.0752                   |
| 9           | 213         | 0.1109                   |
| 12          | 169         | 0.1452                   |
| 15          | 141.0       | 0.1704                   |
| 18          | 122.5       | 0.2130                   |
| 21          | 110.0       | 0.2455                   |
| 24          | 100.0       | 0.2799                   |
| 27          | 92.5        | 0.3130                   |
| 30          | 86.5        | 0.3460                   |
| 33          | 81.5        | 0.3797                   |
| 36          | 77.0        | 0.4166                   |
| 39          | 73.5        | 0.4513                   |
| 42          | 70.5        | 0.4864                   |
| 45          | 68.0        | 0.5208                   |
| 48          | 66.0        | 0.5524                   |
| 51          | 64.0        | 0.5887                   |
| 54          | 62.5        | 0.6198                   |
| 57          | 61.0        | 0.6550                   |

$$R_0 = 47.5 \text{ ohms}$$

$$k = 2.62 \times 10^{-2} \text{ min.}^{-1}$$

$$k = 4.37 \times 10^{-4} \text{ sec.}^{-1}$$



TABLE 15

SOLYLYSIS OF 0.1031 Molar CHLOROPROPYL CARBENYL TRIFLUOROACETATE  
IN 60% DIOXANE-40% WATER AT 50.1°C.

| $t$<br>min. | $R$<br>ohms | $\log \frac{R}{R - R_0}$ |
|-------------|-------------|--------------------------|
| 3           | 300         | 0.0330                   |
| 6           | 149.0       | 0.0693                   |
| 9           | 104.0       | 0.1031                   |
| 12          | 79.5        | 0.1370                   |
| 15          | 65.5        | 0.1729                   |
| 18          | 57.0        | 0.2057                   |
| 21          | 50.0        | 0.2440                   |
| 24          | 45.2        | 0.2803                   |
| 27          | 41.6        | 0.3160                   |
| 30          | 38.5        | 0.3552                   |
| 33          | 36.3        | 0.3897                   |
| 36          | 34.2        | 0.4302                   |
| 39          | 32.7        | 0.4651                   |
| 42          | 31.3        | 0.5043                   |
| 45          | 30.1        | 0.5411                   |
| 48          | 29.1        | 0.5831                   |
| 51          | 28.3        | 0.6193                   |
| 54          | 27.5        | 0.6540                   |

$$R_0 = 21.5 \text{ ohms}$$

$$k = 2.82 \times 10^{-2} \text{ min.}^{-1}$$

$$k = 4.70 \times 10^{-4} \text{ sec.}^{-1}$$

TABLE 16

SOLVOLYSIS OF 0.07283 MOLAR OCTYLPHENYLENEVINYL TRIFLUOROACETATE  
IN 60% DIOXANE-40% WATER AT 59.6°C.

| $t$<br>min. | $R$<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-------------|-------------|---------------------------------|
| 2           | 270         | 0.0157                          |
| 3           | 195         | 0.0618                          |
| 4           | 158         | 0.0814                          |
| 5           | 131.0       | 0.1004                          |
| 6           | 113.0       | 0.1186                          |
| 7           | 100.5       | 0.1358                          |
| 8           | 91.0        | 0.1529                          |
| 9           | 82.5        | 0.1720                          |
| 10          | 77.0        | 0.1875                          |
| 11          | 72.0        | 0.2041                          |
| 12          | 67.5        | 0.2219                          |
| 13          | 63.5        | 0.2406                          |
| 14          | 60.0        | 0.2596                          |
| 15          | 57.5        | 0.2793                          |
| 16          | 55.0        | 0.2931                          |
| 17          | 53.0        | 0.3092                          |
| 18          | 51.0        | 0.3274                          |
| 19          | 49.2        | 0.3456                          |
| 20          | 47.6        | 0.3638                          |
| 21          | 46.1        | 0.3827                          |
| 22          | 44.8        | 0.4009                          |
| 23          | 43.8        | 0.4161                          |
| 24          | 42.7        | 0.4346                          |
| 25          | 41.8        | 0.4509                          |
| 26          | 40.9        | 0.4686                          |
| 27          | 39.9        | 0.4904                          |
| 28          | 39.1        | 0.5093                          |
| 29          | 38.5        | 0.5248                          |
| 30          | 37.9        | 0.5412                          |

$$R_{\infty} = 27.0 \text{ ohms}$$

$$k = 4.07 \times 10^{-2} \text{ min.}^{-1}$$

$$k = 6.78 \times 10^{-4} \text{ sec.}^{-1}$$

TABLE 17

SOLVOLYSIS OF 0.0385M NOLAR CYCLOPROPYLSANBINE TRIFLUOROACETATE  
IN 60% DIOXANE-40% WATER AT 69.1°C.

| t<br>min. | R<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-----------|-----------|---------------------------------|
| 1         | 860       | 0.0228                          |
| 2         | 480       | 0.0418                          |
| 3         | 340       | 0.0603                          |
| 4         | 270       | 0.0774                          |
| 5         | 220       | 0.0949                          |
| 6         | 190       | 0.1113                          |
| 7         | 168       | 0.1279                          |
| 8         | 151       | 0.1400                          |
| 9         | 138.0     | 0.1550                          |
| 10        | 127.0     | 0.1627                          |
| 11        | 119.5     | 0.1770                          |
| 12        | 110.5     | 0.2180                          |
| 13        | 104.0     | 0.2360                          |
| 14        | 99.5      | 0.2504                          |
| 15        | 95.0      | 0.2660                          |
| 16        | 90.5      | 0.2856                          |
| 17        | 87.2      | 0.3010                          |
| 18        | 84.0      | 0.3179                          |
| 19        | 81.0      | 0.3357                          |
| 20        | 78.5      | 0.3520                          |
| 21        | 76.3      | 0.3679                          |
| 22        | 74.3      | 0.3838                          |
| 23        | 72.5      | 0.3995                          |
| 25        | 70.7      | 0.4165                          |

$$R_{\infty} = 43.6 \text{ ohms}$$

$$k = 3.94 \times 10^{-2} \text{ min.}^{-1}$$

$$k = 6.57 \times 10^{-4} \text{ sec.}^{-1}$$

TABLE 18

SOLVOLYSIS OF 0.1032 Molar CHLOROPROPYL CARBINYL TRIFLUOROACRYLATE  
IN 70% DIOXANE-30% WATER AT 29.9° C.

| t<br>min. | R<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-----------|-----------|---------------------------------|
| 20        | 2510      | 0.0378                          |
| 41        | 1610      | 0.0607                          |
| 60        | 1270      | 0.0785                          |
| 80        | 1050      | 0.0969                          |
| 100       | 910       | 0.1133                          |
| 120       | 800       | 0.1316                          |
| 140       | 720       | 0.1489                          |
| 160       | 660       | 0.1652                          |
| 180       | 605       | 0.1811                          |
| 200       | 560       | 0.2028                          |
| 220       | 525       | 0.2204                          |
| 240       | 498       | 0.2363                          |
| 260       | 468       | 0.2570                          |
| 280       | 442       | 0.2781                          |
| 300       | 423       | 0.2960                          |
| 320       | 403       | 0.3174                          |
| 350       | 382       | 0.3440                          |
| 380       | 365       | 0.3770                          |
| 400       | 351       | 0.3930                          |

$$R_{\infty} = 209 \text{ ohms}$$

$$k = 2.11 \times 10^{-3} \text{ min.}^{-1}$$

$$k = 3.56 \times 10^{-5} \text{ sec.}^{-1}$$

TABLE 19

SOLVOLYSIS OF 0.050M N-HEXANOYL CYCLOHEXYLAMMONIUM TRIFLUOROMETHANE  
IN 70% DIOXANE-30% WATER AT 40.3°C.

| $t$<br>min. | $R$<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-------------|-------------|---------------------------------|
| 7           | 3780        | 0.0010                          |
| 10          | 3310        | 0.0073                          |
| 15          | 2780        | 0.0585                          |
| 20          | 2470        | 0.0813                          |
| 25          | 2190        | 0.0733                          |
| 30          | 1990        | 0.0813                          |
| 35          | 1820        | 0.0899                          |
| 40          | 1620        | 0.0976                          |
| 45          | 1580        | 0.1018                          |
| 50          | 1485        | 0.1126                          |
| 55          | 1410        | 0.1199                          |
| 60          | 1340        | 0.1271                          |
| 65          | 1275        | 0.1318                          |
| 70          | 1220        | 0.1408                          |
| 75          | 1170        | 0.1492                          |
| 80          | 1125        | 0.1562                          |
| 85          | 1085        | 0.1632                          |
| 90          | 1050        | 0.1700                          |
| 95          | 1020        | 0.1761                          |
| 100         | 980         | 0.1850                          |
| 121         | 875         | 0.2138                          |
| 160         | 738         | 0.2681                          |
| 201         | 630         | 0.3169                          |
| 296         | 515         | 0.4688                          |

$$R_{\infty} = 340 \text{ ohms}$$

$$k = 3.40 \times 10^{-3} \text{ min.}^{-1}$$

$$k = 5.67 \times 10^{-5} \text{ sec.}^{-1}$$

TABLE 20

SOLVOLYSIS OF 0.1025 Molar CYCLOHEPTYLSANBUTYL TRIFLUOROSULFATE  
IN 70% DICHLOROMETHANE-30% WATER AT 40.3°C.

| t<br>min. | R<br>ohms | $\log \frac{R}{R - R_0}$ |
|-----------|-----------|--------------------------|
| 5         | 2690      | 0.0318                   |
| 10        | 2070      | 0.0618                   |
| 15        | 1810      | 0.0846                   |
| 20        | 1475      | 0.0999                   |
| 25        | 1315      | 0.0878                   |
| 30        | 1180      | 0.0783                   |
| 35        | 1085      | 0.0835                   |
| 40        | 1000      | 0.0917                   |
| 45        | 930       | 0.0993                   |
| 50        | 875       | 0.1062                   |
| 55        | 825       | 0.1136                   |
| 60        | 780       | 0.1212                   |
| 65        | 745       | 0.1278                   |
| 70        | 712       | 0.1348                   |
| 75        | 678       | 0.1427                   |
| 80        | 650       | 0.1501                   |
| 85        | 627       | 0.1569                   |
| 90        | 603       | 0.1644                   |
| 95        | 582       | 0.1717                   |
| 116       | 510       | 0.2025                   |
| 155       | 421       | 0.2608                   |
| 205       | 351       | 0.3385                   |
| 300       | 285       | 0.4771                   |

$$R_0 = 190 \text{ ohms}$$

$$k = 3.37 \times 10^{-3} \text{ min.}^{-1}$$

$$k = 5.62 \times 10^{-5} \text{ sec.}^{-1}$$

TABLE 21

SOLVOLYSIS OF 0.09733 Molar CYCLOHEXYLCARBONYL TRIFLUOROACETATE  
IN 70% DIKANE-30% WATER AT 50.1°C.

| $t$<br>min. | $R$<br>ohms | $\log \frac{R}{R - R_\infty}$ |
|-------------|-------------|-------------------------------|
| 10          | 1910        | 0.0441                        |
| 20          | 1210        | 0.0720                        |
| 30          | 920         | 0.0976                        |
| 40          | 735         | 0.1258                        |
| 50          | 650         | 0.1455                        |
| 60          | 575         | 0.1605                        |
| 70          | 515         | 0.1934                        |
| 80          | 475         | 0.2148                        |
| 90          | 439         | 0.2373                        |
| 100         | 400         | 0.2624                        |
| 110         | 382         | 0.2876                        |
| 120         | 362         | 0.3107                        |
| 130         | 343         | 0.3367                        |
| 140         | 329         | 0.3589                        |
| 150         | 315         | 0.3843                        |
| 160         | 301         | 0.4111                        |
| 170         | 291         | 0.4385                        |
| 180         | 282         | 0.4634                        |
| 190         | 274         | 0.4884                        |
| 200         | 267         | 0.5127                        |

$$R_\infty = 185 \text{ ohms}$$

$$k = 5.63 \times 10^{-3} \text{ min.}^{-1}$$

$$k = 9.38 \times 10^{-5} \text{ sec.}^{-1}$$

TABLE 22

SOLVOLYSIS OF 0.1908 Molar CYCLOPHOPHILCARBINYL TRIFLUOROACETATE  
IN 70% DIKLANE-30% WATER AT 19.8°C.

| $t$<br>min. | $R$<br>ohms | $\log \frac{R}{R - R_0}$ |
|-------------|-------------|--------------------------|
| 10          | 1510        | 0.0737                   |
| 20          | 1225        | 0.0945                   |
| 30          | 1020        | 0.1166                   |
| 40          | 875         | 0.1393                   |
| 50          | 775         | 0.1611                   |
| 60          | 700         | 0.1824                   |
| 80          | 585         | 0.2294                   |
| 100         | 510         | 0.2702                   |
| 120         | 458         | 0.3224                   |
| 140         | 416         | 0.3744                   |
| 160         | 386         | 0.4186                   |
| 180         | 363         | 0.4700                   |
| 200         | 341         | 0.5153                   |
| 220         | 328         | 0.5714                   |
| 240         | 318         | 0.6103                   |
| 270         | 301         | 0.6932                   |

$$R_0 = 240 \text{ ohms}$$

$$k = 5.47 \times 10^{-3} \text{ min.}^{-1}$$

$$k = 9.12 \times 10^{-5} \text{ sec.}^{-1}$$



TABLE 23

DECOMPOSITION OF 0.05731 MOLAR CHLOROPROPYLCAFFEINYL TRIFLUOROACETATE  
IN 70% DIOXANE-30% WATER AT 59.6°C.

| $t$<br>min. | $R$<br>ohms | $\log \frac{R}{R - R_\infty}$ |
|-------------|-------------|-------------------------------|
| 5           | 2800        | 0.0457                        |
| 10          | 1990        | 0.0659                        |
| 15          | 1570        | 0.0839                        |
| 20          | 1320        | 0.1018                        |
| 25          | 1140        | 0.1202                        |
| 30          | 1030        | 0.1355                        |
| 35          | 920         | 0.1550                        |
| 40          | 850         | 0.1706                        |
| 45          | 790         | 0.1867                        |
| 50          | 740         | 0.2028                        |
| 55          | 700         | 0.2177                        |
| 60          | 660         | 0.2353                        |
| 65          | 625         | 0.2531                        |
| 70          | 600         | 0.2676                        |
| 75          | 575         | 0.2840                        |
| 80          | 552         | 0.3010                        |
| 85          | 530         | 0.3195                        |
| 90          | 510         | 0.3383                        |
| 95          | 496         | 0.3531                        |
| 100         | 481         | 0.3703                        |
| 105         | 468         | 0.3869                        |
| 110         | 458         | 0.4007                        |
| 115         | 448         | 0.4158                        |

$$R_\infty = 276 \text{ ohms}$$

$$k = 7.71 \times 10^{-3} \text{ min.}^{-1}$$

$$k = 1.29 \times 10^{-4} \text{ sec.}^{-1}$$

TABLE 24

SOLVOLYSIS OF 0.1126 MOLAR CHLOROPHTHALIC ANHYDRIDE TRIFLUOROACETATE  
IN 70% DIOXANE-30% WATER AT 60.1°C.

| $t$<br>min. | $R$<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-------------|-------------|---------------------------------|
| 3           | 3110        | 0.0275                          |
| 4           | 2630        | 0.0326                          |
| 5           | 2310        | 0.0374                          |
| 10          | 1905        | 0.0528                          |
| 15          | 1160        | 0.0781                          |
| 20          | 965         | 0.0959                          |
| 25          | 824         | 0.1143                          |
| 30          | 727         | 0.1323                          |
| 35          | 655         | 0.1498                          |
| 40          | 600         | 0.1664                          |
| 45          | 551         | 0.1850                          |
| 50          | 513         | 0.2022                          |
| 55          | 480         | 0.2204                          |
| 60          | 452         | 0.2385                          |
| 65          | 427         | 0.2574                          |
| 70          | 406         | 0.2760                          |
| 75          | 388         | 0.2945                          |
| 80          | 371         | 0.3141                          |
| 85          | 356         | 0.3340                          |
| 90          | 342         | 0.3551                          |

$$R_{\infty} = 191 \text{ ohms}$$

$$k = 8.47 \times 10^{-3} \text{ min.}^{-1}$$

$$k = 1.41 \times 10^{-4} \text{ sec.}^{-1}$$

TABLE 25

SOLVOLYSIS OF 0.03807 Molar CHLOROPROPYL CARBINYL TRIFLUOROACETATE  
IN 80% HEXANE-20% WATER AT 40.0°C.

| $t$<br>min. | $R$<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-------------|-------------|---------------------------------|
| 50          | 11150       | 0.0704                          |
| 60          | 10450       | 0.0770                          |
| 90          | 8300        | 0.0997                          |
| 120         | 7050        | 0.1199                          |
| 150         | 6250        | 0.1380                          |
| 180         | 5600        | 0.1571                          |
| 210         | 5120        | 0.1758                          |
| 240         | 4760        | 0.1917                          |
| 270         | 4430        | 0.2103                          |
| 300         | 4160        | 0.2281                          |
| 330         | 3950        | 0.2445                          |
| 360         | 3730        | 0.2611                          |
| 390         | 3570        | 0.2808                          |
| 420         | 3420        | 0.2984                          |
| 450         | 3300        | 0.3143                          |
| 480         | 3180        | 0.3322                          |
| 510         | 3070        | 0.3504                          |
| 540         | 2960        | 0.3670                          |
| 570         | 2890        | 0.3854                          |
| 600         | 2800        | 0.4057                          |

$$R_{\infty} = 1700 \text{ ohms}$$

$$k = 1.39 \times 10^{-3} \text{ min.}^{-1}$$

$$k = 2.32 \times 10^{-5} \text{ sec.}^{-1}$$

TABLE 26

SOLVOLYSIS OF 0.09791 Molar CYCLOPROPYLCARBINYL TRIFLUOROACETATE  
IN 80% DICKANE-20% WATER AT 50.1°C.

| t<br>min. | R<br>ohms | $\log \frac{R}{R - R_0}$ |
|-----------|-----------|--------------------------|
| 20        | 11500     | 0.0438                   |
| 40        | 7200      | 0.0719                   |
| 62        | 5600      | 0.0948                   |
| 82        | 4700      | 0.1159                   |
| 100       | 4110      | 0.1351                   |
| 120       | 3680      | 0.1517                   |
| 140       | 3320      | 0.1746                   |
| 160       | 3040      | 0.1951                   |
| 180       | 2810      | 0.2156                   |
| 200       | 2630      | 0.2353                   |
| 220       | 2490      | 0.2531                   |
| 240       | 2330      | 0.2774                   |
| 260       | 2200      | 0.3010                   |
| 280       | 2100      | 0.3222                   |
| 300       | 2040      | 0.3365                   |
| 320       | 1970      | 0.3519                   |
| 352       | 1860      | 0.3886                   |
| 360       | 1820      | 0.4028                   |
| 380       | 1760      | 0.4260                   |
| 400       | 1710      | 0.4476                   |

$$R_0 = 1100 \text{ ohms}$$

$$k = 2.39 \times 10^{-3} \text{ min.}^{-1}$$

$$k = 3.98 \times 10^{-5} \text{ sec.}^{-1}$$

TABLE 27

SOLVOLYSIS OF 0.08940 Molar CYCLOPROPYLCARBINYL TRIFLUOROACRYATE  
IN 80% DICKANE-20% WATER AT 50.1°C.

| $t$<br>min. | $R$<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-------------|-------------|---------------------------------|
| 20          | 12300       | 0.0770                          |
| 40          | 9750        | 0.0997                          |
| 50          | 8600        | 0.1119                          |
| 60          | 7750        | 0.1335                          |
| 80          | 7150        | 0.1484                          |
| 90          | 6700        | 0.1598                          |
| 100         | 6350        | 0.1684                          |
| 115         | 5900        | 0.1798                          |
| 135         | 5400        | 0.2009                          |
| 150         | 5050        | 0.2191                          |
| 165         | 4800        | 0.2340                          |
| 180         | 4570        | 0.2499                          |
| 210         | 4150        | 0.2826                          |
| 240         | 3910        | 0.3111                          |
| 270         | 3670        | 0.3420                          |
| 330         | 3290        | 0.4065                          |

$$R_{\infty} = 2000 \text{ ohms}$$

$$k = 2.42 \times 10^{-3} \text{ min.}^{-1}$$

$$k = 4.03 \times 10^{-5} \text{ sec.}^{-1}$$

TABLE 28

SOLVOLYSIS OF 0.1025 Molar CYCLOPROPYLCARBINYL TRIFLUOROACETATE  
IN 80% DIOXANE-20% WATER AT 59.6°C.

| t<br>min. | R<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-----------|-----------|---------------------------------|
| 10        | 10400     | 0.0461                          |
| 20        | 7400      | 0.0660                          |
| 30        | 5850      | 0.0853                          |
| 40        | 4950      | 0.1031                          |
| 50        | 4400      | 0.1176                          |
| 60        | 3930      | 0.1342                          |
| 70        | 3600      | 0.1489                          |
| 80        | 3330      | 0.1635                          |
| 90        | 3080      | 0.1801                          |
| 100       | 2870      | 0.1967                          |
| 110       | 2710      | 0.2116                          |
| 120       | 2580      | 0.2256                          |
| 130       | 2440      | 0.2428                          |
| 140       | 2330      | 0.2584                          |
| 150       | 2230      | 0.2746                          |
| 160       | 2130      | 0.2929                          |
| 170       | 2050      | 0.3076                          |
| 180       | 1980      | 0.3259                          |
| 190       | 1910      | 0.3440                          |
| 200       | 1850      | 0.3614                          |
| 210       | 1800      | 0.3773                          |
| 220       | 1750      | 0.3948                          |

$$R_{\infty} = 1045 \text{ ohms}$$

$$k = 3.74 \times 10^{-3} \text{ min.}^{-1}$$

$$k = 6.24 \times 10^{-5} \text{ sec.}^{-1}$$

TABLE 29

SOLVOLYSIS OF 0.07300 MOLAR CYCLOPROPYLCARBINYL TRIFLUOROACETATE  
IN 80% DIOXANE-20% WATER AT 59.6°C.

| t<br>min. | R<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-----------|-----------|---------------------------------|
| 20        | 10250     | 0.0686                          |
| 30        | 8230      | 0.0874                          |
| 40        | 7000      | 0.1048                          |
| 50        | 6220      | 0.1199                          |
| 60        | 5310      | 0.1376                          |
| 70        | 5080      | 0.1520                          |
| 80        | 4680      | 0.1679                          |
| 90        | 4380      | 0.1821                          |
| 100       | 4100      | 0.1978                          |
| 110       | 3890      | 0.2116                          |
| 120       | 3690      | 0.2266                          |
| 130       | 3500      | 0.2430                          |
| 140       | 3370      | 0.2558                          |
| 150       | 3210      | 0.2735                          |
| 160       | 3100      | 0.2871                          |
| 170       | 2990      | 0.3025                          |
| 180       | 2890      | 0.3179                          |
| 190       | 2800      | 0.3333                          |
| 200       | 2710      | 0.3502                          |
| 210       | 2630      | 0.3668                          |
| 220       | 2565      | 0.3817                          |
| 230       | 2505      | 0.3967                          |
| 240       | 2450      | 0.4114                          |

$$R_{\infty} = 1500 \text{ ohms}$$

$$k = 3.57 \times 10^{-3} \text{ min.}^{-1}$$

$$k = 5.95 \times 10^{-5} \text{ sec.}^{-1}$$

TABLE 30

SOLVOLYSIS OF 0.0215 MOLAR NORTHCYCLOHEXANONE TRIFLUOROACETATE  
IN 60% DICHLORETHANE-40% WATER AT 40.0°C.

| $t$<br>min. | $R$<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-------------|-------------|---------------------------------|
| 30          | 503         | 0.0504                          |
| 40          | 411         | 0.0626                          |
| 50          | 350         | 0.0745                          |
| 60          | 308         | 0.0857                          |
| 70          | 277         | 0.0962                          |
| 80          | 251         | 0.1075                          |
| 90          | 231         | 0.1179                          |
| 100         | 213         | 0.1297                          |
| 110         | 201         | 0.1389                          |
| 120         | 189         | 0.1492                          |
| 150         | 162         | 0.1601                          |
| 180         | 145.0       | 0.1671                          |
| 210         | 130.0       | 0.1788                          |
| 240         | 119.0       | 0.1893                          |
| 270         | 110.0       | 0.1910                          |
| 300         | 103.0       | 0.1916                          |

$$R_{\infty} = 55.0 \text{ ohms}$$

$$k = 2.37 \times 10^{-3} \text{ min.}^{-1}$$

$$k = 3.95 \times 10^{-5} \text{ sec.}^{-1}$$



TABLE 31

SOLVOLYSIS OF 0.0512 Molar NORBISCHLITCARBINYL TRIFLUOROACETATE  
IN 60% DIOXANE-40% WATER AT 50.0°C.

| $t$<br>min. | $R$<br>ohms | $\log \frac{R}{R - R_\infty}$ |
|-------------|-------------|-------------------------------|
| 20          | 183         | 0.6924                        |
| 40          | 133.5       | 0.1326                        |
| 60          | 108.5       | 0.1697                        |
| 70          | 100.0       | 0.1878                        |
| 80          | 93.0        | 0.2098                        |
| 90          | 88.0        | 0.2212                        |
| 100         | 83.0        | 0.2388                        |
| 110         | 79.0        | 0.2553                        |
| 120         | 75.5        | 0.2716                        |
| 130         | 72.5        | 0.2876                        |
| 140         | 70.0        | 0.3023                        |
| 150         | 67.5        | 0.3187                        |
| 160         | 65.0        | 0.3373                        |
| 170         | 63.0        | 0.3537                        |
| 180         | 61.5        | 0.3674                        |
| 190         | 60.0        | 0.3820                        |
| 200         | 58.5        | 0.3979                        |
| 220         | 56.0        | 0.4281                        |
| 240         | 53.5        | 0.4635                        |
| 260         | 51.5        | 0.4971                        |

$$R_\infty = 35.1 \text{ ohms}$$

$$k = 3.79 \times 10^{-3} \text{ min.}^{-1}$$

$$k = 6.32 \times 10^{-5} \text{ sec.}^{-1}$$

TABLE 32

SOLVING OF 0.0586 MOLAR NORTHOXYLGLUCAMINE TRIFLUOROACETATE  
IN 60% DIOXANE-40% WATER AT 59.6°C.

| $t$<br>min. | $R$<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-------------|-------------|---------------------------------|
| 10          | 148         | 0.1113                          |
| 20          | 130.0       | 0.1501                          |
| 30          | 110.0       | 0.1811                          |
| 40          | 95.0        | 0.2219                          |
| 45          | 90.0        | 0.2383                          |
| 50          | 85.5        | 0.2553                          |
| 55          | 82.0        | 0.2705                          |
| 60          | 78.5        | 0.2873                          |
| 70          | 73.0        | 0.3193                          |
| 80          | 69.0        | 0.3475                          |
| 90          | 65.5        | 0.3769                          |
| 100         | 62.5        | 0.4067                          |
| 110         | 60.0        | 0.4357                          |
| 120         | 58.0        | 0.4621                          |
| 130         | 56.0        | 0.4928                          |

$$R_{\infty} = 38.0 \text{ ohms}$$

$$k = 7.21 \times 10^{-3} \text{ min.}^{-1}$$

$$k = 1.20 \times 10^{-4} \text{ sec.}^{-1}$$

TABLE 33

SOLVOLYSIS OF 0.0518M NUCLEAR NONHETEROLOGAMINYL TRINUCLEOSIDE  
IN 60% DIOXANE-40% WATER AT 59.6°C.

| t<br>min. | R<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-----------|-----------|---------------------------------|
| 10        | 150.0     | 0.1229                          |
| 20        | 127.0     | 0.1195                          |
| 30        | 107.0     | 0.1811                          |
| 40        | 93.0      | 0.2201                          |
| 50        | 85.0      | 0.2182                          |
| 60        | 78.5      | 0.2769                          |
| 70        | 73.0      | 0.3071                          |
| 80        | 69.0      | 0.3338                          |
| 90        | 65.5      | 0.3613                          |
| 100       | 62.5      | 0.3891                          |
| 110       | 60.0      | 0.4165                          |
| 120       | 58.0      | 0.4412                          |
| 130       | 56.0      | 0.4691                          |
| 140       | 54.0      | 0.5019                          |
| 150       | 52.5      | 0.5298                          |

$$R_{\infty} = 37.0 \text{ ohms}$$

$$k = 6.63 \times 10^{-3} \text{ min.}^{-1}$$

$$k = 1.11 \times 10^{-4} \text{ sec.}^{-1}$$

TABLE 3b

SOLVOLYSIS OF 0.06371 MOLAR NORTHERNELYLOARNINE, TRIFLUOROACETATE  
IN 70% ETHANOL-30% WATER AT 40.1°C.

| t<br>min. | R<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-----------|-----------|---------------------------------|
| 60        | 1840      | 0.0774                          |
| 90        | 1565      | 0.0924                          |
| 120       | 1385      | 0.1039                          |
| 150       | 1265      | 0.1176                          |
| 180       | 1175      | 0.1281                          |
| 210       | 1095      | 0.1389                          |
| 240       | 1030      | 0.1495                          |
| 270       | 975       | 0.1596                          |
| 300       | 930       | 0.1691                          |
| 330       | 885       | 0.1798                          |
| 360       | 855       | 0.1878                          |
| 390       | 810       | 0.2011                          |
| 420       | 785       | 0.2106                          |
| 450       | 755       | 0.2199                          |
| 480       | 730       | 0.2299                          |
| 510       | 685       | 0.2502                          |
| 600       | 645       | 0.2718                          |
| 660       | 615       | 0.2906                          |
| 720       | 585       | 0.3124                          |
| 780       | 555       | 0.3366                          |
| 840       | 510       | 0.3520                          |
| 900       | 520       | 0.3737                          |
| 960       | 500       | 0.3979                          |

$$R_{\infty} = 300 \text{ ohms}$$

$$k = 7.97 \times 10^{-4} \text{ min.}^{-1}$$

$$k = 1.33 \times 10^{-5} \text{ sec.}^{-1}$$

TABLE 35

SOLVOLYSIS OF 0.05713 Molar NORTHOXYLCAINEHYD, TRIFLUOROACETATE  
IN 70% HEXANE-30% WATER AT 50.0°C.

| t<br>min. | R<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-----------|-----------|---------------------------------|
| 40        | 1370      | 0.0874                          |
| 60        | 1180      | 0.1035                          |
| 80        | 1055      | 0.1176                          |
| 100       | 980       | 0.1310                          |
| 120       | 880       | 0.1452                          |
| 140       | 815       | 0.1590                          |
| 160       | 770       | 0.1706                          |
| 180       | 725       | 0.1836                          |
| 200       | 690       | 0.1953                          |
| 220       | 660       | 0.2071                          |
| 240       | 630       | 0.2196                          |
| 260       | 605       | 0.2315                          |
| 280       | 580       | 0.2439                          |
| 300       | 560       | 0.2570                          |
| 320       | 540       | 0.2700                          |
| 340       | 525       | 0.2808                          |
| 360       | 505       | 0.2969                          |
| 380       | 494       | 0.3064                          |
| 400       | 481       | 0.3185                          |
| 420       | 468       | 0.3318                          |
| 440       | 458       | 0.3428                          |
| 460       | 447       | 0.3538                          |
| 480       | 437       | 0.3687                          |
| 500       | 429       | 0.3797                          |
| 520       | 419       | 0.3943                          |

$$R_{\infty} = 250 \text{ ohms}$$

$$k = 1.44 \times 10^{-3} \text{ min.}^{-1}$$

$$k = 2.41 \times 10^{-5} \text{ sec.}^{-1}$$

TABLE 36

SOLVOLYSIS OF 0.0589 MOLAR NORTHEXYLOXYCARBONYL TRIFLUOROACETATE  
IN 70% ETHANOL-30% WATER AT 59.6°C.

| $t$<br>min. | $R$<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-------------|-------------|---------------------------------|
| 20          | 1490        | 0.0976                          |
| 30          | 1330        | 0.1109                          |
| 40          | 1210        | 0.1239                          |
| 50          | 1120        | 0.1354                          |
| 60          | 1050        | 0.1461                          |
| 70          | 980         | 0.1587                          |
| 80          | 930         | 0.1691                          |
| 90          | 885         | 0.1798                          |
| 100         | 850         | 0.1889                          |
| 110         | 815         | 0.1995                          |
| 120         | 785         | 0.2093                          |
| 130         | 755         | 0.2198                          |
| 140         | 730         | 0.2299                          |
| 150         | 710         | 0.2386                          |
| 160         | 690         | 0.2477                          |
| 170         | 671         | 0.2571                          |
| 180         | 652         | 0.2676                          |
| 190         | 635         | 0.2778                          |
| 200         | 620         | 0.2874                          |
| 220         | 590         | 0.3083                          |
| 240         | 563         | 0.3306                          |
| 260         | 545         | 0.3471                          |
| 280         | 527         | 0.3659                          |
| 300         | 513         | 0.3813                          |
| 320         | 498         | 0.4005                          |
| 330         | 490         | 0.4114                          |

$$R_{\infty} = 300 \text{ ohms}$$

$$k = 2.30 \times 10^{-3} \text{ min.}^{-1}$$

$$k = 3.83 \times 10^{-5} \text{ sec.}^{-1}$$

TABLE 37

SOLVOLYSIS OF 0.06348 Molar NORTHEXYLOXANBENYL TRIFLUOROACETATE  
IN 70% DICHLORO-30% WATER AT 59.6° C.

| $t$<br>min. | $R$<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-------------|-------------|---------------------------------|
| 30          | 920         | 0.1307                          |
| 40          | 845         | 0.1443                          |
| 50          | 785         | 0.1569                          |
| 60          | 735         | 0.1709                          |
| 70          | 695         | 0.1830                          |
| 80          | 665         | 0.1924                          |
| 90          | 635         | 0.2052                          |
| 100         | 605         | 0.2183                          |
| 110         | 585         | 0.2281                          |
| 120         | 565         | 0.2388                          |
| 130         | 545         | 0.2507                          |
| 140         | 530         | 0.2603                          |
| 160         | 500         | 0.2824                          |
| 180         | 475         | 0.3042                          |
| 200         | 454         | 0.3247                          |
| 220         | 433         | 0.3457                          |
| 240         | 418         | 0.3683                          |
| 260         | 402         | 0.3920                          |
| 280         | 391         | 0.4103                          |
| 300         | 380         | 0.4306                          |
| 320         | 370         | 0.4509                          |
| 340         | 361         | 0.4711                          |
| 360         | 352         | 0.4935                          |

$$R_{\infty} = 239 \text{ ohms}$$

$$k = 2.50 \times 10^{-3} \text{ min.}^{-1}$$

$$k = 4.17 \times 10^{-5} \text{ sec.}^{-1}$$

TABLE 38

SOLVOLYSIS OF 0.00102 Molar NORTHEXYLOXANOLYL TRIFLUOROACETATE  
IN 80% DIOXANE-20% WATER AT 40.0°C.

| $t$<br>min. | $R$<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-------------|-------------|---------------------------------|
| 180         | 10850       | 0.0792                          |
| 210         | 10200       | 0.0849                          |
| 240         | 9700        | 0.0895                          |
| 270         | 9200        | 0.0952                          |
| 300         | 8720        | 0.1011                          |
| 330         | 8300        | 0.1069                          |
| 360         | 7980        | 0.1116                          |
| 390         | 7650        | 0.1173                          |
| 420         | 7400        | 0.1219                          |
| 450         | 7140        | 0.1277                          |
| 480         | 6920        | 0.1316                          |
| 510         | 6720        | 0.1361                          |
| 540         | 6520        | 0.1411                          |
| 570         | 6320        | 0.1461                          |
| 600         | 6150        | 0.1501                          |
| 660         | 5840        | 0.1611                          |
| 720         | 5550        | 0.1714                          |
| 780         | 5350        | 0.1793                          |
| 840         | 5170        | 0.1869                          |
| 900         | 4970        | 0.1968                          |

$$R_{\infty} = 1810 \text{ ohms}$$

$$k = 3.79 \times 10^{-4} \text{ min.}^{-1}$$

$$k = 6.31 \times 10^{-5} \text{ sec.}^{-1}$$



TABLE 39

SOLVOLYSIS OF 0.07639 MOLAR NORTHOXYLGLUCARINYL TRIFLUOROACETATE  
IN 80% DIOXANE-20% WATER AT 50.0°C.

| t<br>min. | R<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-----------|-----------|---------------------------------|
| 60        | 6700      | 0.0810                          |
| 90        | 5850      | 0.0912                          |
| 120       | 5250      | 0.1042                          |
| 150       | 4840      | 0.1166                          |
| 180       | 4570      | 0.1245                          |
| 210       | 4300      | 0.1339                          |
| 240       | 4080      | 0.1424                          |
| 270       | 3890      | 0.1508                          |
| 300       | 3710      | 0.1596                          |
| 330       | 3520      | 0.1688                          |
| 360       | 3420      | 0.1761                          |
| 390       | 3310      | 0.1833                          |
| 420       | 3190      | 0.1920                          |
| 450       | 3090      | 0.2000                          |
| 480       | 2990      | 0.2084                          |
| 510       | 2900      | 0.2170                          |
| 540       | 2810      | 0.2261                          |
| 570       | 2730      | 0.2354                          |
| 600       | 2650      | 0.2443                          |
| 630       | 2590      | 0.2520                          |
| 660       | 2530      | 0.2601                          |
| 690       | 2480      | 0.2674                          |
| 720       | 2430      | 0.2751                          |
| 750       | 2380      | 0.2831                          |
| 780       | 2330      | 0.2918                          |

$$R_{\infty} = 1140 \text{ ohms}$$

$$k = 6.55 \times 10^{-4} \text{ min.}^{-1}$$

$$k = 1.09 \times 10^{-5} \text{ sec.}^{-1}$$

TABLE 40

SOLVOLYSIS OF 0.07563 MOLAR NITROCHLORIDANINE, TRIFLUOROACETATE  
IN 80% DIOXANE-20% WATER AT 59.6°C.

| t<br>min. | R<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-----------|-----------|---------------------------------|
| 20        | 5350      | 0.0788                          |
| 40        | 5000      | 0.0938                          |
| 60        | 4450      | 0.1069                          |
| 80        | 3980      | 0.1212                          |
| 100       | 3670      | 0.1332                          |
| 120       | 3410      | 0.1455                          |
| 140       | 3200      | 0.1569                          |
| 160       | 3000      | 0.1697                          |
| 180       | 2840      | 0.1816                          |
| 200       | 2720      | 0.1915                          |
| 220       | 2600      | 0.2028                          |
| 240       | 2495      | 0.2138                          |
| 260       | 2400      | 0.2248                          |
| 280       | 2320      | 0.2353                          |
| 300       | 2230      | 0.2480                          |
| 320       | 2160      | 0.2589                          |
| 340       | 2100      | 0.2691                          |
| 360       | 2040      | 0.2803                          |
| 380       | 1990      | 0.2903                          |
| 400       | 1940      | 0.3010                          |
| 420       | 1890      | 0.3126                          |
| 440       | 1850      | 0.3226                          |
| 460       | 1810      | 0.3335                          |
| 480       | 1770      | 0.3448                          |
| 500       | 1735      | 0.3556                          |
| 520       | 1700      | 0.3672                          |
| 540       | 1665      | 0.3795                          |

$$R_{\infty} = 970 \text{ ohms}$$

$$k = 1.30 \times 10^{-3} \text{ min.}^{-1}$$

$$k = 2.16 \times 10^{-5} \text{ sec.}^{-1}$$

The data in Tables 41, 42, 43, 44, 45 and 49 were obtained from the solvolysis of the reaction product obtained in the preparation of cyclopropylmethylearbonyl trifluoroacetate which also contained 2-methylcyclobutyl trifluoroacetate. As 2-methylcyclobutyl trifluoroacetate solvolyzes much slower than the former ester, the latter part of the data (below the solid line in the tables) gave straight lines and the slope of these lines were used to calculate rate constants for this ester in 60% aqueous dioxane.

TABLE 11

SOLVOLYSIS OF 0.05477 MOLAR MIXED ESTER FROM CYCLOPROPYLMETHYL-  
CARBYNOL IN 60% DIOXANE-40% WATER AT 40.1°C.

| t<br>min. | R<br>ohms | $\log \frac{R}{R - R_\infty}$ |
|-----------|-----------|-------------------------------|
| 2         | 51.0      | 0.0094                        |
| 4         | 44.1      | 0.0173                        |
| 6         | 41.0      | 0.0235                        |
| 8         | 39.5      | 0.0285                        |
| 10        | 38.0      | 0.0329                        |
| 12        | 36.0      | 0.0368                        |
| 14        | 350.0     | 0.0404                        |
| 16        | 320.5     | 0.0431                        |
| 18        | 312.5     | 0.0450                        |
| 20        | 306.0     | 0.0461                        |
| 22        | 301.0     | 0.0475                        |
| 24        | 297.0     | 0.0485                        |
| 26        | 293.0     | 0.0496                        |
| 28        | 290.0     | 0.0503                        |
| 30        | 287.0     | 0.0512                        |
| 35        | 282.0     | 0.0528                        |
| 40        | 277.5     | 0.0541                        |
| 45        | 273.5     | 0.0557                        |
| 50        | 270.5     | 0.0571                        |
| 55        | 268.0     | 0.0585                        |
| 65        | 261.0     | 0.0617                        |
| 70        | 262.5     | 0.0628                        |
| 80        | 259.5     | 0.0645                        |
| 85        | 258.0     | 0.0657                        |
| 95        | 256.5     | 0.0670                        |
| 100       | 255.5     | 0.0680                        |
| 110       | 251.0     | 0.0692                        |
| 115       | 252.2     | 0.0707                        |
| 120       | 252.5     | 0.0710                        |

$$R_\infty = 42.0 \text{ ohms}$$

$$k = 9.94 \times 10^{-3} \text{ min.}^{-1}$$

$$k = 1.66 \times 10^{-4} \text{ sec.}^{-1}$$

TABLE 1.2

SOLVOLYSIS OF 0.05493 MOLAR MIXED ESTER FROM CETOLOPENTYL-  
 CANOINOL IN 60% DIOXANE-40% WATER AT 40.1°C.

| $t$<br>min. | $R$<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-------------|-------------|---------------------------------|
| 2           | 520         | 0.0310                          |
| 4           | 278         | 0.0603                          |
| 6           | 196         | 0.0881                          |
| 8           | 156         | 0.1139                          |
| 10          | 133.0       | 0.1358                          |
| 12          | 117.5       | 0.1572                          |
| 14          | 107.0       | 0.1764                          |
| 16          | 98.5        | 0.1951                          |
| 18          | 92.0        | 0.2133                          |
| 20          | 87.0        | 0.2291                          |
| 22          | 83.0        | 0.2443                          |
| 24          | 79.0        | 0.2590                          |
| 26          | 76.0        | 0.2735                          |
| 28          | 74.0        | 0.2860                          |
| 30          | 72.0        | 0.2973                          |
| 32          | 70.0        | 0.3098                          |
| 36          | 66.0        | 0.3381                          |
| 40          | 63.5        | 0.3587                          |
| 44          | 61.0        | 0.3822                          |
| 48          | 59.0        | 0.4035                          |
| 52          | 57.5        | 0.4213                          |
| 56          | 56.0        | 0.4406                          |
| 60          | 54.5        | 0.4622                          |
| 65          | 53.0        | 0.4862                          |
| 70          | 51.6        | 0.5112                          |
| 75          | 50.5        | 0.5330                          |
| 80          | 49.5        | 0.5517                          |
| 85          | 48.5        | 0.5785                          |
| 90          | 47.6        | 0.6012                          |

$$R_{\infty} = 35.7 \text{ ohms}$$

$$k = 1.09 \times 10^{-3} \text{ min.}^{-1}$$

$$k = 1.81 \times 10^{-4} \text{ sec.}^{-1}$$

TABLE 43

SOLVOLYSIS OF 0.05103 MOLAL MIXED ESTER FROM CYCLOPROPYLAMINYL-  
CARBONATE IN 60% DICHLORO-40% WATER AT 19.7°C.

| t<br>min. | R<br>ohms | $\log \frac{R}{R_0 - R_\infty}$ |
|-----------|-----------|---------------------------------|
| 2         | 352       | 0.0480                          |
| 3         | 225       | 0.0781                          |
| 4         | 172       | 0.1052                          |
| 5         | 141.0     | 0.1253                          |
| 6         | 122.0     | 0.1414                          |
| 7         | 110.0     | 0.1552                          |
| 8         | 101.0     | 0.1648                          |
| 9         | 95.0      | 0.1706                          |
| 10        | 90.0      | 0.1753                          |
| 11        | 86.5      | 0.1789                          |
| 12        | 83.0      | 0.1816                          |
| 13        | 80.5      | 0.1841                          |
| 14        | 78.0      | 0.1862                          |
| 15        | 76.0      | 0.1882                          |
| 16        | 74.5      | 0.1895                          |
| 17        | 73.0      | 0.1910                          |
| 18        | 71.5      | 0.1923                          |
| 19        | 70.0      | 0.1931                          |
| 20        | 68.5      | 0.1936                          |
| 21        | 67.5      | 0.1939                          |
| 22        | 66.5      | 0.1943                          |
| 23        | 65.5      | 0.1949                          |
| 24        | 64.5      | 0.1955                          |
| 25        | 63.5      | 0.1961                          |
| 26        | 62.5      | 0.1969                          |
| 27        | 61.5      | 0.1979                          |
| 28        | 61.1      | 0.1981                          |
| 29        | 60.4      | 0.1986                          |
| 30        | 59.8      | 0.1994                          |
| 35        | 57.0      | 0.2010                          |
| 40        | 54.5      | 0.2022                          |
| 45        | 52.0      | 0.2057                          |
| 50        | 50.0      | 0.2087                          |
| 55        | 48.5      | 0.2060                          |

$$R_\infty = 36.5 \text{ ohms}$$

$$k = 1.81 \times 10^{-2} \text{ min.}^{-1}$$

$$k = 3.02 \times 10^{-4} \text{ sec.}^{-1}$$

TABLE 14

SOLFOXIDES OF 0.05233 MOLAR MIXED BUTYL FROM CHLOROPHTHALIC-  
CARBONIC IN 60% DICHLORO-10% WATER AT 60.1°C.

| $t$<br>min. | $R$<br>ohms | $\log \frac{R}{R - R_0}$ |
|-------------|-------------|--------------------------|
| 1.5         | 171         | 0.0962                   |
| 2           | 132.0       | 0.1291                   |
| 3           | 97.0        | 0.1875                   |
| 4           | 82.0        | 0.2385                   |
| 5           | 73.0        | 0.2723                   |
| 6           | 70.0        | 0.2887                   |
| 7           | 66.0        | 0.3115                   |
| 8           | 61.0        | 0.3290                   |
| 9           | 58.3        | 0.3426                   |
| 10          | 56.8        | 0.3558                   |
| 11          | 55.4        | 0.3690                   |
| 12          | 56.2        | 0.3821                   |
| 13          | 57.3        | 0.3908                   |
| 14          | 56.3        | 0.4023                   |
| 15          | 55.3        | 0.4143                   |
| 16          | 54.5        | 0.4247                   |
| 17          | 53.8        | 0.4341                   |
| 18          | 53.0        | 0.4434                   |
| 19          | 52.4        | 0.4545                   |
| 20          | 51.7        | 0.4655                   |
| 21          | 51.0        | 0.4771                   |
| 22          | 50.3        | 0.4894                   |
| 23          | 49.7        | 0.5005                   |
| 24          | 49.1        | 0.5121                   |
| 25          | 48.6        | 0.5233                   |
| 26          | 48.1        | 0.5329                   |
| 27          | 47.6        | 0.5441                   |
| 28          | 47.1        | 0.5557                   |
| 29          | 46.6        | 0.5680                   |
| 30          | 46.2        | 0.5794                   |

$$R_0 = 34.0 \text{ ohms}$$

$$k = 2.54 \times 10^{-3} \text{ min.}^{-1}$$

$$k = 4.23 \times 10^{-4} \text{ sec.}^{-1}$$

TABLE 45

SOLVENTS OF 0.0143 MOLAR NITRO-ENTER FROM CYCLOHEXYLAMINE-  
CANDINOL IN 60% ETHANOL-40% WATER AT 60.1°C.

| t<br>min. | R<br>ohms | $\log \frac{R}{R_0 - R_0}$ |
|-----------|-----------|----------------------------|
| 1         | 230       | 0.0830                     |
| 2         | 188       | 0.1288                     |
| 3         | 159.5     | 0.1678                     |
| 4         | 146.0     | 0.1986                     |
| 5         | 137.5     | 0.2222                     |
| 6         | 131.5     | 0.2455                     |
| 7         | 97.0      | 0.2310                     |
| 8         | 92.5      | 0.2660                     |
| 9         | 88.5      | 0.2878                     |
| 10        | 86.5      | 0.2718                     |
| 11        | 83.2      | 0.2847                     |
| 12        | 80.8      | 0.2989                     |
| 13        | 78.2      | 0.3111                     |
| 14        | 76.5      | 0.3214                     |
| 15        | 74.7      | 0.3330                     |
| 16        | 72.6      | 0.3477                     |
| 17        | 71.0      | 0.3598                     |
| 18        | 69.5      | 0.3722                     |
| 19        | 68.0      | 0.3854                     |
| 20        | 66.8      | 0.3967                     |
| 21        | 65.6      | 0.4086                     |
| 22        | 64.5      | 0.4204                     |
| 23        | 63.3      | 0.4341                     |
| 24        | 62.3      | 0.4462                     |
| 25        | 61.4      | 0.4577                     |
| 26        | 60.5      | 0.4700                     |
| 27        | 59.6      | 0.4830                     |
| 28        | 58.8      | 0.4953                     |
| 29        | 58.2      | 0.5049                     |
| 30        | 57.6      | 0.5150                     |

$$R_0 = 40.0 \text{ ohms}$$

$$k = 2.82 \times 10^{-2} \text{ min.}^{-1}$$

$$k = 4.70 \times 10^{-4} \text{ sec.}^{-1}$$



TABLE 46

SOLVOLYSIS OF 0.0501 MOLAR 2-METHYLSTYLOXYL TRIPHENYLCARBONATE  
IN 70% DICHLOROMETHANE-30% WATER AT 40.0°C.

| t<br>min. | R<br>ohms | $\log \frac{R}{R_0 - R_\infty}$ |
|-----------|-----------|---------------------------------|
| 5         | 1395      | 0.1212                          |
| 10        | 1350      | 0.1281                          |
| 15        | 1275      | 0.1368                          |
| 20        | 1230      | 0.1405                          |
| 25        | 1180      | 0.1477                          |
| 30        | 1140      | 0.1538                          |
| 35        | 1105      | 0.1596                          |
| 40        | 1070      | 0.1661                          |
| 45        | 1045      | 0.1708                          |
| 50        | 1010      | 0.1781                          |
| 55        | 985       | 0.1838                          |
| 60        | 965       | 0.1887                          |
| 70        | 912       | 0.2025                          |
| 80        | 878       | 0.2127                          |
| 90        | 845       | 0.2235                          |
| 100       | 812       | 0.2355                          |
| 110       | 780       | 0.2487                          |
| 120       | 745       | 0.2603                          |
| 150       | 696       | 0.2911                          |
| 180       | 648       | 0.3230                          |
| 210       | 605       | 0.3585                          |

$$R_\infty = 340 \text{ ohms}$$

$$k = 2.65 \times 10^{-3} \text{ min.}^{-1}$$

$$k = 4.41 \times 10^{-5} \text{ sec.}^{-1}$$

TABLE 47

SOLVOLYSIS OF 0.00789 Molar 2-METHYLBENZYLCHLORIDE TRIPHENYLMETHANE  
IN 70% DIETHANE-30% WATER AT 49.9°C.

| t<br>min. | R<br>ohms | $\log \frac{R}{R - R_0}$ |
|-----------|-----------|--------------------------|
| 10        | 1280      | 0.1206                   |
| 15        | 1195      | 0.1306                   |
| 20        | 1125      | 0.1399                   |
| 25        | 1070      | 0.1486                   |
| 30        | 1015      | 0.1584                   |
| 35        | 972       | 0.1664                   |
| 40        | 927       | 0.1767                   |
| 45        | 893       | 0.1853                   |
| 50        | 857       | 0.1951                   |
| 55        | 827       | 0.2043                   |
| 60        | 800       | 0.2103                   |
| 65        | 775       | 0.2219                   |
| 70        | 752       | 0.2307                   |
| 75        | 730       | 0.2400                   |
| 80        | 712       | 0.2482                   |
| 85        | 696       | 0.2560                   |
| 90        | 678       | 0.2653                   |
| 95        | 663       | 0.2737                   |
| 100       | 648       | 0.2826                   |
| 110       | 622       | 0.2997                   |
| 120       | 598       | 0.3172                   |
| 130       | 576       | 0.3339                   |
| 140       | 556       | 0.3522                   |

$$R_0 = 310 \text{ ohms}$$

$$k = 4.09 \times 10^{-3} \text{ min.}^{-1}$$

$$k = 6.81 \times 10^{-5} \text{ sec.}^{-1}$$

TABLE 13

SOLVOLYSIS OF 0.02735 MOLAR 2-METHYLOXYBUTYL TRIFLUOROACETATE  
IN 70% NICOTINE-30% WATER AT 49.9°C.

| t<br>min. | R<br>ohms | $\log \frac{R}{R - R_0}$ |
|-----------|-----------|--------------------------|
| 10        | 1507      | 0.1212                   |
| 15        | 1402      | 0.1300                   |
| 20        | 1330      | 0.1403                   |
| 25        | 1257      | 0.1498                   |
| 30        | 1195      | 0.1593                   |
| 35        | 1142      | 0.1685                   |
| 40        | 1095      | 0.1773                   |
| 45        | 1050      | 0.1867                   |
| 50        | 1010      | 0.1962                   |
| 55        | 977       | 0.2047                   |
| 60        | 947       | 0.2130                   |
| 65        | 920       | 0.2212                   |
| 70        | 894       | 0.2294                   |
| 75        | 868       | 0.2382                   |
| 80        | 843       | 0.2462                   |
| 85        | 820       | 0.2577                   |
| 90        | 800       | 0.2667                   |
| 95        | 780       | 0.2762                   |
| 100       | 763       | 0.2869                   |
| 110       | 733       | 0.3004                   |
| 120       | 706       | 0.3187                   |
| 130       | 680       | 0.3371                   |
| 140       | 658       | 0.3523                   |

$$R_0 = 367 \text{ ohms}$$

$$k = 4.11 \times 10^{-3} \text{ min.}^{-1}$$

$$k = 6.85 \times 10^{-5} \text{ sec.}^{-1}$$

TABLE 49

SOLVOLYSES OF 0.07880 MOLAR MIXED ESTER FROM CYCLOPROPYLENE-1,2-CARBOXYL IN 70% HEXANE-30% WATER AT 49.7°C.<sup>1</sup>

| t<br>min. | R<br>ohms | $\log \frac{R}{R - R_\infty}$ |
|-----------|-----------|-------------------------------|
| 2         | 2600      | 0.0102                        |
| 3         | 2080      | 0.0508                        |
| 5         | 1550      | 0.0897                        |
| 7         | 1275      | 0.0853                        |
| 10        | 1085      | 0.1052                        |
| 15        | 855       | 0.1360                        |
| 20        | 740       | 0.1590                        |
| 25        | 660       | 0.1830                        |
| 30        | 603       | 0.2052                        |
| 35        | 561       | 0.2253                        |
| 40        | 530       | 0.2428                        |
| 45        | 500       | 0.2628                        |
| 50        | 480       | 0.2781                        |
| 60        | 445       | 0.3120                        |
| 70        | 417       | 0.3434                        |
| 80        | 398       | 0.3669                        |
| 90        | 381       | 0.3934                        |
| 100       | 366       | 0.4266                        |
| 150       | 315       | 0.5541                        |
| 225       | 289       | 0.6680                        |

$$R_\infty = 227 \text{ ohms}$$

<sup>1</sup>These data used only for Figure 49, page 59.

TABLE 50

SOLVOLYSIS OF 0.02759 MOLAR 2-METHYLOCTYL-CEPTYL TRIFLUOROACETATE  
IN 70% DIOXANE-30% WATER AT 60.0°C.

| $t$<br>min. | $R$<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-------------|-------------|---------------------------------|
| 10          | 1185        | 0.1348                          |
| 15          | 1305        | 0.1495                          |
| 20          | 1210        | 0.1638                          |
| 25          | 1130        | 0.1781                          |
| 30          | 1085        | 0.1917                          |
| 35          | 1013        | 0.2049                          |
| 40          | 970         | 0.2159                          |
| 45          | 925         | 0.2297                          |
| 50          | 885         | 0.2435                          |
| 55          | 850         | 0.2574                          |
| 60          | 822         | 0.2695                          |
| 65          | 797         | 0.2813                          |
| 70          | 772         | 0.2949                          |
| 75          | 748         | 0.3081                          |
| 80          | 727         | 0.3212                          |
| 85          | 705         | 0.3363                          |
| 90          | 687         | 0.3499                          |
| 95          | 672         | 0.3619                          |
| 100         | 655         | 0.3769                          |
| 105         | 640         | 0.3913                          |

$$R_{\infty} = 380 \text{ ohms}$$

$$k = 6.12 \times 10^{-3} \text{ min.}^{-1}$$

$$k = 1.02 \times 10^{-4} \text{ sec.}^{-1}$$

TABLE 51

SOLVOLYSIS OF 0.0068M NOLAN 2-NHETHYLTOLABUTYL TRIPHENYLOACETATE  
IN 70% DIOXANE-30% WATER AT 60.0°C.

| $t$<br>min. | $R$<br>ohms | $\log \frac{R}{R - R_0}$ |
|-------------|-------------|--------------------------|
| 10          | 1210        | 0.1335                   |
| 15          | 1110        | 0.1484                   |
| 20          | 1035        | 0.1617                   |
| 25          | 980         | 0.1770                   |
| 30          | 925         | 0.1901                   |
| 35          | 877         | 0.2034                   |
| 40          | 840         | 0.2150                   |
| 45          | 805         | 0.2274                   |
| 50          | 770         | 0.2410                   |
| 55          | 740         | 0.2543                   |
| 60          | 713         | 0.2676                   |
| 65          | 690         | 0.2801                   |
| 70          | 670         | 0.2920                   |
| 75          | 650         | 0.3051                   |
| 80          | 631         | 0.3185                   |
| 85          | 612         | 0.3334                   |
| 90          | 598         | 0.3454                   |
| 95          | 585         | 0.3572                   |
| 100         | 572         | 0.3670                   |
| 105         | 560         | 0.3827                   |

$$R_0 = 328 \text{ ohms}$$

$$k = 5.98 \times 10^{-3} \text{ min.}^{-1}$$

$$k = 9.97 \times 10^{-5} \text{ sec.}^{-1}$$

Cyclopropylmethylcarbinyl trifluoroacetate solvolyzed via allyl-oxygen fission and by rearrangement to 2-methylcyclobutyl trifluoroacetate. This latter ester also solvolyzed under the reaction conditions causing the kinetic plots for the solvolysis of cyclopropylmethylcarbinyl trifluoroacetate to have some curvature towards the end of the reaction. Only that portion of the data that gave the initial straight line (above the solid line in the tables) was used in calculating the reported rate constants.

TABLE 52

SOLUBILITIES OF 0.00501 MOLAR CHLOROPROPYLENECARBONITRILE TRIFLUORO-  
ACETATE IN 60% DIOXANE-40% WATER AT 10.0°C.

| t<br>sec. | R<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-----------|-----------|---------------------------------|
| 60        | 253       | 0.0871                          |
| 90        | 203       | 0.1116                          |
| 120       | 170       | 0.1370                          |
| 150       | 150.0     | 0.1590                          |
| 180       | 134.0     | 0.1773                          |
| 210       | 122.0     | 0.2025                          |
| 240       | 113.0     | 0.2271                          |
| 270       | 107.0     | 0.2440                          |
| 300       | 99.0      | 0.2714                          |
| 330       | 94.0      | 0.2918                          |
| 360       | 90.0      | 0.3107                          |
| 390       | 85.5      | 0.3355                          |
| 420       | 82.0      | 0.3575                          |
| 450       | 79.5      | 0.3753                          |
| 480       | 77.0      | 0.3952                          |
| 510       | 74.5      | 0.4173                          |
| 540       | 72.5      | 0.4371                          |
| 570       | 70.8      | 0.4566                          |
| 600       | 69.4      | 0.4728                          |
| 660       | 66.5      | 0.5111                          |
| 720       | 64.0      | 0.5510                          |
| 780       | 62.0      | 0.5883                          |
| 840       | 60.8      | 0.6368                          |
| 900       | 58.5      | 0.6703                          |
| 960       | 57.3      | 0.7051                          |
| 1020      | 56.1      | 0.7446                          |
| 1080      | 55.1      | 0.7821                          |
| 1140      | 54.0      | 0.8293                          |
| 1200      | 53.3      | 0.8634                          |

$$R_{\infty} = 46.0 \text{ ohms}$$

$$k = 9.97 \times 10^{-1} \text{ min.}^{-1}$$

$$k = 1.66 \times 10^{-2} \text{ sec.}^{-1}$$



TABLE 53

SOLVOLYSIS OF 0.08526 MOLAR CYCLOPROPYLMETHYLGLUCONATE TRIFLUORO-  
ACETATE IN 60% DIOXANE-40% WATER AT 49.5° C.

| t<br>sec. | R<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-----------|-----------|---------------------------------|
| 60        | 311.0     | 0.1566                          |
| 80        | 121.5     | 0.2088                          |
| 100       | 100.0     | 0.2116                          |
| 120       | 90.0      | 0.2794                          |
| 140       | 81.5      | 0.3224                          |
| 160       | 75.5      | 0.3621                          |
| 180       | 71.0      | 0.3995                          |
| 200       | 67.0      | 0.4404                          |
| 220       | 64.0      | 0.4778                          |
| 240       | 61.8      | 0.5100                          |
| 260       | 59.2      | 0.5419                          |
| 280       | 57.6      | 0.5873                          |
| 300       | 55.8      | 0.6294                          |
| 320       | 54.5      | 0.6713                          |
| 340       | 53.2      | 0.7047                          |
| 360       | 52.4      | 0.7325                          |
| 380       | 51.1      | 0.7616                          |
| 400       | 50.5      | 0.8112                          |
| 420       | 49.9      | 0.8408                          |
| 440       | 48.1      | 0.9197                          |
| 500       | 47.6      | 0.9874                          |
| 520       | 47.1      | 1.0295                          |
| 540       | 46.8      | 1.0574                          |

$$R_{\infty} = 42.7 \text{ ohms}$$

$$k = 2.66 \times 10^{-1} \text{ min.}^{-1}$$

$$k = 4.44 \times 10^{-3} \text{ sec.}^{-1}$$

TABLE 51

SOLVOLYSIS OF 0.02718 MOLAR CYCLOHEXYLMETHYLOXYMETHYL SULFONOC-  
 ACETATE IN 80% DICHLOROMETHANE-20% WATER AT 60.1°C.

| $t$<br>sec. | $R$<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-------------|-------------|---------------------------------|
| 80          | 89.0        | 0.5069                          |
| 100         | 82.5        | 0.5901                          |
| 120         | 77.0        | 0.6906                          |
| 140         | 73.5        | 0.7799                          |
| 160         | 71.0        | 0.8605                          |
| 180         | 69.0        | 0.9524                          |
| 200         | 67.5        | 1.0399                          |
| 220         | 66.0        | 1.1174                          |
| 240         | 65.0        | 1.2007                          |
| 260         | 64.2        | 1.2661                          |
| 280         | 63.7        | 1.3239                          |

$$R_{\infty} = 63.3 \text{ ohms}$$

$$k = 6.39 \times 10^{-2} \text{ min.}^{-1}$$

$$k = 1.06 \times 10^{-3} \text{ sec.}^{-1}$$

TABLE 55

SOLVOLYSIS OF 0.02887 Molar CYCLOPROPYLMETHYLCARBONYL TRIFLUORO-  
ACETATE IN 70% DICHLORIDE-30% WATER AT 40.0°C.

| t<br>min. | R<br>ohms | $\log \frac{R}{R - R_0}$ |
|-----------|-----------|--------------------------|
| 6         | 2080      | 0.0824                   |
| 8         | 1850      | 0.0941                   |
| 10        | 1670      | 0.1053                   |
| 12        | 1540      | 0.1156                   |
| 14        | 1430      | 0.1258                   |
| 16        | 1340      | 0.1358                   |
| 18        | 1265      | 0.1453                   |
| 20        | 1200      | 0.1550                   |
| 22        | 1145      | 0.1641                   |
| 24        | 1097      | 0.1726                   |
| 26        | 1050      | 0.1824                   |
| 28        | 1020      | 0.1914                   |
| 30        | 977       | 0.1995                   |
| 34        | 920       | 0.2156                   |
| 38        | 870       | 0.2320                   |
| 42        | 825       | 0.2490                   |
| 46        | 780       | 0.2638                   |
| 50        | 750       | 0.2810                   |
| 54        | 720       | 0.3010                   |
| 58        | 700       | 0.3137                   |
| 62        | 675       | 0.3310                   |
| 66        | 658       | 0.3440                   |
| 70        | 640       | 0.3591                   |
| 74        | 623       | 0.3746                   |
| 78        | 605       | 0.3925                   |
| 82        | 590       | 0.4057                   |
| 86        | 581       | 0.4198                   |
| 90        | 572       | 0.4310                   |

$$R_0 = 360 \text{ ohms}$$

$$k = 1.03 \times 10^{-2} \text{ min.}^{-1}$$

$$k = 1.72 \times 10^{-4} \text{ sec.}^{-1}$$

TABLE 54

SOLVENTING OF 0.05% MILAR CELLULOSEPHENYLGLYNNATE TRIFLUORO-  
ACETATE IN 70% DECANOL-30% WATER AT 19.5°C.

| t<br>min. | R<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-----------|-----------|---------------------------------|
| 4         | 1340      | 0.1261                          |
| 5         | 1230      | 0.1396                          |
| 6         | 1185      | 0.1553                          |
| 7         | 1150      | 0.1688                          |
| 8         | 1050      | 0.1833                          |
| 9         | 988       | 0.1970                          |
| 10        | 947       | 0.2106                          |
| 11        | 880       | 0.2249                          |
| 12        | 845       | 0.2360                          |
| 13        | 806       | 0.2487                          |
| 14        | 775       | 0.2610                          |
| 15        | 740       | 0.2725                          |
| 16        | 705       | 0.2853                          |
| 17        | 680       | 0.2984                          |
| 18        | 642       | 0.3103                          |
| 19        | 616       | 0.3216                          |
| 20        | 630       | 0.3340                          |
| 21        | 616       | 0.3456                          |
| 22        | 604       | 0.3562                          |
| 23        | 592       | 0.3675                          |
| 24        | 581       | 0.3786                          |
| 25        | 570       | 0.3904                          |
| 26        | 559       | 0.4030                          |
| 30        | 506       | 0.4469                          |
| 31        | 520       | 0.4559                          |
| 32        | 512       | 0.4688                          |
| 33        | 505       | 0.4806                          |
| 34        | 498       | 0.4930                          |
| 36        | 488       | 0.5120                          |
| 38        | 477       | 0.5354                          |
| 40        | 468       | 0.5560                          |

$$R_{\infty} = 338 \text{ ohms}$$

$$k = 2.87 \times 10^{-2} \text{ min.}^{-1}$$

$$k = 4.78 \times 10^{-4} \text{ sec.}^{-1}$$

TABLE 57

SOLVOLYSES OF 0.02432 MOLAR CYCLOPROPYLMETHYLCARBONYL TRIFLUORO-  
ACETATE IN 70% DICKENS-30% WATER AT 49.8°C.

| t<br>min. | R<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-----------|-----------|---------------------------------|
| 4         | 1455      | 0.1313                          |
| 5         | 1330      | 0.1461                          |
| 6         | 1245      | 0.1581                          |
| 7         | 1165      | 0.1714                          |
| 8         | 1100      | 0.1843                          |
| 9         | 1048      | 0.1954                          |
| 10        | 1000      | 0.2074                          |
| 11        | 953       | 0.2209                          |
| 12        | 920       | 0.2315                          |
| 13        | 884       | 0.2440                          |
| 14        | 855       | 0.2553                          |
| 15        | 828       | 0.2667                          |
| 16        | 805       | 0.2774                          |
| 17        | 780       | 0.2900                          |
| 18        | 765       | 0.2982                          |
| 19        | 748       | 0.3081                          |
| 20        | 730       | 0.3193                          |
| 22        | 700       | 0.3400                          |
| 24        | 673       | 0.3612                          |
| 26        | 650       | 0.3815                          |
| 28        | 630       | 0.4014                          |
| 30        | 613       | 0.4200                          |
| 32        | 597       | 0.4395                          |
| 34        | 583       | 0.4582                          |
| 36        | 570       | 0.4771                          |
| 38        | 558       | 0.4962                          |
| 40        | 548       | 0.5135                          |

$$R_{\infty} = 380 \text{ ohms}$$

$$k = 2.78 \times 10^{-2} \text{ min.}^{-1}$$

$$k = 4.64 \times 10^{-4} \text{ sec.}^{-1}$$

TABLE 58

SOLVOLYSIS OF 0.0277 Molar CYCLOPROPYLMETHYLAMMONIUM TRIFLUORO-  
ACETATE IN 70% DICHLORO-30% WATER AT 60.1°C.

| $t$<br>sec. | $R$<br>ohms | $\log \frac{R}{R - R_\infty}$ |
|-------------|-------------|-------------------------------|
| 120         | 985         | 0.2794                        |
| 150         | 889         | 0.3096                        |
| 180         | 850         | 0.3155                        |
| 210         | 823         | 0.3210                        |
| 240         | 797         | 0.3275                        |
| 270         | 772         | 0.3331                        |
| 300         | 750         | 0.3384                        |
| 330         | 730         | 0.3435                        |
| 360         | 713         | 0.3483                        |
| 390         | 697         | 0.3517                        |
| 420         | 682         | 0.3552                        |
| 450         | 670         | 0.3584                        |
| 480         | 655         | 0.3617                        |
| 510         | 647         | 0.3649                        |
| 540         | 634         | 0.3680                        |
| 570         | 624         | 0.3707                        |
| 600         | 615         | 0.3733                        |
| 630         | 605         | 0.3767                        |
| 660         | 598         | 0.3795                        |
| 690         | 590         | 0.3823                        |
| 720         | 582         | 0.3850                        |
| 780         | 570         | 0.3986                        |
| 840         | 557         | 0.4139                        |
| 900         | 547         | 0.4246                        |
| 960         | 538         | 0.4351                        |
| 1020        | 530         | 0.4452                        |
| 1080        | 524         | 0.4559                        |
| 1140        | 518         | 0.4667                        |
| 1200        | 512         | 0.4760                        |

$$R_\infty = 439 \text{ ohms}$$

$$k = 7.52 \times 10^{-3} \text{ min.}^{-1}$$

$$k = 1.25 \times 10^{-3} \text{ sec.}^{-1}$$

TABLE 59

SOLVOLYSIS OF 0.002M N-ETHYL-N-ETHYL-2-AMINO-2-FLUOROPROPANESULFONATE IN 70% DIMETHYL-SULFONE-30% WATER AT 60.1°.

| t<br>sec. | R<br>ohms | $\log \frac{R}{R_\infty}$ |
|-----------|-----------|---------------------------|
| 120       | 1100      | 0.1339                    |
| 150       | 1055      | 0.1583                    |
| 180       | 1115      | 0.1700                    |
| 210       | 1060      | 0.1873                    |
| 240       | 975       | 0.2079                    |
| 270       | 920       | 0.2213                    |
| 300       | 870       | 0.2311                    |
| 330       | 825       | 0.2504                    |
| 360       | 785       | 0.2778                    |
| 390       | 755       | 0.2916                    |
| 420       | 730       | 0.3081                    |
| 450       | 705       | 0.3215                    |
| 480       | 680       | 0.3386                    |
| 510       | 660       | 0.3587                    |
| 540       | 640       | 0.3764                    |
| 570       | 625       | 0.3911                    |
| 600       | 610       | 0.4074                    |
| 660       | 585       | 0.4368                    |
| 720       | 565       | 0.4602                    |
| 780       | 545       | 0.4958                    |
| 840       | 528       | 0.5287                    |
| 900       | 515       | 0.5534                    |
| 960       | 502       | 0.5814                    |
| 1020      | 490       | 0.6117                    |
| 1080      | 481       | 0.6408                    |
| 1140      | 471       | 0.6730                    |
| 1200      | 462       | 0.7056                    |
| 1320      | 451       | 0.7510                    |
| 1440      | 440       | 0.8046                    |

$$R_\infty = 371 \text{ ohms}$$

$$k = 7.61 \times 10^{-3} \text{ min.}^{-1}$$

$$k = 1.27 \times 10^{-3} \text{ sec.}^{-1}$$

TABLE 60

SOLVOLYSIS OF 0.0260M NUCLEAR CYCLOPROPYLMETHYLOCARBONYL TRIFLUORO-  
ACETATE IN 70% ETHANOL-30% WATER AT 60.1°C.

| t<br>min. | R<br>ohms | $\log \frac{1}{1-R}$ |
|-----------|-----------|----------------------|
| 60        | 1700      | 0.1169               |
| 90        | 1530      | 0.1310               |
| 120       | 1375      | 0.1483               |
| 150       | 1255      | 0.1655               |
| 180       | 1160      | 0.1824               |
| 210       | 1080      | 0.1978               |
| 240       | 1020      | 0.2118               |
| 270       | 965       | 0.2210               |
| 300       | 910       | 0.2297               |
| 330       | 875       | 0.2364               |
| 360       | 840       | 0.2427               |
| 390       | 805       | 0.2482               |
| 420       | 780       | 0.2531               |
| 450       | 755       | 0.2573               |
| 480       | 730       | 0.2612               |
| 510       | 710       | 0.2647               |
| 540       | 695       | 0.2682               |
| 570       | 675       | 0.2719               |
| 600       | 660       | 0.2752               |
| 660       | 635       | 0.2800               |
| 720       | 615       | 0.2824               |
| 780       | 595       | 0.2860               |
| 840       | 578       | 0.2906               |
| 900       | 563       | 0.2930               |
| 960       | 550       | 0.2958               |
| 1020      | 538       | 0.2987               |
| 1080      | 527       | 0.3012               |
| 1140      | 520       | 0.3029               |
| 1200      | 512       | 0.3052               |
| 1320      | 497       | 0.3075               |

$$R_{\infty} = 398 \text{ ohms}$$

$$k = 7.32 \times 10^{-3} \text{ min.}^{-1}$$

$$k = 1.22 \times 10^{-3} \text{ sec.}^{-1}$$



TABLE 61

SOLYLYSIS OF 0.02598 MOLAR CYCLOHEXYLMETHYL CARBENYL TRIFLUORO-  
ACETATE IN 8% DICKENS-20% WATER AT 40.0°C.

| $t$<br>min. | $R$<br>ohms | $\log \frac{R}{R - R_0}$ |
|-------------|-------------|--------------------------|
| 5           | 9920        | 0.0962                   |
| 10          | 9100        | 0.1059                   |
| 15          | 8400        | 0.1333                   |
| 20          | 7820        | 0.1261                   |
| 25          | 7350        | 0.1351                   |
| 30          | 7000        | 0.1434                   |
| 35          | 6700        | 0.1511                   |
| 40          | 6400        | 0.1590                   |
| 45          | 6140        | 0.1679                   |
| 50          | 5870        | 0.1775                   |
| 60          | 5500        | 0.1826                   |
| 70          | 5100        | 0.2110                   |
| 80          | 4870        | 0.2250                   |
| 90          | 4640        | 0.2400                   |
| 100         | 4440        | 0.2527                   |
| 110         | 4280        | 0.2693                   |
| 120         | 4100        | 0.2814                   |
| 130         | 3980        | 0.2967                   |
| 140         | 3870        | 0.3090                   |
| 150         | 3770        | 0.3210                   |
| 160         | 3650        | 0.3371                   |
| 170         | 3570        | 0.3485                   |

$$R_0 = 1970 \text{ ohms}$$

$$k = 3.65 \times 10^{-5} \text{ min.}^{-1}$$

$$k = 6.08 \times 10^{-5} \text{ sec.}^{-1}$$

TABLE 62

SOLVOLYSIS OF 0.00628 MOLAR CYCLOPROPYLMETHYLCARBONYL TRIFLUORO-  
ACETATE IN 80% DIOXANE-20% WATER AT 49.5°C.

| t<br>min. | R<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-----------|-----------|---------------------------------|
| 6         | 10050     | 0.1028                          |
| 8         | 9080      | 0.1150                          |
| 10        | 8270      | 0.1271                          |
| 12        | 7680      | 0.1386                          |
| 14        | 7200      | 0.1498                          |
| 16        | 6770      | 0.1614                          |
| 18        | 6440      | 0.1714                          |
| 20        | 6160      | 0.1810                          |
| 22        | 5850      | 0.1931                          |
| 24        | 5650      | 0.2019                          |
| 26        | 5450      | 0.2114                          |
| 28        | 5270      | 0.2206                          |
| 30        | 5090      | 0.2310                          |
| 32        | 4930      | 0.2410                          |
| 34        | 4800      | 0.2499                          |
| 36        | 4650      | 0.2608                          |
| 38        | 4550      | 0.2688                          |
| 40        | 4450      | 0.2774                          |

$$R_{\infty} = 2100 \text{ ohms}$$

$$k = 1.18 \times 10^{-3} \text{ min.}^{-1}$$

$$k = 1.96 \times 10^{-4} \text{ sec.}^{-1}$$

TABLE 63

SOLVOLYSIS OF 0.057M N-ALCOYL-2-ETHYL-2-ETHYLMETHYLCARBONYL TRIFLUORO-  
ACETATE IN 80% DIOXANE-20% WATER AT 60.1°C.

| t<br>sec. | R<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-----------|-----------|---------------------------------|
| 60        | 5150      | 0.2378                          |
| 90        | 5000      | 0.2172                          |
| 120       | 4860      | 0.2570                          |
| 150       | 4720      | 0.2694                          |
| 180       | 4610      | 0.2762                          |
| 210       | 4510      | 0.2819                          |
| 240       | 4420      | 0.2931                          |
| 270       | 4320      | 0.3030                          |
| 300       | 4240      | 0.3113                          |
| 360       | 4090      | 0.3284                          |
| 420       | 3970      | 0.3436                          |
| 480       | 3870      | 0.3572                          |
| 540       | 3780      | 0.3707                          |
| 600       | 3690      | 0.3852                          |
| 720       | 3530      | 0.4140                          |
| 840       | 3420      | 0.4371                          |
| 960       | 3310      | 0.4629                          |
| 1080      | 3230      | 0.4839                          |
| 1200      | 3160      | 0.5041                          |
| 1320      | 3100      | 0.5228                          |
| 1440      | 3020      | 0.5506                          |
| 1560      | 2970      | 0.5696                          |
| 1680      | 2920      | 0.5962                          |
| 1800      | 2870      | 0.6128                          |
| 2100      | 2780      | 0.6587                          |
| 2400      | 2690      | 0.7137                          |
| 2700      | 2610      | 0.7732                          |
| 3000      | 2560      | 0.8172                          |

$$R_{\infty} = 2170 \text{ ohms}$$

$$k = 4.09 \times 10^{-2} \text{ min.}^{-1}$$

$$k = 6.81 \times 10^{-4} \text{ sec.}^{-1}$$

Methylmercaptopyridineyl trifluoroacetate was not obtained pure. The data in Tables 64, 66, 68, 70 and 72 are those obtained directly on the impure ester. The data in Tables 65, 67, 69, 71 and 73 were calculated from the respective original tables using assumed value of  $k_p$  (calculated as mentioned in the section "Discussion and Results" of the first part of this thesis). These latter data gave initial straight lines from which the reported solvolysis rate constants for this ester were calculated.

TABLE 61

SOLVOLYSIS OF 0.00026 Molar METHYLNORADRETYLGLUCAMINE TRIFLUORO-  
ACETATE IN 70% DIKANE-30% WATER AT 49.9°C.

| t<br>sec. | R<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-----------|-----------|---------------------------------|
| 60        | 300       | 0.8365                          |
| 90        | 243       | 0.8175                          |
| 120       | 235       | 0.8031                          |
| 150       | 197       | 0.8433                          |
| 180       | 185       | 0.8939                          |
| 210       | 176       | 0.8465                          |
| 240       | 171       | 0.8798                          |
| 300       | 164       | 0.8807                          |
| 360       | 161       | 0.6657                          |
| 420       | 159       | 0.6882                          |
| 480       | 157       | 0.7046                          |
| 540       | 156       | 0.7160                          |
| 600       | 155       | 0.7280                          |
| 720       | 154       | 0.7404                          |
| 840       | 153       | 0.7533                          |
| 960       | 152.5     | 0.7699                          |
| 1080      | 151.5     | 0.7739                          |
| 1200      | 151.0     | 0.7810                          |
| 1440      | 150.0     | 0.7959                          |
| 3300      | 142.4     | 0.9367                          |
| 6300      | 137.0     | 1.0952                          |
| 7200      | 136.0     | 1.1335                          |
| 8100      | 135.0     | 1.1761                          |
| 9000      | 134.0     | 1.2240                          |

$$R_{\infty} = 126 \text{ ohms}$$

TABLE 65

DERIVED DATA FROM THE SOLVOLYSIS OF 0.02025 MOLAR METHYLPHOSPHORYL-  
CYCLICCARBONATE TRIPHOSPHATE IN 70% DIMETHYL-  
30% WATER AT 19.9°C.

| $t$<br>sec. | $R$<br>ohms | $\log \frac{R}{R - R_0}$ |
|-------------|-------------|--------------------------|
| 60          | 300         | 0.3128                   |
| 90          | 285         | 0.1362                   |
| 120         | 275         | 0.572                    |
| 150         | 267         | 0.6610                   |
| 180         | 265         | 0.7709                   |
| 210         | 276         | 0.9032                   |
| 240         | 271         | 1.0824                   |

$$R_0 = 154 \text{ ohms}$$

$$k = 5.31 \times 10^{-2} \text{ min.}^{-1}$$

$$k = 8.84 \times 10^{-3} \text{ sec.}^{-1}$$

TABLE 66

SOLVOLYSIS OF 0.02405 MOLAR METHYLHEPTICALLYCARBINYL TRIFLUORO-  
ACETATE IN 70% DICHLORIDE-30% WATER AT 49.9°C.

| $t$<br>sec. | $R$<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-------------|-------------|---------------------------------|
| 50          | 420         | 0.1578                          |
| 60          | 370         | 0.1844                          |
| 80          | 293         | 0.2194                          |
| 100         | 267         | 0.2535                          |
| 120         | 241         | 0.2890                          |
| 140         | 215         | 0.3239                          |
| 160         | 202         | 0.3462                          |
| 180         | 194         | 0.3682                          |
| 200         | 188         | 0.3960                          |
| 220         | 183         | 0.4220                          |
| 240         | 178.5       | 0.4484                          |
| 300         | 170.0       | 0.5144                          |
| 360         | 165.0       | 0.6072                          |
| 420         | 162.0       | 0.6781                          |
| 480         | 160.5       | 0.6935                          |
| 540         | 159.5       | 0.7044                          |
| 600         | 158.5       | 0.7229                          |
| 900         | 155.0       | 0.7590                          |
| 1200        | 154.5       | 0.7657                          |
| 1800        | 151.0       | 0.8172                          |
| 2400        | 148.0       | 0.8692                          |
| 3000        | 146.0       | 0.9091                          |
| 3600        | 144.5       | 0.9424                          |
| 4200        | 142.5       | 0.9925                          |
| 5400        | 141.0       | 1.0354                          |
| 7200        | 136.0       | 1.2304                          |
| 9000        | 134.0       | 1.3489                          |

$R_{\infty} = 128$  ohms

TABLE 67

DERIVED DATA FROM THE SOLVELEN OF 0.02105 MOLAR NITRILONGITRIL-  
CYCLOHEXANENE. TRIPHENYLACETATE IN 70% DICKANE-  
30% WATER AT 49.9°C.

| $t$<br>sec. | $R$<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-------------|-------------|---------------------------------|
| 50          | 120         | 0.2049                          |
| 60          | 170         | 0.2118                          |
| 80          | 293         | 0.3365                          |
| 100         | 267         | 0.3822                          |
| 120         | 211         | 0.4639                          |
| 140         | 215         | 0.5766                          |
| 160         | 202         | 0.6619                          |
| 180         | 194         | 0.7315                          |
| 200         | 188         | 0.7971                          |
| 220         | 183         | 0.8645                          |
| 240         | 178.5       | 0.9399                          |

$$R_{\infty} = 158 \text{ ohms}$$

$$k = 5.42 \times 10^{-1} \text{ min.}^{-1}$$

$$k = 9.03 \times 10^{-2} \text{ sec.}^{-1}$$



TABLE 68

SOLUBILITY OF 0.02023 MOLAR METHYLOROTRISTULYLCARBINYL TRIFLUORO-  
ACRYATE IN 70% DIETHANE-30% WATER AT 19.9°C.

| $t$<br>sec. | $R$<br>ohms | $\log \frac{R}{R - R_0}$ |
|-------------|-------------|--------------------------|
| 50          | 1440        | 0.1870                   |
| 60          | 1400        | 0.2111                   |
| 80          | 1400        | 0.2420                   |
| 100         | 1308        | 0.3096                   |
| 120         | 1285        | 0.3377                   |
| 140         | 1260        | 0.3897                   |
| 160         | 1244        | 0.4331                   |
| 180         | 1213        | 0.4667                   |
| 200         | 1226        | 0.4968                   |
| 220         | 1221        | 0.5144                   |
| 240         | 1216        | 0.5321                   |
| 260         | 1212        | 0.5629                   |
| 280         | 1209        | 0.5798                   |
| 300         | 1207        | 0.5917                   |
| 360         | 1201        | 0.6311                   |
| 420         | 1198        | 0.6532                   |
| 480         | 1196        | 0.6731                   |
| 540         | 1195        | 0.6772                   |
| 600         | 1194        | 0.6857                   |
| 900         | 1192        | 0.7035                   |
| 1200        | 1190        | 0.7225                   |
| 1800        | 1187        | 0.7533                   |
| 2400        | 1185        | 0.7758                   |
| 3000        | 1183        | 0.7998                   |
| 3600        | 1181        | 0.8129                   |
| 5400        | 1174        | 0.9395                   |
| 7200        | 1170        | 1.0261                   |
| 9900        | 1165        | 1.1761                   |

$$R_0 = 154 \text{ ohms}$$

TABLE 69

DERIVED DATA FROM THE SOLVOLYSIS OF 0.02023 MOLAR METHYLNITRIL-  
CYCLICAMINEYL TRIFLUOROACETATE IN 70% DIOXANE-  
30% WATER AT 49.9°C.

| $t$<br>sec. | $R$<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-------------|-------------|---------------------------------|
| 50          | 440         | 0.2190                          |
| 60          | 400         | 0.2240                          |
| 80          | 340         | 0.3222                          |
| 100         | 302         | 0.4385                          |
| 120         | 285         | 0.4861                          |
| 140         | 260         | 0.5285                          |
| 160         | 244         | 0.5714                          |
| 180         | 233         | 0.7516                          |
| 200         | 226         | 0.8226                          |
| 220         | 221         | 0.8820                          |
| 240         | 216         | 0.9212                          |

$$R_{\infty} = 192 \text{ ohms}$$

$$k = 5.22 \times 10^{-1} \text{ min.}^{-1}$$

$$k = 8.70 \times 10^{-3} \text{ sec.}^{-1}$$

TABLE 70

SOLUBILITIES OF 0.020M N-METHYLNORADICETYLGLANINE SULFINO-  
ACETATE IN 70% ETHANOL-30% WATER AT 15.9° C.

| $t$<br>sec. | $R$<br>ohms | $\log \frac{R}{R - R_0}$ |
|-------------|-------------|--------------------------|
| 60          | 620         | 0.1611                   |
| 80          | 525         | 0.2085                   |
| 100         | 451         | 0.2408                   |
| 120         | 410         | 0.2714                   |
| 140         | 381         | 0.3013                   |
| 160         | 362         | 0.3282                   |
| 180         | 349         | 0.3549                   |
| 200         | 337         | 0.3682                   |
| 220         | 328         | 0.3821                   |
| 240         | 319         | 0.4000                   |
| 260         | 312         | 0.4160                   |
| 300         | 302         | 0.4385                   |
| 360         | 297         | 0.4516                   |
| 420         | 291         | 0.4602                   |
| 480         | 286         | 0.4771                   |
| 540         | 285         | 0.4864                   |
| 600         | 283         | 0.4928                   |
| 660         | 281         | 0.4993                   |
| 900         | 279         | 0.5061                   |
| 1200        | 276         | 0.5167                   |
| 1500        | 272         | 0.5315                   |
| 1800        | 270         | 0.5393                   |
| 2400        | 265         | 0.5599                   |
| 3000        | 260         | 0.5825                   |
| 3600        | 258         | 0.5921                   |
| 5400        | 249         | 0.6403                   |
| 7200        | 240         | 0.6990                   |
| 9000        | 233         | 0.7546                   |
| 10800       | 230         | 0.7820                   |

$$R_0 = 192 \text{ ohms}$$

TABLE 71

DERIVED DATA FROM THE SOLYLYSIS OF 0.02027 Molar NITROLYNORTH-  
CHOLYLCHAMPHYL TRIFLUOROMETHANE IN 70% DIOXANE-  
30% WATER AT 49.9°C.

| $t$<br>sec.                                                                                                                   | $R$<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-------------------------------------------------------------------------------------------------------------------------------|-------------|---------------------------------|
| 60                                                                                                                            | 600         | 0.2634                          |
| 80                                                                                                                            | 515         | 0.3644                          |
| 100                                                                                                                           | 451         | 0.4284                          |
| 120                                                                                                                           | 410         | 0.5056                          |
| 140                                                                                                                           | 381         | 0.5888                          |
| 160                                                                                                                           | 362         | 0.6586                          |
| 180                                                                                                                           | 349         | 0.7187                          |
| 200                                                                                                                           | 337         | 0.7873                          |
| 220                                                                                                                           | 328         | 0.8531                          |
| 240                                                                                                                           | 319         | 0.9356                          |
| $R_{\infty} = 282 \text{ ohms}$<br>$k = 5.07 \times 10^{-1} \text{ min.}^{-1}$<br>$k = 8.46 \times 10^{-3} \text{ sec.}^{-1}$ |             |                                 |

TABLE 72

SOLVOLYSIS OF 0.02285 MOLAR METHYLNORTHCELYLCARBINYL TRIFLUORO-  
ACETATE IN 60% DIKANE-20% WATER AT 19.9°C.

| t<br>sec. | R<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-----------|-----------|---------------------------------|
| 60        | 1690      | 0.1073                          |
| 90        | 1350      | 0.1392                          |
| 120       | 1150      | 0.1685                          |
| 140       | 1055      | 0.1875                          |
| 160       | 980       | 0.2060                          |
| 180       | 925       | 0.2219                          |
| 200       | 873       | 0.2343                          |
| 220       | 830       | 0.2502                          |
| 240       | 800       | 0.2695                          |
| 260       | 770       | 0.2844                          |
| 280       | 745       | 0.2982                          |
| 300       | 722       | 0.3120                          |
| 320       | 703       | 0.3245                          |
| 340       | 688       | 0.3353                          |
| 360       | 673       | 0.3466                          |
| 390       | 650       | 0.3657                          |
| 420       | 635       | 0.3795                          |
| 480       | 613       | 0.4019                          |
| 540       | 593       | 0.4247                          |
| 600       | 577       | 0.4415                          |
| 660       | 568       | 0.4577                          |
| 720       | 560       | 0.4694                          |
| 840       | 552       | 0.4819                          |
| 900       | 547       | 0.4900                          |
| 960       | 542       | 0.4985                          |
| 1050      | 535       | 0.5108                          |
| 1200      | 530       | 0.5202                          |
| 1500      | 524       | 0.5319                          |
| 1800      | 520       | 0.5400                          |

$$R_{\infty} = 370 \text{ ohms}$$

TABLE 73

DERIVED DATA FROM THE SOLVOLYSIS OF 0.02026 MOLAR METHYLNORTRI-  
CYLYLCARBONYL TRIFLUOROACETATE IN 80% DIOXANE-  
20% WATER AT 49.9°C.

| $t$<br>sec. | $R$<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-------------|-------------|---------------------------------|
| 60          | 1490        | 0.1569                          |
| 90          | 1390        | 0.2071                          |
| 120         | 1350        | 0.2598                          |
| 140         | 1025        | 0.2885                          |
| 160         | 980         | 0.3210                          |
| 180         | 925         | 0.3503                          |
| 200         | 873         | 0.3821                          |
| 220         | 830         | 0.4144                          |
| 240         | 800         | 0.4437                          |
| 260         | 770         | 0.4748                          |
| 280         | 745         | 0.5018                          |
| 300         | 722         | 0.5363                          |
| 320         | 703         | 0.5660                          |
| 340         | 688         | 0.5971                          |
| 360         | 673         | 0.6212                          |
| 390         | 650         | 0.6730                          |
| 420         | 635         | 0.7129                          |

$$R_{\infty} = 512 \text{ ohms}$$

$$k = 2.13 \times 10^{-2} \text{ min.}^{-1}$$

$$k = 3.51 \times 10^{-4} \text{ sec.}^{-1}$$

TABLE 74

SOLVOLYSIS OF 0.05123 Molar n-BUTYL TRIPHTHOSPHATE IN 70%  
DIOXANE-30% WATER AT 45.1°C.

| t<br>min. | R<br>ohms | $\log \frac{R}{R - R_\infty}$ |
|-----------|-----------|-------------------------------|
| 15        | 2400      | 0.0986                        |
| 20        | 2170      | 0.0822                        |
| 45        | 1660      | 0.0835                        |
| 60        | 1390      | 0.1018                        |
| 75        | 1190      | 0.1212                        |
| 90        | 1060      | 0.1389                        |
| 105       | 960       | 0.1562                        |
| 120       | 877       | 0.1744                        |
| 135       | 810       | 0.1928                        |
| 150       | 755       | 0.2106                        |
| 165       | 705       | 0.2299                        |
| 180       | 673       | 0.2448                        |
| 195       | 640       | 0.2622                        |
| 210       | 610       | 0.2806                        |
| 225       | 580       | 0.3010                        |
| 240       | 560       | 0.3170                        |

$$R_\infty = 290 \text{ ohms}$$

$$k = 2.81 \times 10^{-3} \text{ min.}^{-1}$$

$$k = 4.69 \times 10^{-5} \text{ sec.}^{-1}$$

TABLE 75

SOLVOLYSIS OF 0.05123 MOLAR *n*-BUTYL TRIFLUOROACETATE  
IN 70.7% ACETONE-29.3% WATER AT 45.1°C.

| $t$<br>min. | $R$<br>ohms | $\log \frac{R}{R - R_{\infty}}$ |
|-------------|-------------|---------------------------------|
| 15          | 825         | 0.0318                          |
| 30          | 458         | 0.0588                          |
| 45          | 328         | 0.0846                          |
| 60          | 262         | 0.1086                          |
| 75          | 221         | 0.1323                          |
| 90          | 192         | 0.1563                          |
| 105         | 171         | 0.1798                          |
| 120         | 155         | 0.2036                          |
| 135         | 142.0       | 0.2279                          |
| 150         | 132.0       | 0.2514                          |
| 165         | 123.0       | 0.2769                          |
| 180         | 116.5       | 0.2991                          |
| 195         | 110.0       | 0.3253                          |
| 210         | 105.0       | 0.3491                          |
| 225         | 100.5       | 0.3738                          |
| 240         | 97.0        | 0.3957                          |

$$R_{\infty} = 58.0 \text{ ohms}$$

$$k = 3.70 \times 10^{-3} \text{ min.}^{-1}$$

$$k = 6.17 \times 10^{-5} \text{ sec.}^{-1}$$



Figure 19. Plot of  $\log k$  versus  $1/T$  for the Solvolysis of Cyclopropylcarbinyl Trifluoroacetate in 60% Dioxane-40% Water.

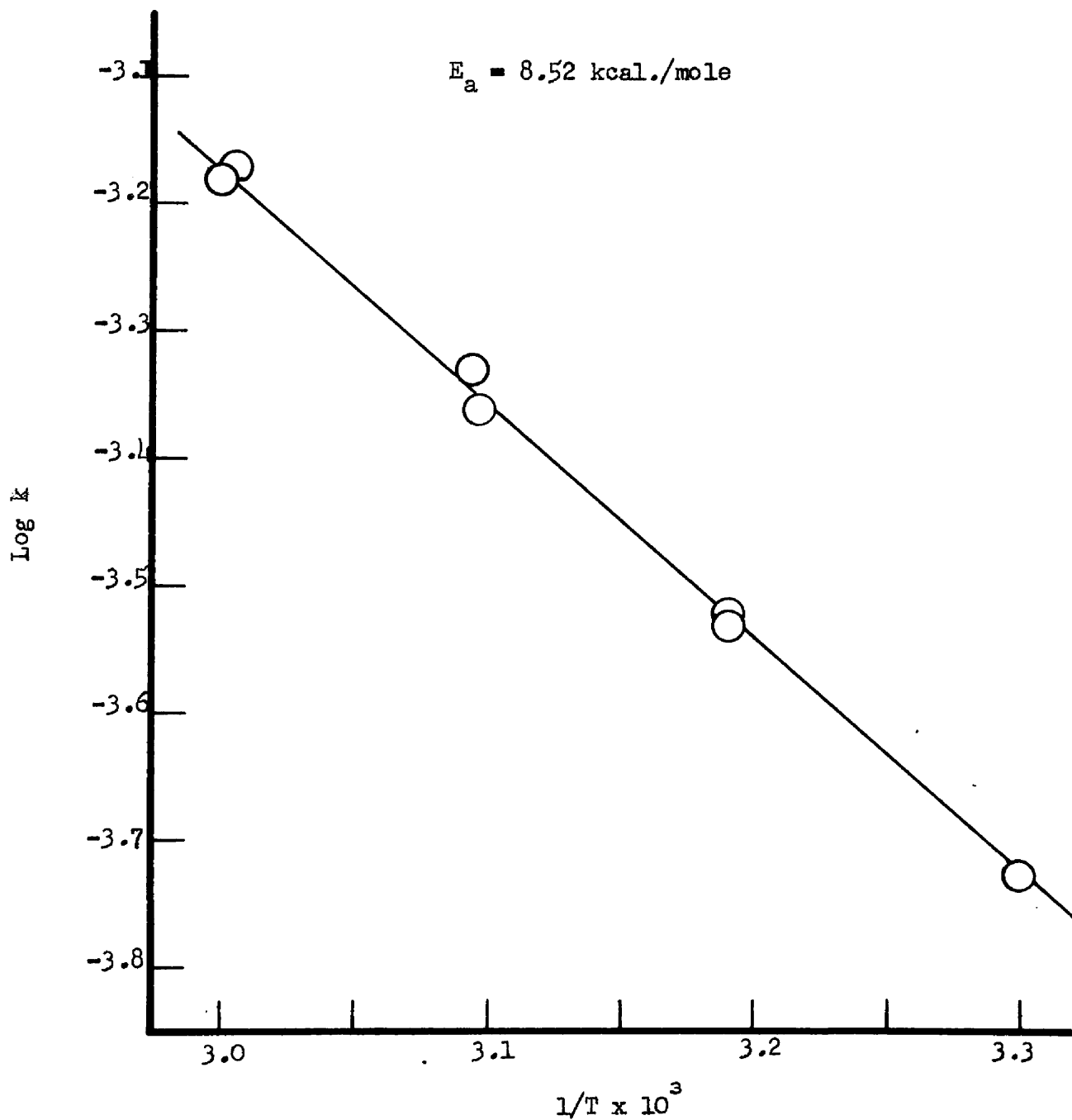


Figure 20. Plot of  $\log k$  versus  $1/T$  for the Solvolysis of Cyclopropylcarbinyl Trifluoroacetate in 70% Dioxane-30% Water.

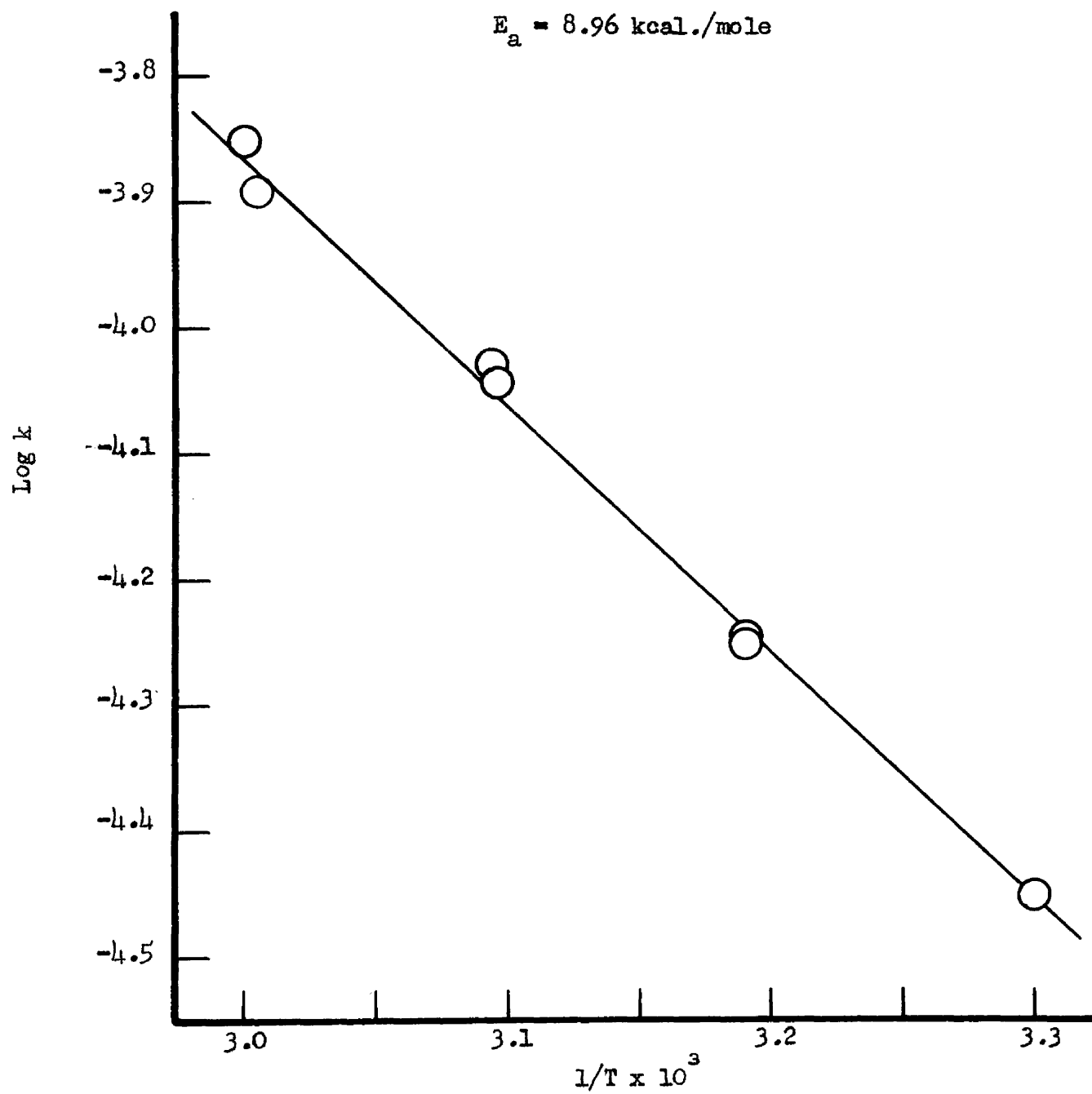


Figure 21. Plot of  $\log k$  versus  $1/T$  for the Solvolysis of Cyclopropylcarbinyl Trifluoroacetate in 80% Dioxane-20% Water.

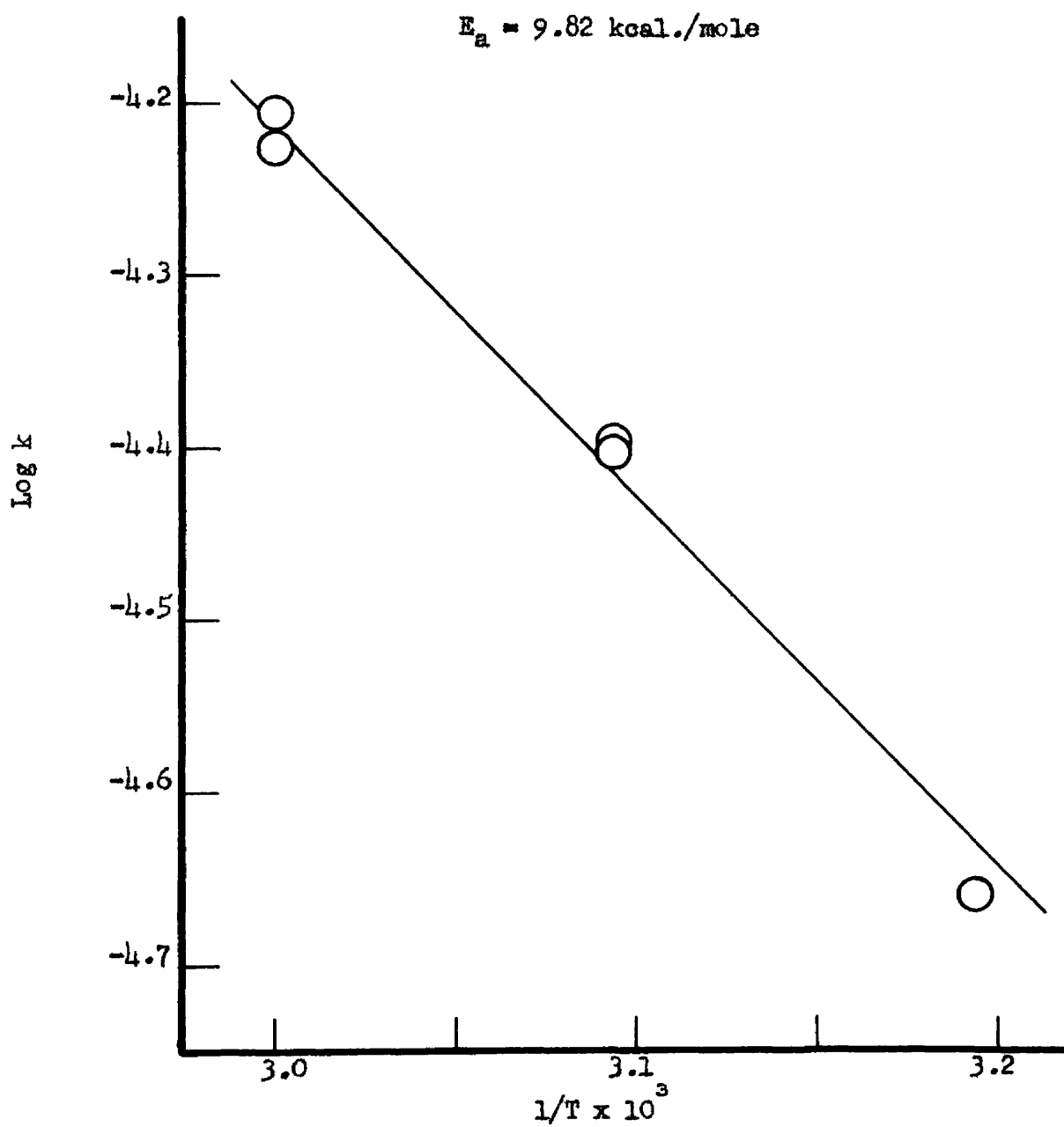


Figure 22. Plot of  $\log k$  versus  $1/T$  for the Solvolysis of Nortricyclylcarbonyl Trifluoroacetate in 60% Dioxane-40% Water.

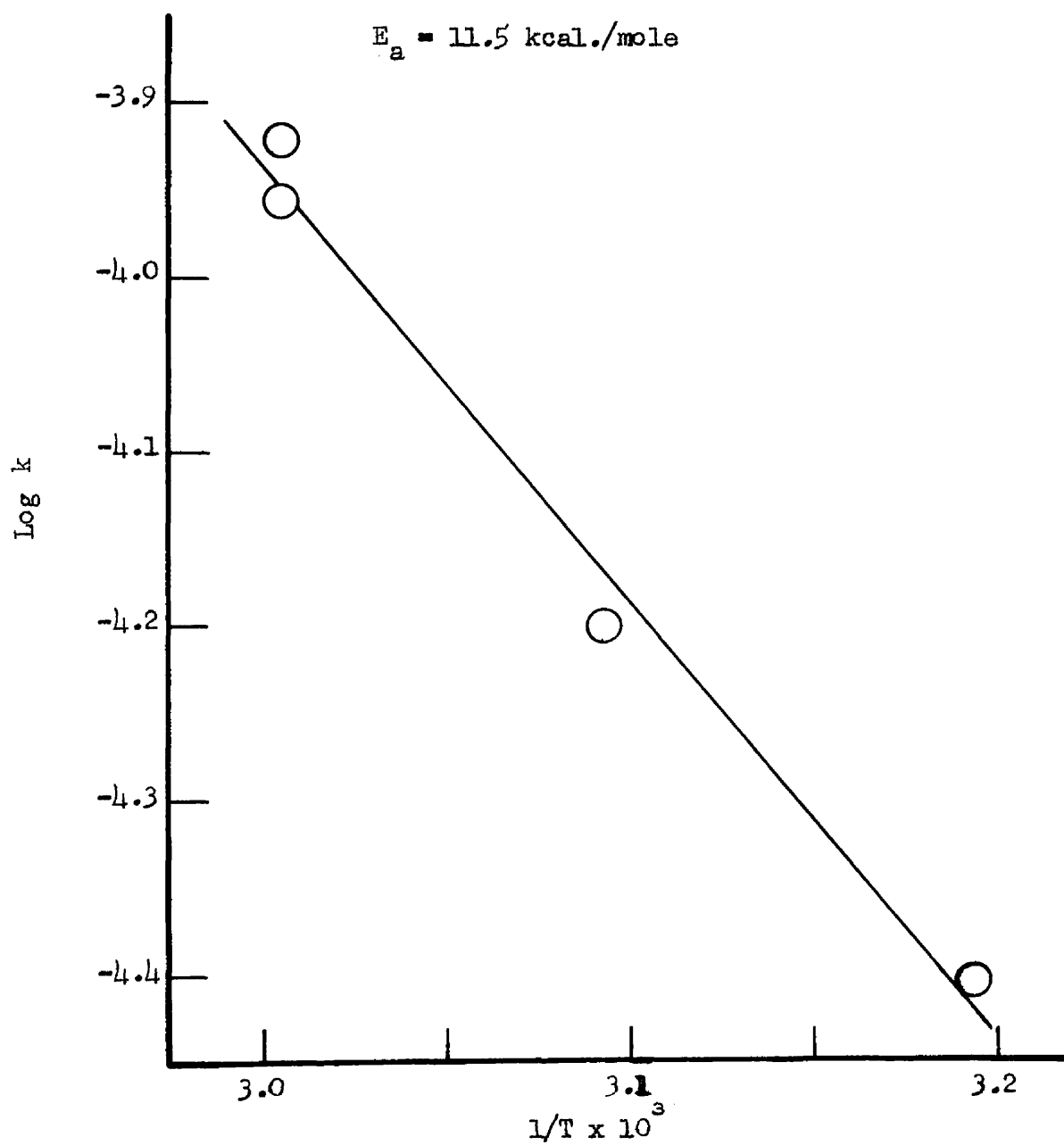


Figure 23. Plot of  $\log k$  versus  $1/T$  for the Solvolysis of Nortricyclylcarbiny1 Trifluoroacetate in 70% Dioxane-30% Water.

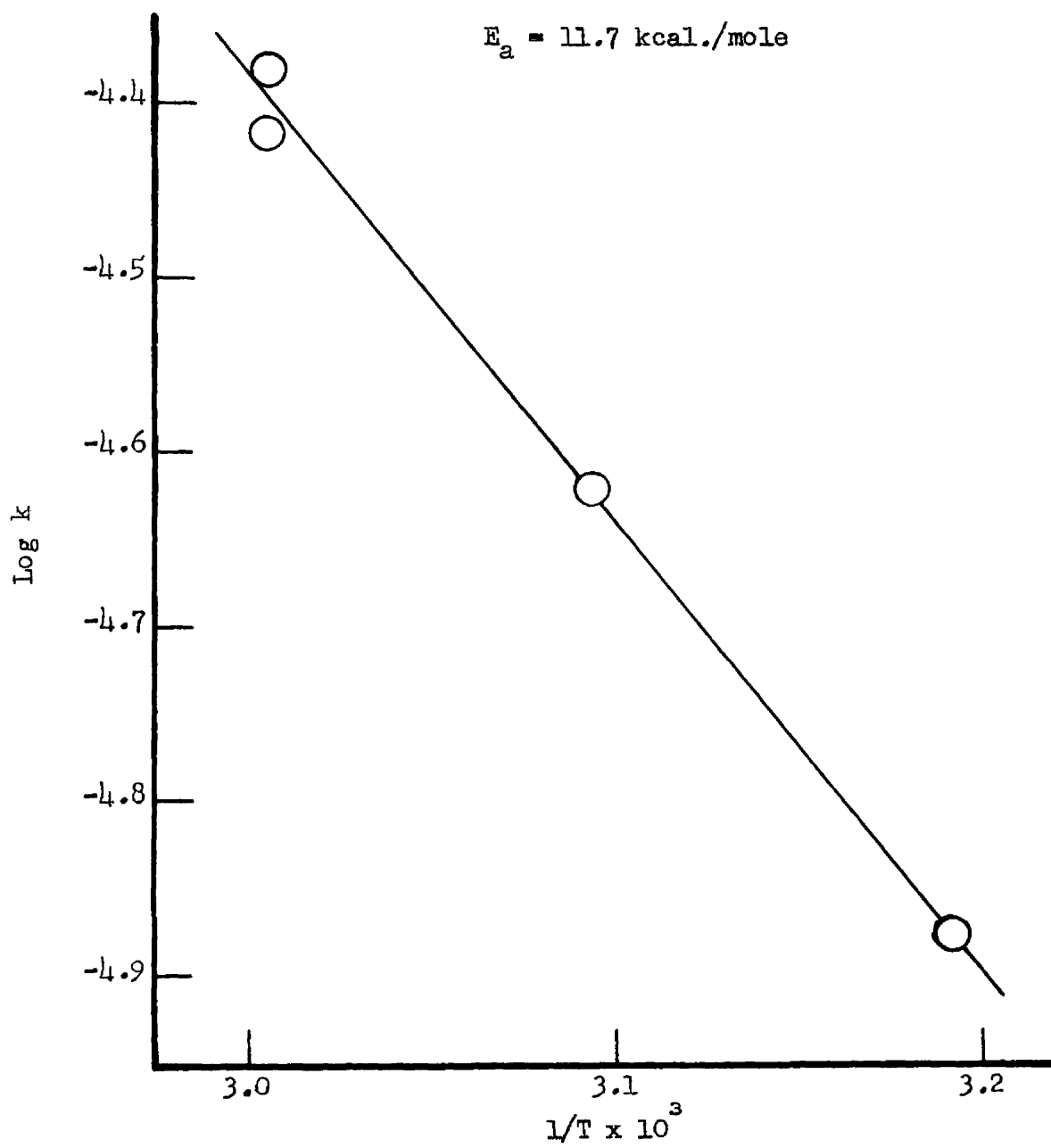


Figure 24. Plot of  $\log k$  versus  $1/T$  for the Solvolysis of Nortricyclylcarbiny1 Trifluoroacetate in 80% Dioxane-20% Water.

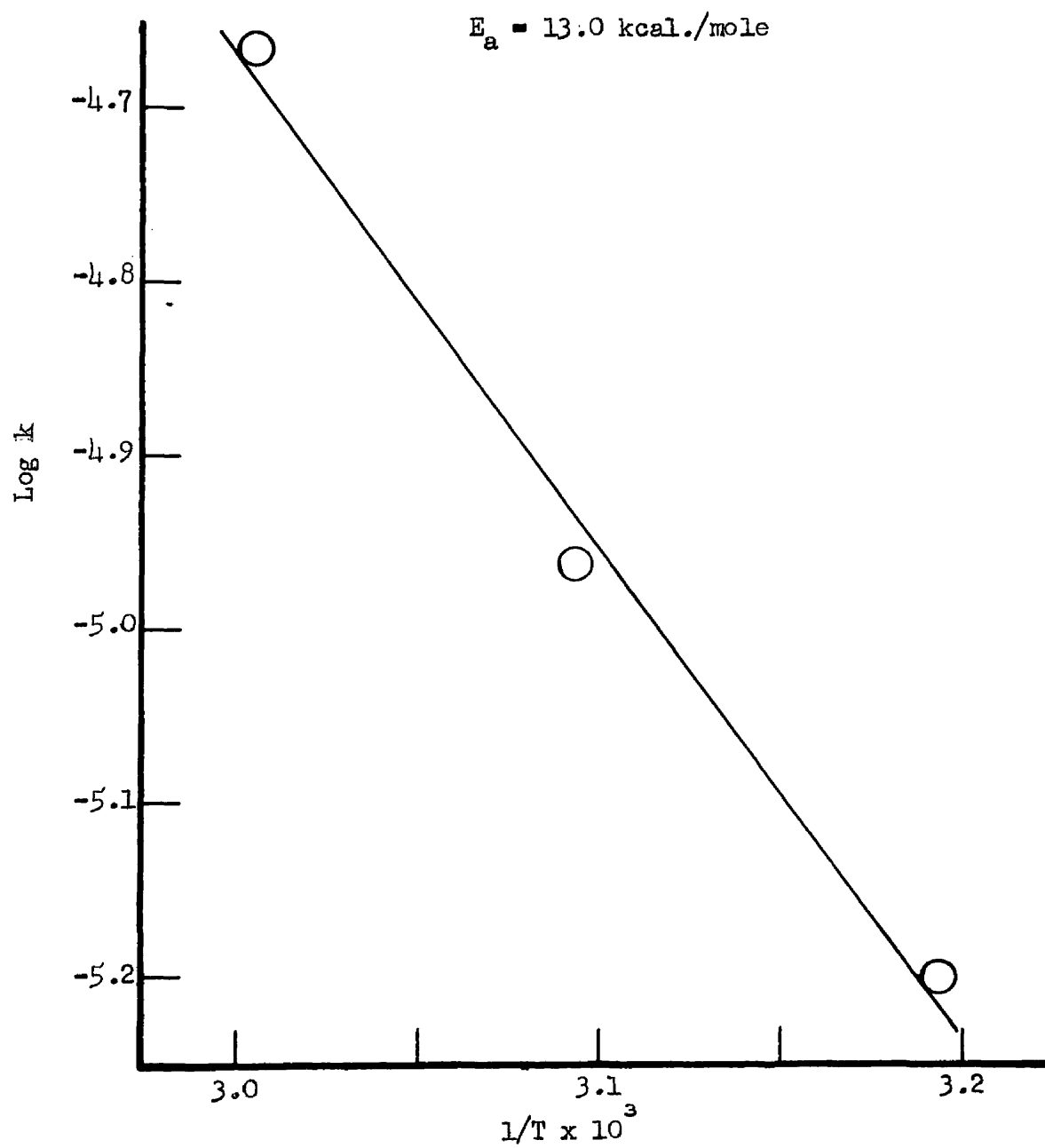


Figure 25. Plot of  $\log k$  versus  $1/T$  for the Solvolysis of 2-Methylcyclobutyl Trifluoroacetate in 60% Dioxane-40% Water.

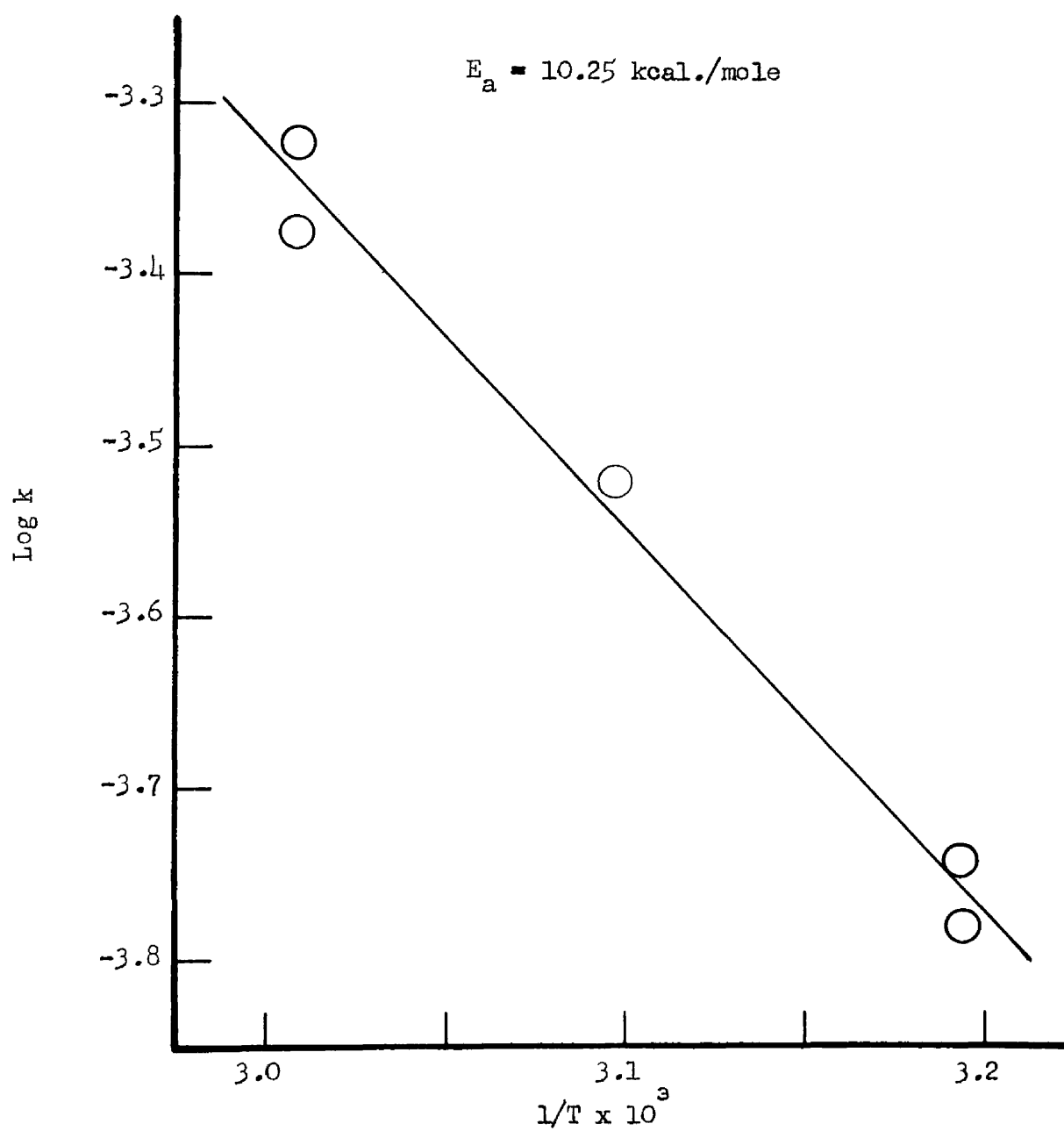


Figure 26. Plot of  $\log k$  versus  $1/T$  for the Solvolysis of 2-Methylcyclobutyl Trifluoroacetate in 70% Dioxane-30% Water.

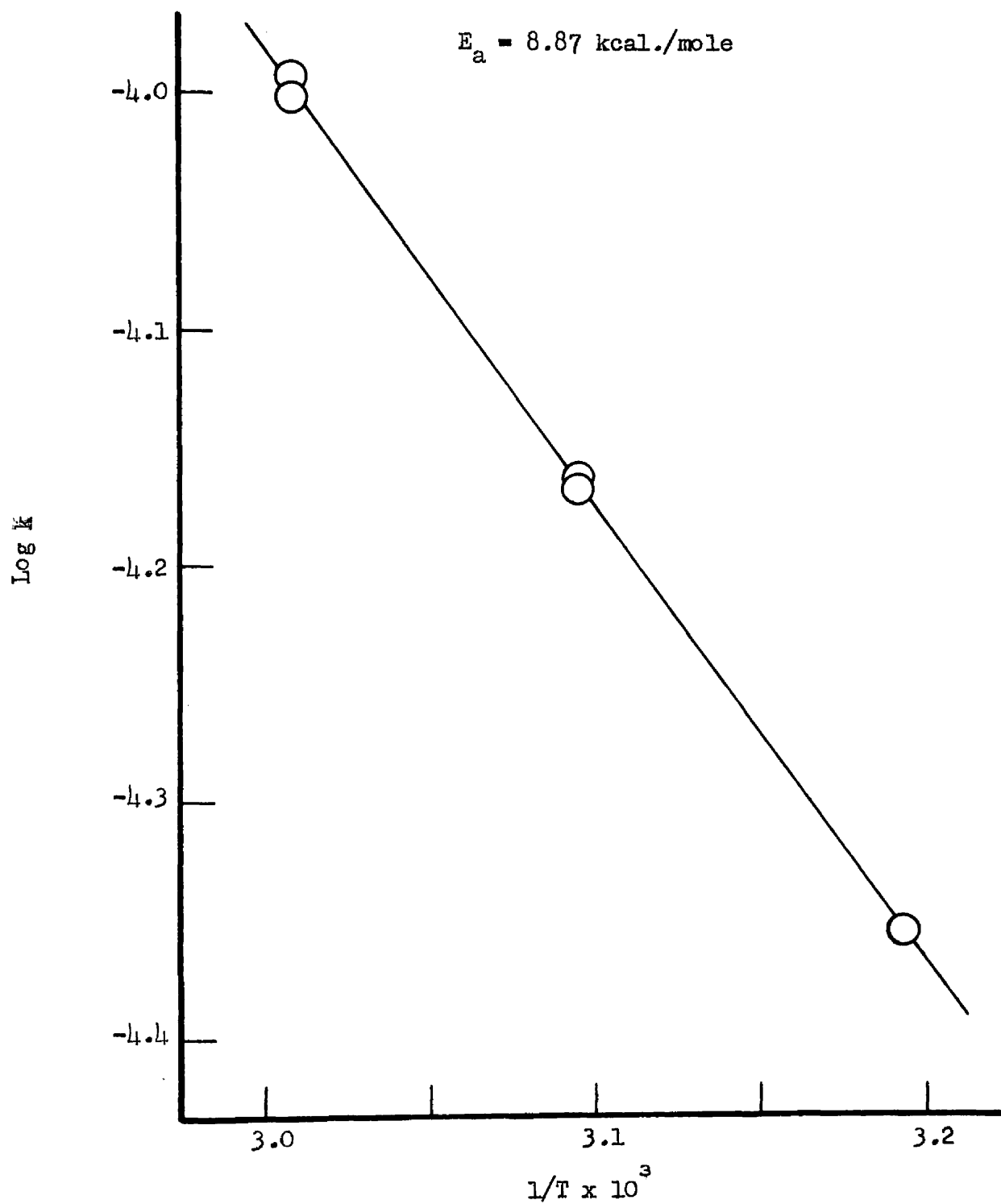




Figure 27. Plot of  $\log k$  versus  $1/T$  for the Solvolysis of Cyclopropylmethylcarbonyl Trifluoroacetate in 60% Dioxane-40% Water.

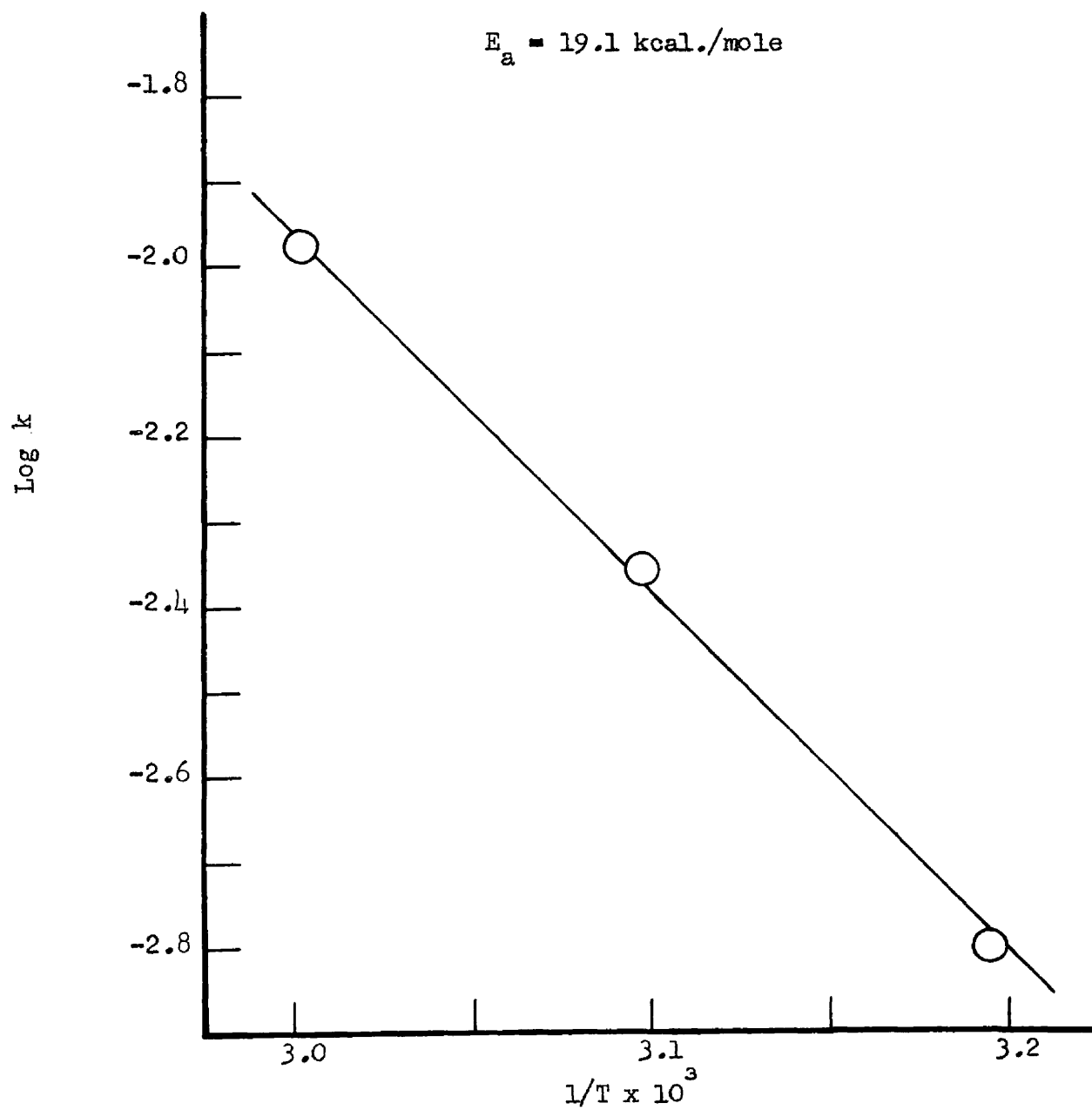


Figure 28. Plot of  $\log k$  versus  $1/T$  for the Solvolysis of Cyclopropylmethylcarbonyl Trifluoroacetate in 70% Dioxane-30% Water.

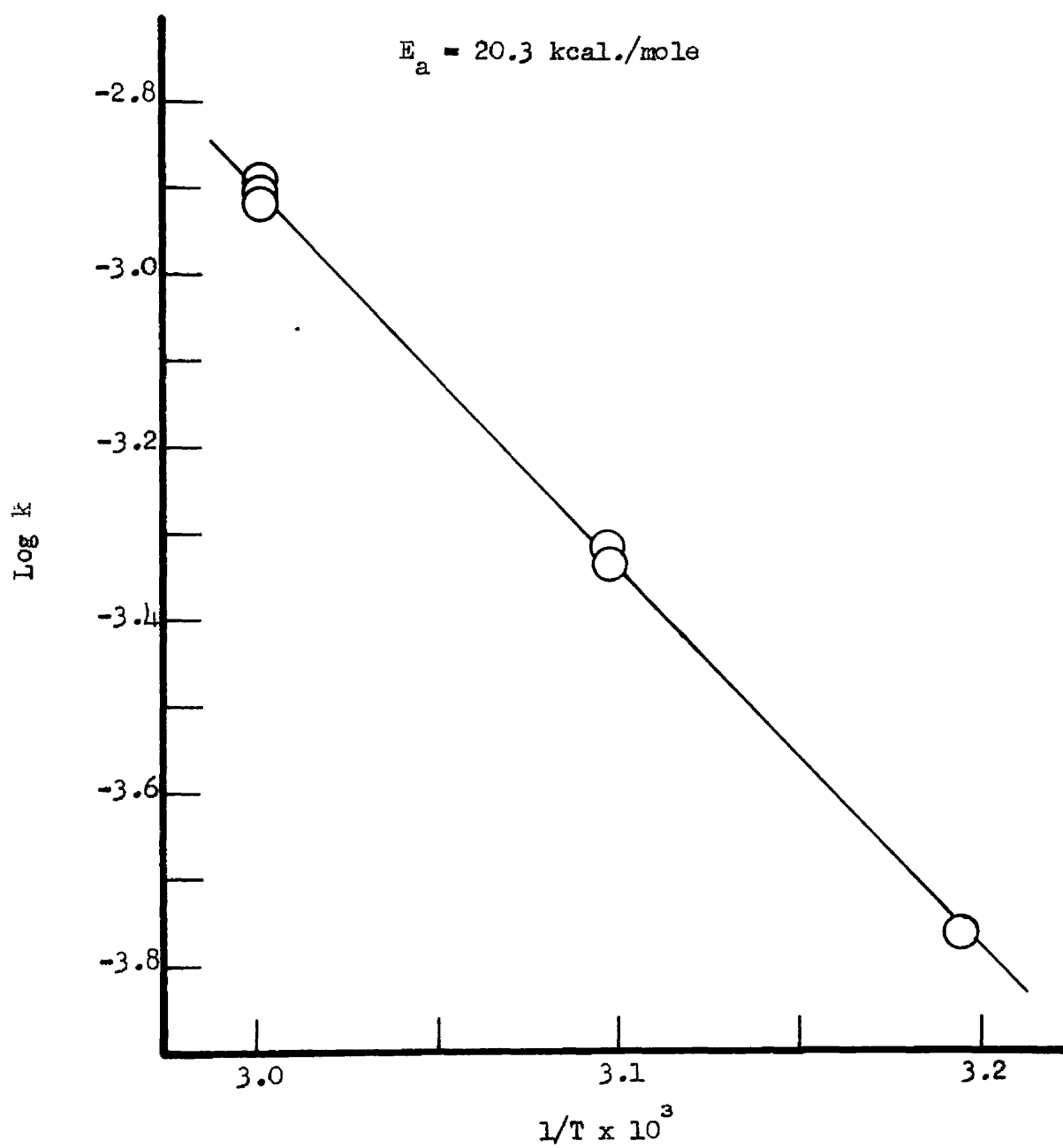


Figure 29. Plot of  $\log k$  versus  $1/T$  for the Solvolysis of Cyclopropylmethylcarbonyl Tri-fluoroacetate in 80% Dioxane-20% Water.

