SOLVOLYSIS, REARRANGEMENT AND HYDROGENOLYSIS OF TRICYCLOPROPYLCARBINOL DERIVATIVES

Thesis for the Degree of Ph. D.
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ABSTRACT

SOLVOLYSIS, REARRANGEMENT AND HYDROGENOLYSIS OF TRICYCLOPROPYLCARBINOL DERIVATIVES

by Paul Arthur Law

The present investigation involved the study of some reactions of tricyclopropylcarbinol and dicyclopropylcarbinol.

The benzoate of tricyclopropylcarbinol was prepared and its solvolysis rate measured. In 95% aqueous dioxane at 25°, it solvolyzed remarkably rapidly, with a first order specific rate constant 1.23 x $10^{-3}sec^{-1}$. Solvolysis occurred with alkyl-oxygen fission; methanolysis produced the corresponding methyl ether. No rearrangement of the alcohol occurred and the sole products of hydrolysis were tricyclopropylcarbinol and benzoic acid.

Under the same solvolysis conditions dicyclopropylisopropylcarbinyl benzoate solvolyzed with a first order specific rate constant of 1.14 x $10^{-6}sec^{-1}$. Thus, the substitution of a third cyclopropyl group for isopropyl caused a rate enhancement of 1080 fold, an even greater increase than previously observed (1) for the first and second cyclopropyl.

Tricyclopropylcarbinyl benzoate rearranged quantitatively to 4,4-dicyclopropylbut-3-en-1-yl benzoate when heated at 100° for 30 minutes.

The nuclear magnetic resonance (n.m.r.) spectrum of tricyclopropylcarbinol in concentrated sulfuric acid (2, 3) consists of a single, sharp peak at 7.79 τm (methane sulfonic acid, internal standard). This is in contrast with its n.m.r. spectrum in carbon tetrachloride

which consists of a complex pattern in the 9-10 τ region. Dicyclopropylcarbinol, in sulfuric acid, also has an n.m.r. spectrum consisting of a single peak at the same position.

When tricyclopropylcarbinol was heated with a trace of sulfuric acid, rearrangement occurred (4). The products were 2, 2-dicyclopropyltetrahydrofuran (synthesized independently from γ-butyrolactone and cyclopropyl lithium) and bis (4, 4-dicyclopropylbut-3-en-1-yl) ether. The alcohol 4, 4-dicyclopropylbut-3-en-1-ol may be an intermediate, since it also gave the tetrahydrofuran on treatment with sulfuric acid. When dicyclopropylcarbinol was treated similarly, the products were 2-cyclopropyltetrahydrofuran and bis (4-cyclopropylbut-3-en-1-yl) ether.

Catalytic reduction of tricyclopropylcarbinol using hydrogen and copper oxide-chromium oxide catalyst produced tricyclopropylmethane in 36% yield. Other products were 1, 1-dicyclopropyl-1-butene, 1, 1-dicyclopropylbutane, 4-cyclopropylheptane and 4-propylheptane. Reduction of dicyclopropylcarbinol yielded only a small amount (8.1%) of dicyclopropylmethane. The major product was 21.5% of 1-cyclopropylbutane. Other products were n-heptane and a dimer, probably 1, 1-dicyclopropyl-2-(cyclopropylmethyl)butane.

All of the reactions mentioned above may be explained in terms of exceptionally stable aliphatic carbonium ions such as the tricyclopropylcarbinyl and dicyclopropylcarbinyl cations.

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(4) T. A. Favorskaya, Zhur. Obshchei Khim., 27, 1179 (1957). C. A., 52, 3800f, (1958).

SOLVOLYSIS, REARRANGEMENT AND HYDROGENOLYSIS OF TRICYCLOPROPYLCARBINOL DERIVATIVES

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DEDICATION

This thesis is dedicated to my wife, Donna, for patience and encouragement beyond the call of duty.

TABLE OF CONTENTS

TABLE OF CONTENTS - Continued

LIST OF TABLES

LIST OF TABLES - Continued

TABLE Page

LIST OF FIGURES

LIST OF FIGURES - Continued

FIGURE Page

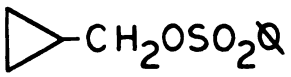
LIST OF FIGURES - Continued

LIST OF FIGURES - Continued

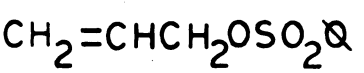
FIGURE Page

INTRODUCTION

The ability of a cyclopropyl group to act as an electron donor has been shown in studies of cyclopropylcarbinyl systems. The enhanced rate of ester solvolysis of such systems is well-known (1, 2, 3). For example, the rate of ethanolysis (1) of cyclopropylcarbinyl benzenesulfonate (I) is ten times that of allyl benzenesulfonate (II) and 1000 times that of allylcarbinyl benzenesulfonate (III)



I



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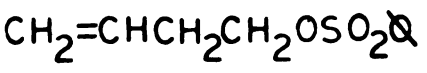
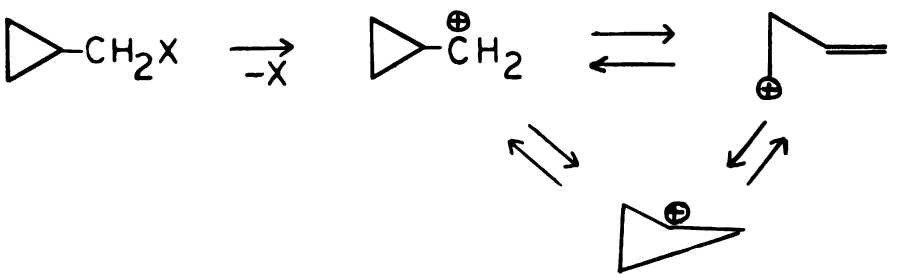


III

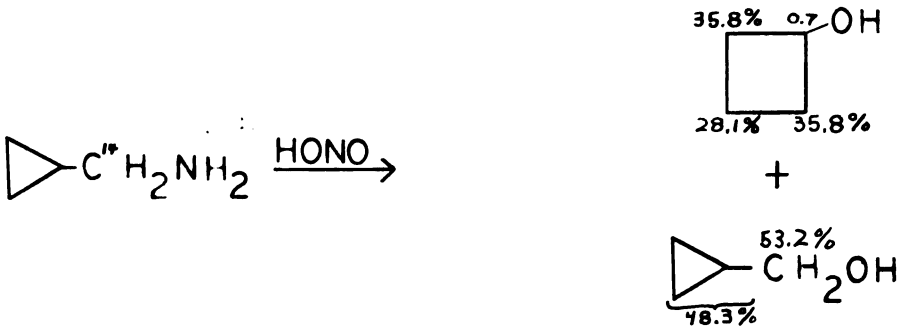
The solvolysis products are derivatives not only of cyclopropylcarbinol, but of cyclobutanol and allylcarbinol as well. Such rearranged products could arise from classical carbonium ion rearrangements. But in



aliphatic systems primary carbonium ions are not favored and solvolysis via such an ion could not explain the observed enhanced rate.

Roberts (4, 5, 6) investigated the C^{14} scrambling which occurred in the nitrous acid deamination of cyclopropylcarbinylamine labelled in the

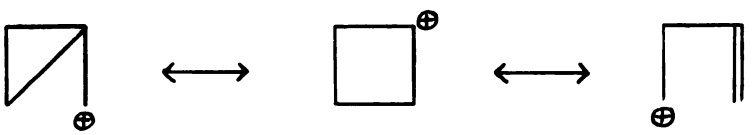
α-position. The distribution of the label is shown below.



In order to explain these results, participation by the cyclopropyl ring is necessary but the intermediate cannot be the symmetrical tricyclobutonium ion (IV) (see Figure 1) since the cyclobutyl carbons are not labelled equally. Three equilibrating bicyclobutonium ions (V, VI, VII) explain the results adequately and are preferred by Roberts to equilibrating classical carbonium ions because of the enhanced solvolysis rates.

Sneen (7), in order to refine the bicyclobutonium ion concept, studied the effect of a phenyl substituent on the cyclopropyl ring of cyclopropylcarbinyl β-naphthalenesulfonates. Only a very small kinetic effect was observed, indicating that "little excess positive charge is concentrated at the ring methylene carbon atom of the cyclopropylcarbinyl system in the transition state." Thus, if Roberts' ion (VIII) represents a resonance hybrid of the structures IX, X and XI, XI contributes "in only a minor way."

VIII



IX X XI

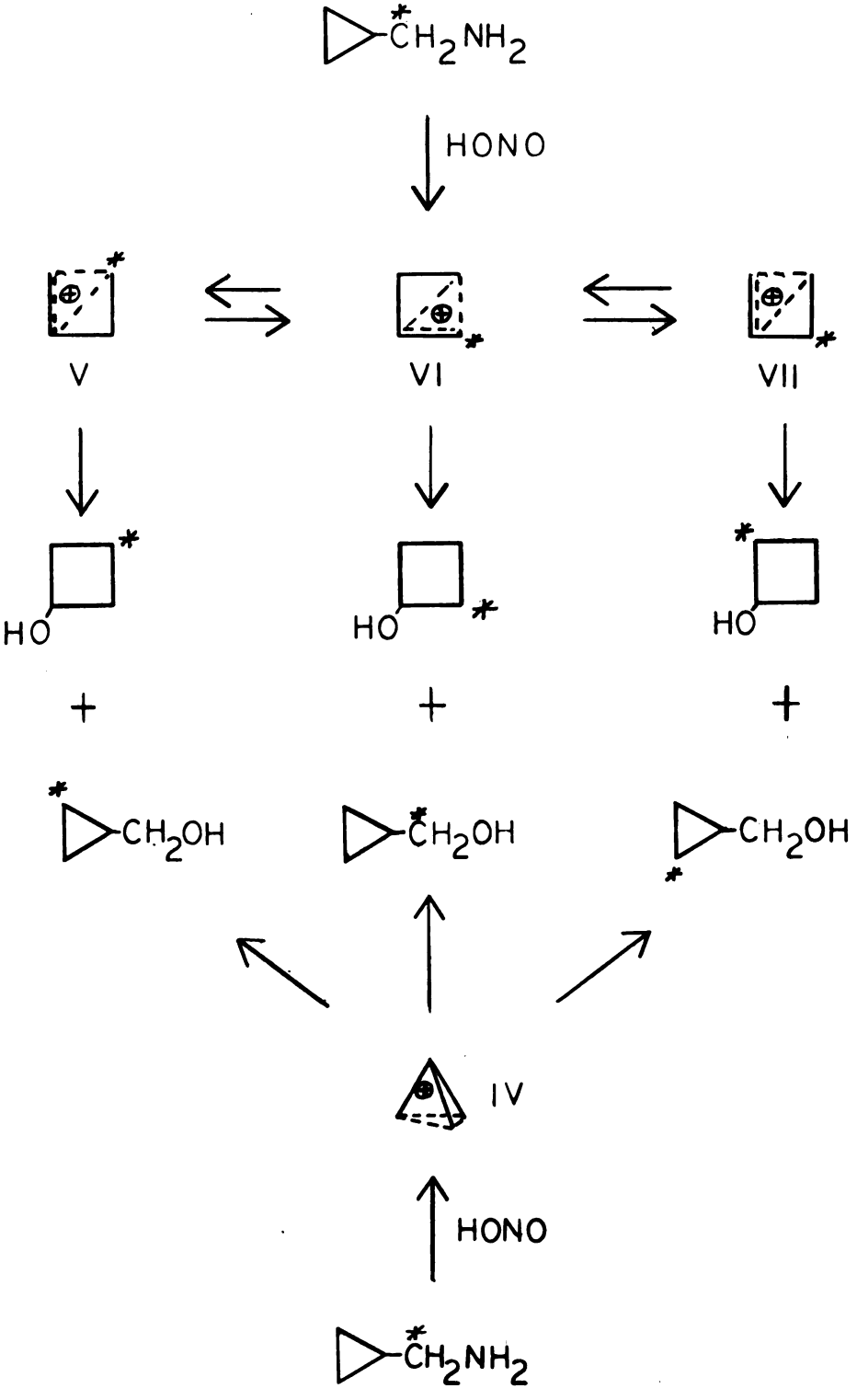
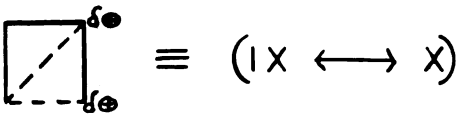
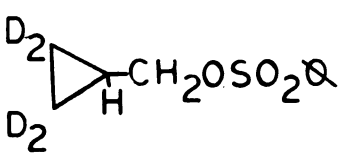


Figure 1. The C^{14} Labelling in the Nitrous Acid Deamination Products of Cyclopropylcarbinyl-C^{14}-amine.

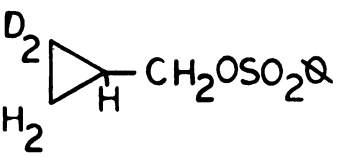
The electronic description of the bicyclobutonium ion can then be simplified to:



The solvolysis studies of deuterated cyclopropylcarbinyl benzenesulfonates added evidence favoring participation of the cyclopropyl ring in the transition state. Borčić (9) found that substitution of deuterium on the cyclopropyl ring, as in XII and XIII, caused a rate increase in ethanolysis and acetolysis.



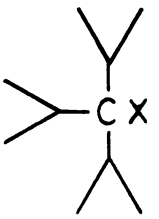
XII



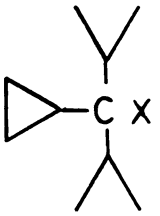
XIII

Deuterium induces a negative charge on the methylene carbon atoms in the cyclopropane ring increasing its ability to accommodate a positive charge. The slower reaction, ethanolysis, should have a transition state which resembles starting material less than does the transition state of the acetolysis reaction. This hypothesis is an extension of Hammond's postulate (10, 11). The ethanolysis will then have more non-classical character and should be more affected by the deuterium. In fact, the deuterium isotope effect was greater for the ethanolysis and this is "considered indicative for the formation of a non-classical carbonium ion in the rate determining step of these reactions."

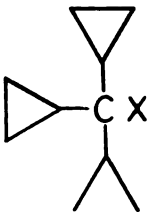
Hart and Sandri (12) showed that the effect of cyclopropyl groups was cumulative. The solvolysis rate of diisopropylcyclopropylcarbinyl p-nitrobenzoate (XV) in aqueous dioxane was 246 times that of triisopropylcarbinyl p-nitrobenzoate (XIV). A second cyclopropyl group, as in dicyclopropylisopropylcarbinyl p-nitrobenzoate (XVI), caused a further 95 fold increase in the rate.



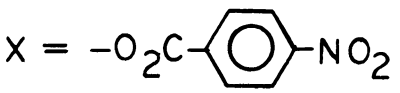
XIV



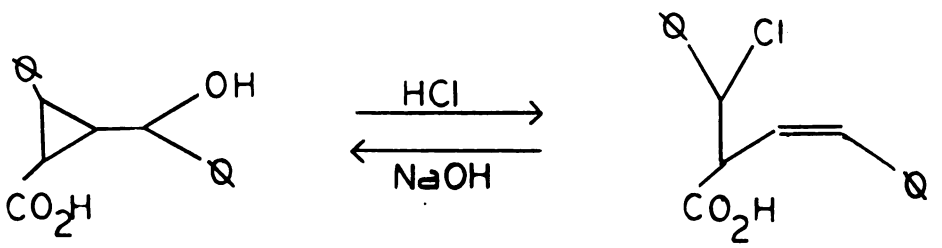
XV



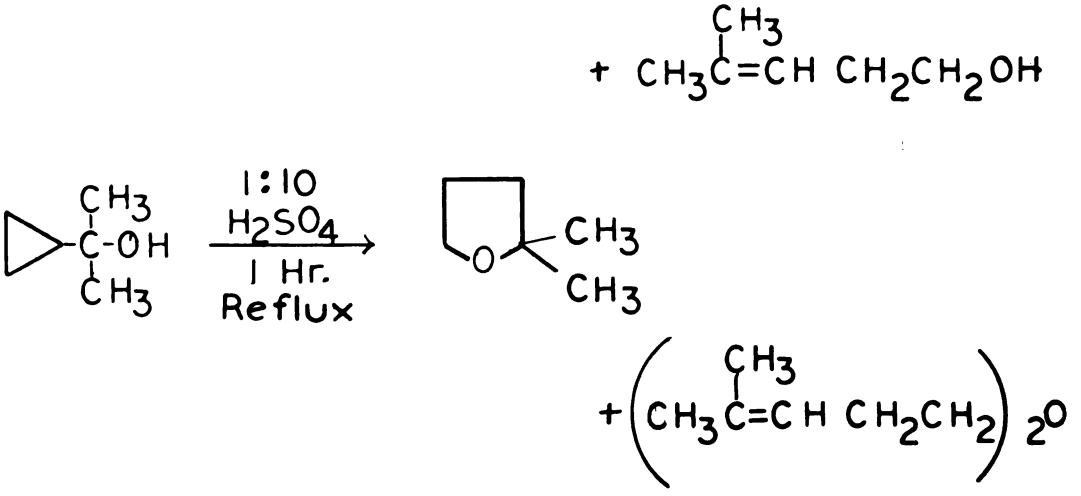
XVI



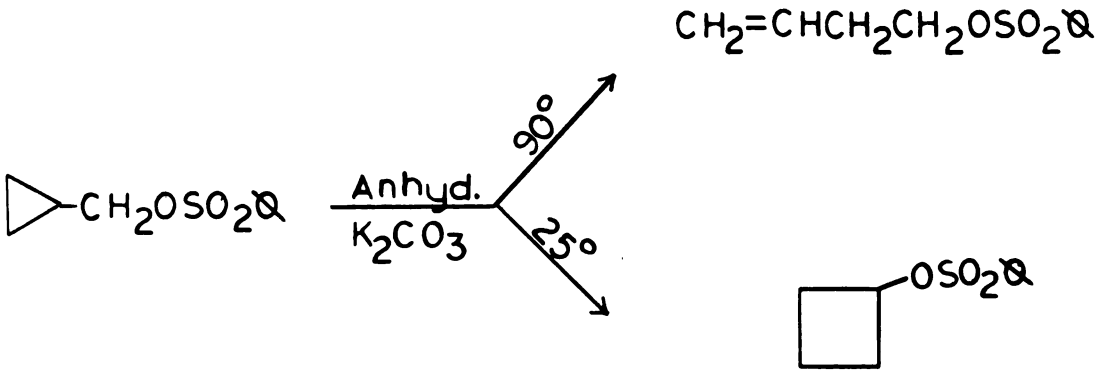
Another interesting property of the cyclopropyl group is the ease with which it undergoes isomerization under acidic, solvolytic or thermal conditions. There are many examples of isomerizations and rearrangements in acid media (12-18, 24). Stoermer and Schenk (13) treated 2-phenyl-3-(hydroxybenzyl) cyclopropane-1-carboxylic acid with hydrochloric acid and obtained the rearranged chloride, 4-phenyl-2-(chlorobenzyl)but-3-enoic acid. This reaction could be reversed by treatment with sodium hydroxide.



Favorskaya (25) obtained a variety of products from the acid treatment of tertiary alcohols containing one cyclopropyl group. Typical is the reaction of 2-cyclopropyl-2-propanol with aqueous sulfuric acid which yielded 2, 2-dimethyltetrahydrofuran, 4-methylpent-3-en-1-ol and bis (4-methylpent-3-en-1-yl) ether.

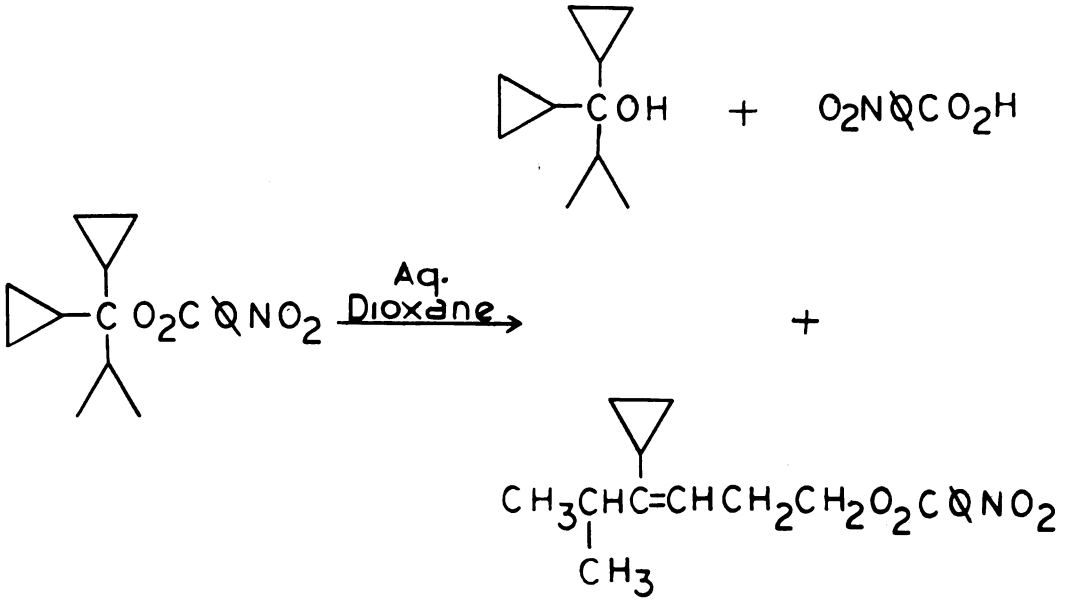


Thermal rearrangement (19-23) occurs during pyrolysis of cyclopropylcarbinyl esters (19) to give olefins. However, less rigorous conditions can cause rearrangement to a new ester. Cyclopropylcarbinyl benzenesulfonate, when heated in the presence of anhydrous potassium carbonate at 90°, resulted in but-3-en-1-yl benzenesulfonate but at 25° the product was cyclobutyl benzenesulfonate (23).



It is interesting that starting material labelled with O^{18} in the ether position retained only one-third of the label in the ether position of the products, indicating complete equilibration of the oxygens during the course of the reaction (23).

Solvolytic rearrangement of cyclopropylcarbinyl systems has been shown (12), for example, to occur during hydrolysis of dicyclopropylisopropylcarbinyl p-nitrobenzoate, resulting in small amounts of rearranged ester, 4-cyclopropyl-5-methylhex-3-en-1-yl p-nitrobenzoate.



The primary purpose of the present investigation was to examine the effect of a third cyclopropyl group on reactions related to those discussed above. If the effect of cyclopropyl groups were cumulative, the presence of three such groups could be expected to give the tricyclopropylcarbinyl cation unusual stability.

This thesis is primarily concerned with the chemistry of tricyclopropylcarbinol. The hydrogenolysis and acid catalyzed rearrangement of the alcohol, and the solvolysis and thermal rearrangement of its benzoate have been studied in an attempt to assess the effect of the third cyclopropyl ring.

RESULTS AND DISCUSSION

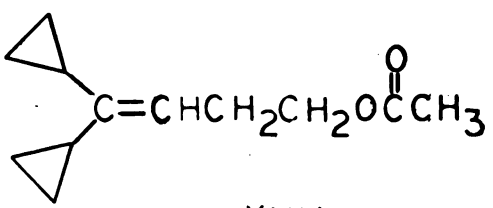
I. Solvolysis of Tricyclopropylcarbinyl Benzoate

A. Discussion of Synthetic Methods

The study of the effect of cyclopropyl groups on the solvolysis rates of some cyclopropylcarbinyl p-nitrobenzoates (12) could not be completed due to the lack of a solvolyzable tricyclopropylcarbinyl ester. Such an ester has been synthesized and is described herein. Examination of the rate increase caused by the presence of a second cyclopropyl group, as in dicyclopropylisopropylcarbinyl p-nitrobenzoate, indicates that the presence of a third ring may result in an ester with a large solvolysis rate. For this reason, preparation of an ester which would react more slowly than a p-nitrobenzoate seemed desirable.

The synthesis of tricyclopropylcarbinyl acetate was attempted by several methods. Hurd (26) prepared t-butyl acetate by treating t-butyl alcohol with ketene in the presence of a small amount of sulfuric acid or p-toluenesulfonic acid. Using adaptations of these methods no reaction was obtained with tricyclopropylcarbinol. Boron trifluoride etherate was also ineffective as a catalyst.

Distillation of the reaction products of potassium tricyclopropylcarbinolate with acetyl chloride resulted in a 71% recovery of the starting alcohol. The only ester isolated was 4,4-dicyclopropylbut-3-en-1-yl acetate (XVII) in 4.6% yield. Its infrared and n.m.r. spectra are



XVII

shown in Figures 2 and 3. Similar results were obtained using the lithium alcoholate.

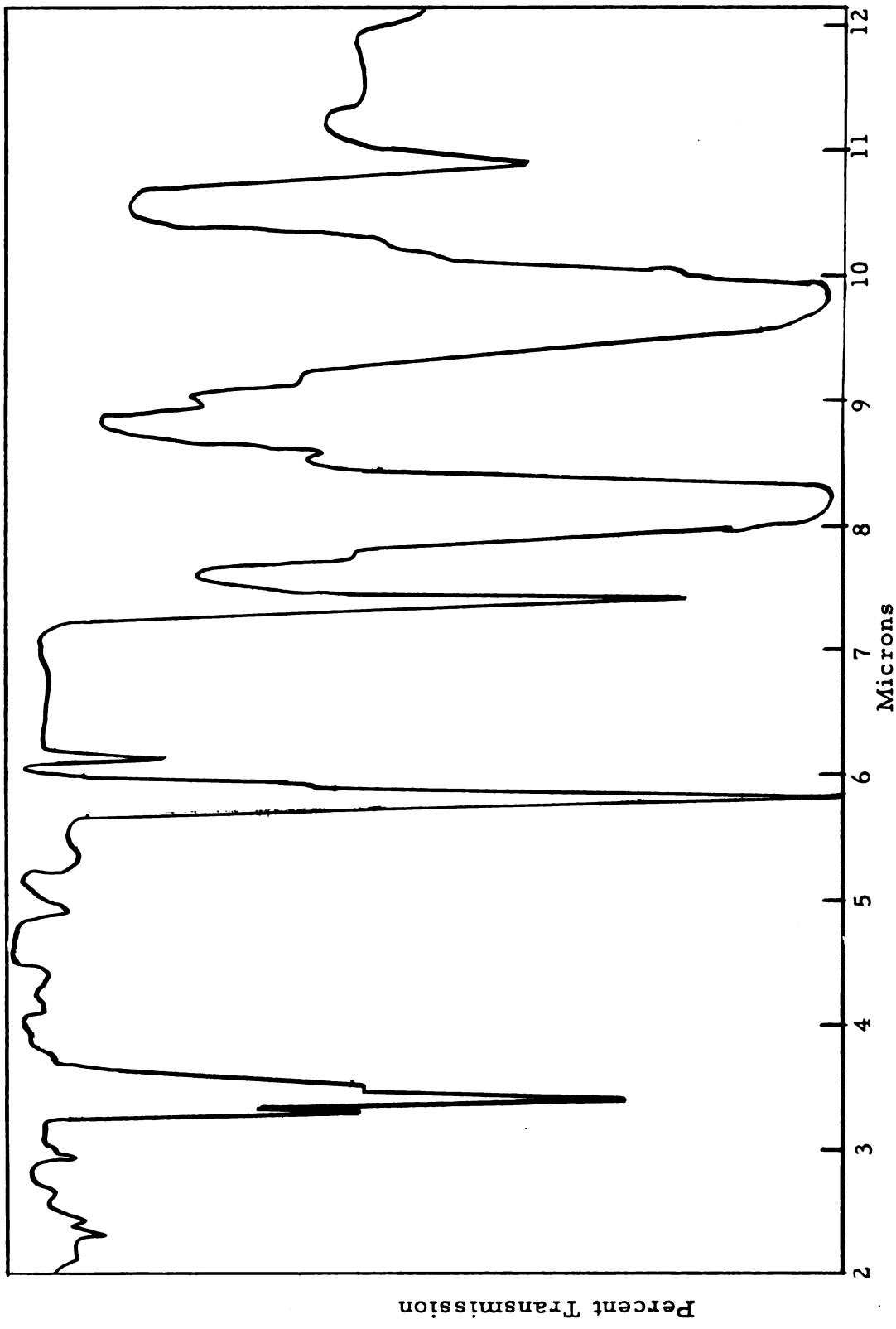


Figure 2. The Infrared Spectrum of 4,4-Dicyclopropylbut-3-en-1-yl Acetate in Carbon Tetrachloride.

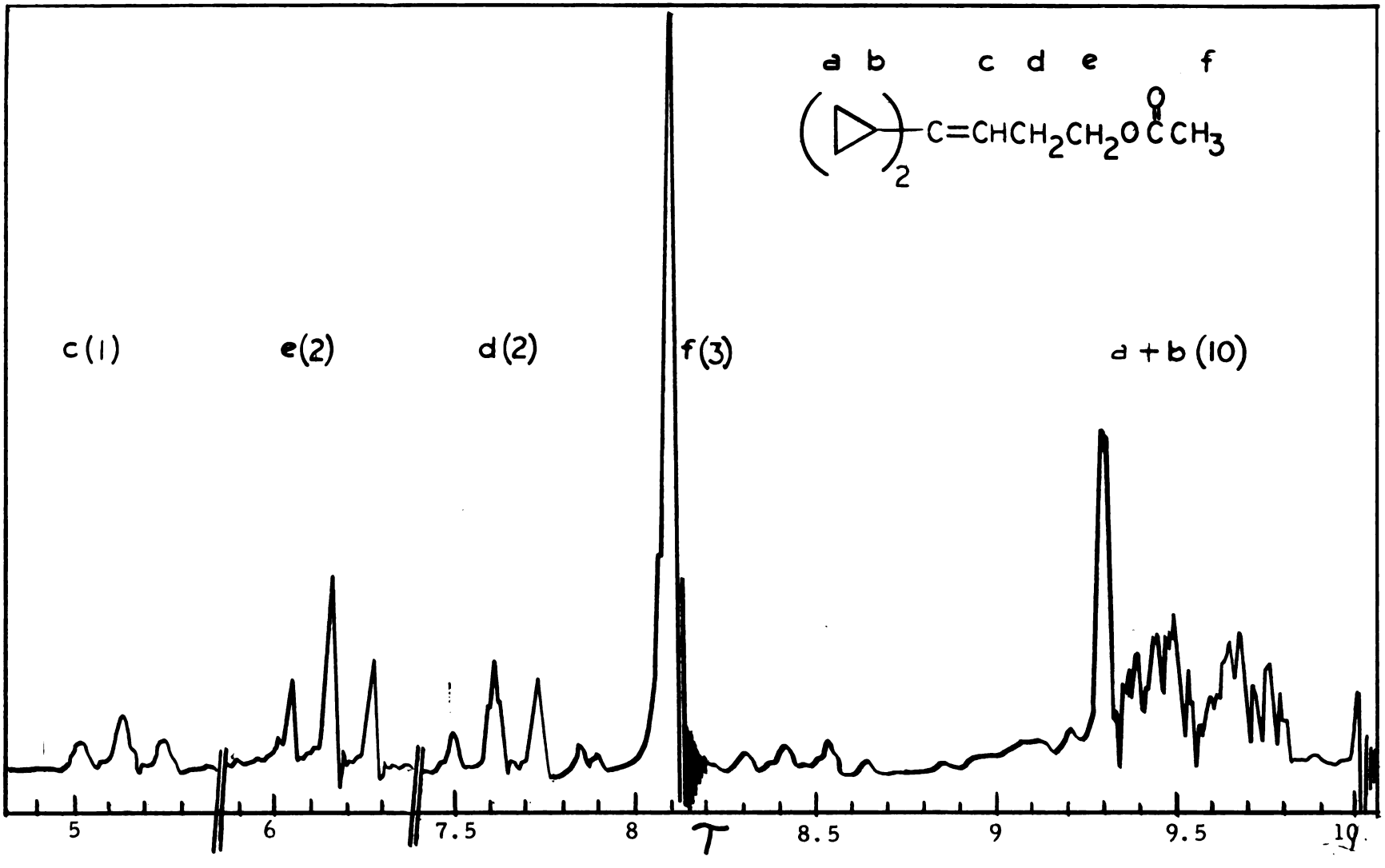
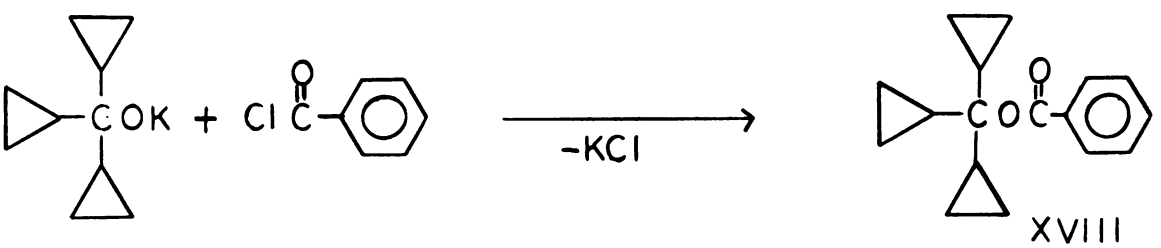


Figure 3. The N.M.R. Spectrum of 4,4-Dicyclopropylbut-3-en-1-yl Acetate in Carbon Tetrachloride. All spectra were taken on the Varian Associates spectrometer, model A-60, using tetramethylsilane as internal standard ($\tau = 10.0$). Spectral solutions were about 30% by volume unless otherwise noted.

Later work revealed the thermal and solvolytic instability of tricyclopropylcarbinyl esters. The distillation conditions in the above work-up would have been sufficient to destroy any desired ester, were it present. No further attempts at acetate synthesis were made due to the successful synthesis of tricyclopropylcarbinyl benzoate.

In a re-examination of an earlier attempt (Cf. Hart and Sandri, ref. 12) to prepare tricyclopropylcarbinyl p-nitrobenzoate, p-nitrobenzoyl chloride was added to the potassium salt of tricyclopropylcarbinol. The crude reaction product showed no nitro absorption in the infrared spectrum. It is suspected that the nitro group itself may have caused side reactions preventing synthesis of the desired ester. The obvious alternative was the preparation of the unsubstituted benzoate.

Tricyclopropylcarbinyl benzoate (XVIII) was prepared in almost quantitative yield by the reaction of benzoyl chloride with the potassium salt of tricyclopropylcarbinol in pentane. Attempts to purify the liquid



XVIII

product by distillation or chromatography lead to decomposition or rearrangement. The purity of the ester was determined by a saponification equivalent. Although elemental analysis was not possible, the infrared and n.m.r. spectra, shown in Figures 4 and 5, in addition to the products of solvolysis clearly substantiated the assigned structure.

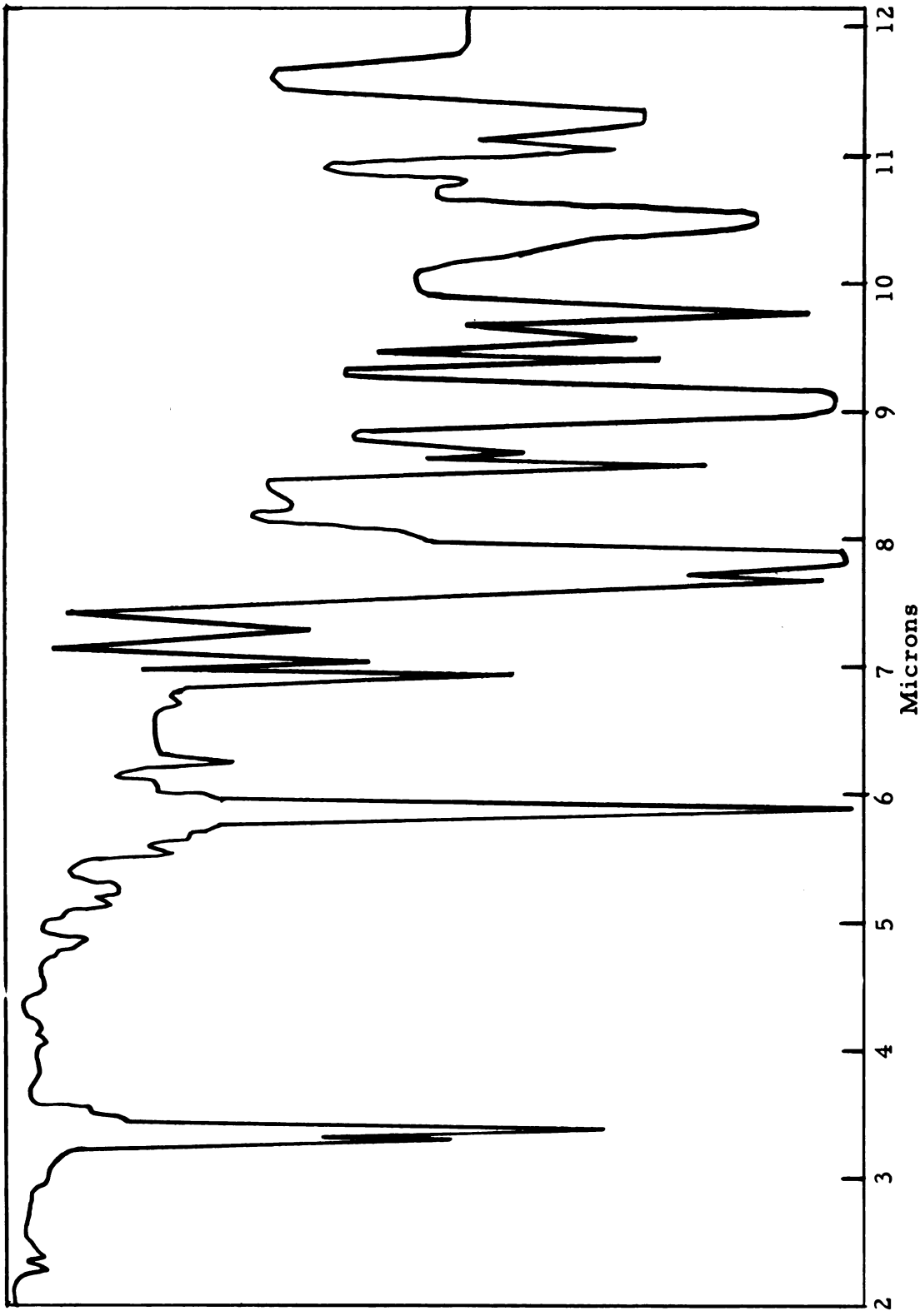


Figure 4. The Infrared Spectrum of Tricyclopropylcarbinyl Benzoate in Carbon Tetrachloride.

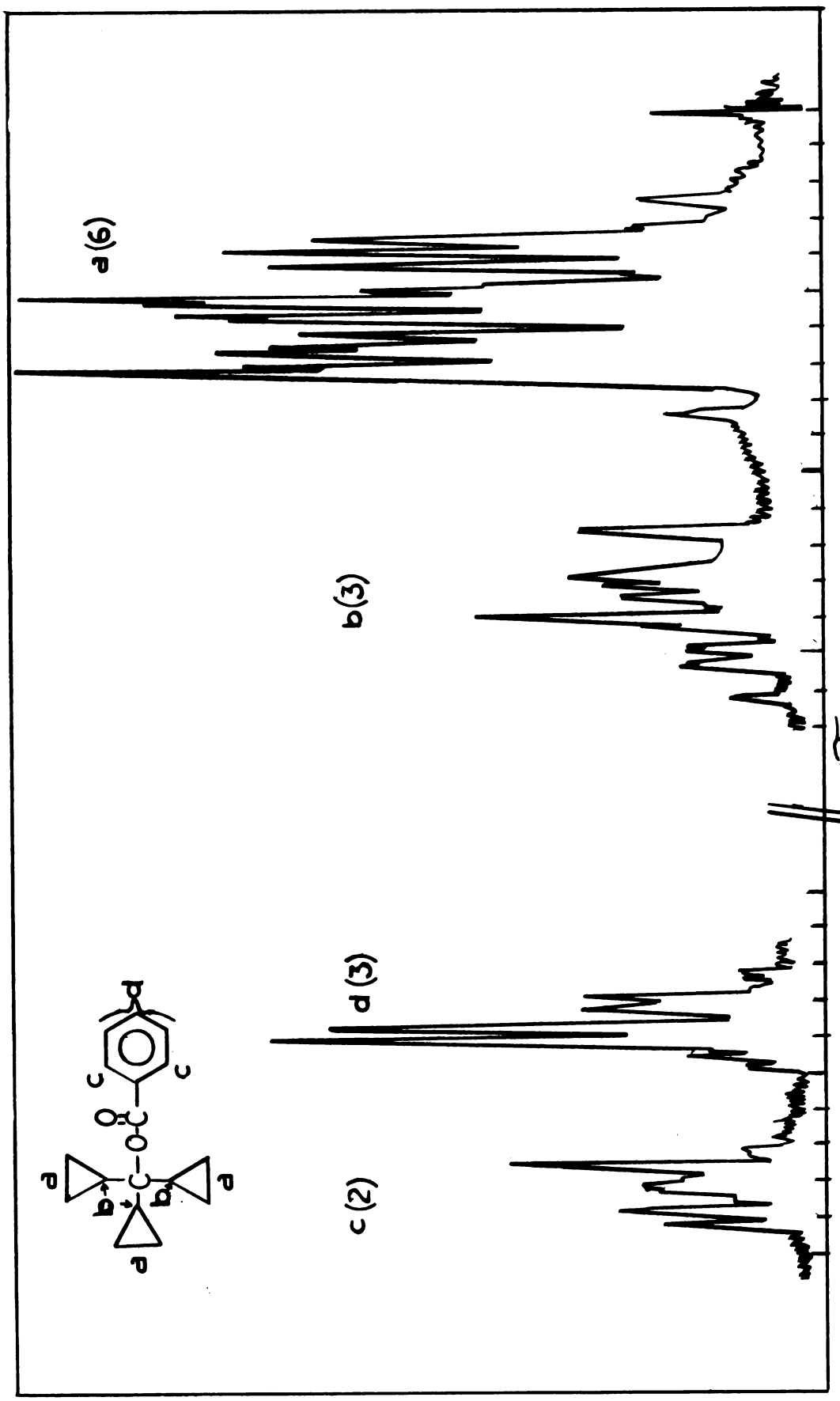
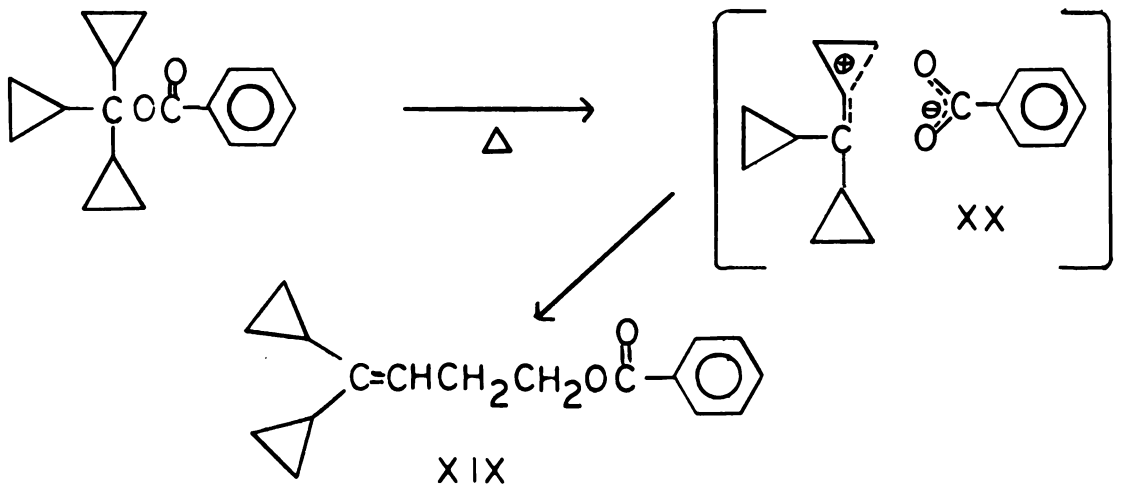


Figure 5. The N.M.R. Spectrum of Tricyclopropylcarbinyl Benzoate in Carbon Tetrachloride.

Tricyclopropylcarbinyl benzoate was stable when refrigerated but at room temperature it slowly rearranged to an unsaturated ester. At 100° the rearrangement was complete in 30 minutes. The new ester was shown by its n.m.r. and infrared spectra, in addition to elemental analysis, to be 4,4-dicyclopropylbut-3-en-1-yl benzoate (XIX). The spectra of XIX are shown in Figures 6 and 7.



XX

XIX

This rearrangement may be explained in terms of an ion pair such as XX. Relief of steric repulsions would be expected to favor internal return (27) to the open chain isomer.

In order to obtain a cross-over point for rate comparisons, it became necessary to prepare the benzoate of an alcohol studied as the p-nitrobenzoate in the previous work. Dicyclopropylisopropylcarbinol was chosen since its p-nitrobenzoate solvolysis rate was the fastest of the series and would, therefore, be nearest the rate of the tricyclopropylcarbinyl ester.

The benzoate (XXI) was prepared by the reaction of the potassium salt of dicyclopropylisopropylcarbinol with benzoyl chloride.

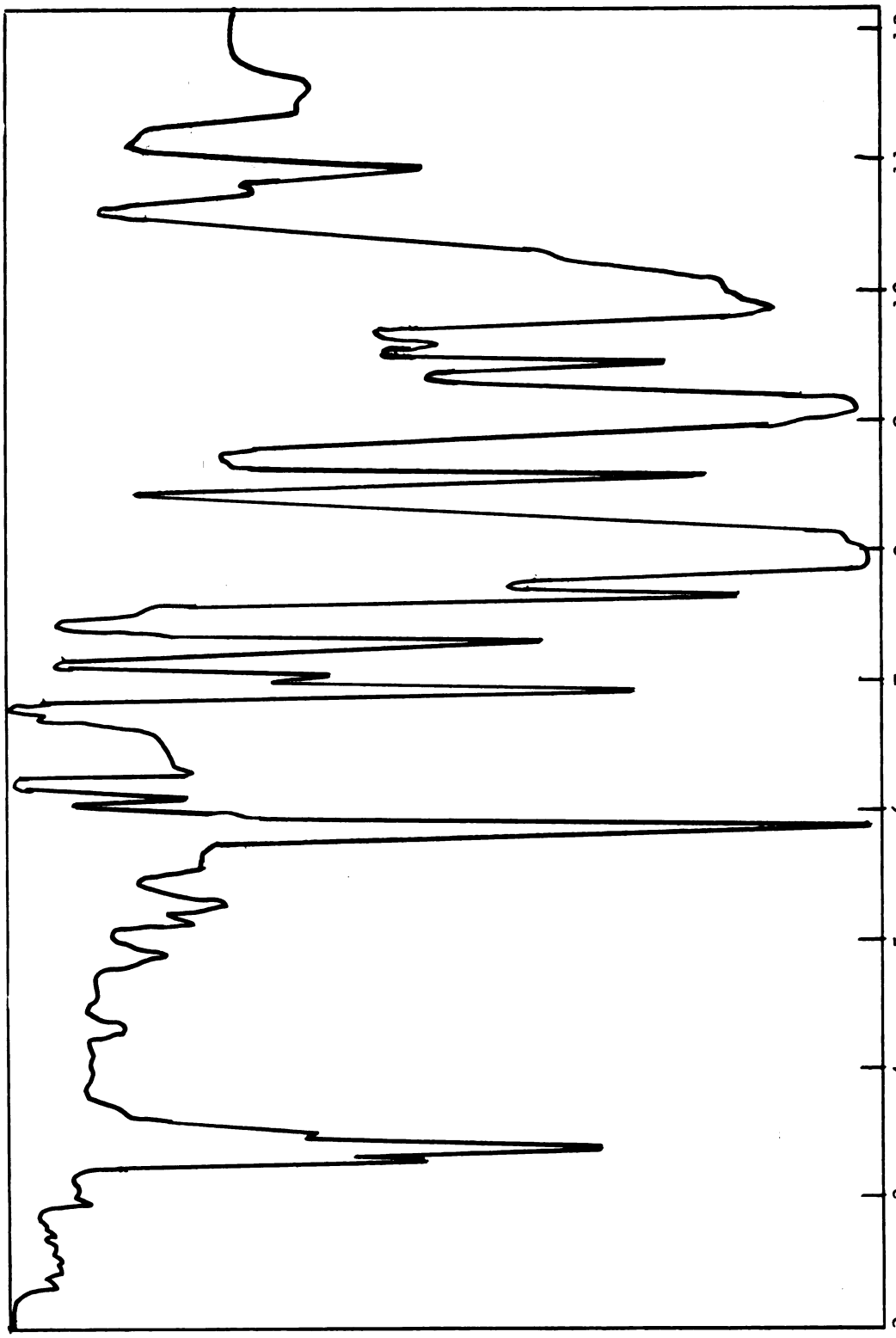


Figure 6. The Infrared Spectrum of 4,4-Dicyclopropylbut-3-en-1-yl Benzoate in Carbon Tetrachloride.

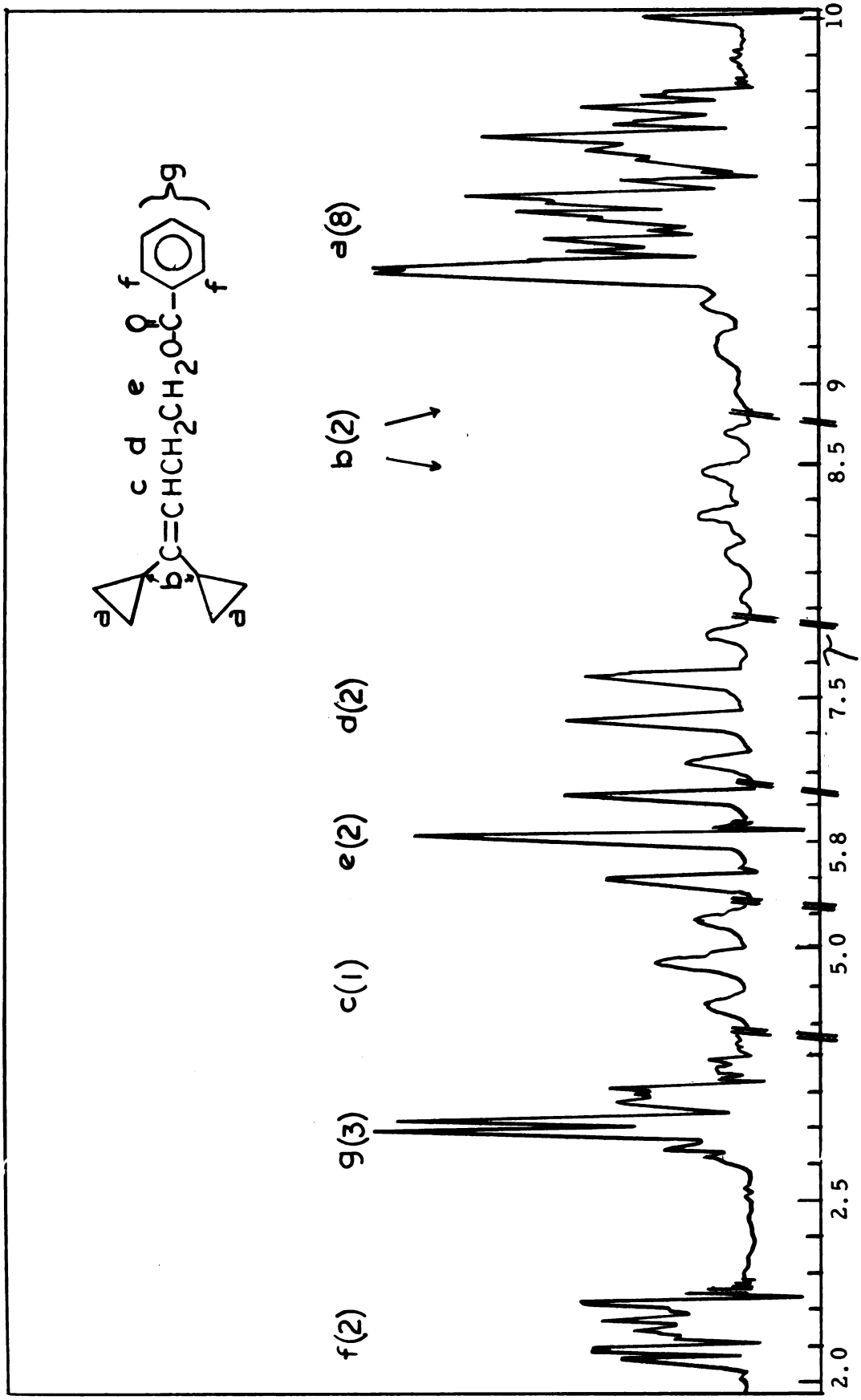
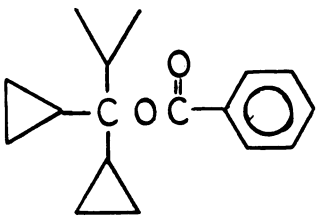
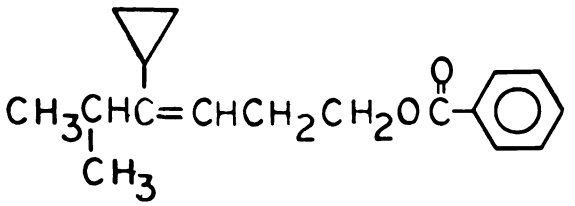


Figure 7. The N.M.R. Spectrum of 4,4-Dicyclopropylbut-3-en-1-yl Benzoate in Carbon Tetrachloride.



XXI

The purity of this liquid ester was determined by a saponification equivalent since chromatography either failed to purify it or caused rearrangement to an unsaturated compound, presumably the ester XXII. The infrared and n.m.r. spectra of XXI are shown in Figures 50 and 51 (see pages 87 and 88).



XXII

It is interesting to note that the thermal rearrangement of XXI (presumably to XXII) is only 30% complete after 290 minutes at 100°. Thus, tricyclopropylcarbinyl benzoate rearranges at least 20 times faster than does XXI. The amount of rearrangement was followed by the appearance of olefinic protons at 4.96, 5.8 and 7.5 τ in the n.m.r. spectrum. The rearrangements were run in absence of solvent; therefore any rate comparison of thermal rearrangement vs. solvolysis is not valid.

Vinyldicyclopropylcarbinyl benzoate would be an interesting ester to solvolyze because it presents the opportunity for direct comparison of a vinyl vs. a cyclopropyl group. This ester (XXIII) was successfully prepared from the potassium salt of the corresponding carbinol and benzoyl chloride. The infrared and n.m.r. spectra are shown in Figures 8 and 9.

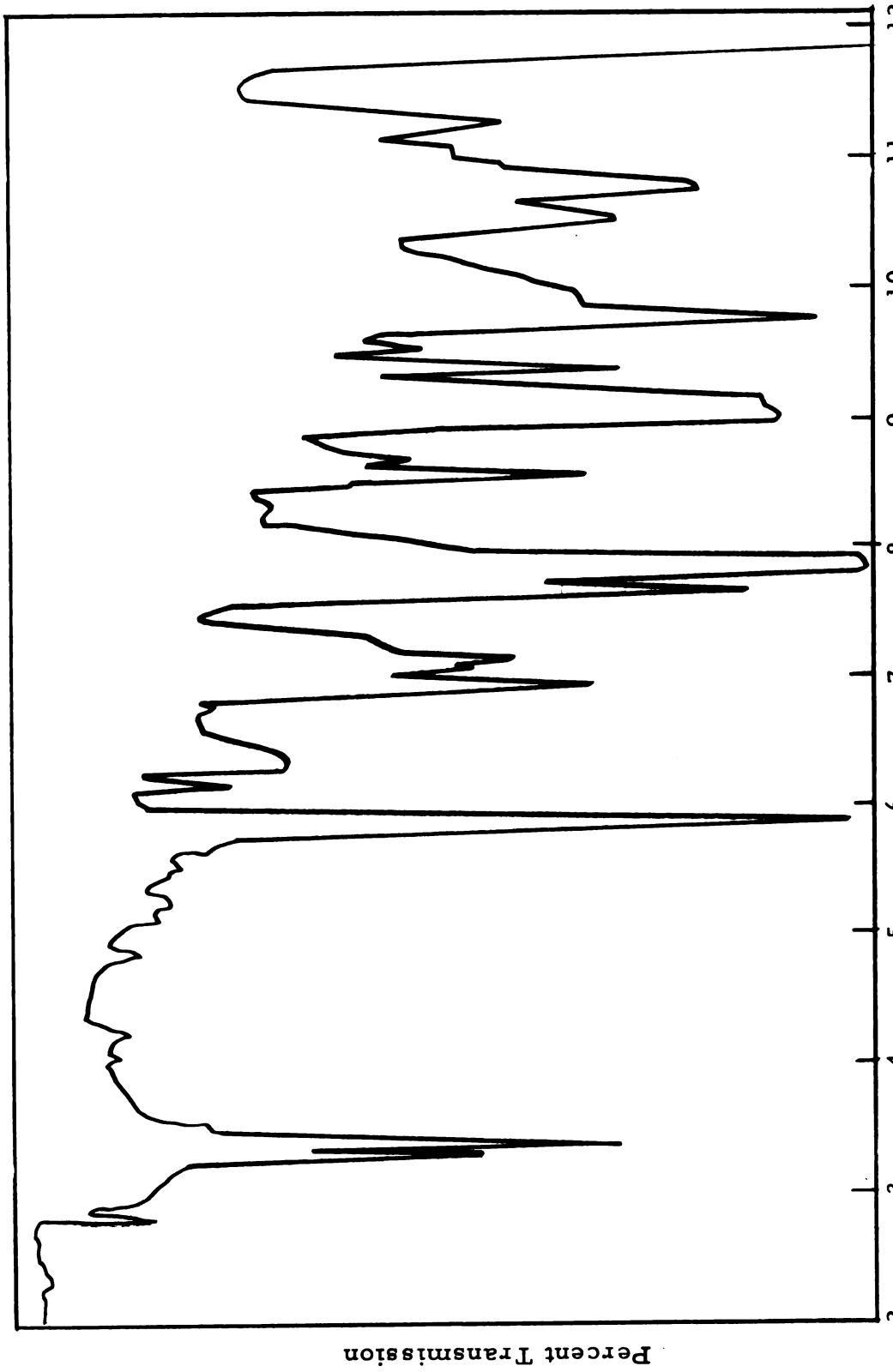


Figure 8. The Infrared Spectrum of Vinyldicyclopropylcarbinyl Benzoate in Carbon Tetrachloride.

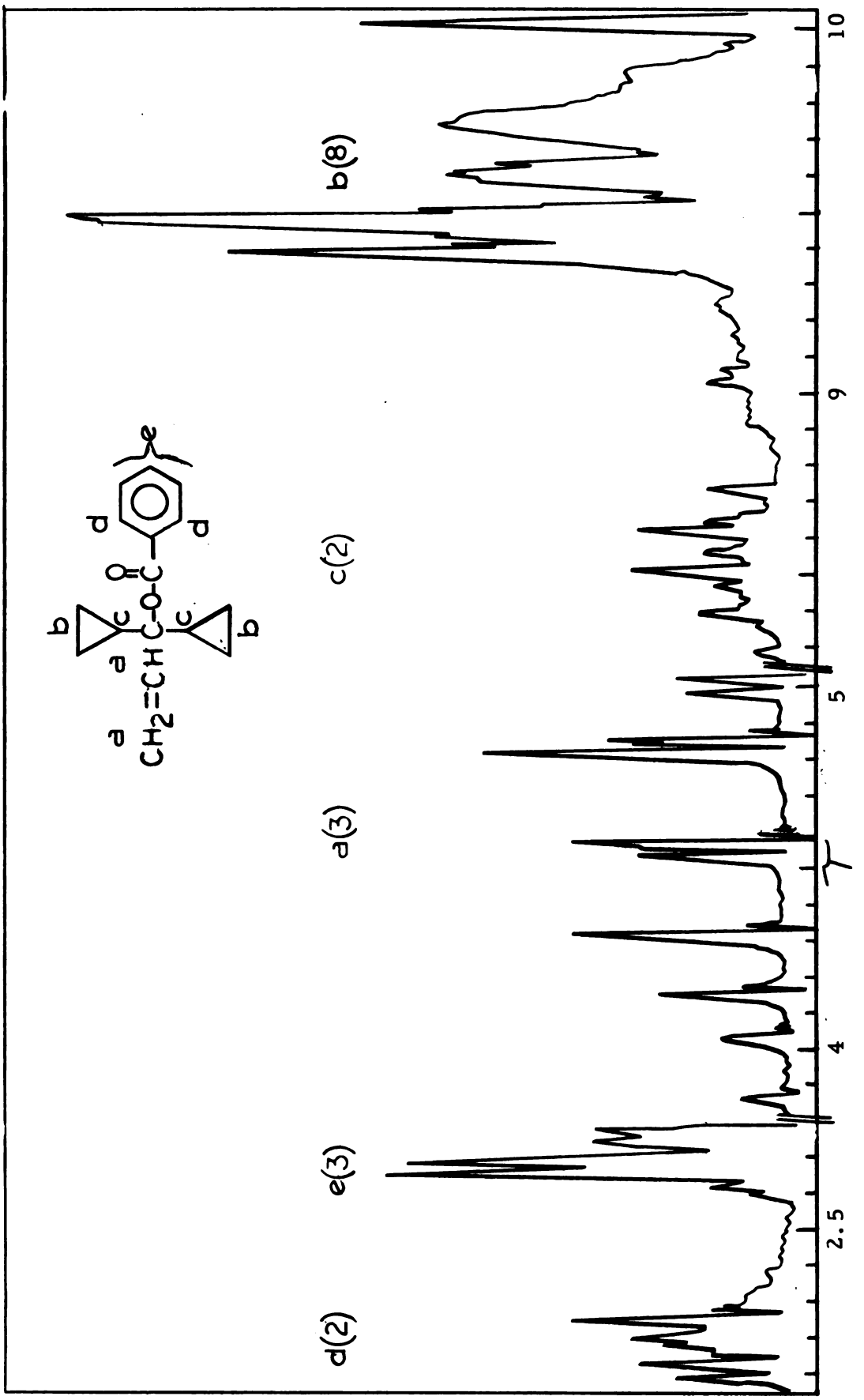
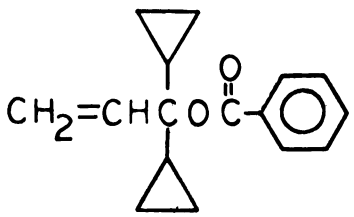
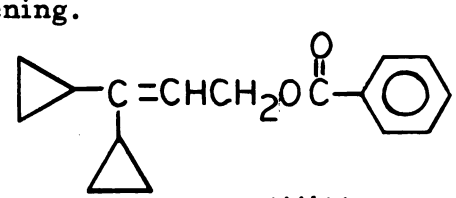


Figure 9. The N.M.R. Spectrum of Vinyldicyclopropylcarbinyl Benzoate in Carbon Tetrachloride.



XXIII

However, after one day at room temperature new peaks began to appear in the n.m.r. spectrum. These were in the vinyl and allyl regions and were not present originally. When a sample of vinyldicyclopropylcarbinyl benzoate was heated for six hours at 100°, and the resulting liquid purified by distillation, a new ester was obtained. This was shown by its n.m.r. spectrum (Figure 10) to be 3,3-dicyclopropylprop-2-en-1-yl benzoate (XXIV). The vinyl and allyl proton signals in its n.m.r. spectrum correspond to those mentioned above. It is interesting that no rearrangement of the cyclopropane ring was observed. The allylic rearrangement was therefore much more facile than the homoallylic which required ring opening.



XXIV

The infrared spectrum (Figure 11) and elemental analysis are consistent with the structural assignment but, of course, are not unique as they cannot aid in differentiation between XXIII and XXIV.

This rearrangement is an example of internal return in an allylic system (28), the release of steric repulsions being the driving force.

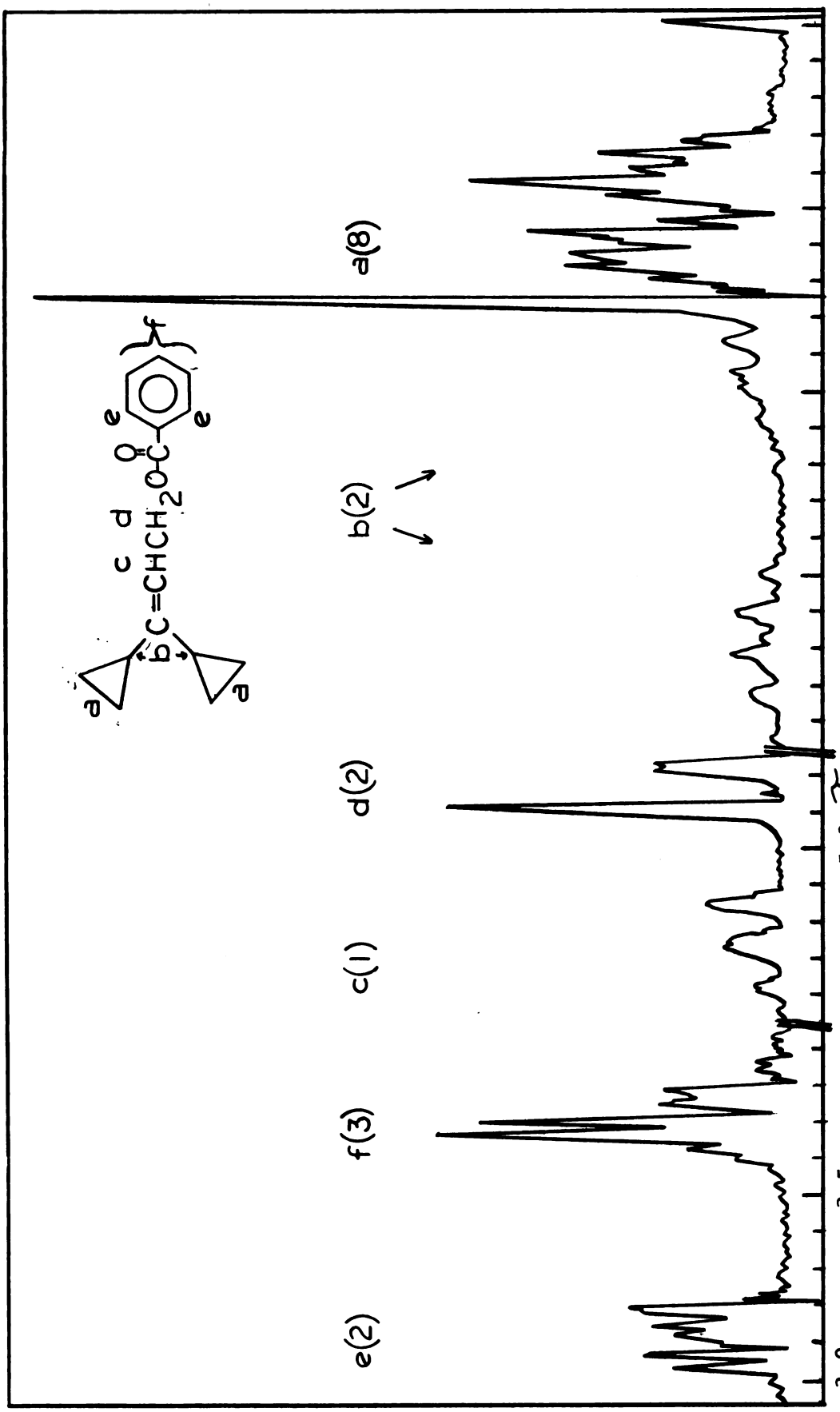


Figure 10. The N.M.R. Spectrum of 3,3-Dicyclopropylprop-2-en-1-yl Benzoate in Carbon Tetrachloride.

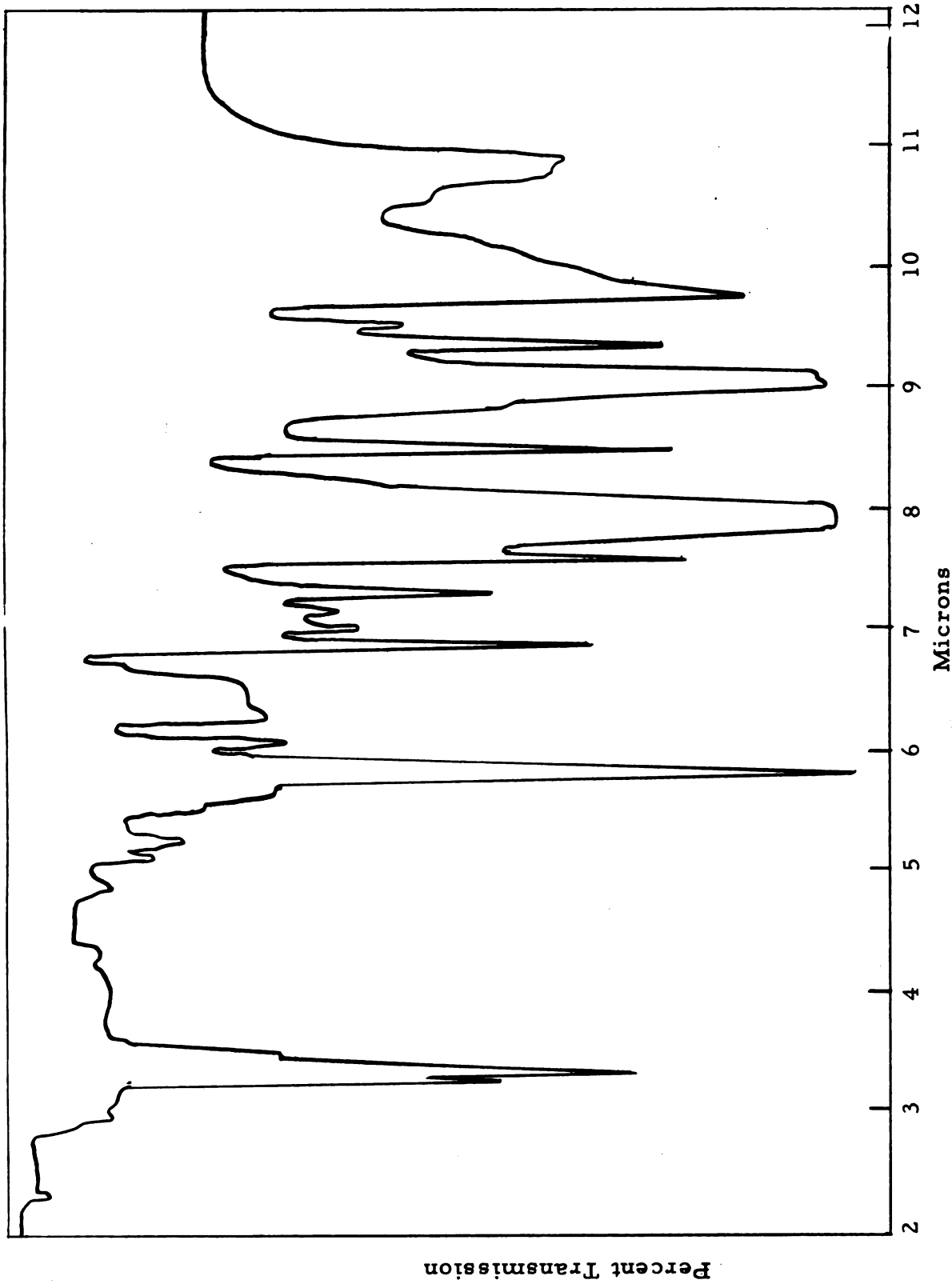
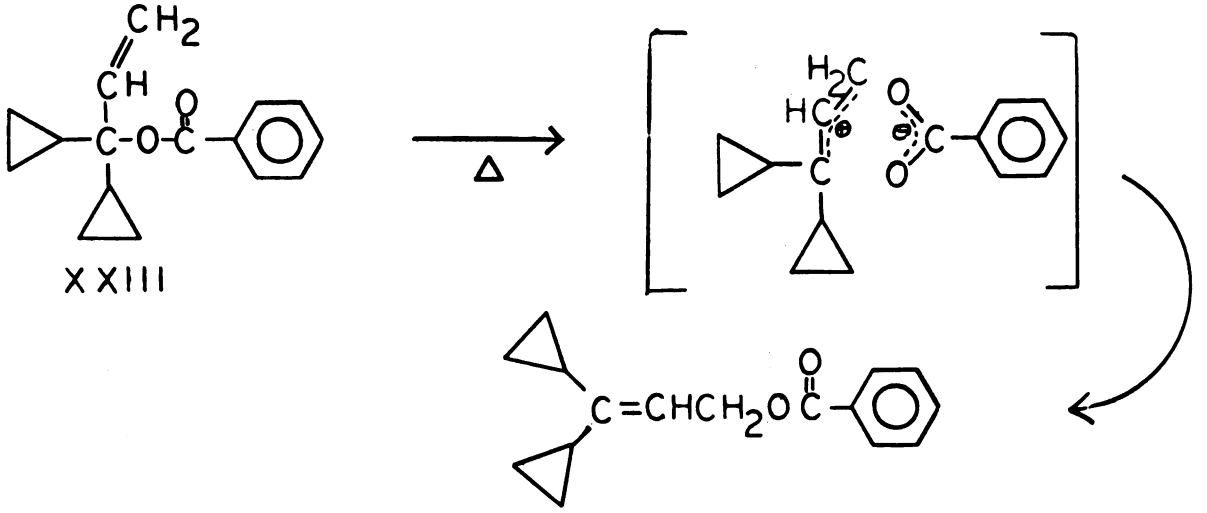


Figure 11. The Infrared Spectrum of 3,3-Dicyclopropylprop-2-en-1-yl Benzoate in Carbon Tetrachloride.



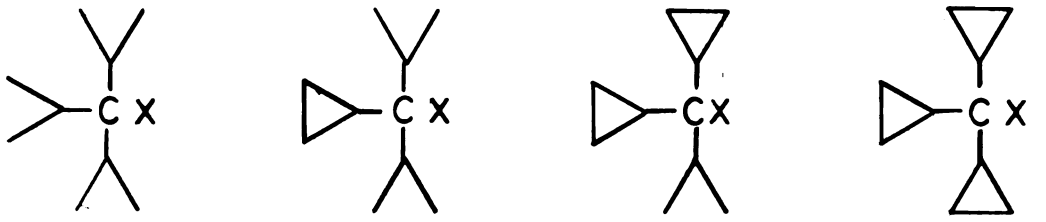
XXIII

XXIV

The rearranged ester XXIV, being allylic, should solvolyze at an appreciable rate under the conditions of solvolysis of XXIII. Its formation, whether caused by thermal or solvolytic influences, would thus complicate rate studies. For this reason, and due to lack of time, no solvolysis rates for vinyldicyclopropylcarbinyl benzoate were examined.

B. Kinetic Study

In their examination of the solvolyses of the p-nitrobenzoates of the cyclopropylcarbinols XXV-XXVIII, Hart and Sandri (12) showed the



XXV XXVI XXVII XXVIII

PNB, x = p-nitrobenzoate

B, x = benzoate

effect of substitution of cyclopropyl groups for isopropyl groups to be cumulative. The relative rates of solvolysis in 80% aqueous dioxane at 60° are shown in Table 1.

Table 1. The Relative Rates of Solvolysis of the p-Nitrobenzoates of Some Cyclopropylcarbinols in 80% Dioxane at 60°

Ester		Relative Rate
XXV	(PNB)	1
XXVI	(PNB)	246
XXVII	(PNB)	23500

With the synthesis of an ester containing three cyclopropane rings (XXVIII-B) this series was completed. Initial examination showed the solvolysis of XXVIII-B to be very rapid in 90% aqueous dioxane, even at 8° C. In order to eliminate the need to carry out solvolyses at temperatures below 0°, the solvent was changed to 95% aqueous dioxane. The advantage of being able to use higher temperatures was partly offset by the poor end point afforded by phenolphthalein when titrating in this solvent. The solvolysis of dicyclopropylisopropylcarbinyl benzoate (XXVII-B), at 25° in 95% aqueous dioxane, allowed convenient comparison with the other members of this series of alcohols.

The rates were followed by titration of the liberated benzoic acid with standard base. As in the p-nitrobenzoate work, the rates were first order in disappearance of ester (Figure 12).

The data in Table 2 show clearly that the third cyclopropyl group caused a rate enhancement even greater than that of the second ring.

A plot of 1/T vs. log k is shown in Figure 13. The E_a calculated from the slope of this curve was 28.8 K. cal. Other activation parameters calculated (see Appendix) were ΔS^*, 24.3±0.2 e.u., and ΔH^*, 28.2 K. cal.

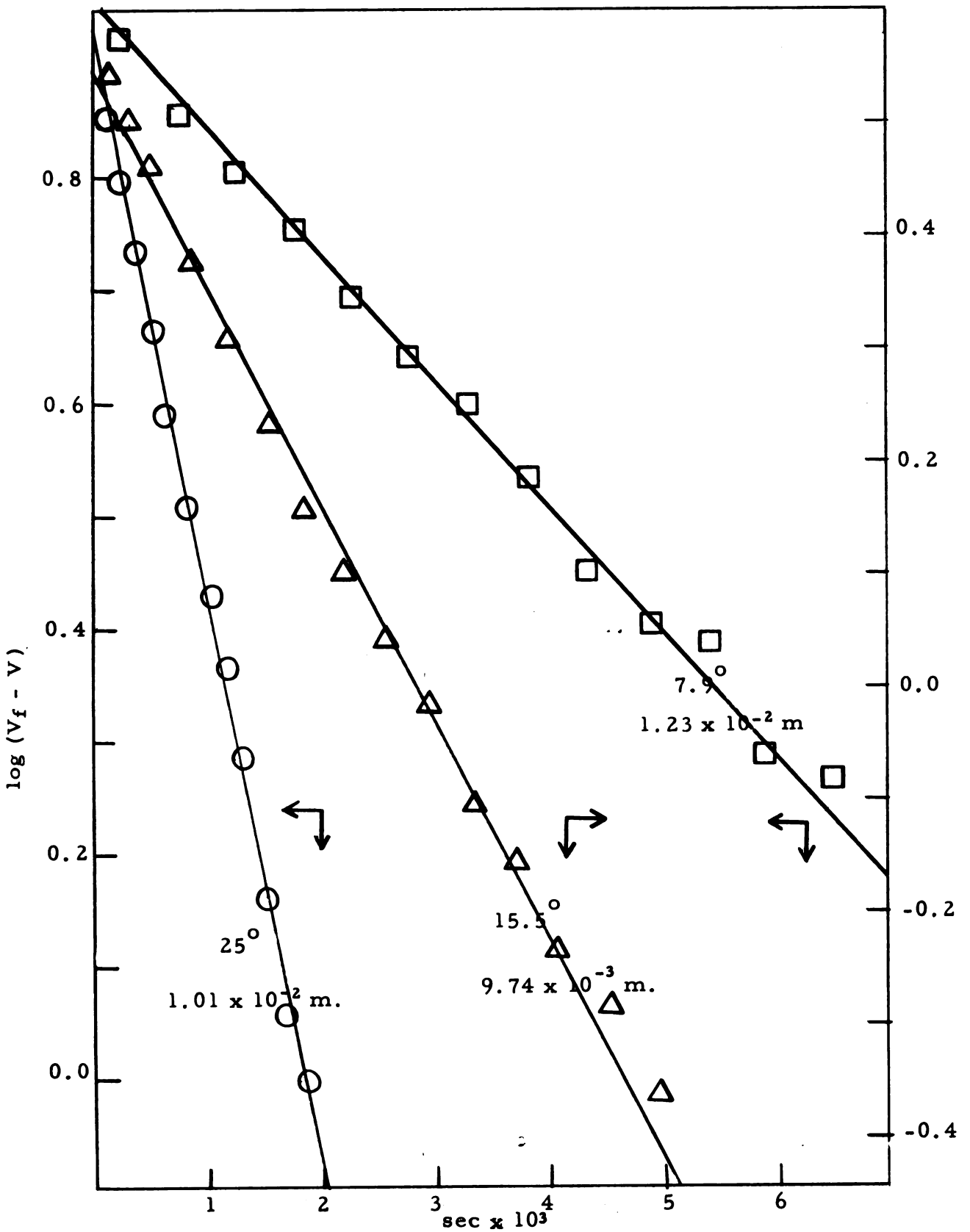


Figure 12. Plot of log (V_f - V) vs. t for the Solvolysis of Tricyclopropylcarbinyl Benzoate in 95% Aqueous-Dioxane at 7.9°, 15.5° and 25.0°.

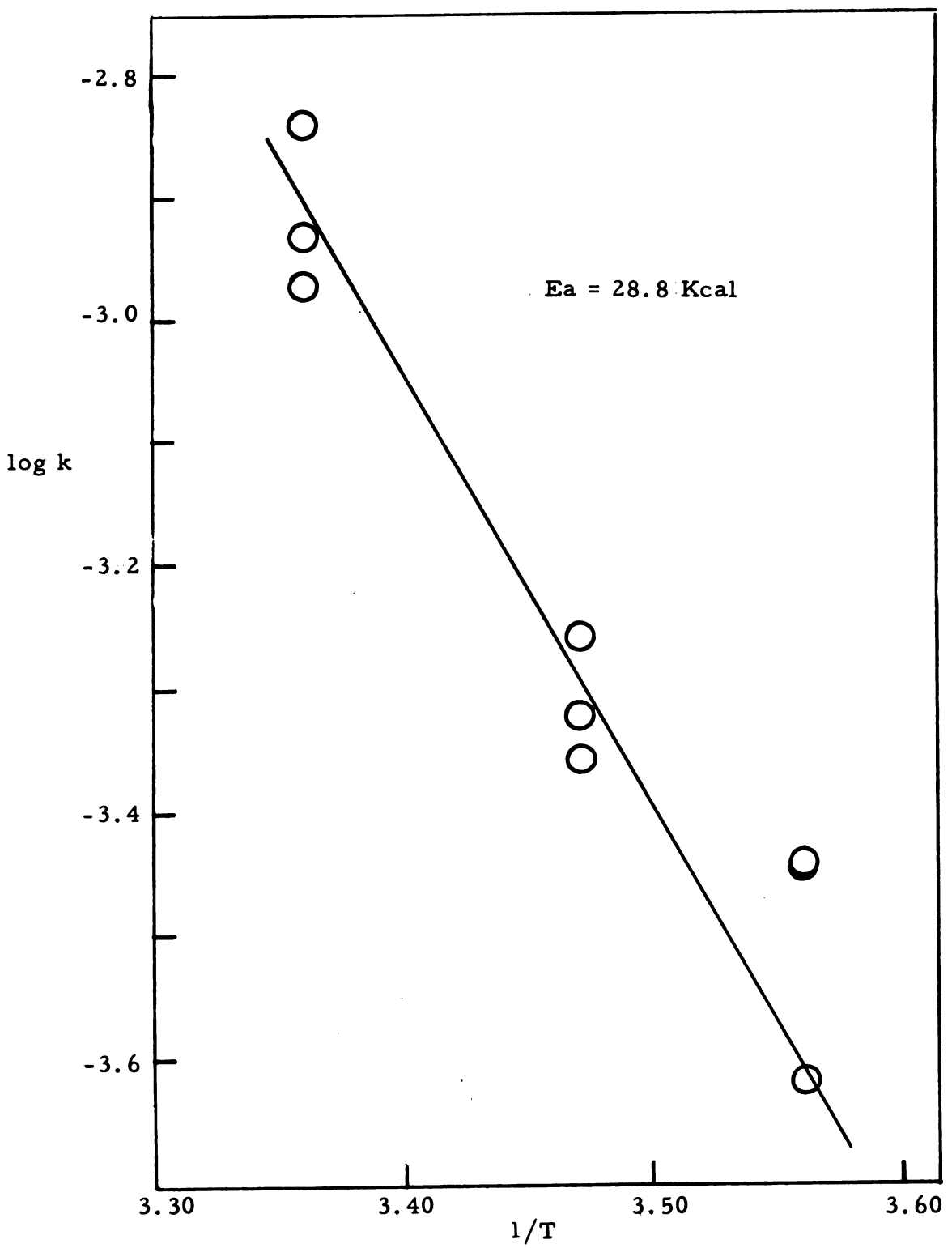


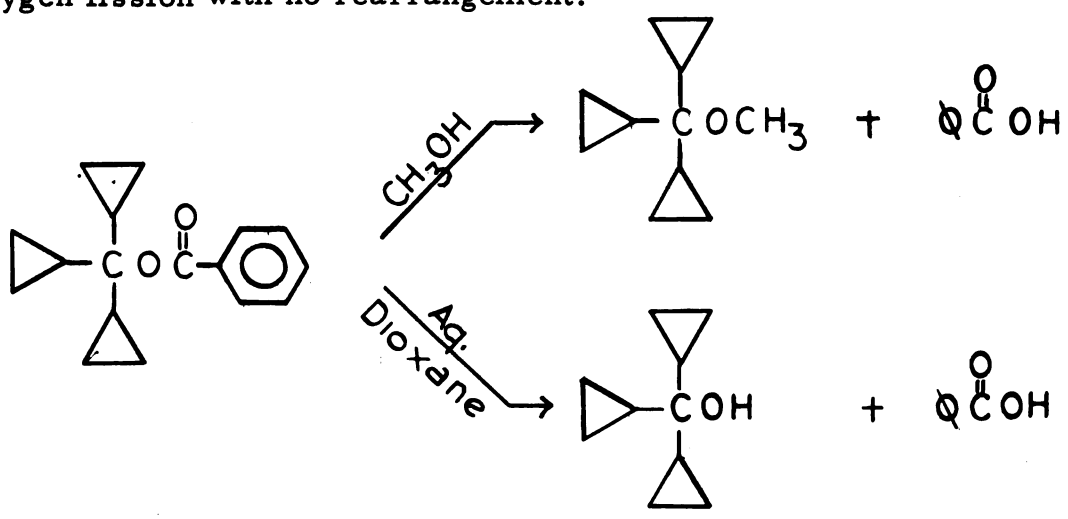
Figure 13. Plot of 1/T vs. log k for the Solvolysis of Tricyclopropylcarbinyl Benzoate in 95% Aqueous-Dioxane.

Table 2. Specific Rate Constants and Relative Rates for the Solvolysis of Tricyclopropylcarbinyl Benzoate and Dicyclopropylisopropylcarbinyl Benzoate

Ester	% Dioxane	Solvolysis Rates t, °C	k x 10^4 sec^{-1}	Relative Rate
XXVII-B	95	25.0	0.0114[a]	1
XXVIII-B	95	25.0	12.3[b]	1080
		15.5	4.37	
		7.9	2.52	
	90	7.9	22.9	

(a) Total rate including solvolysis and rearrangement.
(b) XXVIII-B underwent only solvolysis, no rearrangement.

The sole product of solvolysis of XXVIII-B was tricyclopropylcarbinol. This was shown by the identity of the cyclopropyl region of the n.m.r. spectrum of the solvolysis product with that of an authentic sample of the carbinol (Figures 14 and 15). Methanolysis yielded a mixture which, after removal of solvent and benzoic acid, had an n.m.r. spectrum consisting of a singlet at 6.75 τ (2.9 protons) and a complex multiplet from 8.8 to 10 τ (15 protons) (Figure 16). This was taken to be the spectrum of the methyl ether of tricyclopropylcarbinol(XXVIII, x = OCH_3), the sole methanolysis product. Thus, solvolysis occurs with alkyl-oxygen fission with no rearrangement.



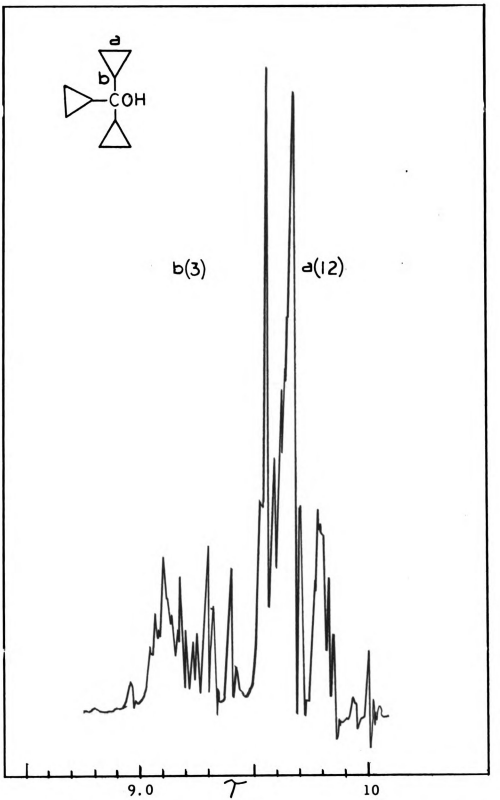


Figure 14. The N.M.R. Spectrum of Tricyclopropylcarbinol in Carbon Tetrachloride.

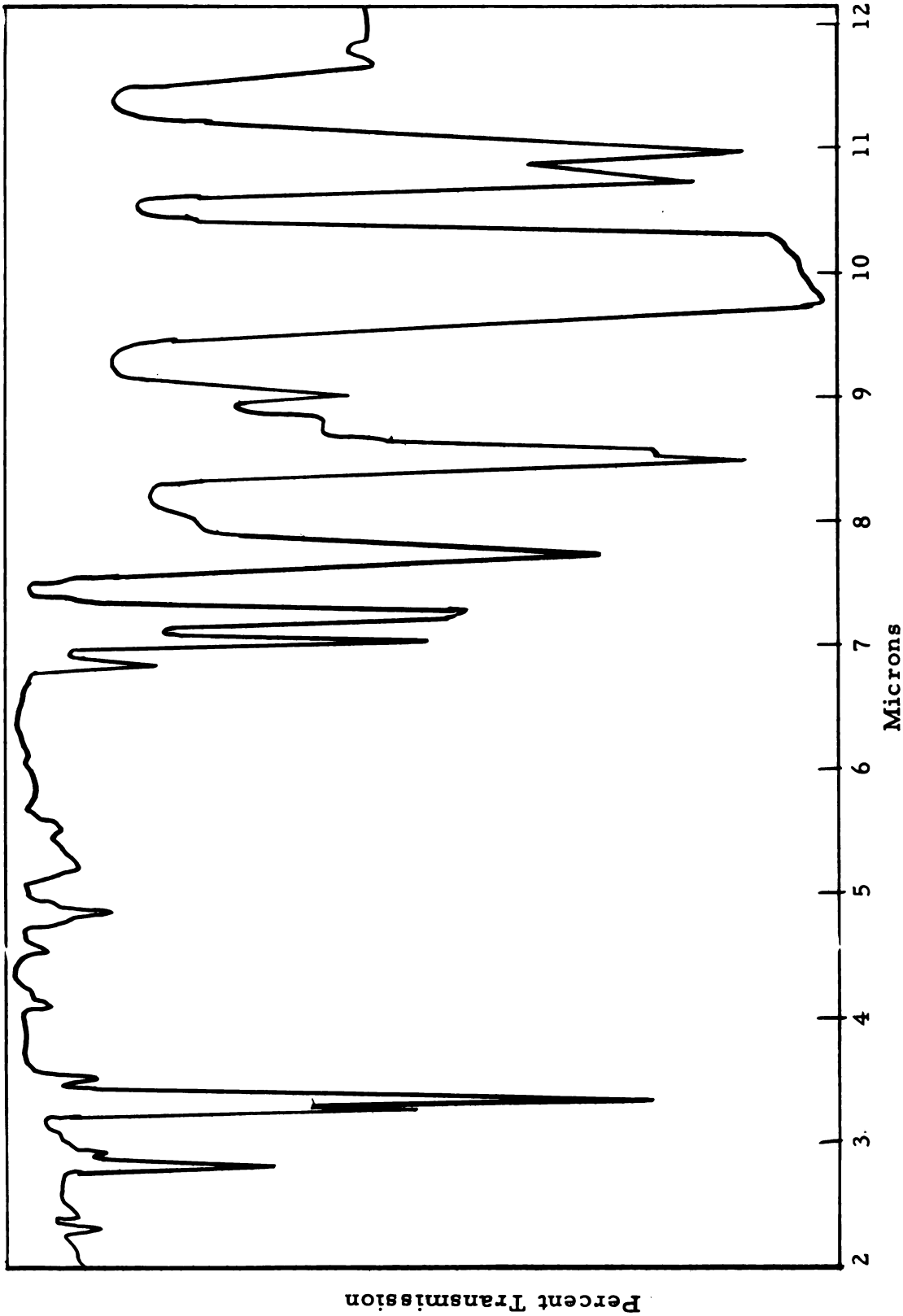


Figure 15. The Infrared Spectrum of Tricyclopropylcarbinol in Carbon Tetrachloride.

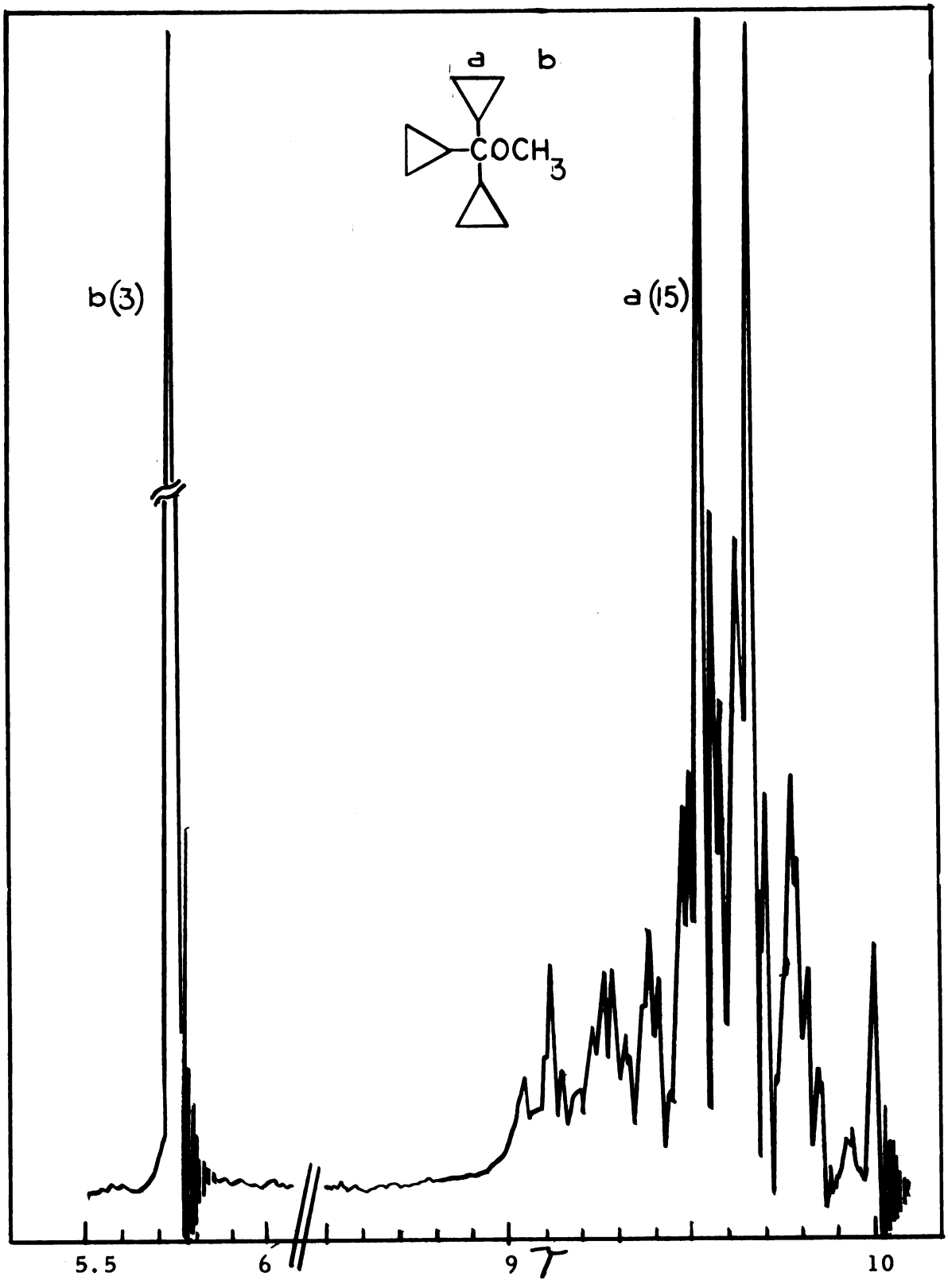
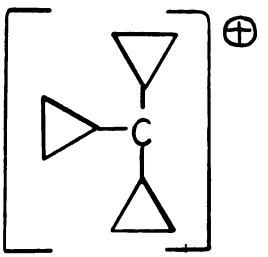


Figure 16. The N.M.R. Spectrum of the Methyl Ether of Tricyclopropylcarbinol in Carbon Tetrachloride.

No evidence of 4,4-dicyclopropylbut-3-en-1-yl benzoate was found in the n.m.r. spectrum.

This greatly enhanced solvolysis rate indicates exceptional stability for the tricyclopropylcarbinyl cation.



The fact that each additional cyclopropyl ring causes a rate increase implies that each ring must be involved in stabilizing the positive charge. The mode of stabilization is more profitably discussed in a later section of this thesis.

II. N.M.R. Spectra of Some Cyclopropylcarbinols in Concentrated Sulfuric Acid

A. Tricyclopropylcarbinol

The exceptional stability of the tricyclopropylcarbinyl cation is further demonstrated by the n.m.r. spectrum of tricyclopropylcarbinol in concentrated sulfuric acid (29, 30). The n.m.r. spectrum of tricyclopropylcarbinol in carbon tetrachloride consists of a complex pattern in the 9-10 τ region (Figure 14). However, in 96% sulfuric acid only a single sharp peak (Figure 17) is observed at 7.79 τ m. (See page 92 for the definition of τ m.) Deno (29) also reported a single peak at 7.06 τ, using a benzene capillary as an external reference.

The spectral solutions were yellow-brown when first mixed but darkened after standing at room temperature. The darkening was accompanied by polymer formation, seen both visibly and as broad peaks

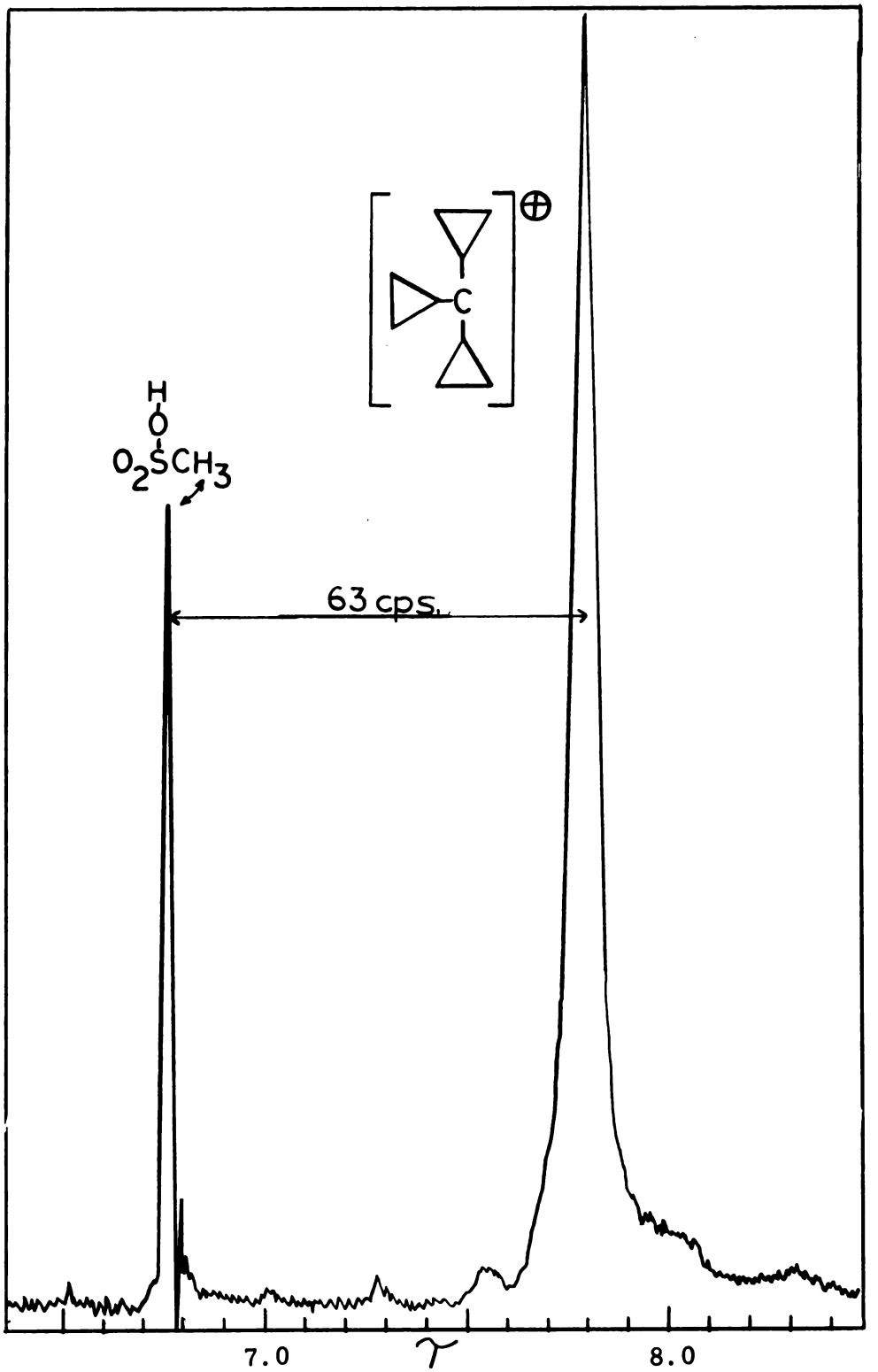
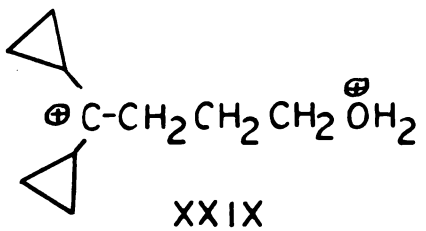


Figure 17. The N.M.R. Spectrum of Tricyclopropylcarbinol in 96% Sulfuric Acid.

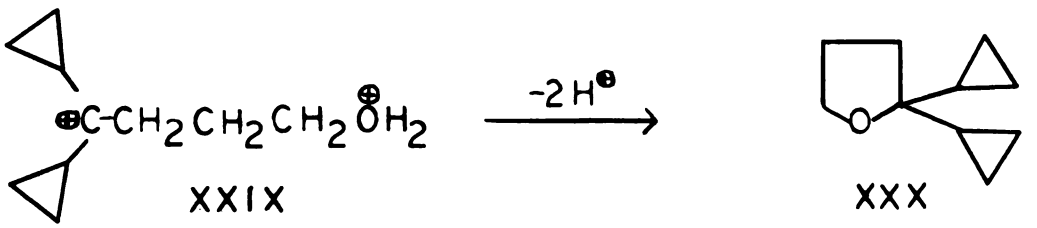
at 5.54 and 7.96 τ in the n.m.r. spectrum. As the polymer peaks increased, the original sharp signal decreased in intensity and ultimately disappeared.

The nature of the cationic species present in this solution was investigated by Deno (29). The ultraviolet spectrum of tricyclopropylcarbinol in 96% sulfuric acid (λ_{max} 270 mμ, ϵ 22,000) slowly changed and at the end of one hour a new ion (λ_{max} 285 mμ, ϵ 3000) was being formed. This ion was tentatively assigned the structure XXIX.



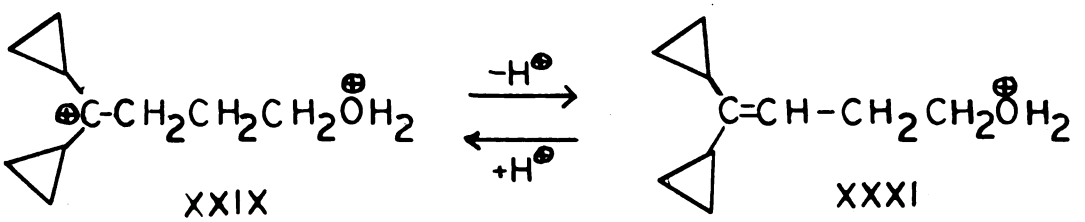
XXIX

Immediate addition of the sulfuric acid solution to water allowed 63% recovery of tricyclopropylcarbinol. However, drowning of the solution after XXIX had formed gave 2,2-dicyclopropyltetrahydrofuran (XXX).



XXIX XXX

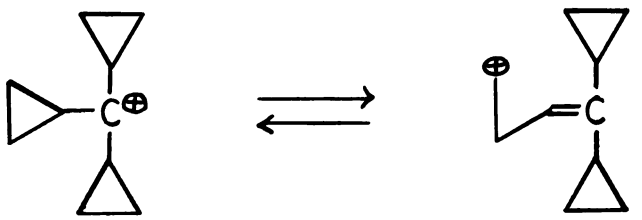
The possibility of an olefin (XXXI) as a contributing species in the



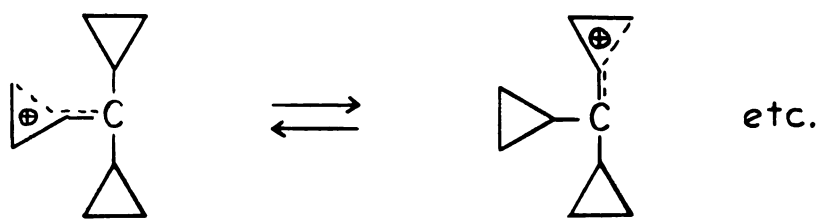
XXIX XXXI

equilibrium was eliminated by running the n.m.r. spectrum in D_2SO_4. After one hour the spectrum was unchanged showing that no deuterium exchange had occurred.

The rearrangement products (see also page 60) and the unusual n.m.r. spectrum could be explained by a series of rapidly equilibrating classical ions, such as below. There is, however, evidence against such an explanation (see introduction and references 7 and 9).

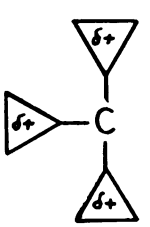


The observed properties of tricyclopropylcarbinyl systems can also be explained by an equilibrating mixture of homoallylic ions such as XXXII, XXXIII, etc., where the charge is delocalized by first one ring and then another. Another possibility is a cation such as XXXIV in which



XXXII XXXIII

the rings simultaneously share the charge, as in the triphenylmethyl cation. The difference, if any, between these explanations is a time factor. Any non-equivalence of the ring protons in the n.m.r. spectrum

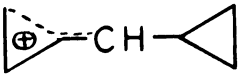


XXXIV

may be masked due to the width of the peak (ca. 4 c.p.s. at half height). Also, the twelve methylene protons may obscure the three methine protons precluding resolution of the peaks.

B. Dicyclopropylcarbinol

Dicyclopropylcarbinol, in 96% sulfuric acid, gives an n.m.r. spectrum identical (see Figure 17) with that of tricyclopropylcarbinol in sulfuric acid. Here, again, equilibrating non-classical structures such as XXXV offer an explanation for the n.m.r. spectrum and the rearrangement products (see page 69). Any non-equivalence of the protons in the



XXXV

cation may be of such small magnitude that resolution to a multiplet is not possible. Polymer formed more rapidly in this case than with tricyclopropylcarbinol. Formation of the polymer lead to broad n.m.r. peaks at 5.76, 8.18, 8.46 and 9.01 τ m. This was not an unexpected phenomenon as the secondary cation should be less stable and undergo further reaction more easily.

III. Hydrogenolysis of Some Cyclopropylcarbinols

A. Tricyclopropylcarbinol

The ease with which aryl carbinols are catalytically reduced to the corresponding aryl hydrocarbons is well-known (31). Benzyl alcohol when reduced with hydrogen and nickel at 125° yields, in ten minutes, 88% of toluene. As the phenyl group is moved further from the hydroxyl,

reduction of the ring occurs at the expense of hydrogenolysis. For instance, β-phenylethanol is reduced to a mixture consisting of 75% cyclohexylethanol and 25% ethylbenzene (200°, nickel), 2-phenylbutanol yields 68% of 2-cyclohexylbutanol and 32% of sec-butylbenzene (300°, Raney nickel) while 3-phenylbutanol gives 91% of 3-cyclohexylbutanol (200°, Raney nickel). The conclusion is that the phenyl group stabilizes the intermediate species involved in the reduction of the hydroxyl function.

If this conclusion is valid, the tricyclopropylcarbinyl group may possess sufficient stability to allow a similar reaction, i.e., the reduction of tricyclopropylcarbinol to tricyclopropylmethane. This reaction was successfully carried out using copper oxide-chromium oxide (copper chromite) catalyst. This catalyst was used because of its known preference for reduction of oxygen functions. (β-Phenylethanol yields 95% of ethylbenzene with copper chromite versus 68% of ethylcyclohexane with nickel under the same reaction conditions.)

The reduction products were tricyclopropylmethane (XXXVI) 35.9%, 1, 1-dicyclopropyl-1-butene (XXXVII) 4.2%, 1, 1-dicyclopropylbutane (XXXVIII) 18.6%, 4-cyclopropylheptane (XXXIX) 2%, 4-propylheptane (XL) 1%, and an unidentified product (1%). All of the products may be explained on the basis of a reduction intermediate such as the tricyclopropylcarbinyl cation (or alternately in absence of further evidence, the corresponding anion).

The structure of tricyclopropylmethane was shown by its infrared spectrum (Figure 18), which showed no hydroxyl absorption and no olefin. Its n.m.r. spectrum (Figure 19) showed no protons in the olefinic regions. The infrared spectrum (Figure 20) of 1, 1-dicyclopropyl-1-butene showed olefin at 6.01 μ and cyclopropyl absorption at 3.26 μ. Its n.m.r. spectrum (Figure 21) showed olefin at 4.95 τ and integrated satisfactorily for the assigned structure. The structure of 1, 1-dicyclopropylbutane was shown by its infrared (Figure 22) and n.m.r.

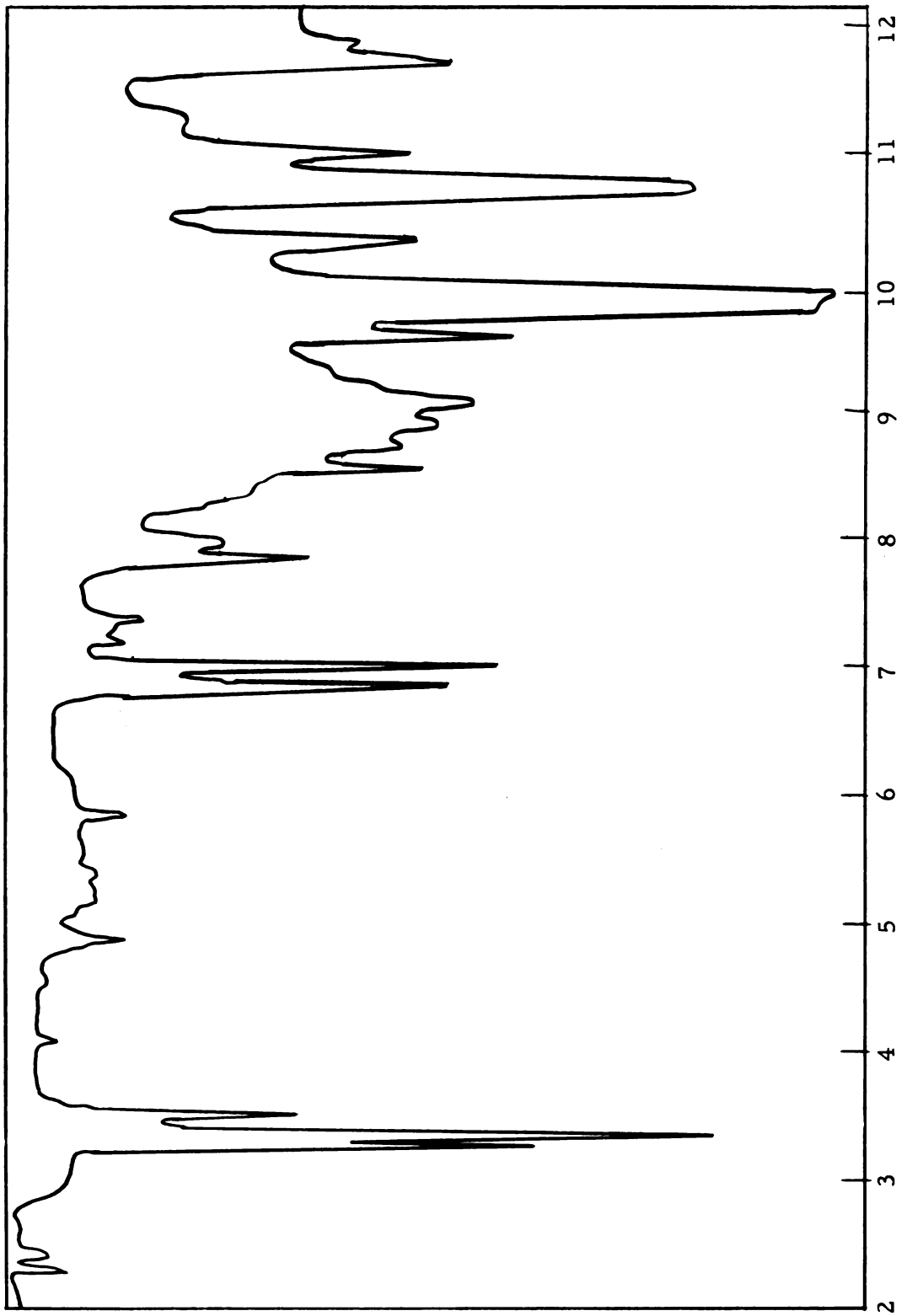


Figure 18. The Infrared Spectrum of Tricyclopropylmethane in Carbon Tetrachloride.

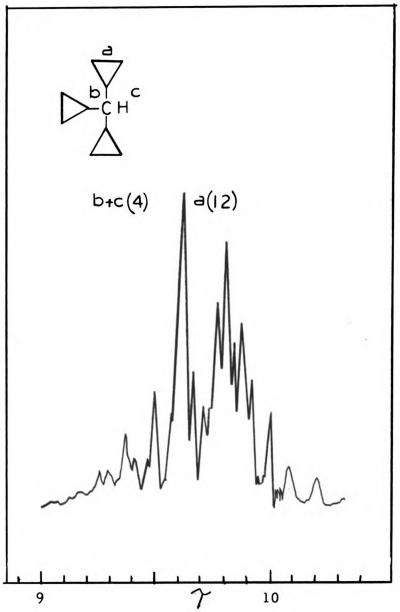


Figure 19. The N.M.R. Spectrum of Tricyclopropylmethane in Carbon Tetrachloride.

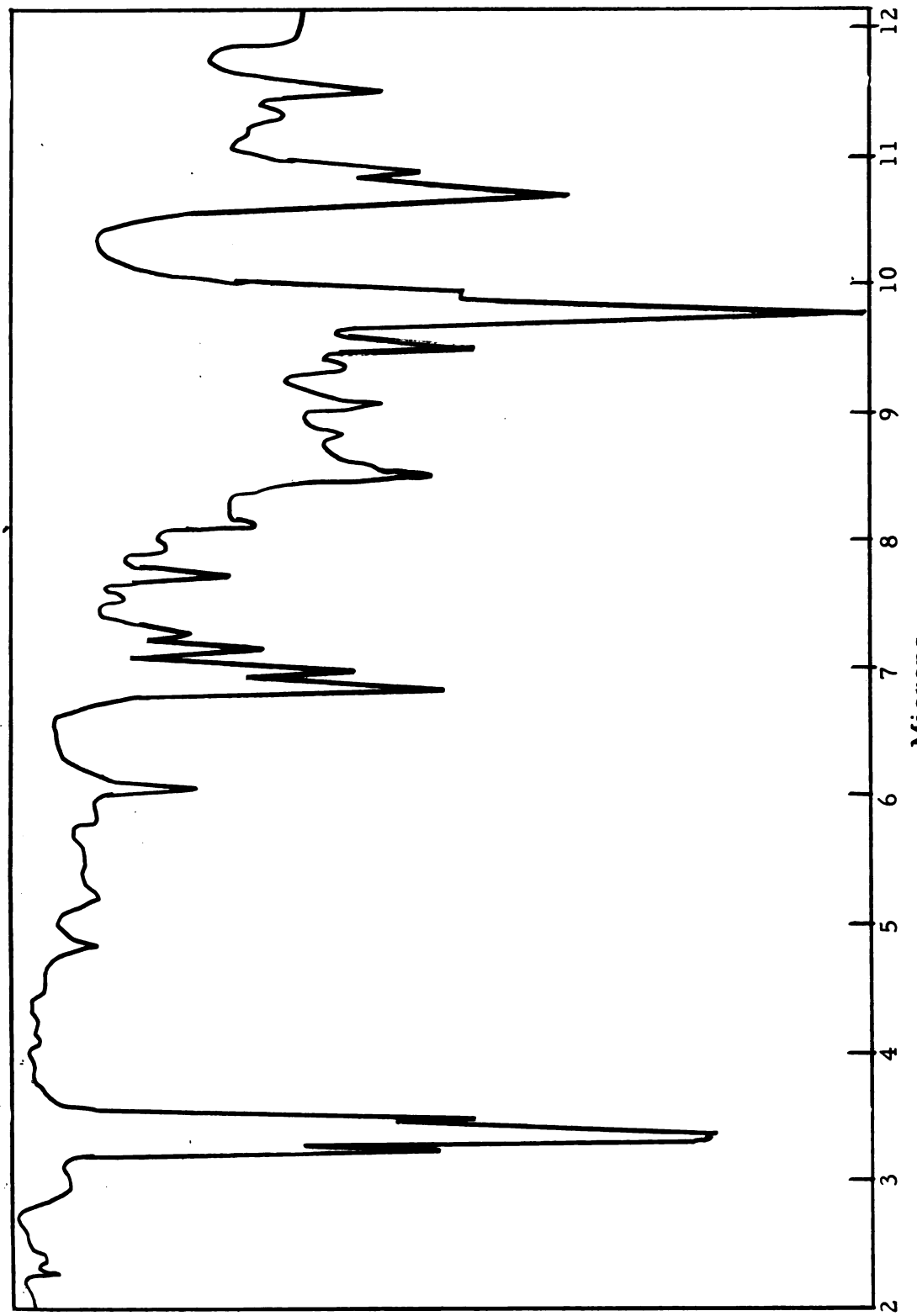


Figure 20. The Infrared Spectrum of 1,1-Dicyclopropyl-1-butene in Carbon Tetrachloride.

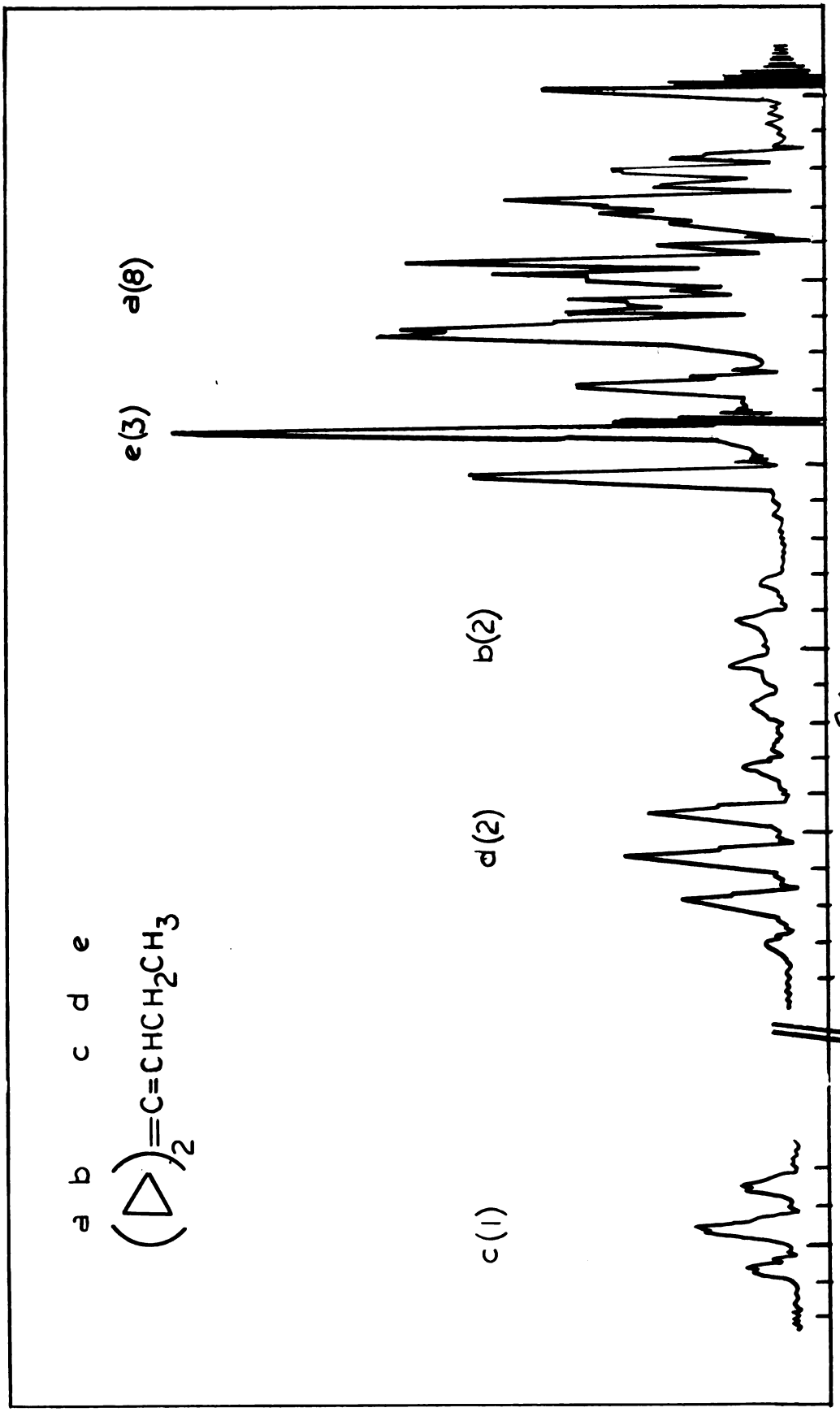


Figure 21. The N.M.R. Spectrum of 1,1-Dicyclopropyl-1-butene in Carbon Tetrachloride.

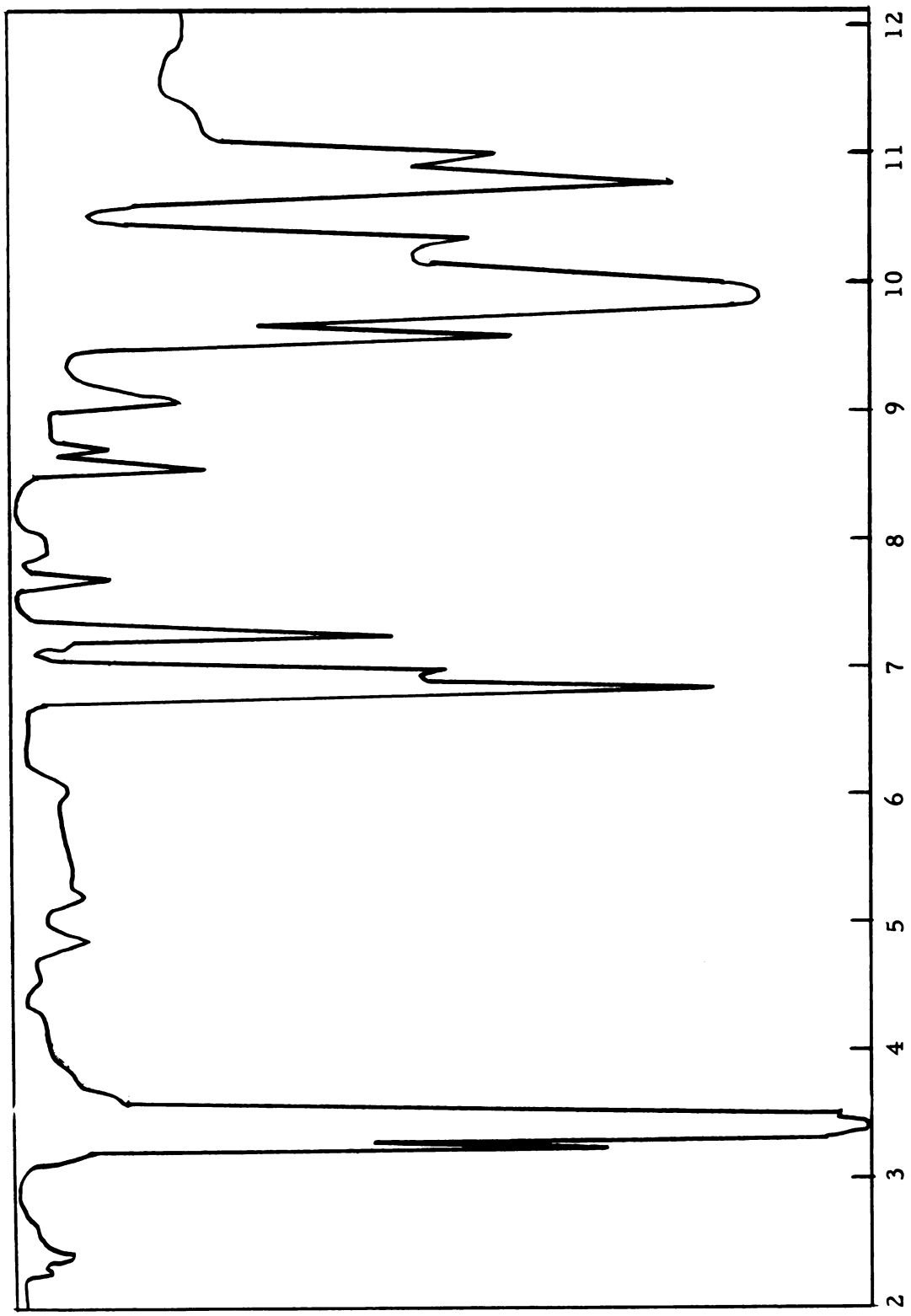
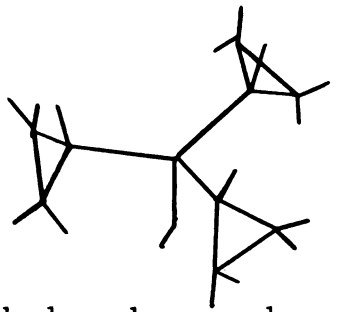


Figure 22. The Infrared Spectrum of 1,1-Dicyclopropylbutane in Carbon Tetrachloride.

(Figure 23) spectra. 4-Cyclopropylheptane gave infrared (Figure 24) and n.m.r. (Figure 25) spectra consistent with the structure. The position of the cyclopropyl group was deduced from the starting material and no rigid proof of its position was made. The structure of 4-propylheptane was indicated by its infrared (Figure 26) and n.m.r. (Figure 27) spectra.

All compounds had satisfactory elemental analyses. Yields were calculated from the integrated areas under gas chromatographic curves.

Tricyclopropylcarbinol appeared, from Dreiding models to be an umbrella shaped molecule. If this molecule were to be adsorbed on the



catalyst surface with the hydroxyl group down, it would be in a position favorable for receiving a proton from the catalyst (32). Loss of a water molecule from the protonated species would result in a tricyclopropylcarbinyl cation. Hydride attack at a ring methylene carbon in competition with attack at the carbinyl carbon accounts for the products, as shown in Figure 28. These processes may occur on or off the catalyst surface. Protonation of olefin product is followed by hydride attack, with or without ring opening, to give a saturated product and its olefinic isomer, which again reacts. All of the compounds with the exception of 4-propyl-3-heptene (probably the unidentified component) have been isolated thus giving support to this scheme.

(It should be noted that initial hydride attack on the hydroxyl, loss of water and a similar sequence of reactions involving anions also explains the products, see references 46 and 47. It is felt, however, that this explanation is less satisfactory than that involving initial protonation of the hydroxyl group.)

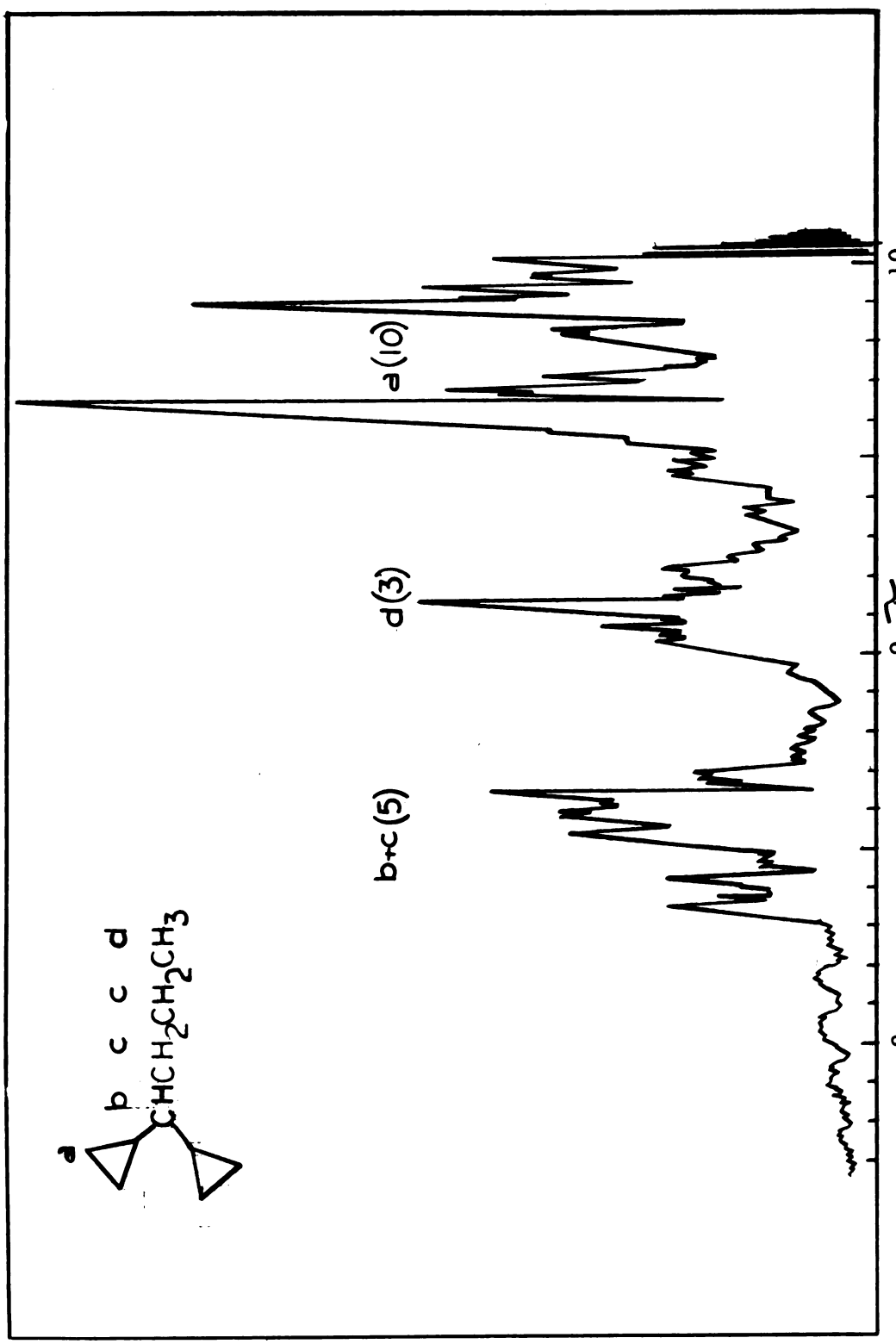


Figure 23. The N.M.R. Spectrum of 1, 1-Dicyclopropylbutane in Carbon Tetrachloride.

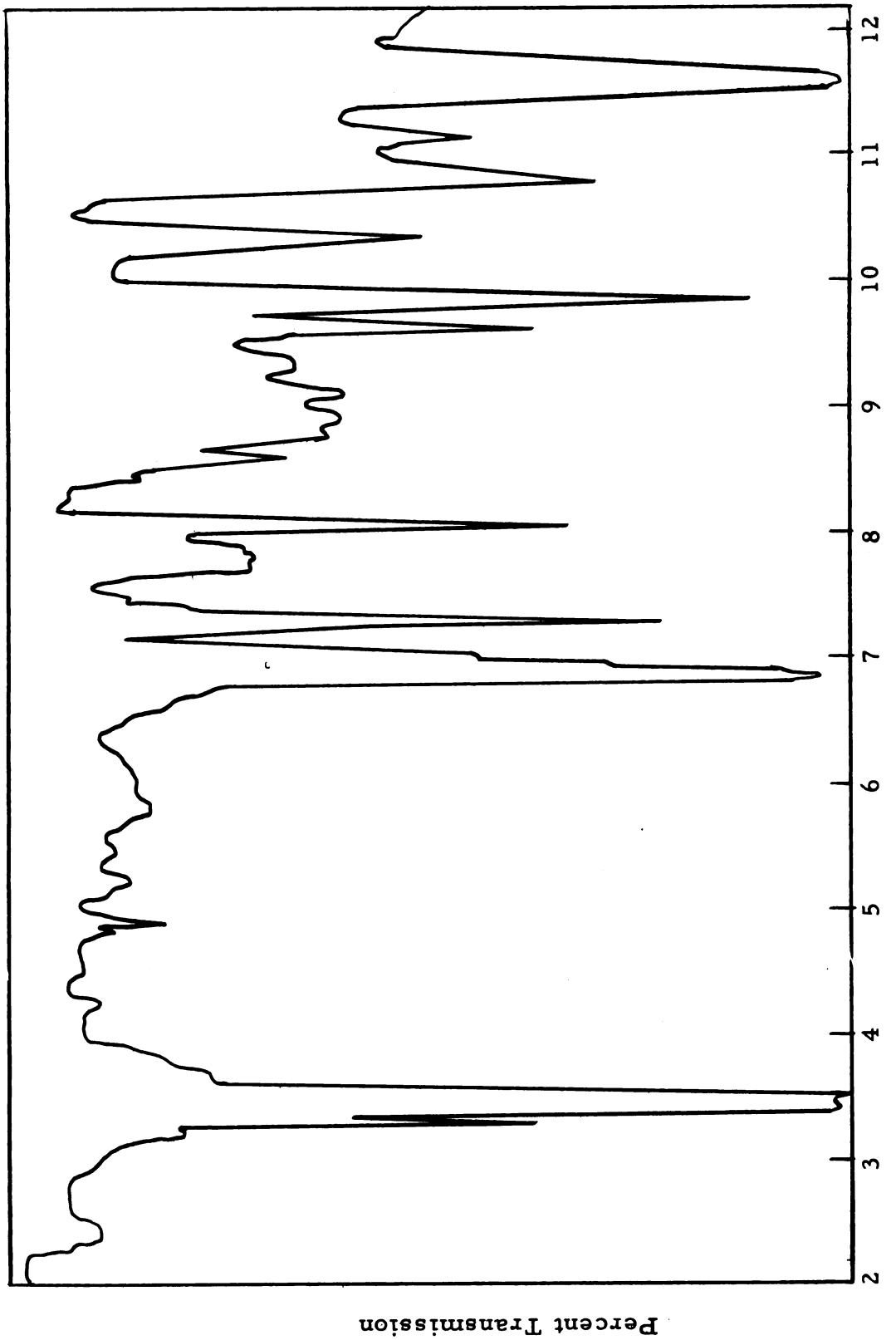


Figure 24. The Infrared Spectrum of 4-Cyclopropylheptane in Carbon Tetrachloride.

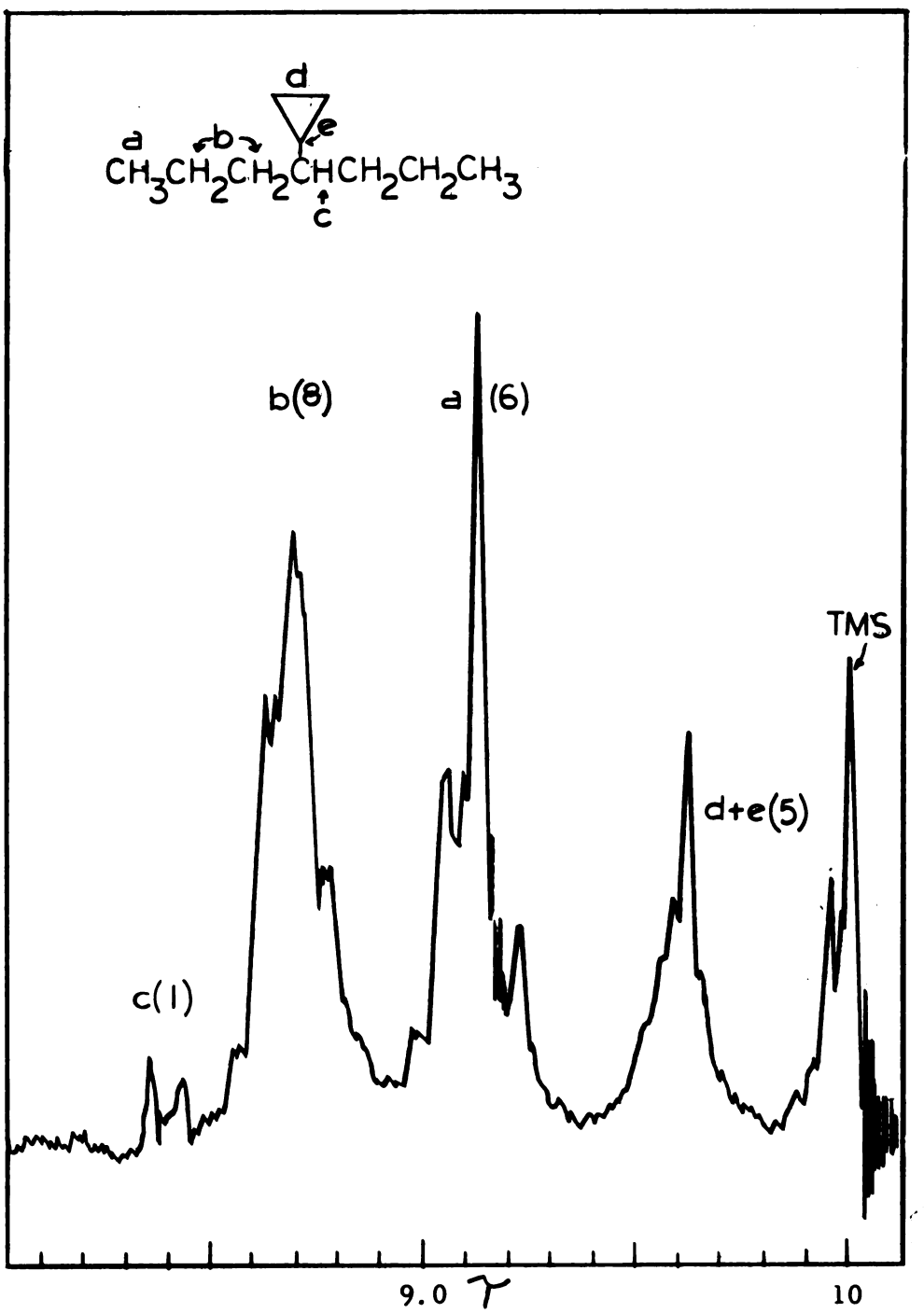


Figure 25. The N.M.R. Spectrum of 4-Cyclopropylheptane in Carbon Tetrachloride.

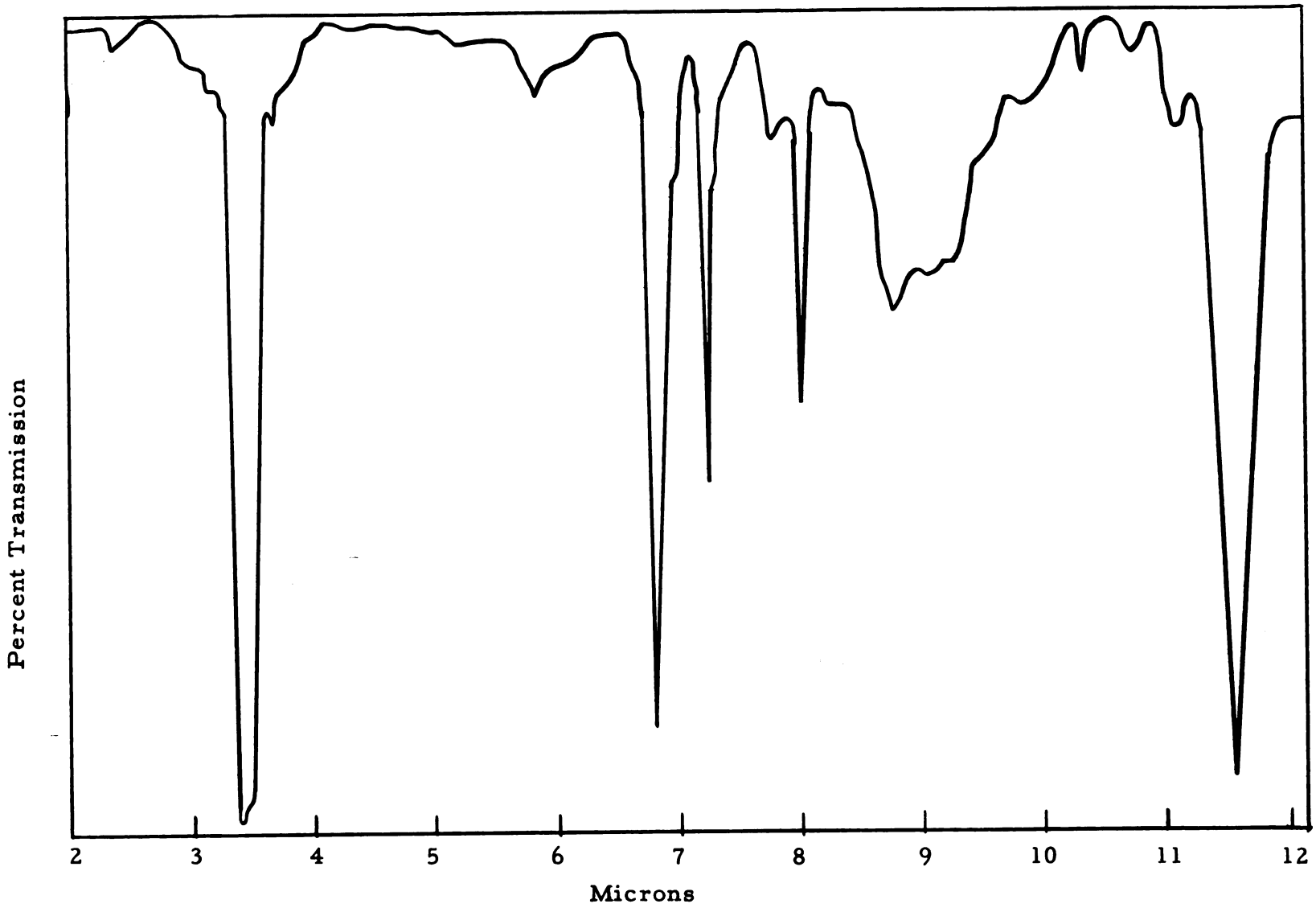


Figure 26. The Infrared Spectrum of 4-Propylheptane in Carbon Tetrachloride.

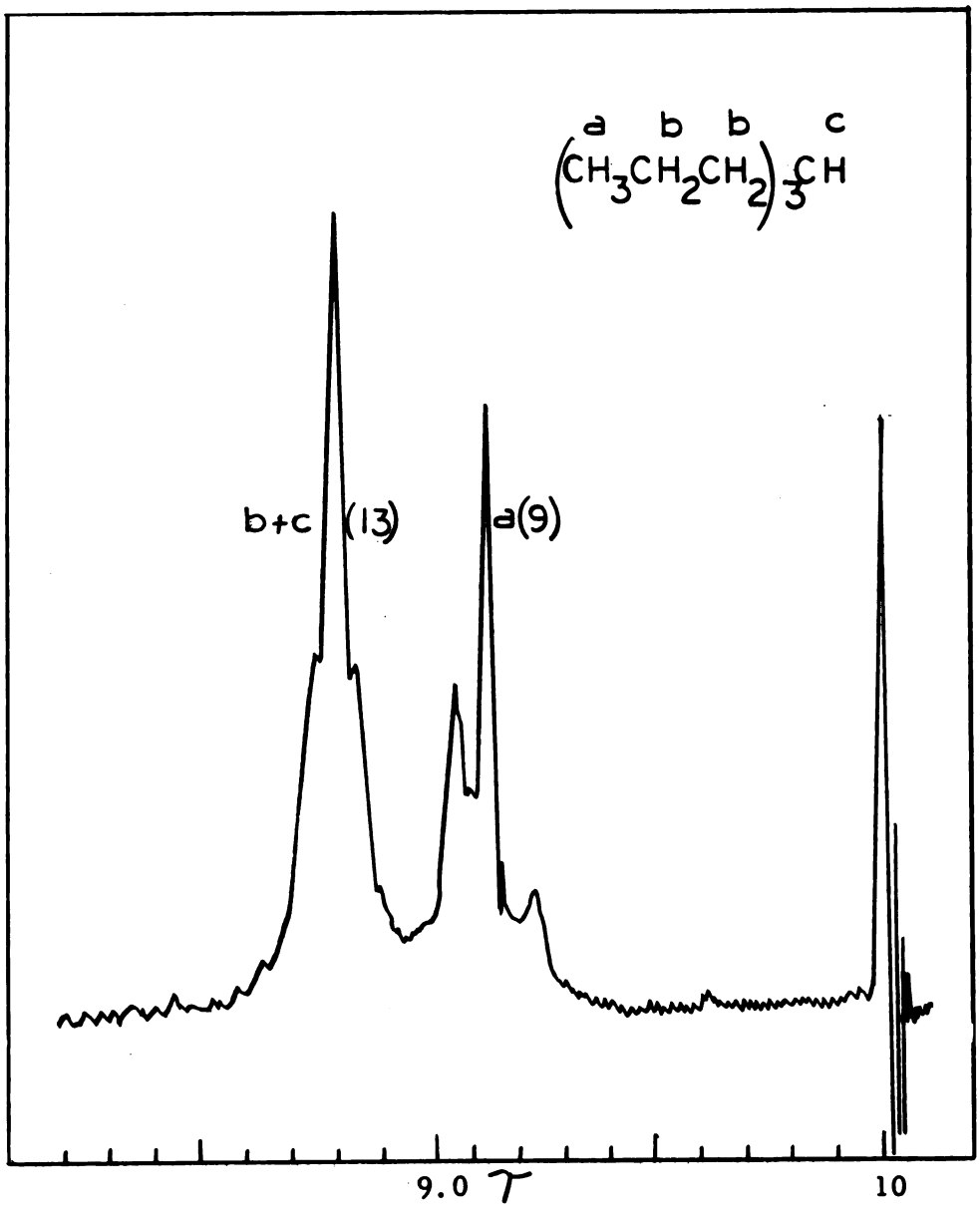


Figure 27. The N.M.R. Spectrum of 4-Propylheptane in Carbon Tetrachloride.

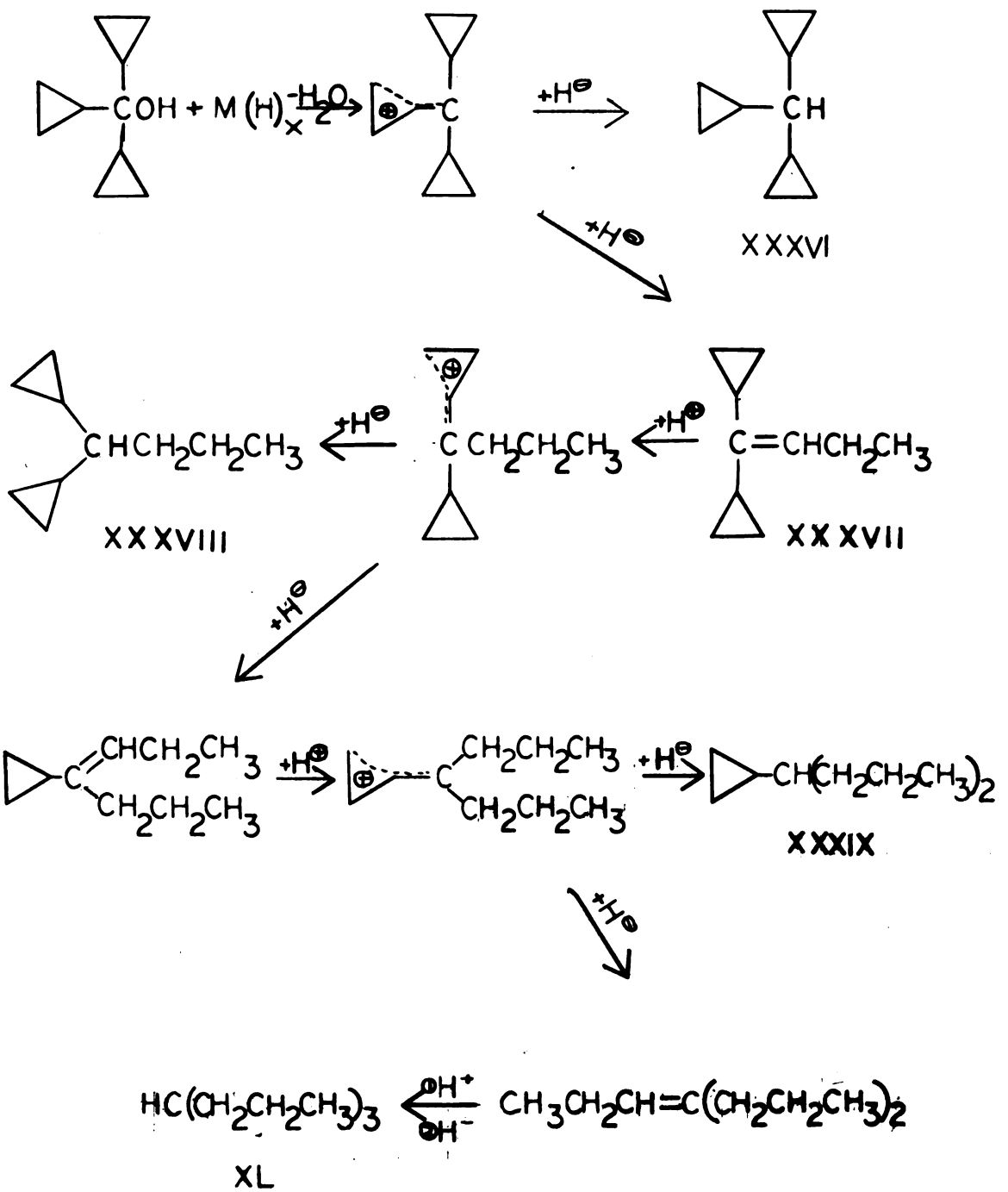


Figure 28. The Scheme for the Reduction of Tricyclopropylcarbinol.

That tricyclopropylmethane was not the source of further reduction products was shown by treating a mixture of this compound and 1, 1-dicyclopropyl-1-butene under the reduction conditions. The amount of tricyclopropylmethane remained unchanged but the olefin disappeared and in its place 1, 1-dicyclopropylbutane, 4-cyclopropylheptane and 4-propylheptane were found.

When carbinol and catalyst were heated at 200° for three hours, the resulting liquid had an n.m.r. spectrum identical with that of the starting material thus showing that no dehydration occurred.

After this section of work was completed a dimer was discovered as a product of the reduction of dicyclopropylcarbinol. Re-examination of the reduction products of tricyclopropylcarbinol, by gas chromatography, revealed a previously unnoticed component with a retention time much greater than that of any C_{10} hydrocarbon product. This was probably a C_{20} dimer analogous to that found in the dicyclopropyl case (see following section).

B. Dicyclopropylcarbinol

Catalytic reduction of dicyclopropylcarbinol (n.m.r. Spectrum Figure 28a) with copper chromite and hydrogen resulted in seven products in addition to recovered carbinol. The four which were identified, plus recovered carbinol, account for about 84% of the reaction mixture but, since the compound of greatest interest, dicyclopropylmethane, was a minor product, a complete study was not made.

The products identified were n-heptane (XLI) 2%, 1-cyclopropylbutane (XLII) 21.5%, dicyclopropylmethane (XLIII) 8.1% and 1, 1-dicyclopropyl-2-(cyclopropylmethyl)butane (XLIV) 15.7%. There remained 36.5% of the starting carbinol. n-Heptane was identified by comparison of its gas chromatographic retention time with that of an authentic sample.

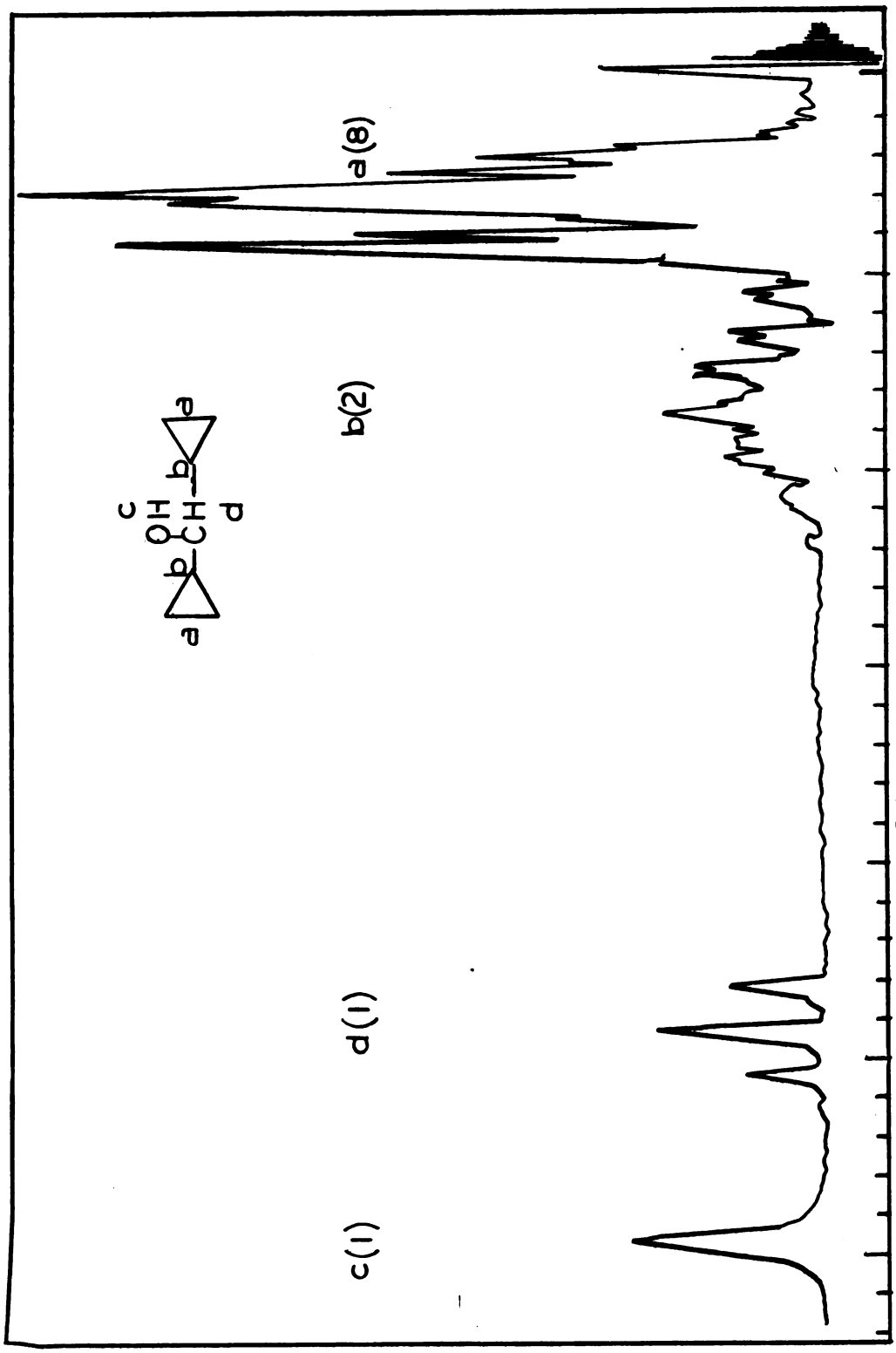


Figure 28a. The N.M.R. Spectrum of Dicyclopropylcarbinol in Carbon Tetrachloride.

The structure of 1-cyclopropylbutane was shown by its infrared (Figure 29) and n.m.r. (Figure 30) spectra. Dicyclopropylmethane was identified by comparison of its retention time and n.m.r. spectrum (Figure 31) with that of an authentic sample (33). The dimer, 1, 1-dicyclopropyl-2-cyclopropylmethylbutane was tentatively identified by its infrared spectrum (Figure 32) which showed no olefin and its n.m.r. (Figure 33) spectrum which showed about 15 cyclopropyl and 9 aliphatic protons. The position of the cyclopropane rings could not be proved and was deduced from its expected mode of formation (Figure 34). Satisfactory elemental analyses for these compounds were obtained. The proposed reaction scheme is shown in Figure 34 and is similar to that of tricyclopropylcarbinol. Not all of the compounds shown were isolated but a complete product study would, no doubt, prove their presence.

All of the reaction steps, except possibly that of dimerization, probably occur on the catalyst surface with adsorption-desorption processes between the steps. The dimer may be formed by the reaction of the dicyclopropylcarbinyl cation with 1-cyclopropyl-1-butene.

This reduction occurred at a much lower temperature than did the tricyclopropyl system (145° vs. 200°) probably because the geometry of dicyclopropylcarbinol is more suitable for intimate contact with the catalyst. It is also interesting to note that at 115° little of the C_7 hydrocarbons were produced but the C_{14} dimer was still formed. The reason why dicyclopropylcarbinol yielded more ring-opened products than did tricyclopropylcarbinol is not fully understood. The dicyclopropylcarbinyl cation would be expected to undergo reaction more readily than the more stable tricyclopropylcarbinyl cation but the preference for ring opening is not easily explained on this basis. It may be that under optimum reaction conditions dicyclopropylcarbinol would give a higher yield of unrearranged hydrocarbon. A full examination of the effect of catalyst ratio and temperature would clarify this point.

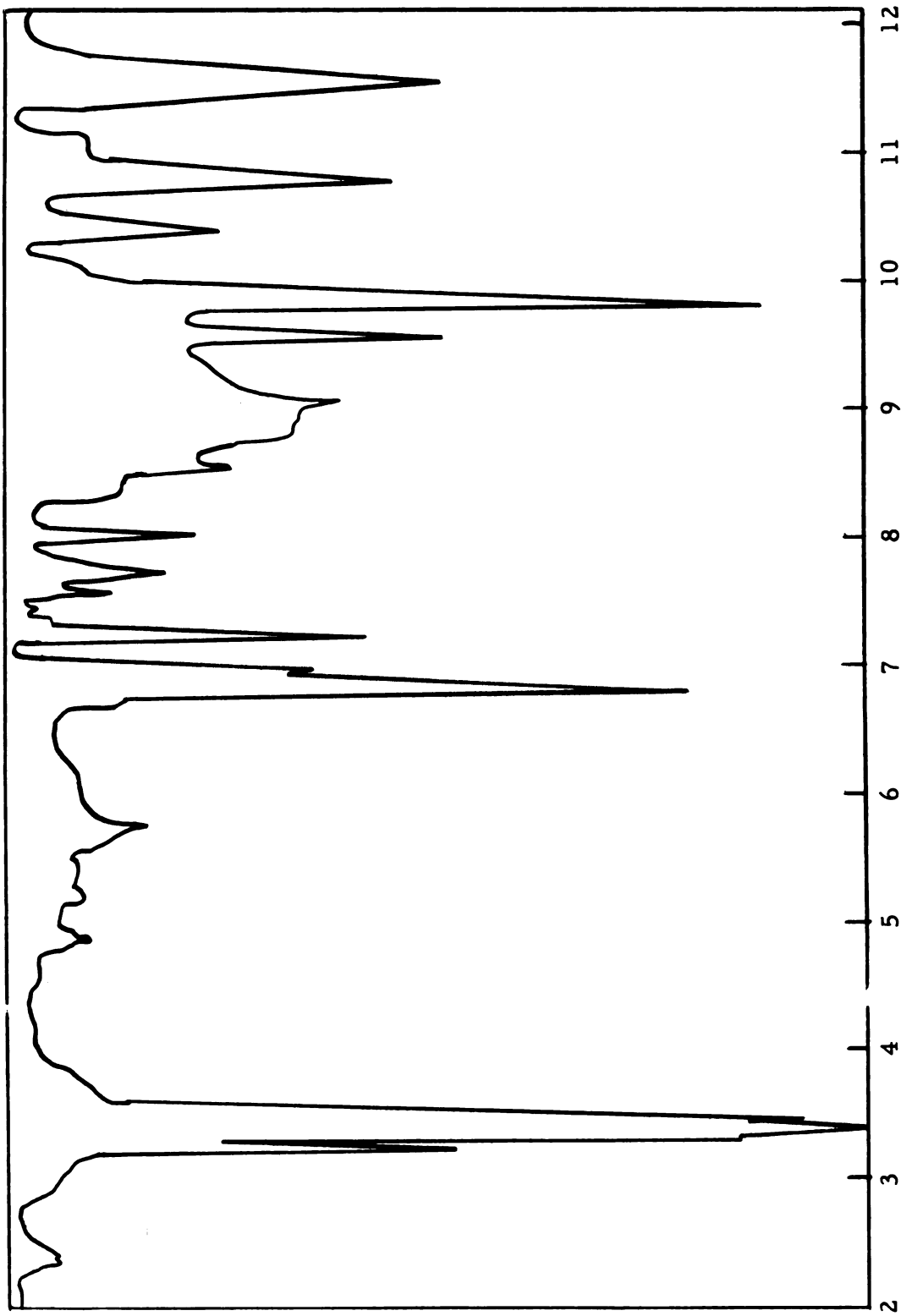


Figure 29. The Infrared Spectrum of 1-Cyclopropylbutane in Carbon Tetrachloride.

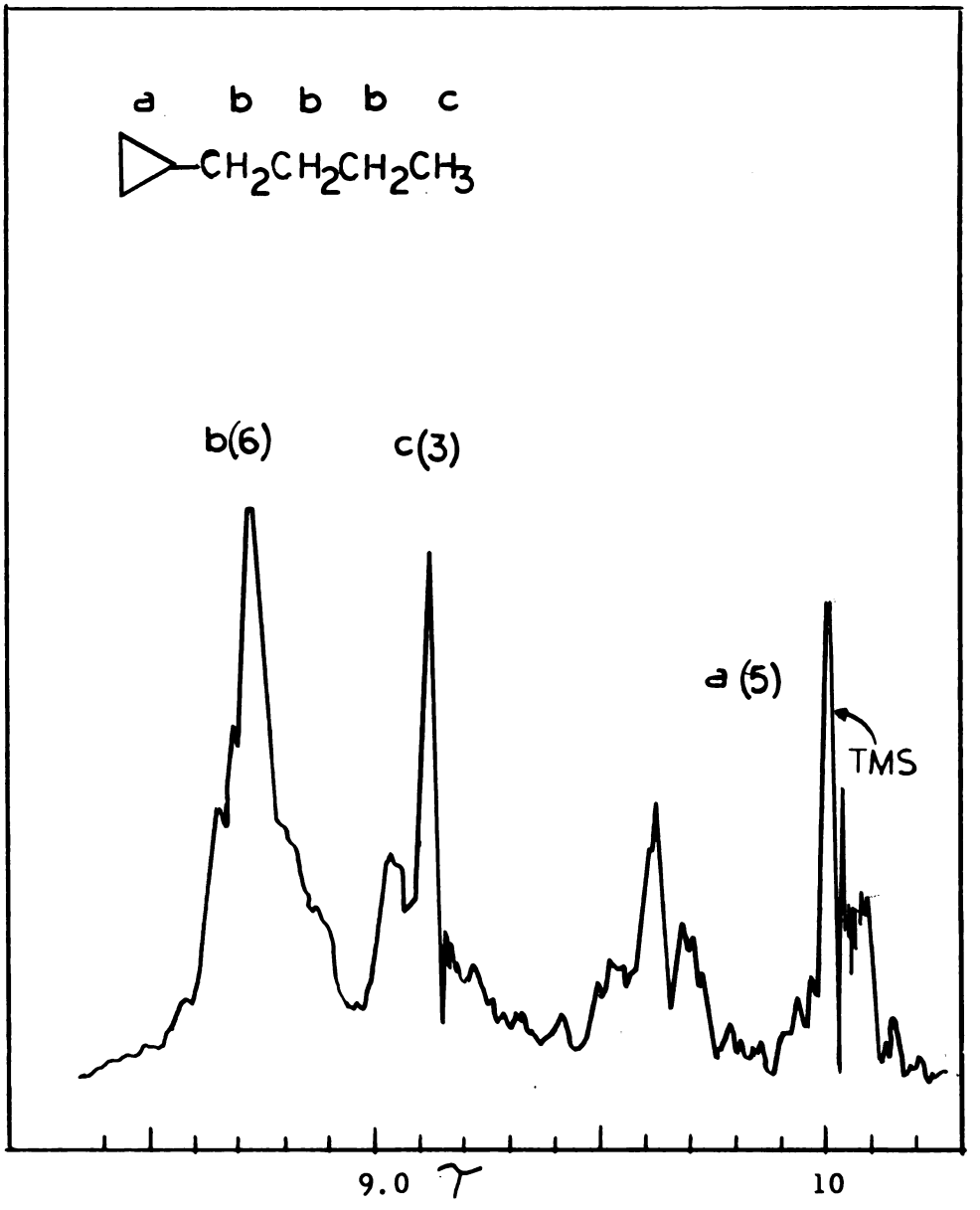


Figure 30. The N.M.R. Spectrum of 1-Cyclopropylbutane in Carbon Tetrachloride.

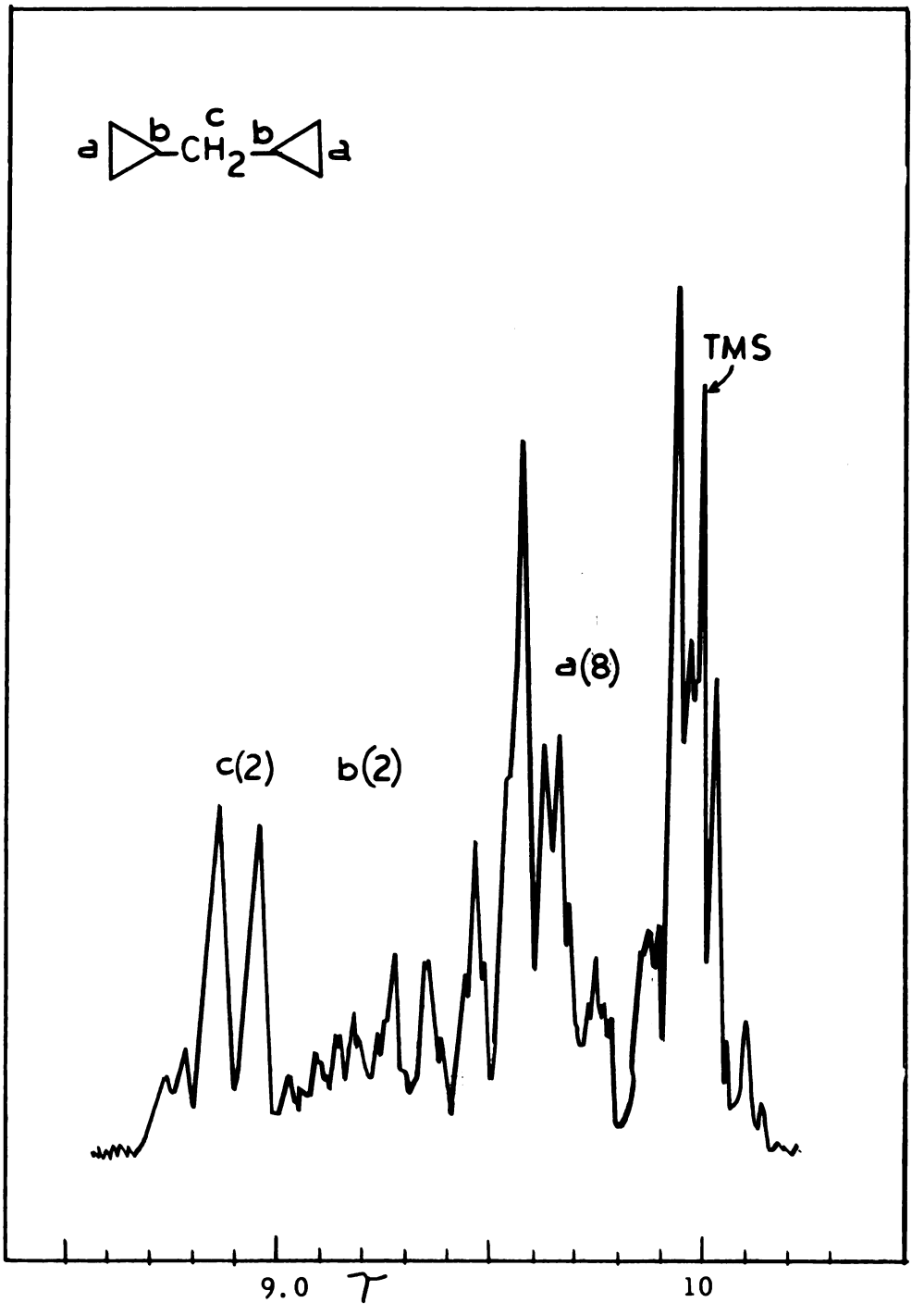


Figure 31. The N.M.R. Spectrum of Dicyclopropylmethane in Tetrachloride.

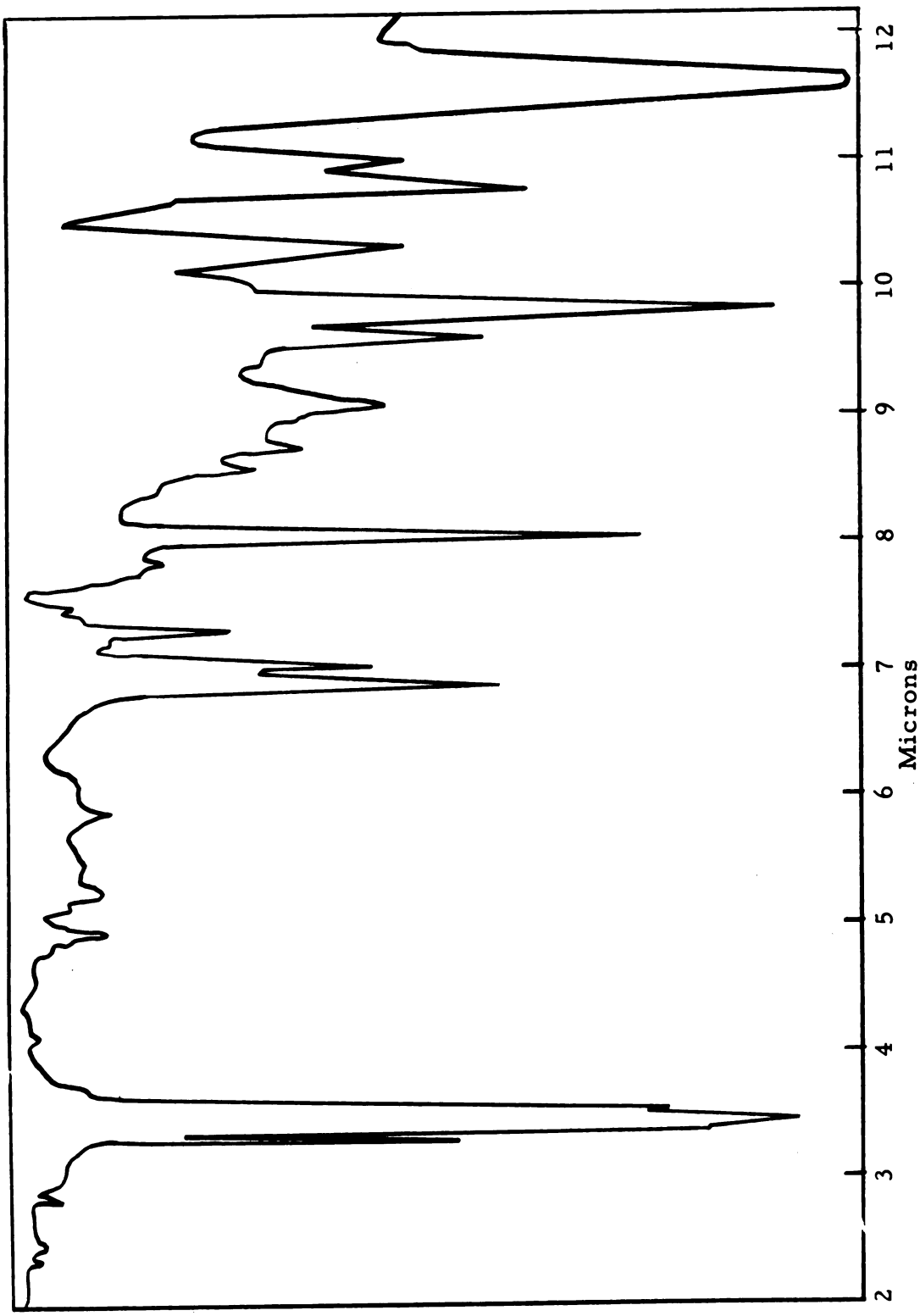


Figure 32. The Infrared Spectrum of 1,1-Dicyclopropyl-2-(cyclopropylmethyl)butane in Carbon Tetrachloride.

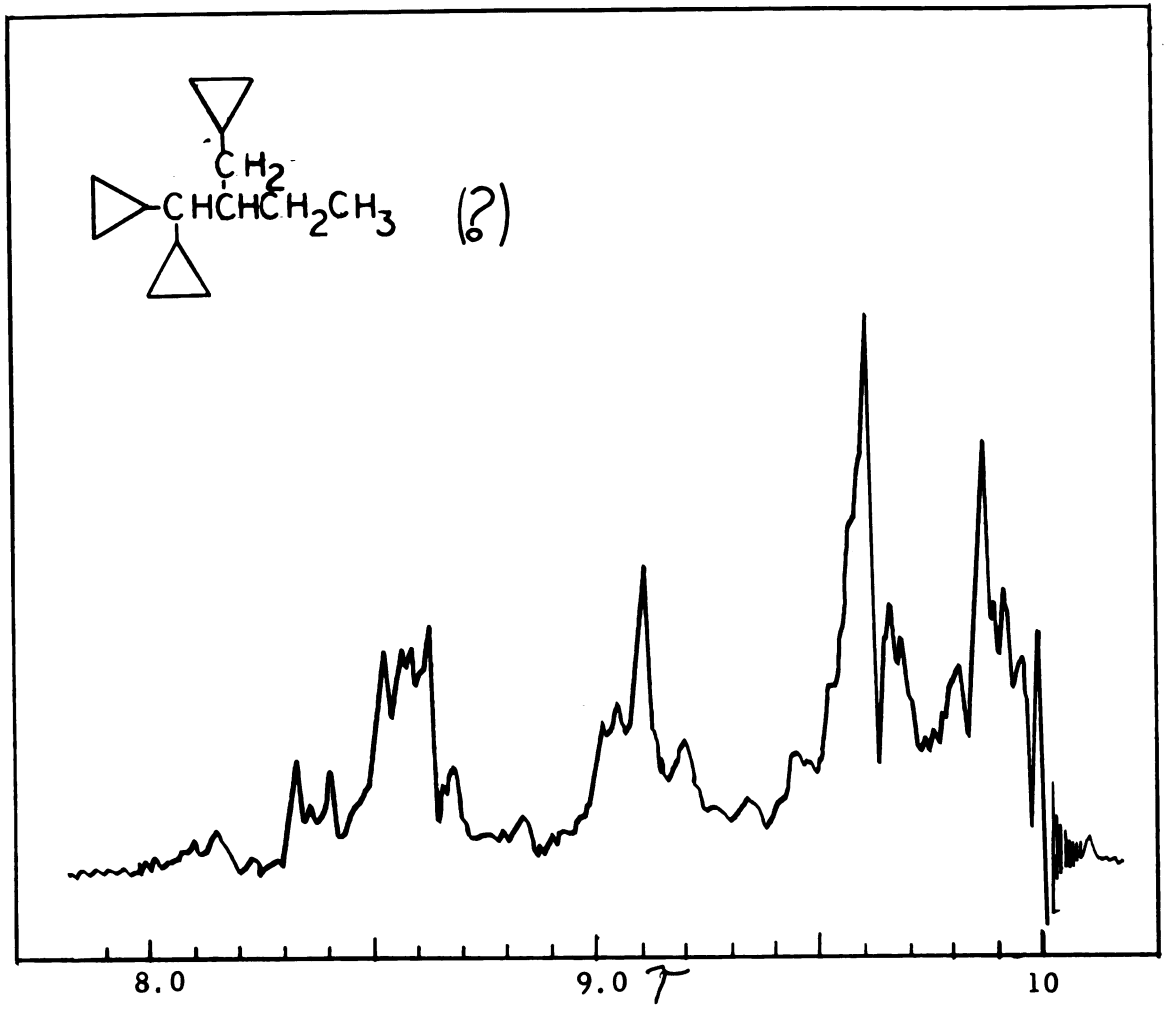


Figure 33. The N.M.R. Spectrum of 1, 1, -Dicyclopropyl-2-(cyclopropylmethyl)butane in Carbon Tetrachloride.

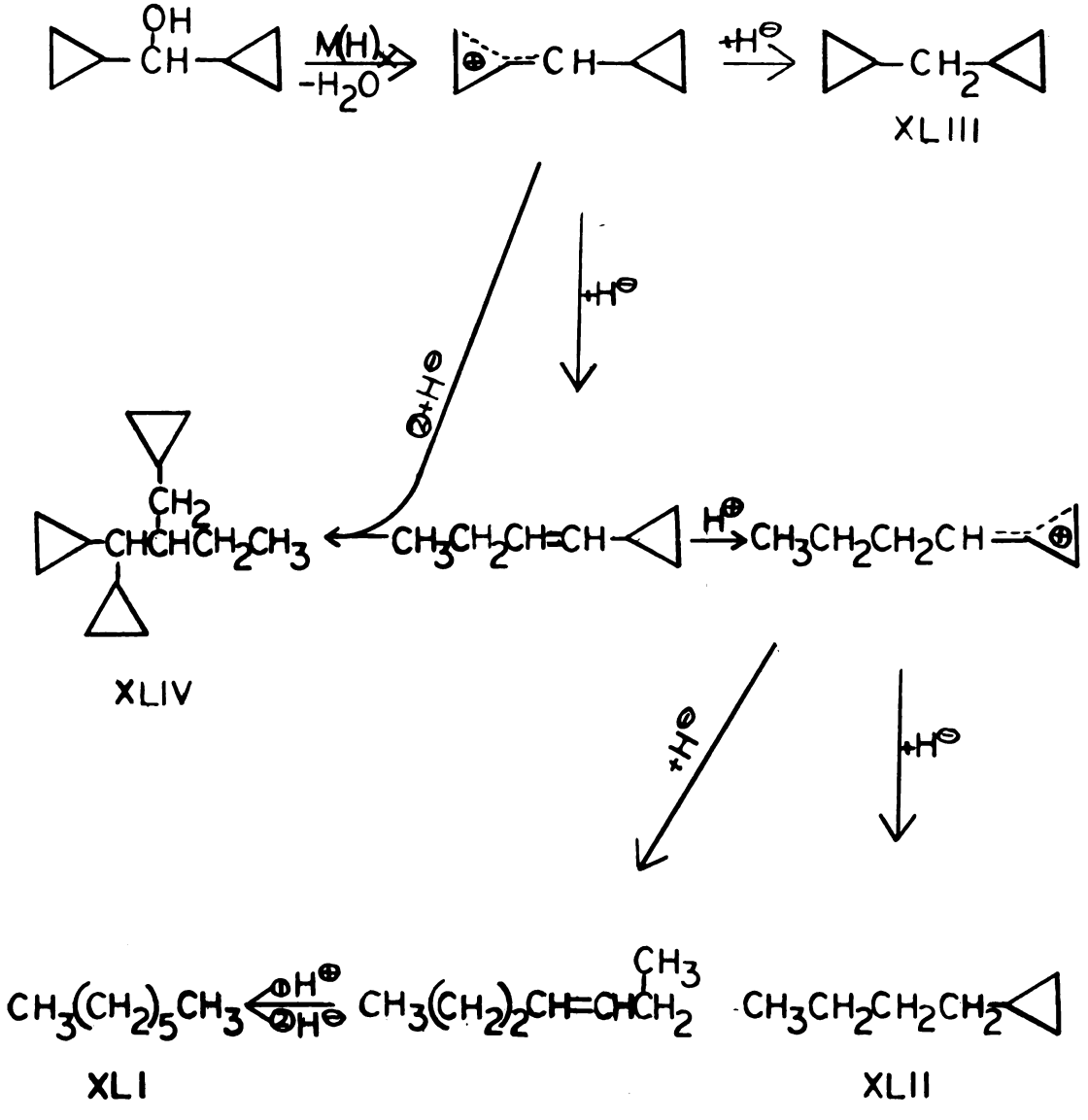


Figure 34. Scheme for the Reduction of Dicyclopropylcarbinol.

IV. Acid Catalyzed Rearrangement of Some Cyclopropylcarbinols

A. Tricyclopropylcarbinol

Favorskaya reported (15, 25) that in the presence of aqueous sulfuric acid, 2-cyclopropyl-2-propanol rearranged to yield 2, 2-dimethyltetrahydrofuran, 4-methylpent-3-en-1-ol and bis (4-methylpent-3-en-1-yl) ether. It was hoped that the stability of the tricyclopropylcarbinyl cation would allow tricyclopropylcarbinol to follow a reaction path differing from that of the above case.

When tricyclopropylcarbinol was heated with a trace of concentrated sulfuric acid, rearrangement occurred. The products (Figure 35) were 2, 2-dicyclopropyltetrahydrofuran (XLV) and bis (4, 4-dicyclopropylbut-3-en-1-yl) ether.

2, 2-Dicyclopropyltetrahydrofuran was synthesized independently by the reaction of cyclopropyl lithium and γ-butyrolactone using a method patterned after that of Henry (39). Its infrared (Figure 36) and n.m.r. (Figure 37) spectra were identical with that of the 2, 2-dicyclopropyltetrahydrofuran isolated from the reaction. The structure of bis (4, 4-dicyclopropylbut-3-en-1-yl) ether was indicated by its infrared (Figure 38) and n.m.r. (Figure 39) spectra. Elemental analyses for these compounds was satisfactory.

Since no 4, 4-dicyclopropylbut-3-en-1-ol (XLVI) was isolated, it was assumed that the reaction conditions had caused its further reaction. When XLVI, infrared spectrum (Figure 40) and n.m.r. spectrum (Figure 41), prepared by reduction of 4, 4-dicyclopropylbut-3-en-1-yl acetate with lithium aluminumhydride, was treated with sulfuric acid under the reaction conditions, the only product isolated was XLV.

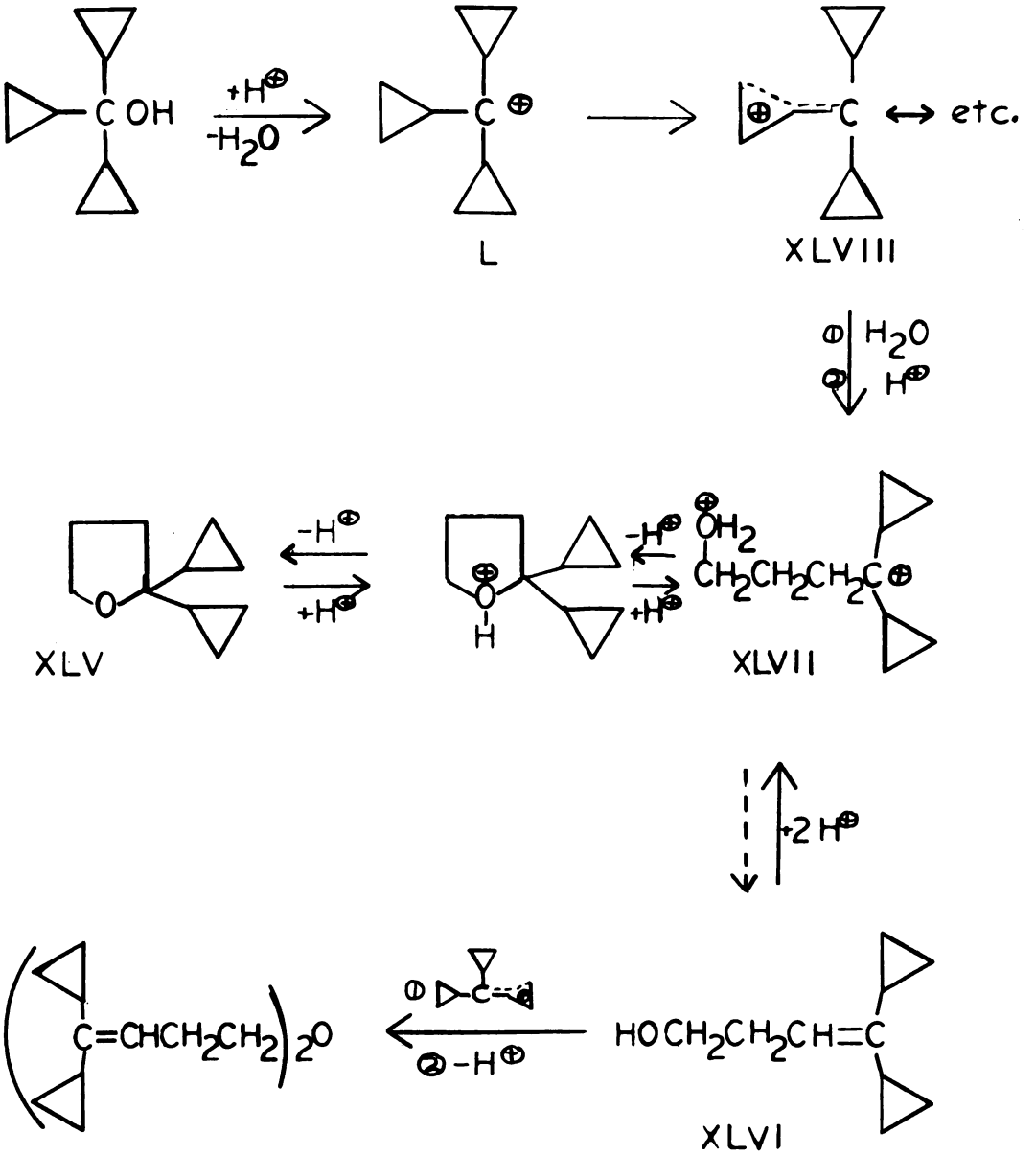


Figure 35. Scheme for the Acid Catalyzed Rearrangement of Tricyclopropylcarbinol.

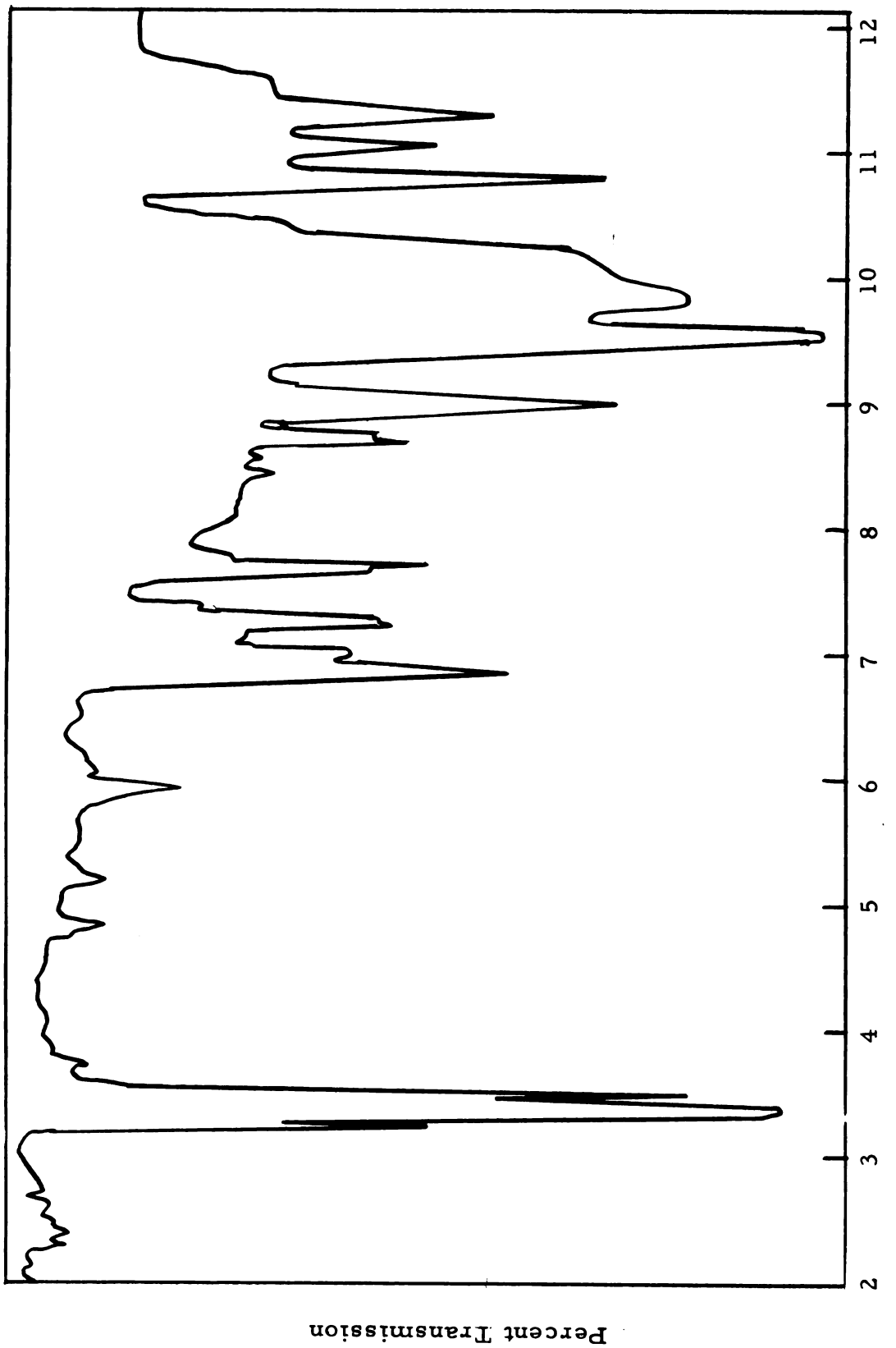


Figure 36. The Infrared Spectrum of 2, 2-Dicyclopropyltetrahydrofuran in Carbon Tetrachloride.

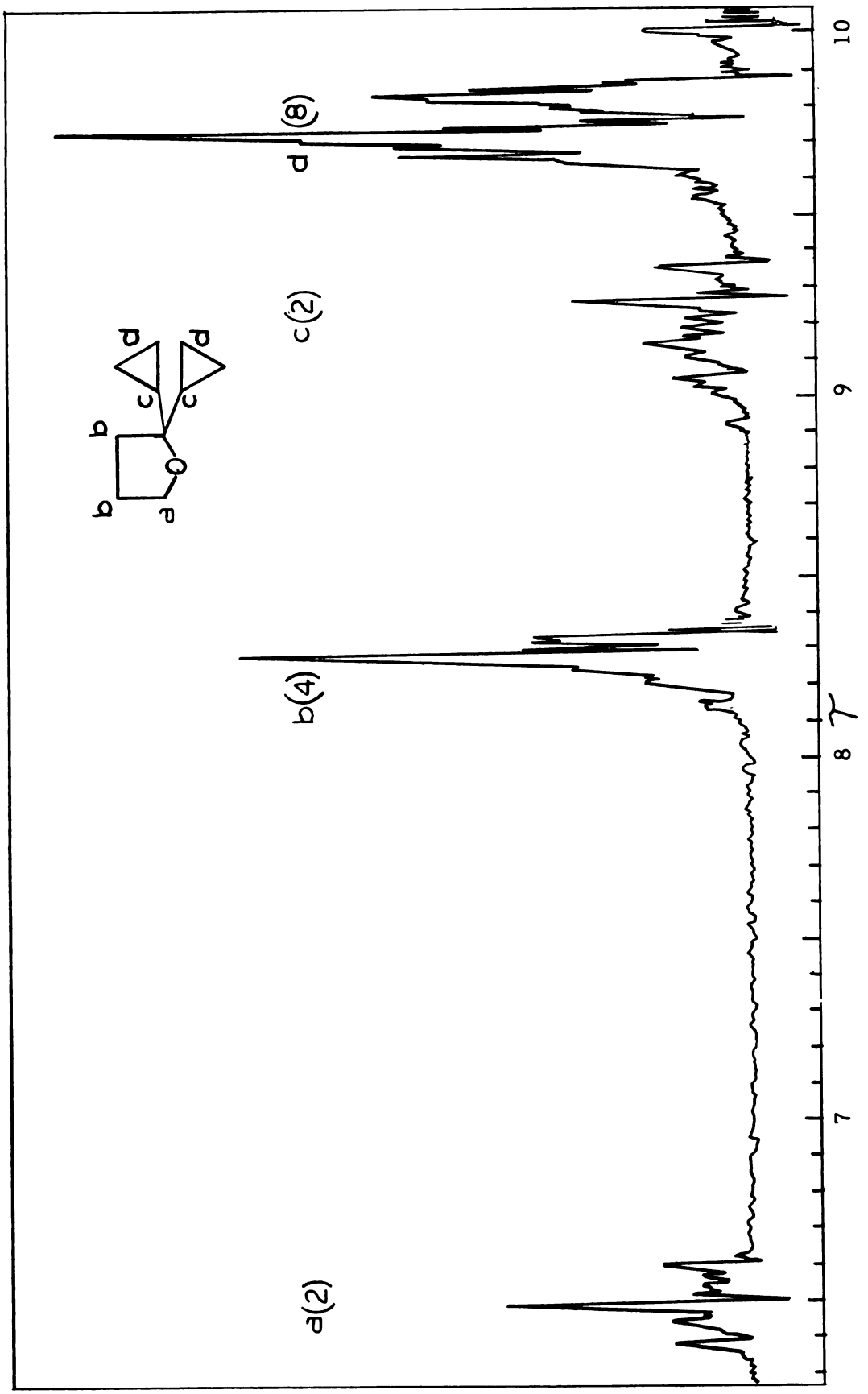


Figure 37. The N.M.R. Spectrum of 2, 2-Dicyclopropyltetrahydrofuran in Carbon Tetrachloride.

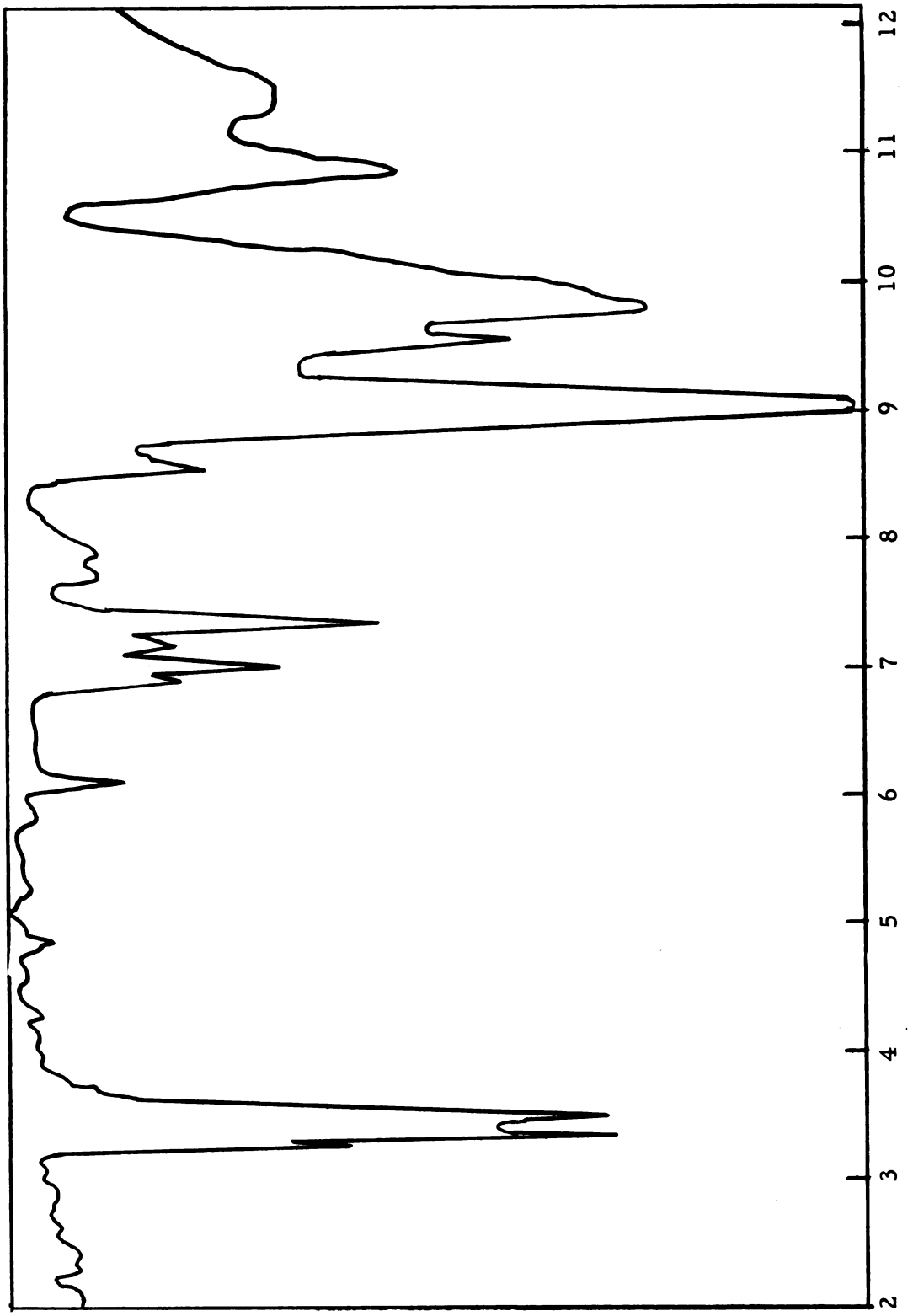


Figure 38. The Infrared Spectrum of bis (4,4-Dicyclopropylbut-3-en-1-yl) ether in Carbon Tetrachloride.

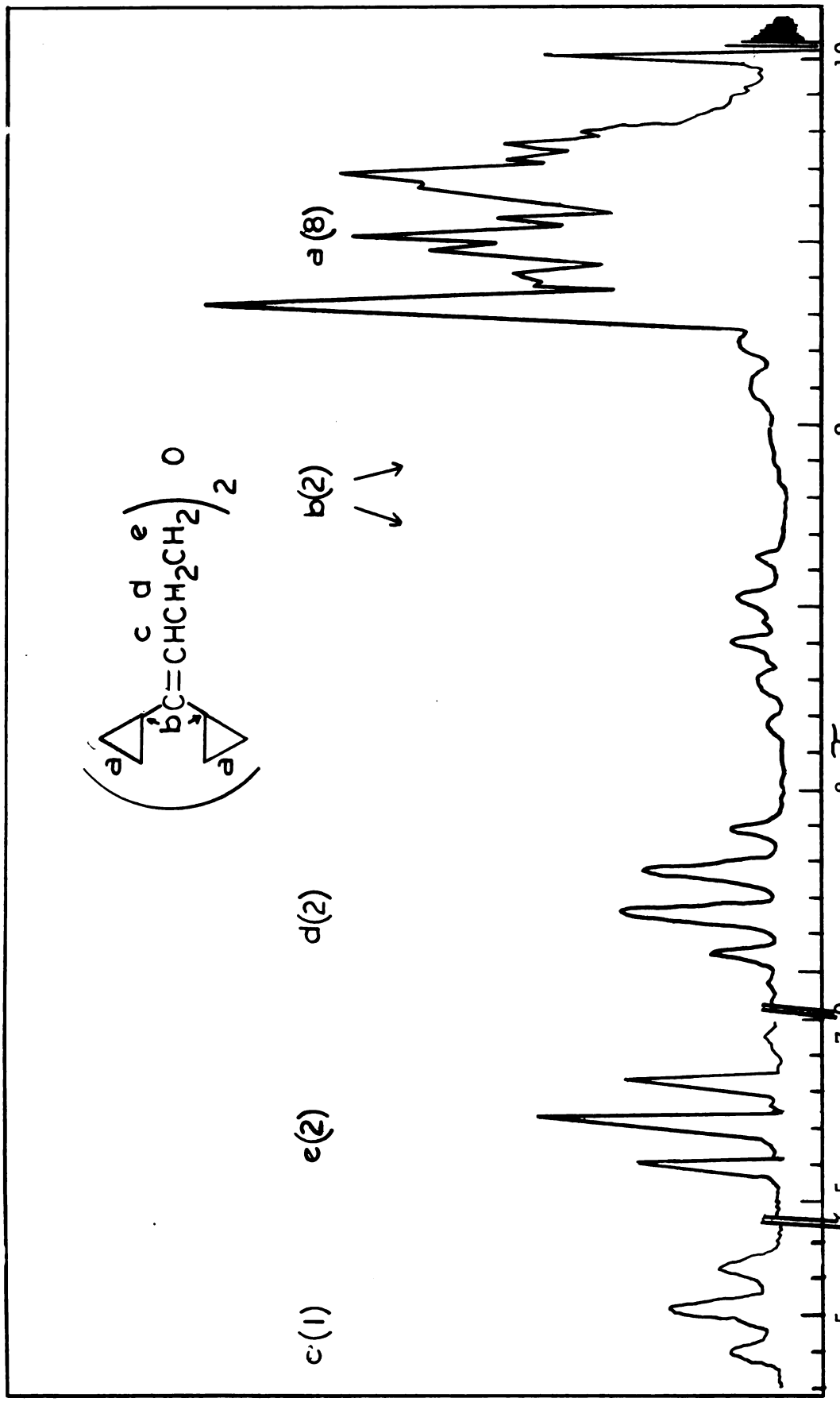


Figure 39. The N.M.R. Spectrum of bis (4,4-Dicyclopropylbut-3-en-1-yl) ether in Carbon Tetrachloride.

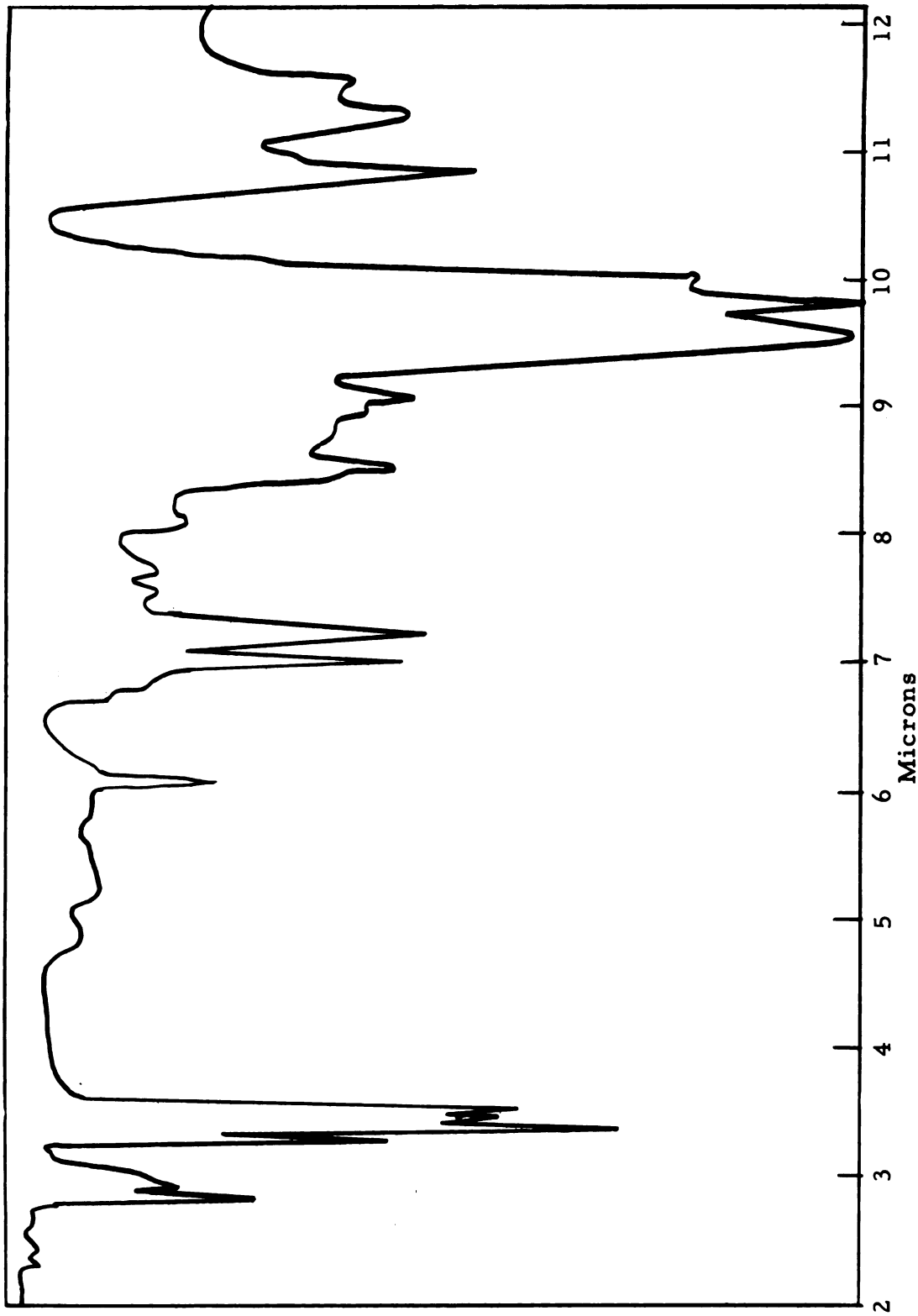


Figure 40. The Infrared Spectrum of 4,4-Dicyclopropylbut-3-en-1-ol in Carbon Tetrachloride.

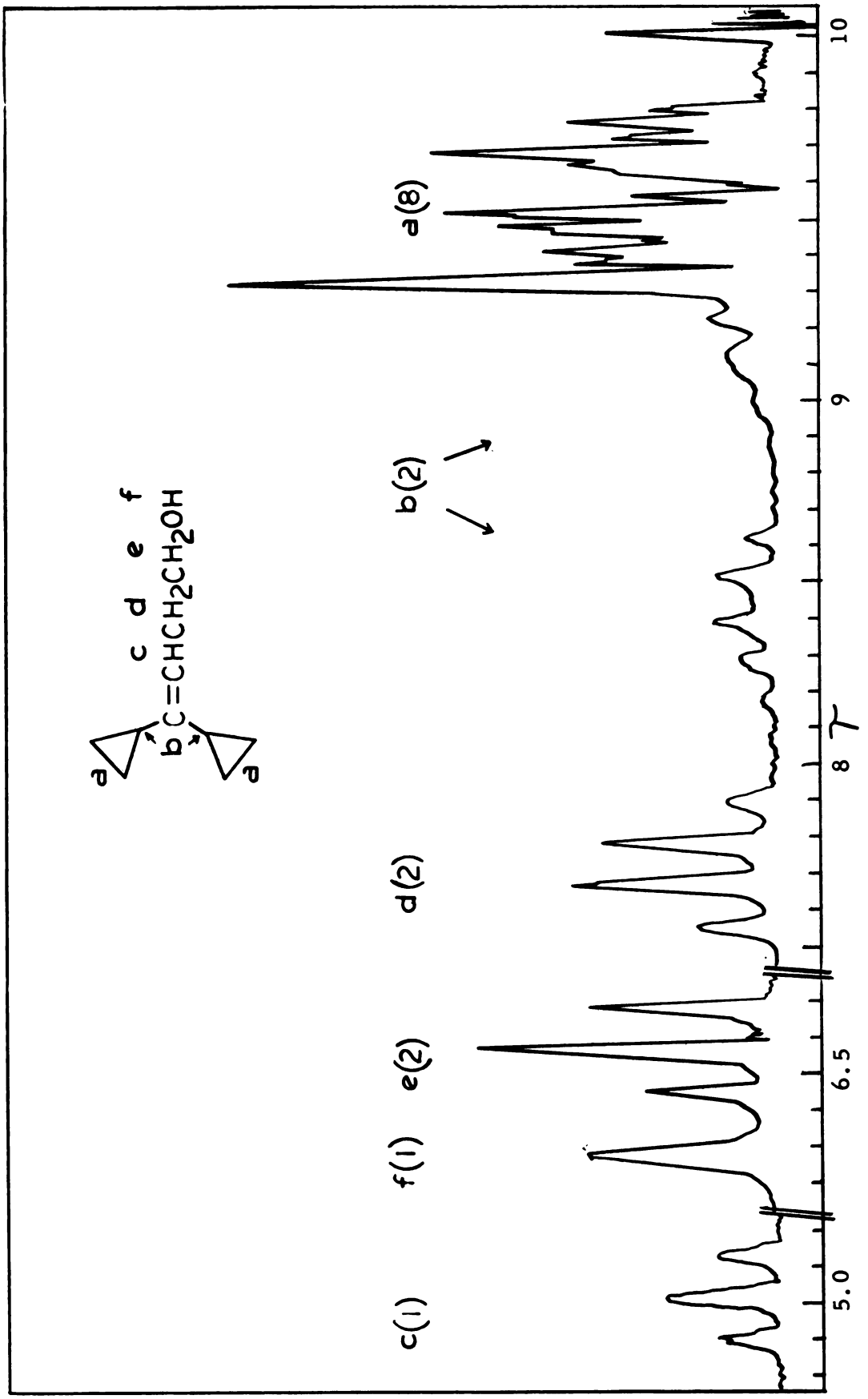
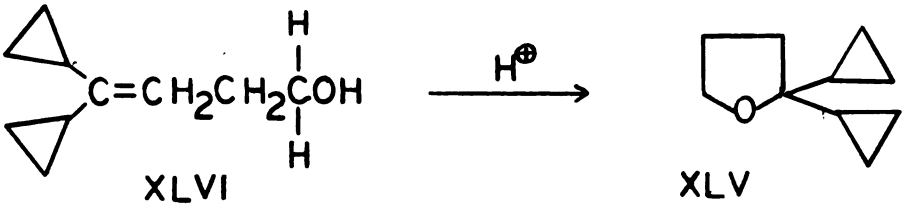


Figure 41. The N.M.R. Spectrum of 4,4-Dicyclopropylbut-3-en-1-ol in Carbon Tetrachloride.

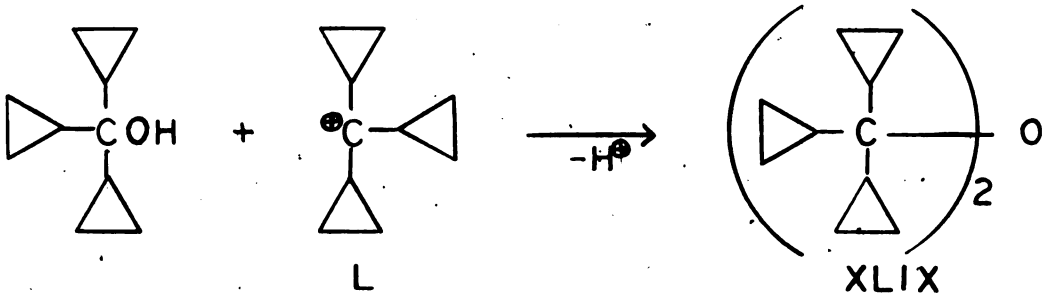


XLVI XLV

This indicated that XLVI may indeed be an intermediate compound. The ease with which 4,4-dicyclopropyl-3-buten-1-ol (XLVI) cyclizes to form the tetrahydrofuran derivative (XLV) is demonstrated by examination of the n.m.r. spectrum of the alcohol, XLVI. After eight hours at room temperature, a carbon tetrachloride solution of XLVI showed evidence of rearrangement. Multiplets at 6.37 and 8.07 τ, corresponding to tetrahydrofuran ring protons, were found indicating the slow formation of 2,2-dicyclopropyltetrahydrofuran.

Figure 35 shows the entire reaction scheme. Spectral evidence for the existence of the ion XLVII has been presented (see page 35). All open chain products may be explained by the attack of water on the methylene carbon of the cyclopropane ring. Reaction of 4,4-dicyclopropylbut-3-en-1-ol (XLVI) with the cation XLVIII leads to formation of the ether.

That the charge of the cation is distributed onto the ring is further indicated by the absence of any of the symmetrical ether (XLIX) which would result from the reaction of tricyclopropylcarbinol with the

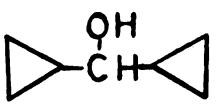


L XLIX

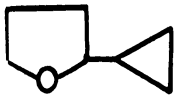
classical tertiary cation L.

B. Dicyclopropylcarbinol

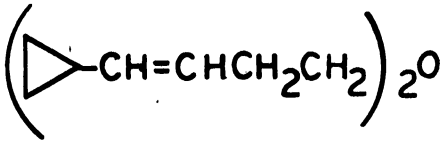
When dicyclopropylcarbinol (LI) was similarly heated with a trace of sulfuric acid, analogous products were obtained. They were 2-cyclopropyltetrahydrofuran (LII) and bis (4-cyclopropylbut-3-en-1-yl)ether (LIII). The structure of 2-cyclopropyltetrahydrofuran was shown by its infrared (Figure 42) and its n.m.r. (Figure 43) spectra. The infrared (Figure 44) spectrum of bis(4-cyclopropylbut-3-en-1-yl) ether showed olefin at 6.1 μ and ether (C-O band) at 9.5 μ. The n.m.r. spectrum (Figure 45) was consistent with the assigned structure. Satisfactory elemental analyses were obtained for these compounds.



LI



LII



LIII

The reaction scheme (Figure 46) is similar to that of tricyclopropylcarbinol and the products are similarly explained.

C. Diphenylcyclopropylcarbinol

Diphenylcyclopropylcarbinol, treated with sulfuric acid, as in the previous examples, results in only one isolable product, i.e., a 73% yield of bis (4,4-diphenylbut-3-en-1-yl) ether (LIV).

The infrared spectrum (Figure 47) showed olefin at 6.1 μ and ether (C-O band) at 9.5 μ. The n.m.r. spectrum (Figure 48) was consistent with the assigned structure.

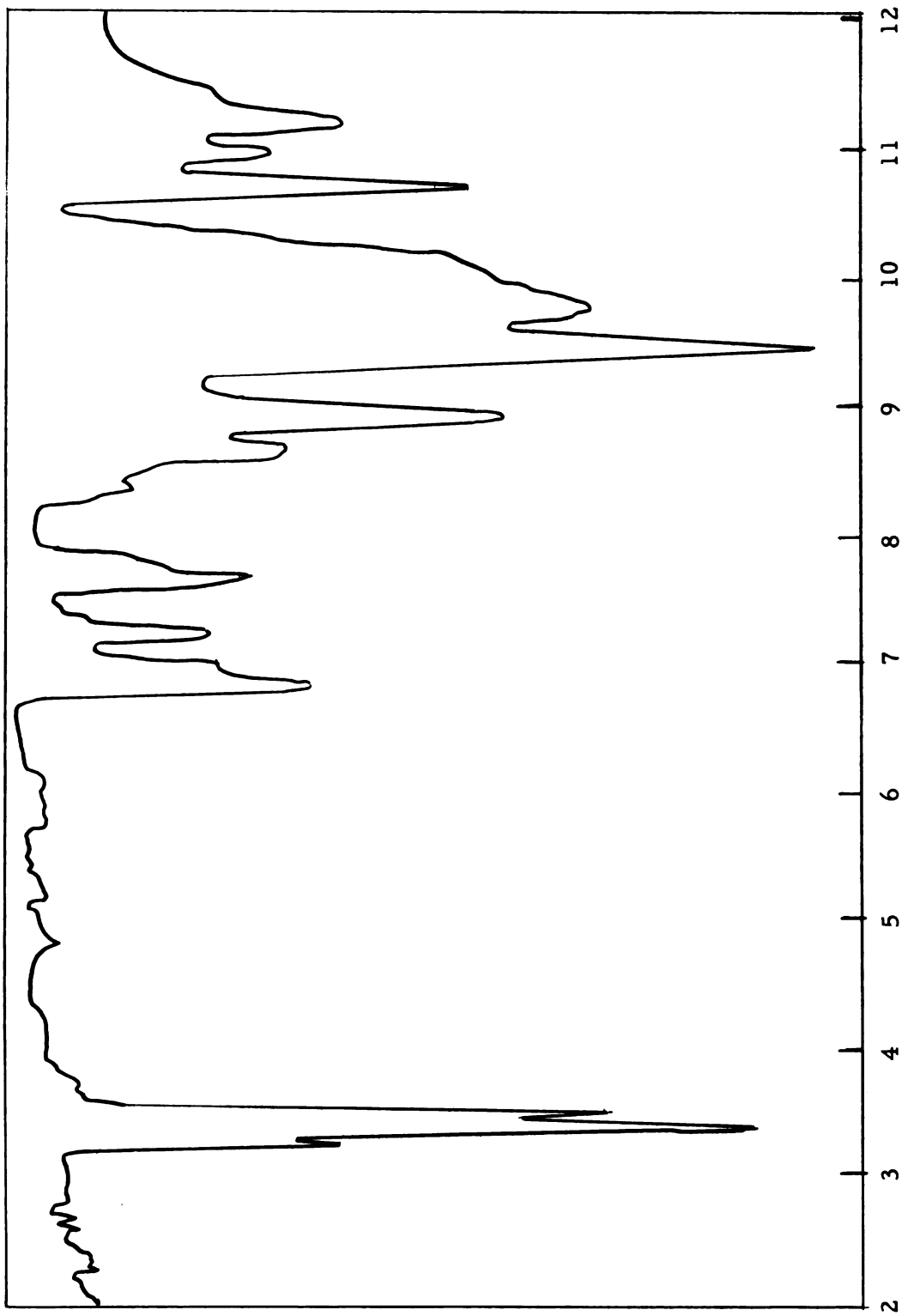


Figure 42. The Infrared Spectrum of 2-Cyclopropyltetrahydrofuran in Carbon Tetrachloride.

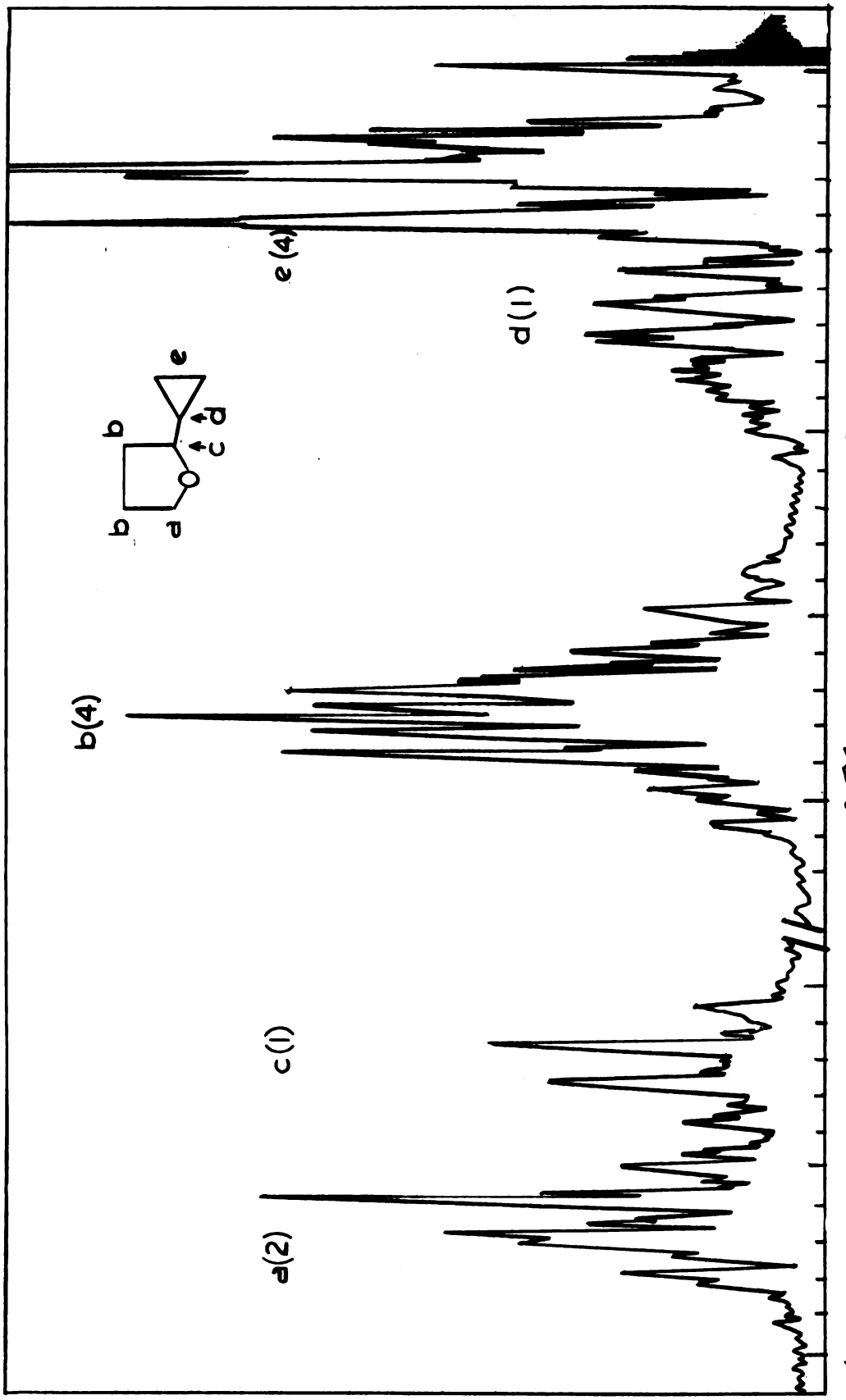


Figure 43. The N.M.R. Spectrum of 2-Cyclopropyltetrahydrofuran in Carbon Tetrachloride.

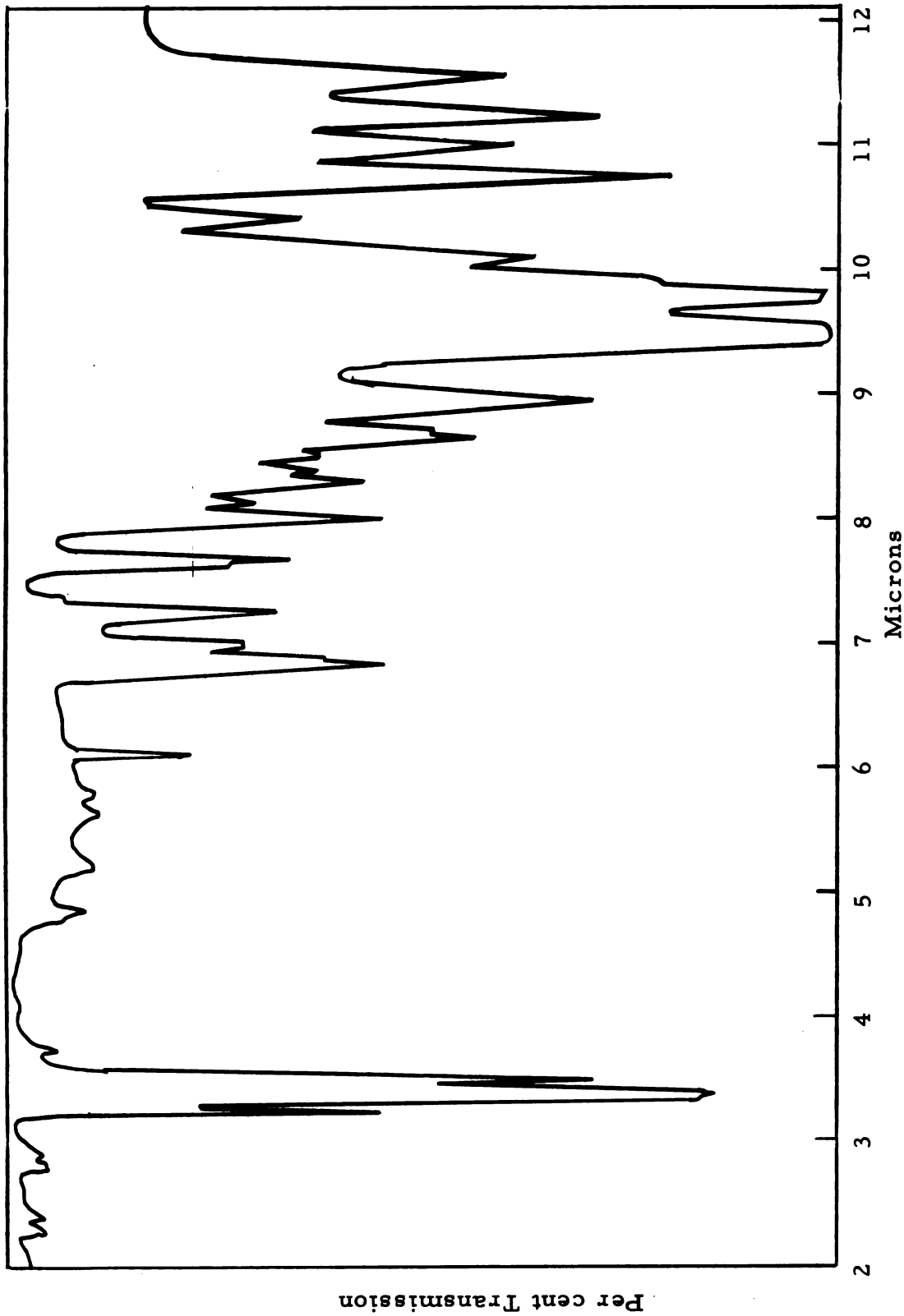


Figure 44. The Infrared Spectrum of bis (4-Cyclopropylbut-3-en-1-yl) ether in Carbon Tetrachloride.

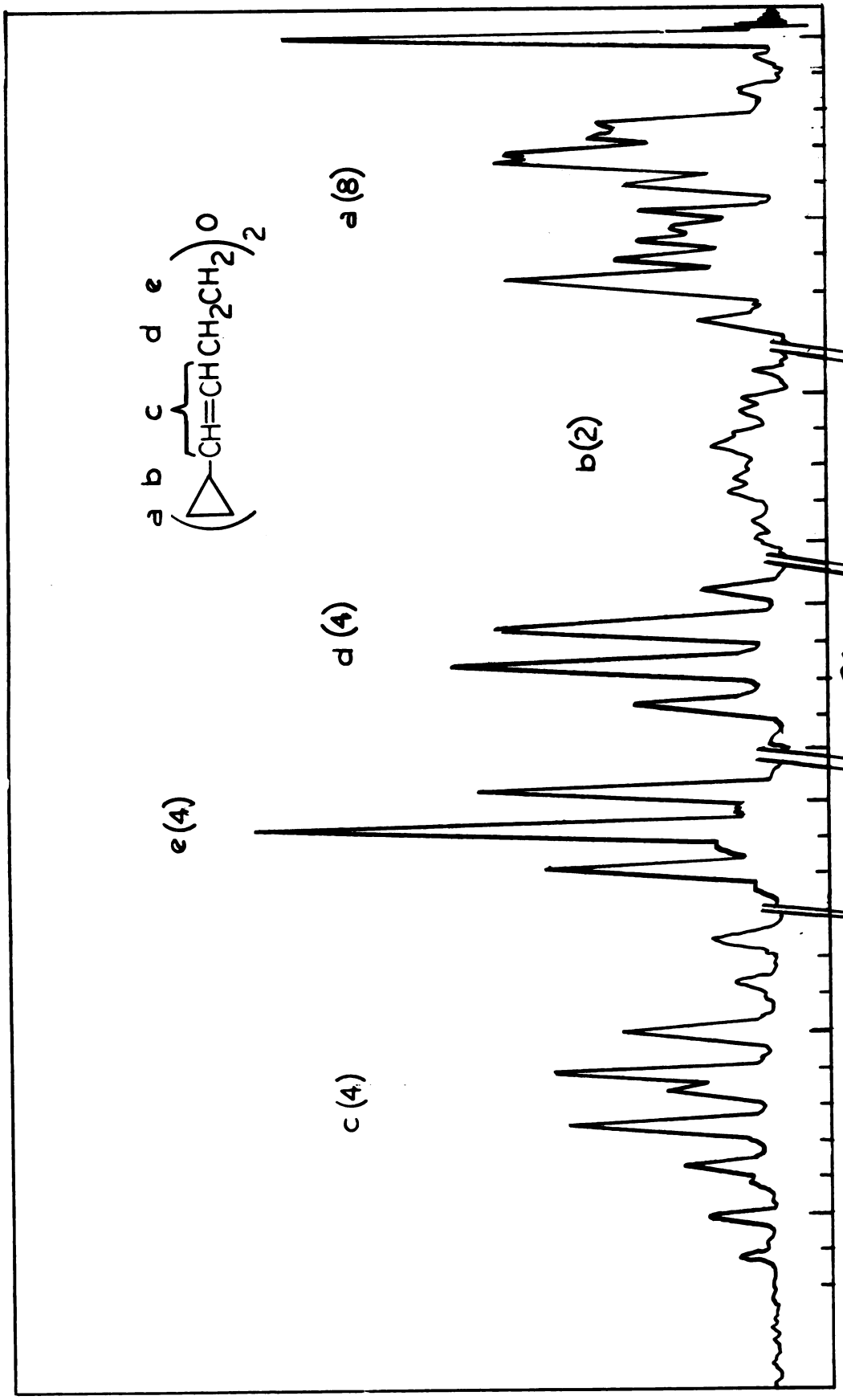


Figure 45. The N.M.R. Spectrum of bis (4-Cyclopropylbut-3-en-1-yl) ether in Carbon Tetrachloride.

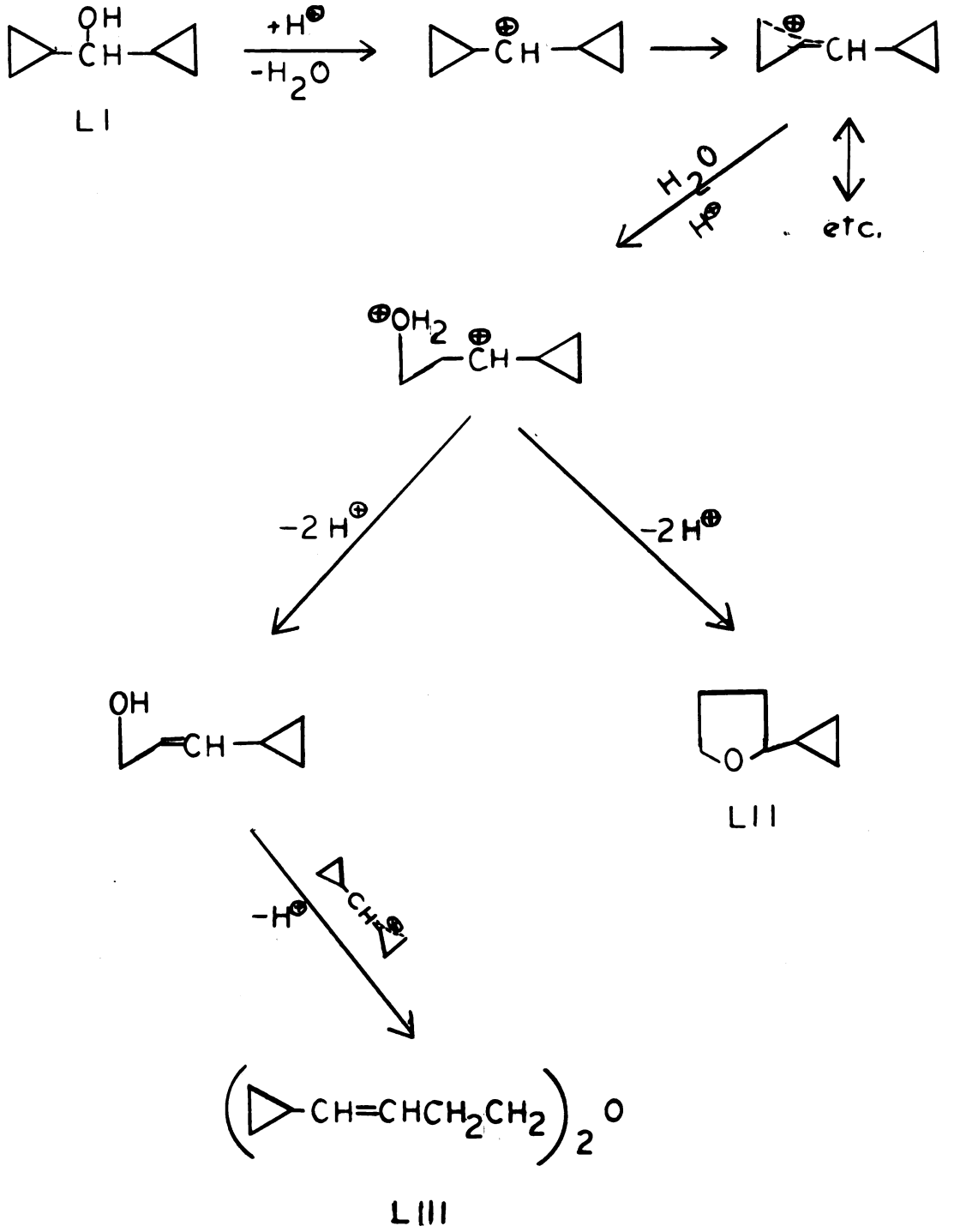


Figure 46. The Scheme for the Acid Catalyzed Rearrangement of Dicyclopropylcarbinol.

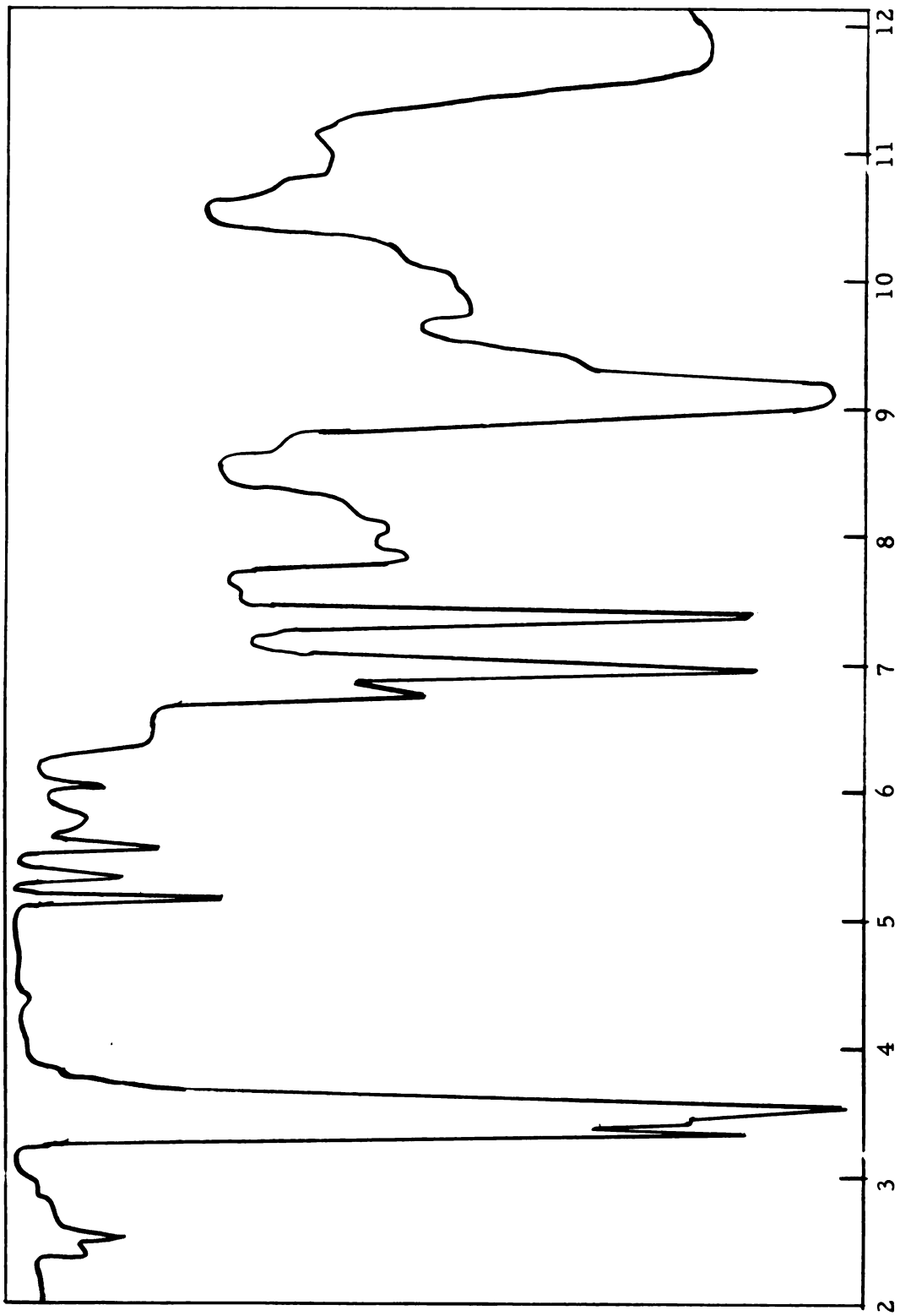


Figure 47. The Infrared Spectrum of bis (4, 4-Diphenylbut-3-en-1-yl) ether in Carbon Tetrachloride.

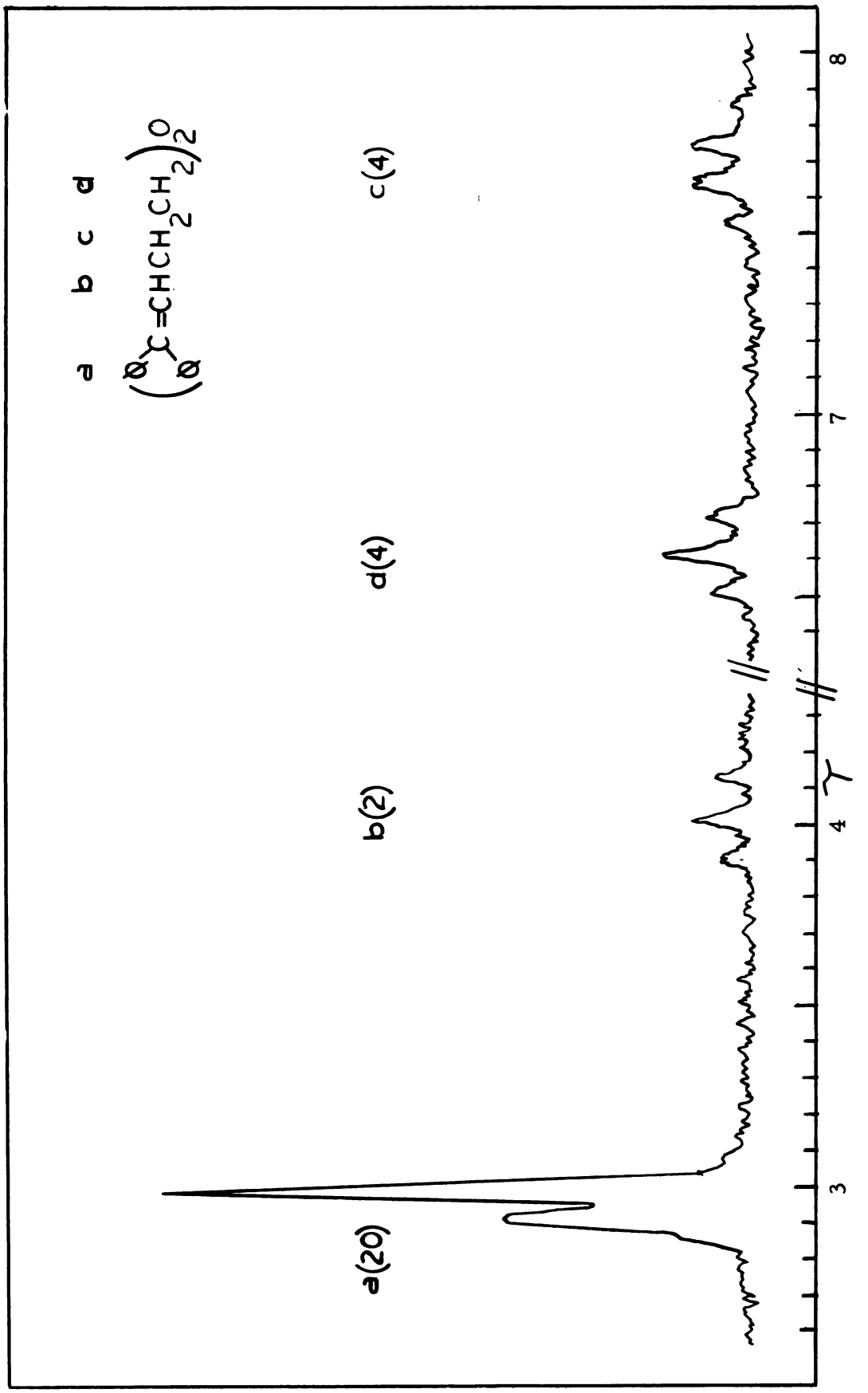
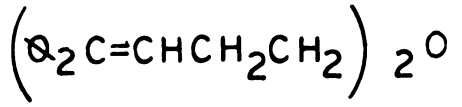
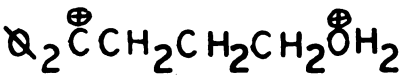


Figure 48. The N.M.R. Spectrum of bis (4, 4-Diphenylbut-3-en-1-yl) ether in Carbon Tetrachloride.



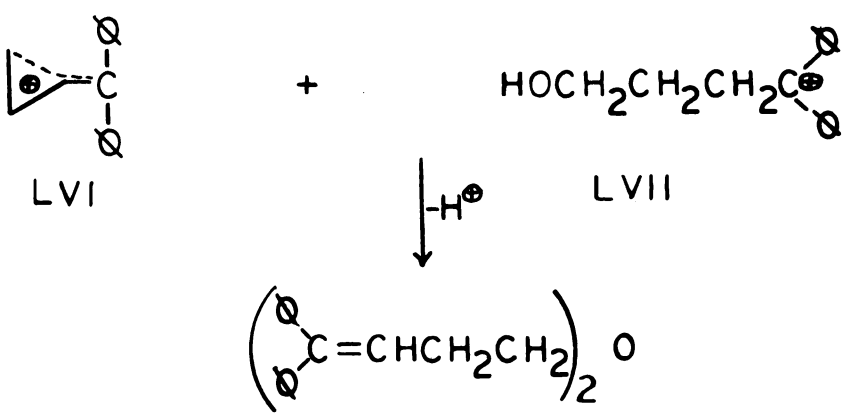
LIV

In this case, the stability of the intermediate ion LV must preclude



LV

cyclization to 2, 2-diphenyltetrahydrofuran. This tetrahydrofuran derivative was synthesized by the reaction of phenylmagnesium bromide and γ-butyrolactone (41). However, even with an authentic sample as a guide, none could be found in the reaction mixture. The preferred reaction is apparently that of LVII with the homoallylic ion LVI to form the ether (LIV).



LVI LVII LIV

Thus in both aliphatic cases rearrangement produces the same types of products as found with 2-cyclopropyl-2-propanol. The extra stabilization caused by more than one cyclopropane ring is of little importance in determining the products. However, in the aromatic system, diphenylcyclopropylcarbinol, the stability of the alkyldiphenylmethyl cation (LV) is the controlling factor in product formation.

EXPERIMENTAL

Attempted Synthesis of Tricycloproylcarbinyl Acetate

A. Using Ketene (Acid Catalyzed)

Using a method similar to that of Hurd (26), ketene (34) was bubbled through a solution of 7.6 g. (0.05 mole) of tricyclopropylcarbinol and one drop of sulfuric acid for two hours. A temperature rise of only 5° was noted. (In a pilot experiment, using t-butyl alcohol and sulfuric acid, a temperature rise of 26° was noted after 30 minutes.) An infrared spectrum of the crude reaction mixture showed a large amount of alcohol (2.8 μ) plus ketene (4.67, 5.85 μ).

In another experiment a few crystals of p-toluene sulfonic acid were used as catalyst. After one hour of ketene addition the temperature had risen only 2°. An infrared spectrum of the crude products showed starting alcohol (2.8 μ) plus ketene (4.67, 5.85 μ).

B. Using Ketene and Borontrifluoride-etherate

Ketene was bubbled into an ether solution of 0.055 mole of borontrifluoride-etherate for 15 min. after which 1 g.(0.0066 mole) of tricyclopropylcarbinol was added. The solution turned dark red. Attempts to identify or isolate products of this reaction were unsuccessful.

In another experiment 1.52 g. (0.01 mole) of tricyclopropylcarbinol was dissolved in 20 ml. of dry ether and ketene bubbled through this solution for 15 min. A one degree temperature rise was noted. To this solution 0.25 mole of borontrifluoride-etherate was added dropwise. There was no temperature rise but the solution did become cloudy and on further addition of ketene (1 1/2 hour) became deep red in color. All attempts to isolate or identify products of this reaction were fruitless.

C. Using Acetyl Chloride and Lithium Tricyclopropylmethoxide

The lithium salt of tricyclopropylcarbinol was prepared from the interrupted synthesis of tricyclopropylcarbinol from 24.0 g. (0.305 mole) of

cyclopropyllithium (40) and 35.2 g. (0.32 mole) of dicyclopropyl ketone (12, 33).

Acetyl chloride (20.2 g., 0.256 mole) in 50 ml. of ether was added to the salt in 50 ml. of ether at 0°. A brown precipitate formed and was removed by filtration under a stream of dry nitrogen. The ether was removed in vacuo yielding a dark brown liquid.

This residue was distilled at 0.5 mm. through a 12 x 1/2 in. column packed with 1/4 in. glass helices. Five fractions were taken. The first was 6.57 g. boiling at less than 27°. Its infrared spectrum indicated that it was a mixture of acetic anhydride, acetic acid and dicyclopropyl ketone. The second, 0.85 g. (0.008 mole), b.p. 40-48°, was shown by its infrared spectrum to be dicyclopropyl ketone. The third, 19.5 g. (0.128 mole), b.p. 48°, had an infrared spectrum identical with that of tricyclopropylcarbinol (Figure 15). The fourth, 1.1 g. (0.006 mole) b.p. 53-61°, had an infrared spectrum identical with that of 1, 1-dicyclopropyl-4-chloro-1-butene (12). The fifth, 3.1 g., b.p. 61-71°, was a mixture of 1, 1-dicyclopropyl-4-chloro-1-butene and a small amount of 4, 4-dicyclopropylbut-3-en-1-yl acetate shown by comparison of its infrared spectrum and gas chromatogram with those of authentic samples.

D. Using Acetyl Chloride and Potassium Tricyclopropylmethoxide

The potassium salt of tricyclopropylcarbinol was prepared in pentane (25 ml.) by the reaction of 3.36 g. (0.086 g. atom) of clean potassium and 13.0 g. (0.086 mole) of tricyclopropylcarbinol. The resulting solution was yellow. Redistilled acetyl chloride (6.57 g., 0.084 mole) dissolved in 30 ml. of pentane was added dropwise, with stirring and cooling by a Dry Ice-alcohol bath, over a half hour period. A brown precipitate formed and was removed by filtration under a nitrogen atmosphere. The infrared spectrum of this crude product showed hydroxyl (2.76 μ), ester carbonyl (5.82 μ) and olefin (6.09 μ). Distillation at 0.2

mm. yielded three fractions. The first, 0.9 g., boiling below 30°, was shown by its infrared spectrum to be a mixture of acetic acid and acetyl chloride. The second, 9.3 g. (0.061 mole), 71.0%, b.p. 41°, was shown by its infrared spectrum to be tricyclopropylcarbinol (Figure 15). The third, 0.8 g. (0.004 mole), 4.6%, had an infrared spectrum identical with that of 4,4-dicyclopropylbut-3-en-1-yl acetate (Figure 2).

Attempted Preparation of Tricyclopropylcarbinyl p-Nitrobenzoate

To the potassium salt of tricyclopropylcarbinol, prepared from 10 g. (0.066 mole) of tricyclopropylcarbinol and 2.57 g. (0.066 g. atom) of potassium in 25 ml. of pentane, was added 12.2 g. (0.066 mole) of p-nitrobenzoyl chloride dissolved in 25 ml. of ether (not soluble in pentane). The reaction mixture turned purple. After stirring overnight, a dark brown precipitate was filtered and the solvent removed by distillation.

An infrared spectrum of the crude residue showed hydroxyl at 2.30 μ, cyclopropyl at 3.26 μ, but no carbonyl and no nitro bands at 6.5 and 7.35 μ.

Isolation of Potassium Tricyclopropylmethoxide

Ten grams (0.066 mole) of tricyclopropylcarbinol was allowed to react with 2.57 g. (0.066 g. atom) of clean potassium metal in 50 ml. of anhydrous pentane. After the reaction was complete, the pentane was removed from the yellow solution. Distillation, using a 6 x 1/2" vacuum jacketed Vigreux column and distillation head, at 0.8 mm. yielded 0.5 g. of alcohol (the infrared spectrum of which was identical with that of the starting material) at which point the contents of the distillation flask solidified.

Water (30 ml.) was added and the solid slowly hydrolyzed giving an oily organic layer. Twenty ml. of ether was added and after shaking, the layers were separated. The ether was removed from the organic layer

yielding 9.0 g. (90%) of tricyclopropylcarbinol, the infrared spectrum of which was identical with that of the starting material (Figure 15).

Synthesis of Tricyclopropylcarbinyl Benzoate

In a 250 ml. flask dried at 110° and fitted with a reflux condenser, dropping funnel and drying tubes, was placed 50 ml. of anhydrous pentane, 2.57 g. (0.066 g. atom) of clean potassium and 10.0 g. (0.066 mole) of tricyclopropylcarbinol. After stirring with a magnetic stirrer for four hours at room temperature only a minute trace of potassium remained.

To the clear light yellow solution, redistilled benzoyl chloride 8.4 g., (0.060 mole) in 50 ml. of pentane was added dropwise over a one hour period. A vigorous reaction occurred and the flask was cooled in an ice bath. A light yellow precipitate of potassium chloride formed during the addition. This precipitate was removed by filtration, in a nitrogen atmosphere, through a dry Buchner funnel. The pentane was removed by cautious evaporation under reduced pressure.

After solvent removal, the sample container was swept with nitrogen, placed in a desiccator and stored at -10°.

The n.m.r. spectrum, Figure 5, showed only aromatic and cyclopropyl protons.

A saponification equivalent showed 98.6% ester.

The infrared spectrum, Figure 4, showed no hydroxyl at 2.75 μ, no olefin at 6.05 μ but did show ester carbonyl at 5.86 μ.

Isolation of 4,4-Dicyclopropylbut-3-en-1-yl Benzoate

Five grams of impure tricyclopropylcarbinyl benzoate were heated at 120° for one hour and the reaction product distilled through a 20 x 1/4" vacuum jacketed tantalum spiral column. Two grams of distillate boiling at 115-120° at 0.04 mm. were collected. The infrared spectrum of this

material showed contamination by benzoic anhydride. The anhydride was removed by chromatography using Florosil (activated at 200° for 18 hours) and anhydrous pentane as the solvent.

After removal of the solvent from the collected eluents, 1.5 g. (75%) of a compound, shown to be 4,4-dicyclopropylbut-3-en-1-yl benzoate by its infrared (Figure 6) and n.m.r. (Figure 7) spectra, was obtained. Anal. Calcd. for $C_{17}H_{20}O_2$: C, 79.69; H, 7.86. Found: C, 79.44; H. 7.68.

Preparation of Dicyclopropylisopropylcarbinol (12)

2-Bromopropane (49.2 g., 0.4 mole) dissolved in 100 ml. of anhydrous ether was added to magnesium (9.71 g., 0.4 g. atom) in 50 ml. of ether at a rate to cause reflux. After the addition was complete, the reaction mixture was heated at reflux temperature for 30 minutes and then cooled to room temperature. Dicyclopropyl ketone (33.0 g., 0.3 mole) in 100 ml. of ether was added at a rate to cause reflux of the solvent. The reaction mixture was heated at reflux for an additional four hours, cooled and the complex decomposed by the addition of aqueous ammonium chloride solution. The organic layer was separated and the water layer washed with two 50-ml. portions of ether. The combined ether layers were dried over magnesium sulfate, filtered and the ether removed by distillation. The crude product was distilled at reduced pressure yielding 31.0 g., 67%, of dicyclopropylisopropylcarbinol, the infrared spectrum of which was identical with that of an authentic sample. The n.m.r. spectrum is shown in Figure 49.

Preparation of Dicyclopropylisopropylcarbinyl Benzoate

Dicyclopropylisopropylcarbinol (5.0 g., 0.0325 mole) and clean potassium (1.28 g., 0.0325 g. atom) were allowed to react at room temperature in 40 ml. of anhydrous pentane. After four hours only

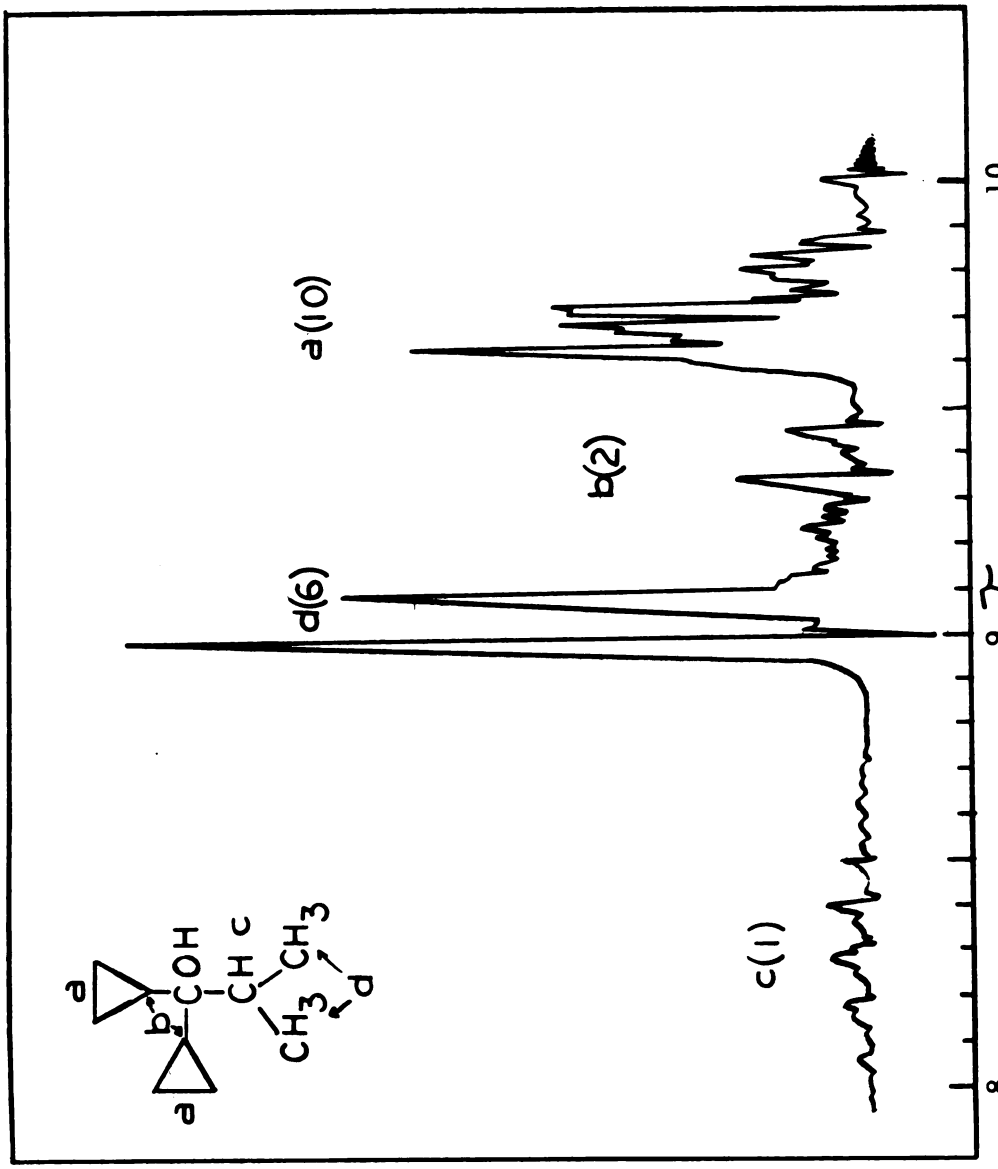


Figure 49. The N.M.R. Spectrum of Dicyclopropylisopropylcarbinol in Carbon Tetrachloride.

trace potassium remained. Freshly redistilled benzoyl chloride (4.56 g., 0.0325 mole) in 40 ml. of pentane was added dropwise over a one hour period. The reaction mixture was then filtered to remove potassium chloride and the solvent was removed in vacuo. An infrared spectrum of the crude product showed that benzoyl chloride remained as an impurity. This was removed by repeated stirring with one gram portions of activated alumina in ligroin (b.p. 60-90°).

The ligroin was removed in vacuo. The infrared spectrum (Figure 50) showed contamination by alcohol. The n.m.r. spectrum (Figure 51) did not integrate satisfactorily for the desired structure, showing an excess of cyclopropyl and methyl protons in accord with the fact that alcohol was present in the infrared spectrum.

A saponification equivalent showed the presence of 86.72% ester.

Attempts to purify the sample by chromatography using activated alumina or Florosil resulted in extensive rearrangement to an unsaturated ester, presumably 5-methyl-4-cyclopropylbut-3-en-1-yl benzoate. Charcoal, while not causing rearrangement, did not effect purification.

Preparation of Vinyldicyclopropylcarbinol

Vinyldicyclopropylcarbinol was prepared by the reaction of vinylmagnesium chloride (35) with dicyclopropyl ketone (33) by Dr. R. A. Cipriani.

Preparation of Vinyldicyclopropylcarbinyl Benzoate

Five grams (0.0362 mole) of vinyldicyclopropylcarbinol was dissolved in 40 ml. of pentane (which had been distilled from sodium metal) and placed in a dry 100-ml. flask equipped with reflux condenser, dropping funnel and magnetic stirrer. To this was added 1.41 g. (0.0362 g. at.) of clean potassium. The reaction was vigorous, at first causing the solvent to reflux. The potassium was allowed to react at room

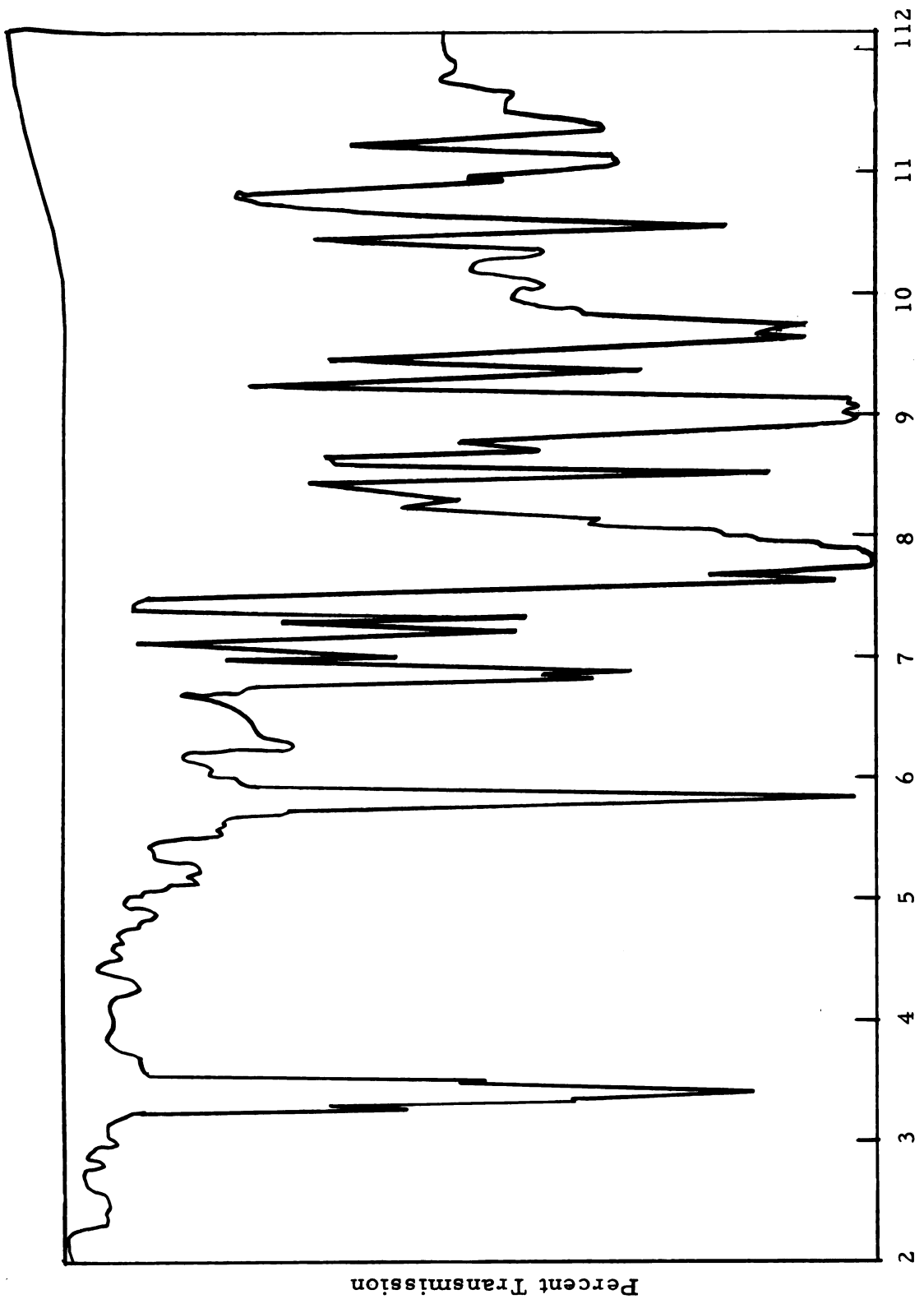


Figure 50. The Infrared Spectrum of Dicyclopropylisopropylcarbinyl Benzoate in Carbon Tetrachloride.

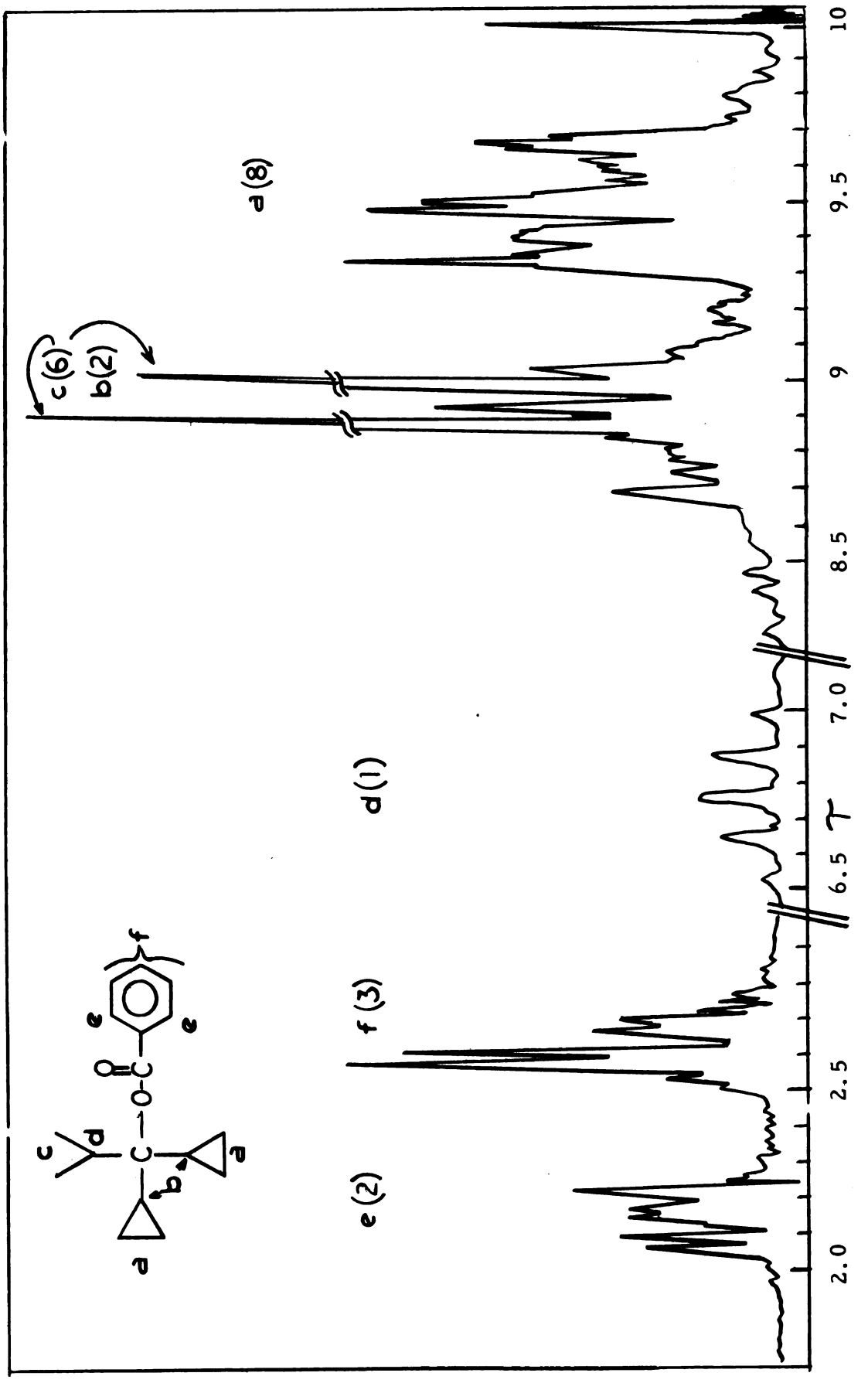


Figure 51. The N.M.R. Spectrum of Dicyclopropylisopropylcarbinyl Benzoate in Carbon Tetrachloride.

temperature for four hours at which time only traces of potassium remained. To the cloudy, light yellow solution, cooled in an ice bath, was added 5.09 g. (0.0362 mole) of freshly distilled benzoyl chloride dissolved in 50 ml. of pentane. The dropwise addition was complete at the end of 20 min. After stirring 1 hour at room temperature the precipitate, potassium chloride, was removed by filtration in a nitrogen atmosphere. After removal of the solvent in vacuo, the infrared spectrum of the yellow residue showed the presence of benzoic anhydride as impurity. This was removed by dissolving the sample in pentane and stirring with two 3-g. portions of activated alumina for one half hour each. Following filtration and solvent removal, a clear yellow liquid remained. A saponification equivalent showed the presence of 90% ester. The infrared spectrum (Figure 8) and n.m.r. spectrum (Figure 9) were consistent with the assigned structure.

Thermal Rearrangement of Vinyldicyclopropylcarbinyl Benzoate

Vinyldicyclopropylcarbinyl benzoate (3.0 grams, 0.13 mole) was heated 6.5 hrs. at 100°. The resulting liquid was distilled, b.p. 100-5° at 0.08 mm.

The n.m.r. and infrared spectra (Figures 10 and 11) and elemental analysis identified this compound as 3, 3-dicyclopropylprop-2-en-1-yl benzoate. Anal. Calcd. for $C_{16}H_{18}O_2$: C. 79.33, H, 7.81. Found: C, 77.16 ; H, 7.16 .

Solvolysis Studies

A. Solvents

The dioxane used was purified by Fieser's procedure (36).

Carbon dioxide-free distilled water was prepared by boiling distilled water for 15 minutes. After cooling, this was was employed for making up solvent mixtures and reagents.

The methanol was purified by distillation over magnesium methoxide.

The kinetic studies were carried out in water-dioxane solvents of several weight per cent compositions. Product analyses were carried out in 95% aqueous dioxane and also in pure methanol.

B. Standardization of Reagents

The sodium hydroxide was made up in aqueous dioxane solution of the highest dioxane concentration possible (approximately 70% dioxane). The 0.01 normal base was standardized immediately before each run against Baker and Adams primary standard grade benzoic acid in an aqueous dioxane solution of the same percentage composition as the solvent being used in the particular run. The indicator was phenolphthalein. If the run lasted longer than three hours the base was restandardized.

The titrant was transferred by nitrogen pressure and Ascarite tubes were used in order to prevent contact with carbon dioxide. All titrations were made in a nitrogen atmosphere.

C. Kinetic Procedure

Approximately 0.01 molar solutions of ester were employed and the reaction was followed by titrating the liberated benzoic acid with standard sodium hydroxide. The reactions were conducted in a constant temperature bath maintained at $\pm 0.1^{\circ}$ of the desired temperature. When a temperature greatly below room temperature (7.9°) was desired, a heat transfer unit was employed. This system allowed alcohol to be pumped first through a coil immersed in a Dry-Ice bath and then through a coil in the constant temperature bath.

The aqueous dioxane solvent was equilibrated in the constant temperature bath before each run was started. Approximately 0.001 mole of the ester was accurately weighed into a dry 100 ml. volumetric flask. At zero time, 100 ml. of the equilibrated solvent was pipetted into the

flask containing the ester and the solution was thoroughly mixed. The pipettes were preheated for runs at 60°. At various time intervals, a 5-ml. aliquot was removed, quenched by adding to 5 ml. of acetone at -10° and immediately titrated (with cooling in an ice-salt bath) with the standard base using phenolphthalein as the indicator. Usually 10 to 15 points were taken for each run and at least two runs were made for each set of conditions.

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

Solvolysis Product Analysis

A. Solvolysis of Tricyclopropylcarbinyl Benzoate in 100% Methanol at 25°.

Tricyclopropylcarbinyl benzoate (1.1667 g., 0.00457 mole) was dissolved in 100 ml. of anhydrous methanol and kept at 25° for 48 hours. The solvent was removed in vacuo at room temperature. The residue, consisting of a mixture of white needles and liquid, was dissolved in pentane and washed with two 10-ml. portions of 1 N. sodium hydroxide. The organic layer was separated and washed with 10-ml. portions of water until neutral to pH paper. After drying over anhydrous magnesium sulfate and filtering, the pentane was removed by heating with a steam bath. The infrared spectrum of the residue showed strong ether oxygen absorption at 9.2 μ plus a trace of ester carbonyl at 5.8 μ. The n.m.r. spectrum showed methyl ether protons at 6.75 τ and cyclopropyl protons from 8.8 to 10.0 τ in the ratio of 2.9 to 15 respectively (Figure 16).

A very slight amount (much too small for integration) of aromatic and olefinic protons were found which would correspond to the ester carbonyl found in the infrared spectrum and indicated the presence of a trace of 4,4-dicyclopropylbut-3-en-1-yl benzoate (Figure 6).

B. Solvolysis of Tricyclopropylcarbinyl Benzoate in 95% Dioxane -5% Water at 25°

Tricyclopropylcarbinyl benzoate (10 g., 0.066 mole) was dissolved in 300 ml. of 95% dioxane -5% water and kept at 25° for 19 hours. The solvent was removed at 30 mm. by heating with a warm water bath.

An infrared spectrum of the residue showed the presence of broad hydroxyl absorption in the 2.75 μ region characteristic of acids, acid carbonyl at 5.8 μ and no olefin at 6.10 μ. The n.m.r. spectrum of this residue showed no olefin in the vinyl (4.95 τ), allyl (7.47 τ) and ester (-CH_2O_2C-; 5.80 τ) regions thus indicating the absence of the rearranged ester, 4,4-dicyclopropylbut-3-en-1-yl benzoate. The cyclopropyl region (9-10 τ) contained a complex pattern identical with that of tricyclopropylcarbinol. Also present were peaks due to benzoic acid (2.10 and 2.60 τ) and dioxane (6.43 τ).

N.M.R. Spectra in Sulfuric Acid

A 10% solution of carbinol in 96% sulfuric acid was prepared by adding the carbinol dropwise, with stirring, to the acid which was cooled with an ice bath. The resulting solution was yellow and slowly grew darker as resinous polymer formed. If the spectrum was taken immediately after mixing no evidence of polymer was seen in the n.m.r.

Methanesulfonic acid was used as an internal reference. The value of 6.76 τ assigned to the methyl group was measured directly against tetramethylsilane in trifluoroacetic acid as mutual solvent by Dr. C-Y Wu. In this thesis, all τ values measured from methane--sulfonic acid are indicated as τm.

All spectra were taken with the Varian Associates nuclear magnetic resonance spectrometer, model A-60.

Hydrogenolysis of Tricyclopropylcarbinol

Twenty grams (0.133 mole) of tricyclopropylcarbinol and 2.0 grams of copper oxide-copper chromite catalyst (37) were placed in a 100 ml. Magnadash hydrogenation bomb (38). The bomb was sealed, purged and pressured with hydrogen to 1910 p.s.i. and stirring begun. The temperature was gradually raised until a drop in pressure was noted. At this point the pressure was 2230 p.s.i. and the temperature 193°. The rate of heating was reduced and the temperature was maintained at 178-182° and the reaction allowed to continue until the rate of pressure drop, which was almost linear, decreased sharply. The total drop in pressure (at 26°) was 450 p.s.i.

After cooling, venting, rinsing the bomb with ether, drying with magnesium sulfate, filtration and removal of the ether by distillation, there remained 18.0 g. of water white liquid.

Gas chromatography (130°, 72 x $\frac{1}{4}$ in. column packed with 30% silicone gum, SE-30, on chromosorb W) showed the presence of seven peaks (Figure 52). These were separated by repeated injection and collection of the components.

The first peak was 4-propylheptane (1%), identified by its n.m.r. and infrared spectra, Figures 26 and 27.

Anal. Calcd. for $C_{10}H_{22}$: C, 84.51; H, 15.49.

Found: C, 84.38; H, 15.52.

The second component (1%) could not be purified sufficiently to allow identification.

The third was 4-cyclopropylheptane (2%), identified by its n.m.r. and infrared spectra, Figures 24 and 25.

Anal. Calcd. for $C_{10}H_{20}$: C, 85.70; H, 14.30.

Found: C, 85.62; H, 13.90.

The fourth was 1,1-dicyclopropylbutane (18.6%). The infrared (Figure 22) and n.m.r. spectra (Figure 23) were consistent with this structure.

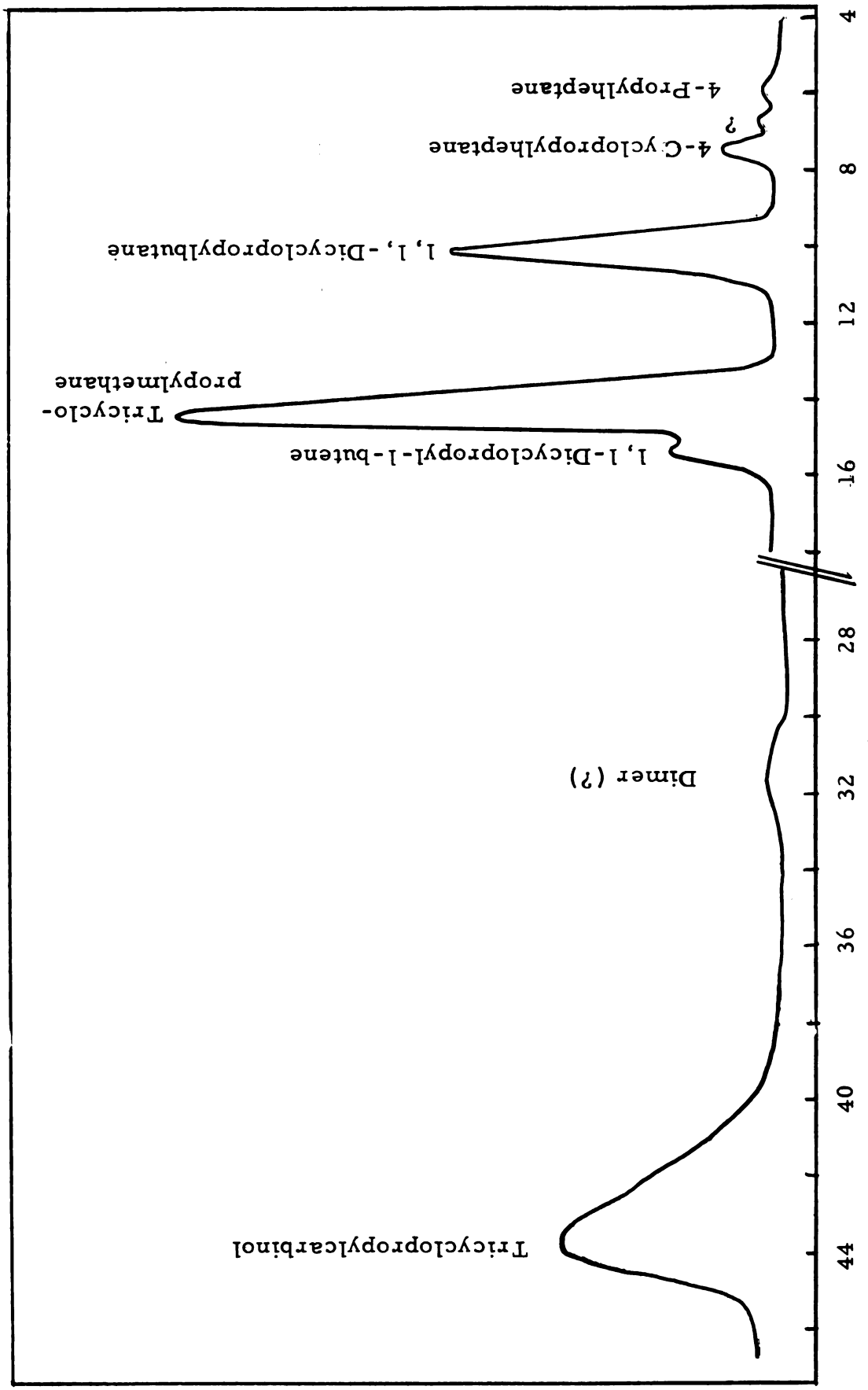


Figure 52. Gas Chromatogram of the Products of Hydrogenolysis of Tricyclopropylcarbinol.

Anal. Calcd. for $C_{10}H_{18}$: C, 87.00; H, 13.00.

Found: C, 86.89; 86.94; H, 13.08; 12.97.

The boiling point was 161° at 732 mm.; $n_D^{24.8}$ 1.4426.

The fifth fraction, amounting to 35.9% of the mixture, was shown to be tricyclopropylmethane. Its infrared and n.m.r. spectra are shown in Figures 18 and 19.

The boiling point was 66° at 28 mm.; n_D^{20} 1.4596.

Anal. Calcd. for $C_{10}H_{16}$: C, 88.24; H, 11.76.

Found: C, 88.53; H, 11.50.

Fraction six, 4.2% was 1,1-dicyclopropyl-1-butene, boiling point 66° at 28 mm.; n_D^{20} 1.4737. Its infrared and n.m.r. spectra, Figures 20 and 21, substantiate the structural assignment.

Anal. Calcd. for $C_{10}H_{16}$: C, 88.24; H, 11.76.

Found: C, 87.57, 87.44; H, 11.99, 11.85.

The last fraction is unreacted tricyclopropylcarbinol (37.7%). Its n.m.r. spectrum is shown in Figure 14.

Hydrogenolysis of Tricyclopropylmethane

Five grams of a mixture consisting of 84.3% tricyclopropylmethane, 14.7% 1,1-dicyclopropyl-1-butene and 1% 1,1-dicyclopropylbutane and 0.5 g. of copper chromite catalyst were placed in a 100 ml. Magnadash hydrogenation bomb and after purging was pressured with hydrogen to 1900 p.s.i. The temperature was raised to, and maintained at 200-210°. The initial pressure at this temperature was 2600 p.s.i. The rate of pressure drop, which was almost constant, was followed and when this rate decreased the bomb was cooled to room temperature. The pressure drop during the reaction was 160 p.s.i. measured at 25°.

Gas chromatographic analysis of the filtered reaction products showed a mixture consisting of 76.0% tricyclopropylmethane, 12.6% 1,1-dicyclopropylbutane, 4.5% 4-cyclopropylheptane and 7.7% of 4-propylheptane. No 1,1-dicyclopropyl-1-butene remained. Quantitative estimation

of the amount of tricyclopropylmethane indicated a decrease of only ca. 2% in its concentration. This is within the range of experimental error and the decrease in relative percentage is apparently due to variations in thermal conductivity (a thermal conductivity detector was used on the gas chromatograph), the absolute amount having remained constant.

Hydrogenolysis of Dicyclopropylcarbinol

Five grams (0.45 mole) of dicyclopropylcarbinol, prepared by the reduction of dicyclopropyl ketone with lithium aluminumhydride (33), and 0.5 g. of copper chromite catalyst were placed in a 100 ml. stainless steel Magnadash hydrogenation bomb. The system was purged with hydrogen and pressured to 1840 p.s.i. The temperature was raised to 167° where the pressure was 2230 p.s.i. The rate of heating was reduced and the temperature was maintained at 140-5°. The rate of pressure drop was almost linear and was followed until a change in the rate was noticed. Stirring was stopped and the bomb allowed to cool to room temperature. The pressure was 1660 p.s.i. After venting, rinsing with ether, filtration and drying over magnesium sulfate, the ether was removed by distillation.

Gas chromatography of the resulting liquid (50° on a 72 x $\frac{1}{4}$ in. column packed with 30% silicone gum, SE-30, on Chromosorb W) showed the presence of nine components in addition to ether (Figure 53). The first was shown, by comparison of its retention time with that of an authentic sample to be n-heptane (2.0%). The second and third components (5.1%) were unresolvable and thus unidentified.

1-Cyclopropylbutane (21.5%) was the fourth peak. It was identified by its infrared and n.m.r. spectra (Figures 29 and 30).

Anal. Calcd. for C_7H_{14}: C, 85.71; H, 14.29.

Found: C, 85.85; H, 13.73.

The fifth (6.1%) was not identified.

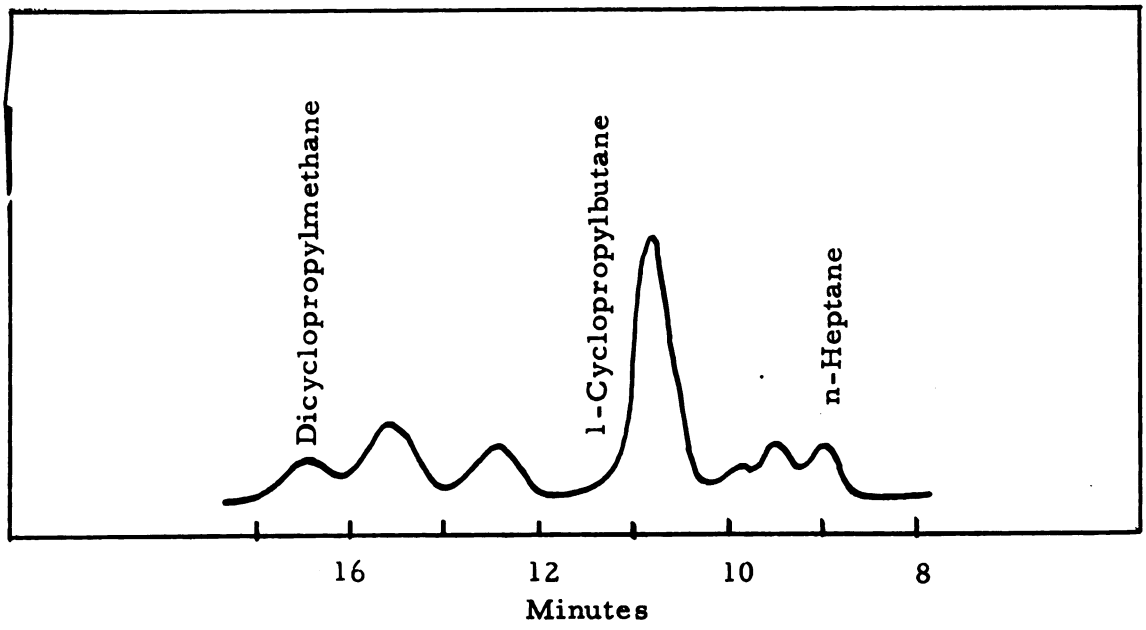


Figure 53a. Gas Chromatogram of the Products of Hydrogenolysis of Dicyclopropylcarbinol. a) Hydrocarbons only (50°)

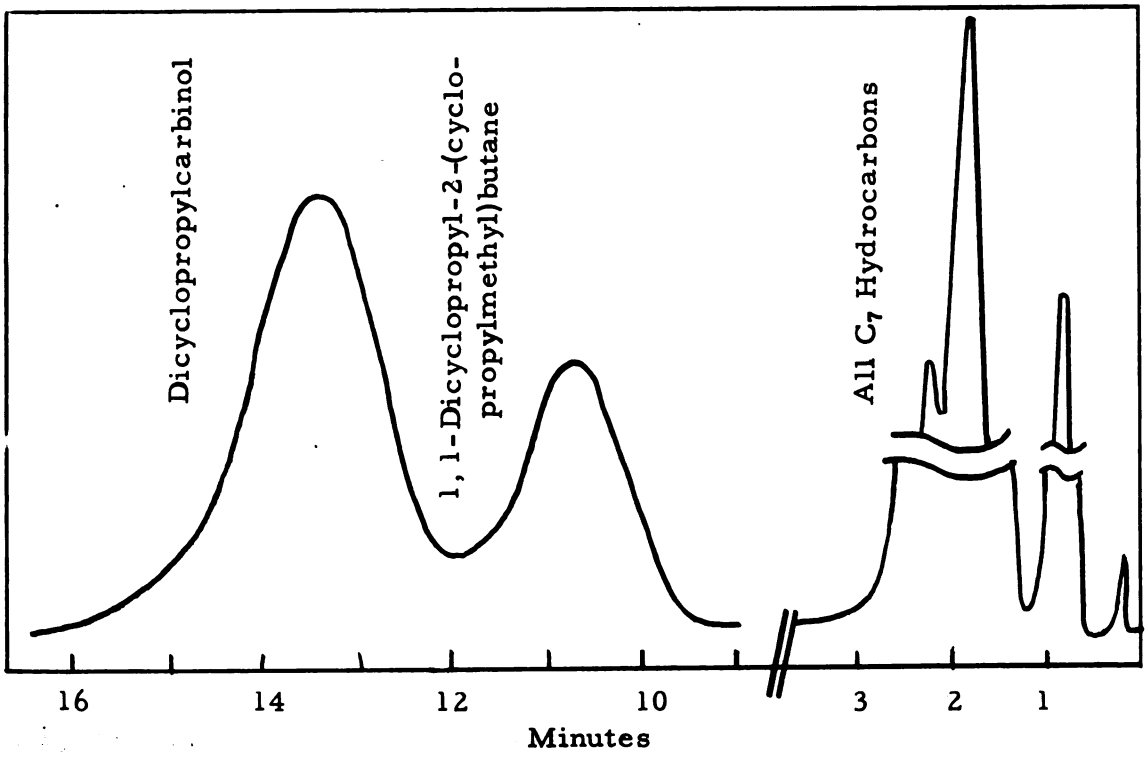


Figure 53b. Gas Chromatogram of the Products of Hydrogenolysis of Dicyclopropylcarbinol. b) Total Product Mixture (130°)

Dicyclopropylmethane (8.1%) was the sixth component and was identified by comparison of its retention time and n.m.r. spectrum (Figure 31) with that of an authentic sample (33).

The seventh component (5.1%) remained unidentified.

A component appearing near unreacted dicyclopropylcarbinol (36.5%) was shown to be probably 1, 1-dicyclopropyl-2-(cyclopropylmethyl)butane by its infrared and n.m.r. spectra (Figures 32 and 33).

Anal. Calcd. for $C_{14}H_{24}$: C, 87.50; H, 12.50.

Found: C, 85.78; H, 12.36 .

Similar results were obtained when the reduction was run at 180°, 205° or 225°. However, at 115° little reduction to C_7 hydrocarbons occurred. 1, 1-Dicyclopropyl-2-cyclopropylmethylbutane (ca. 15%) was the only product found in an appreciable amount.

Attempted Dehydration of Tricyclopropylcarbinol

A. Alumina

Ten grams (0.066 mole) of tricyclopropylcarbinol were passed through a column of activated alumina at 260° with nitrogen used as the carrier gas. The residence time was one minute. The products were trapped in an ice trap. The trap's contents, when subjected to gas chromatography, showed four major and eighteen minor components. The crude products showed no hydroxyl but olefin at 6.1-6.2 μ was present in the infrared spectrum. Carbonization was found at the center of the column.

B. Iodine

One gram (0.0066 mole) of tricyclopropylcarbinol was distilled at atmospheric pressure from three crystals of iodine. The product had n.m.r. and infrared spectra (except for weak absorbtion at 5.6-5.8 μ) essentially identical with the original alcohol. However, gas chromatography

showed one additional component which was not identified. Tricyclopropylcarbinol was unchanged after distillation at atmospheric pressure.

C. Trifluoroacetic acid

A mixture of 0.5 g. (0.0044 mole) of trifluoroacetic acid and 1.0 g. (0.0066 mole) of tricyclopropylcarbinol was heated under nitrogen, with stirring at 135° for two hours. The reaction products were allowed to cool, diluted with 10 ml. of ether and washed once with 10 ml. of 5% aqueous sodium bicarbonate. The layers were separated and the ether layer dried over anhydrous magnesium sulfate. After removal of the ether, gas chromatography showed the presence of three components. The first had a retention time equal to that of 2, 2-dicyclopropyltetrahydrofuran and amounted to ca. 5% of the mixture. The second was tricyclopropylcarbinol (45% of the mixture) as shown by its retention time and the presence of hydroxyl absorbtion at 2.75 μ in the infrared. The third was not identified but is presumed to be the cause of both the strong ester carbonyl absorption in the infrared at 5.62 μ, which is characteristic of trifluoroacetate esters, and the olefin absorption at 6.08 μ.

Reaction of Tricyclopropylcarbinol with Sulfuric Acid

Twenty grams (0.13 mole) of tricyclopropylcarbinol and eight drops of concentrated sulfuric acid were heated with stirring under a nitrogen atmosphere at 138° for 2.17 hours. The resulting clear brown liquid was dissolved in ether, washed with water until the washings were neutral, dried over magnesium sulfate, filtered and the ether removed by distillation.

Distillation of the residue at reduced pressure resulted in three fractions. The first was 6.7 g. of 2, 2-dicyclopropyltetrahydrofuran, b.p. 32° at 0.7 mm. The infrared and n.m.r. spectra were identical with that of a sample synthesized by an independent method (see page 100).

The second was 8.4 g. (0.0294 mole) of bis(4, 4-dicyclopropylbut-3-en-1-yl) ether boiling at 140-145° at 0.2 mm, $n_D^{26.5}$ 1.5080. The infrared (Figure 38) and n.m.r. (Figure 39) spectra are consistent with this structure.

Anal. Calcd. for $C_{20}H_{30}O$: C, 82.53; H, 9.95.

Found: C, 82.47, 82.54; H, 10.34, 10.46.

The distillation flask contained 3.5 g. of dark viscous residue.

Reaction of Tricyclopropylcarbinol with Phosphorus Pentoxide

One gram (0.0066 mole) of tricyclopropylcarbinol and 0.2 g. (0.0014 mole) of phosphorus pentoxide were stirred under a nitrogen atmosphere; after one minute heat evolution was noticed. After stirring fifteen minutes, vacuum (0.1 mm.) was applied and the flask warmed to 60° C. Only 0.2 g. of distillate was obtained. It consisted of ca. 50%, 2, 2-dicyclopropyltetrahydrofuran (infrared spectrum and gas chromatography) and 50% unreacted starting material. The flask contents decomposed, as evidenced by evolution of brown fumes, when additional heat was applied. No other products were observed.

When an equimolar amount of phosphorus pentoxide was used, decomposition occurred immediately after mixing.

Preparation of 2, 2-Dicyclopropyltetrahydrofuran (39)

Cyclopropyllithium, prepared from 15.7 g. (0.2 mole) of cyclopropyl chloride and 4.2 g. (0.4 g. atom) of lithium sand (40) at room temperature, was dispersed in 100 ml. of ether and then 8.6 g. (0.1 mole) of redistilled (88-90° at 16 mm.) commercial γ-butyrolactone in 130 ml. ether was added over a two hour period. Heat was evolved during the addition. Water was added to decompose the complex and salts. The water solution was saturated with calcium chloride with the intention of dehydrating the diol, but only an emulsion resulted. The dehydration was affected by

distillation of the organic products at about 160°. There resulted 3.0 g. of an unidentified compound, the infrared spectrum of which showed intramolecular hydrogen bonded hydroxyl at 2.90 μ (assumed to be 1, 1-dicyclopropylbutane-1, 4-diol) and 2.56 g. (0.0168 mole) of 2, 2-dicyclopropyltetrahydrofuran. The yield of the latter was 16.8%.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.80; H, 10.59.

Found: C, 78.91; H, 10.79.

The n.m.r. spectrum (Figure 37) and the infrared spectrum (Figure 36) were consistent with this structure. Also found was 6.7 g. (0.052 mole) of 1-cyclopropyl-4-hydroxybutan-2-one resulting from addition of only one mole of cyclopropyllithium. The 2, 4-dinitrophenylhydrazone of this ketone was prepared and was recrystallized from 95% ethanol, m.p. 173-174°.

Anal. Calcd. for $C_{13}H_{16}O_4N_4$: C, 50.64; H, 5.23; N, 18.12

Found: C, 50.61; H, 5.29; N, 18.00.

Preparation of 4, 4-Dicyclopropylbut-3-en-1-yl Acetate and 4, 4-Dicyclopropylbut-3-en-1-ol

Using a method analogous to that of Bruylants (14) 25.0 g. (0.147 mole) of 1, 1-dicyclopropyl-4-chloro-1-butene, (12) 14.4 g. (0.147 mole) of potassium acetate and 1.75 ml. of glacial acetic acid were heated at 125-135° C. for 44 hours. The mixture was added to water, extracted with ether, dried over anhydrous magnesium sulfate and the ether was removed by distillation.

Distillation of the residue at 0.7 mm. gave 8.4 g. (0.055 mole) of starting material and 14.0 g. (0.074 mole) of 4, 4-dicyclopropylbut-3-en-1-yl acetate with a b.p. 80-85° at 0.7 mm., $n_D^{25.3}$ 1.4782. Its infrared spectrum (Figure 2) shows ester carbonyl at 5.79 μ, olefin at 6.06 μ, acetate at ca. 8.2 μ and 9.8 μ and no carbon-chlorine at 13.75 μ. The n.m.r. spectrum is shown in Figure 3. The yield, based on unrecovered chloride, was 72%.

The above acetate (8.70 g., 0.05 mole), dissolved in 75 ml. of anhydrous ether, was added over a period of one hour to 1.25 g. (0.031 mole) of lithium aluminum hydride (95% pure) dispersed in 75 ml. of ether and cooled with an ice bath. After the addition was complete, the reaction mixture was refluxed for one-half hour. Water was added (with cooling) until no more hydrogen was evolved. After filtration, drying of the filtrate over anhydrous magnesium sulfate and removal of the ether by distillation, the products were distilled yielding 1.0 g. of unidentified material boiling at 44-89° at 2 mm. and 4.5 g. (0.03 moles) of 4,4-dicyclopropylbut-3-en-1-ol boiling at 82-92° at 2 mm., $n_D^{24.9}$ 1.4987. The yield was 60%.

The infrared (Figure 40) and n.m.r. (Figure 41) spectra are consistent with the structure assigned.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.80; H, 10.59.

Found: C, 78.41; H, 10.09.

Reaction of 4,4-Dicyclopropylbut-3-en-1-ol with Sulfuric Acid

One gram (0.066 mole) of 4,4-dicyclopropylbut-3-en-1-ol and one drop of concentrated sulfuric acid were heated at 137°, with stirring, under nitrogen for four hours. The product was dissolved in ether and washed with water until the washings were neutral. After drying over anhydrous magnesium sulfate, the ether was removed by distillation. The remaining organic material was exclusively 2,2-dicyclopropyltetrahydrofuran (0.9 g., 0.06 mole) as shown by its infrared spectrum (Figure 36) and retention time (gas chromatography) which were identical with that of authentic 2,2-dicyclopropyltetrahydrofuran. The yield was 91%.

Reaction of Dicyclopropylcarbinol with Sulfuric Acid

Five grams (0.033 mole) of dicyclopropylcarbinol and five drops of concentrated sulfuric acid (ca. 1.9×10^{-3} mole) were heated with stirring

in a nitrogen atmosphere at 145° for 3.5 hours. Reaction began immediately, generating water. The reaction mixture was dissolved in ether, washed with water, dried over magnesium sulfate, filtered and the ether removed by distillation. Infrared analysis of the crude product showed no hydroxyl absorption at 2.8 μ.

Distillation yielded 2.0 g. (0.018 mole) of 2-cyclopropyltetrahydrofuran, b.p. 65° at 6.5 mm., $n_D^{25.3}$ 1.4715. The yield was 54.5%.

Anal. Calcd. for $C_7H_{12}O$: C, 74.95; H, 10.78.

Found: C, 77.14 ; H, 10.14.

The infrared (Figure 42) and n.m.r. (Figure 43) spectra are consistent with the assigned structure.

Continued distillation at 0.3 mm. gave 0.9 g. (0.0043 mole) of bis(4-cyclopropylbut-3-en-1-yl)ether, b.p. 144° at 0.3 mm., $n_D^{25.5}$ 1.5000. The infrared (Figure 44) and n.m.r. (Figure 45) spectra are consistent with this structure.

Anal. Calcd. for $C_{14}H_{22}O$: C, 81.50; H, 10.75.

Found: C, 80.26; H, 10.64.

The contents of the distillation flask decomposed at 240° forming 1.5 g. of dark, viscous residue.

Preparation of Cyclopropyldiphenylcarbinol

To 36.5 g. (0.2 mole) of benzophenone in 150 ml. anhydrous ether was added cyclopropyllithium (prepared from 0.3 mole of cyclopropyl chloride) in 100 ml. ether with cooling and stirring. The contents of the flask turned pale blue and after refluxing one hour, turned pink. Water was added, with cooling, and the ether layer separated. The water layer was extracted with two 100-ml. portions of ether. The combined ether layers were dried over anhydrous magnesium sulfate. Filtration and removal of the solvent by distillation resulted in a deep yellow liquid. Infrared showed no carbonyl absorption.

Distillation through a six inch Vigreux column gave 43.0 g. (0.19 mole) of crystalline distillate in 95% yield (b.p. 114-116° at 0.2 mm., m.p. 82.5-84.5°, literature value: (41, 48) 82-83°). Recrystallization from ligroin (b.p. 69-90°) gave 39.0 g. (88%) melting at 83-84.5°C.

Reaction of Cyclopropyldiphenylcarbinol with Sulfuric Acid

Five grams (0.033 mole) of cyclopropyldiphenylcarbinol and two drops of concentrated sulfuric acid were heated with stirring for five hours at 140° in a nitrogen atmosphere. The reaction mixture was recrystallized from ligroin (b.p. 90-120°). Some starting material was recovered in crystalline form. The solvent was removed from the filtrate and the residue recrystallized from methanol. Solid bis(4, 4-diphenyl-but-3-en-1-yl) ether, melting at 112-113°, (0.5 g., 0.0012 mole, 73% yield) was recovered. The infrared spectrum (Figure 47) shows aromatic ether, carbon-hydrogen stretch at 3.32 μ (vinyl hydrogen) and no cyclopropyl absorption. The n.m.r. spectrum is shown in Figure 48. Lipp (41) reported that an ether, $C_{32}H_{30}O$, melting at 113°, was obtained from the reaction of this alcohol and potassium acid sulfate.

No 2, 2-diphenyltetrahydrofuran could be isolated by crystallization from methanol (see preparation of 2, 2-diphenyltetrahydrofuran).

Preparation of 2, 2-Diphenyltetrahydrofuran

The addition of phenylmagnesium bromide, prepared from 71.0 g. (0.45 mole) of bromobenzene in 75 ml. of ether and 12.0 g. (0.5 g. atom) of magnesium in 100 ml. of ether, to 12.9 g. (0.15 mole) of γ-butyrolactone in 200 ml. ether was followed by a 1-1/2 hour reflux period. Aqueous ammonium chloride solution was added to decompose the complex. The layers were separated and the water layer washed with two 75-ml. portions of ether. The combined ether layers were dried over anhydrous

magnesium sulfate and a small amount of activated charcoal. After filtration and removal of the ether by distillation, the residue was recrystallized from benzene yielding 19.0 g. (0.079 mole) of white needles melting at 106-107° (literature value (42), 108°). This was 1, 1-diphenylbutan-1, 4-diol in 53% yield. The infrared spectrum (chloroform) showed hydrogen bonded hydroxyl at 3.02 μ (polymeric association).

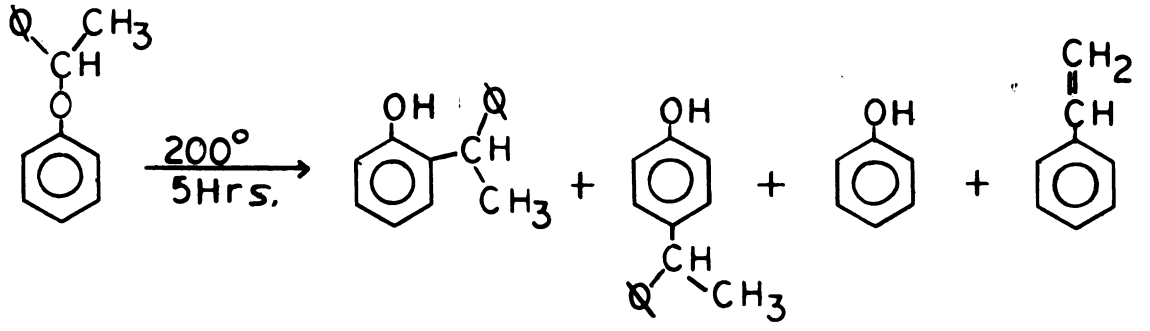
An additional twenty-three grams (0.095 mole) of crude product was found in the filtrate from recrystallization.

This diol (10.0 g., 0.041 mole) was refluxed with 50 ml. of 30% sulfuric acid for two hours, washed twice with 100-ml. portions of ether, dried over anhydrous magnesium sulfate with a small amount of activated charcoal, filtered and the ether removed by distillation. Recrystallization from methanol gave 5.4 g. (0.004 mole, 60% yield) of white needles melting at 66-67° (literature (42) value; 65-66°). The infrared spectrum shows a C-O band (ether) at 9.57 μ but no hydroxyl. The n.m.r. spectrum showed 10 phenyl protons at 2.8 τ, 2 α-tetrahydrofuran protons at 6.08 τ. Two β protons (7.55 τ) next to the phenyl containing carbon and two β protons (8.1 τ) across the ring from the phenyl groups were also found.

MISCELLANEOUS

Attempted Kinetic Study of the Thermal Rearrangement of α-Phenylethyl Aryl Ethers

The stereochemistry of the thermal rearrangement of α-phenylethyl aryl ethers was studied by Hart, et al., (43,44). α-Phenylethyl phenyl ether rearranged at 200° in five hours to give a 33% yield of α-phenylethylphenols. Similar results were obtained with the ethers of p-cresol



and 2,6-xylenol, the latter giving 4-α-phenylethyl-2,6-dimethylphenol (26%). With optically active ethers appreciable optical activity was retained and the α-phenylethyl group migrated with retention of configuration, even on para migration. When optically active α-phenylethyl mesityl ether was treated with an excess of phenol at 200° for seven hours, a 44% yield of racemic α-phenylethylphenols was obtained. Thus, the reaction can apparently proceed in at least two manners: intramolecularly, with retention of configuration and intermolecularly, via a symmetrical intermediate. In the present investigation it was hoped that a study of substituent effects would yield information concerning the nature of this intermediate.

Examination of the kinetics of the α-phenethyl p-tolyl ether rearrangement using gas chromatography showed the ether disappearance to be first order with a rate 6.24×10^{-2} sec^{-1} at 244.5°. But the appearance of p-cresol (cleavage product) and o-α-phenylethyl-p-cresol (rearrangement product) was of no integral order (see Figure 54).

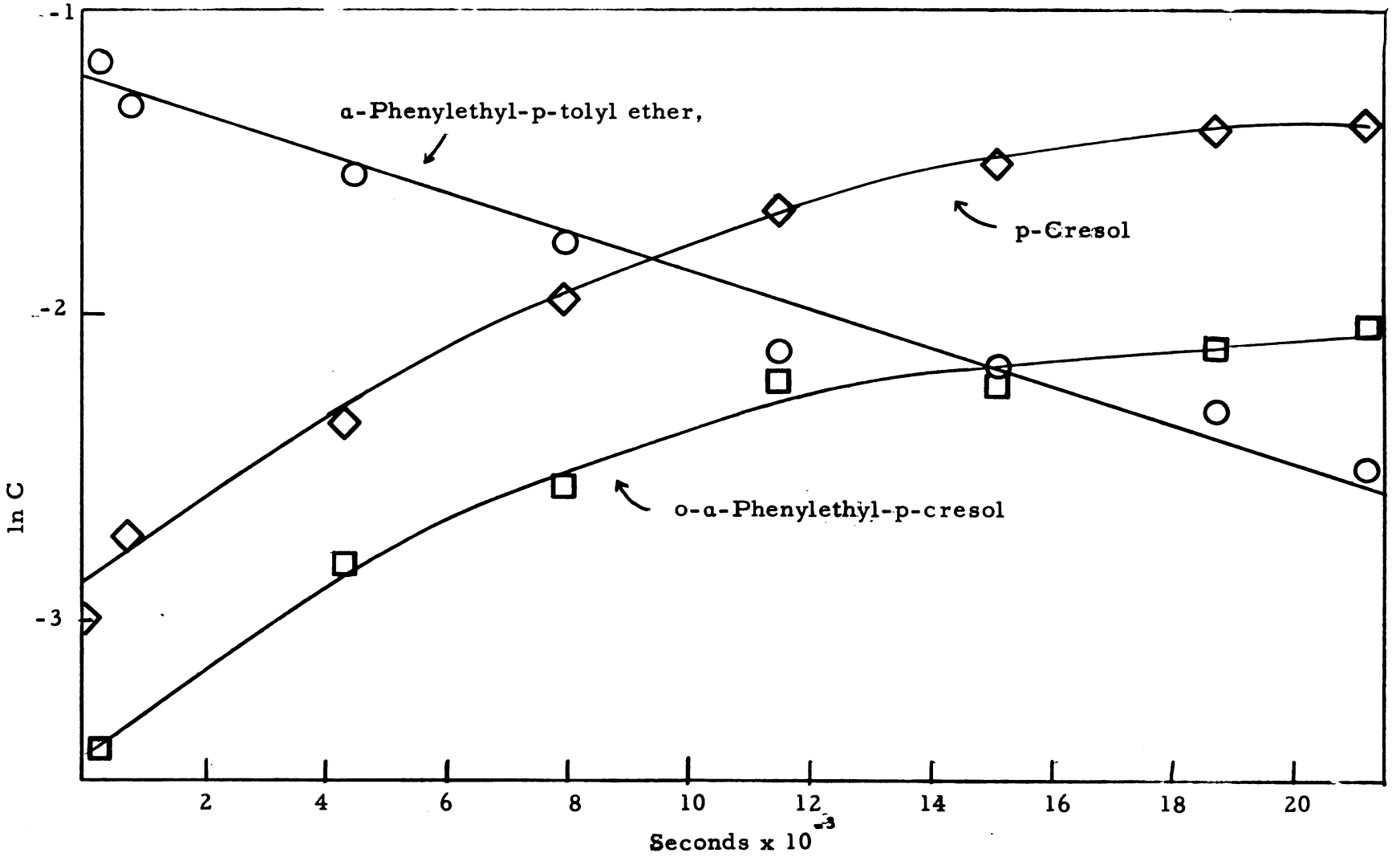


Figure 54. Plot of ln Concentration vs. t for the Thermal Rearrangement of α-Phenylethyl-p-tolyl Ether.

Careful examination of the reaction products, using higher resolution than for the kinetic study, revealed two additional products. These compounds appeared as shoulders on the p-cresol and o-α-phenethyl-p-cresol peaks. Thus, the rate of appearance of two compounds was being followed when the p-cresol or o-α-phenylethyl p-cresol peaks were examined. This led to non-integral orders.

It is apparent that the reaction is more complex than previously believed. The optical activity data of Hart (44) may require reinvestigation. In the older work, the absence of gas chromatography necessitated product isolation by distillation which may have allowed an isomer mixture to be disguised as a single compound.

Due to the fact that an examination of substituent effects on the ratio of rearrangement to cleavage was one of the primary objects of this investigation no further work was attempted. Product identification and re-evaluation of the gas chromatographic technique will be necessary before meaningful kinetic data can be obtained by this method.

EXPERIMENTAL

Solvent

Diphenyl ether was redistilled, b.p. 62° at 0.08 mm., before use. All volumes were measured at 30.0°.

Kinetic Procedure

Approximately 0.5 molar solutions of the α-phenylethyl aryl ether were employed and the reaction was followed by gas chromatography. The reactions were conducted in a constant temperature bath (silicone oil) maintained at 244.5 ± 0.1°.

Approximately 0.2 ml. of the solution was placed in each 1 ml. ampoule. The time at which the ampoules were placed in the bath was

taken as zero time. At various time intervals duplicate samples were removed and quenched by cooling in a water bath at room temperature. The ampoules were opened and thermostatted at 30.0°. A sample of size convenient for gas chromatographic analysis was taken with a 50 μl. syringe. The chromatographic column used was 72 x 1/4 in., packed with 30% silicone gum (SE-30) on 60-80 mesh Chromosorb. Calibration plots of area under the chromatogram curve vs. grams of compound had been previously constructed using authentic samples of the starting materials and products. (No rearrangement of the α-phenethyl aryl ether occurred during gas chromatographic analysis.) With the aid of these plots the concentrations of the components in the sample were determined.

SUMMARY

1. The benzoate of tricyclopropylcarbinol was prepared and its solvolysis rate measured. In 95% aqueous dioxane at 25°, it solvolyzed remarkably rapidly, with a first order specific rate constant 1.23×10^{-3} sec^{-1}. Solvolysis occurred with alkyl-oxygen fission; methanolysis produced the corresponding methyl ether. No rearrangement of the alcohol occurred and the sole products of hydrolysis were tricyclopropylcarbinol and benzoic acid.

2. Under the same solvolysis conditions dicyclopropylisopropylcarbinyl benzoate solvolyzed with a first order specific rate constant of 1.14×10^{-6} sec^{-1}. Thus the substitution of a third cyclopropyl group for isopropyl caused a rate enhancement of 1080 fold, an even greater increase than previously observed for the first and second cyclopropyl.

3. Tricyclopropylcarbinyl benzoate rearranged quantitatively to 4,4-dicyclopropylbut-3-en-1-yl benzoate when heated at 100° for 30 minutes.

4. The nuclear magnetic resonance (n.m.r.) spectrum of tricyclopropylcarbinol in concentrated sulfuric acid consists of a single, sharp peak at 7.79 τ m (methane sulfonic acid, internal standard). This is in contrast with its n.m.r. spectrum in carbon tetrachloride which consists of a complex pattern in the 9-10 τ region. Dicyclopropylcarbinol, in sulfuric acid, also has an n.m.r. spectrum consisting of a single peak at the same position.

5. When tricyclopropylcarbinol was heated with a trace of sulfuric acid, rearrangement occurred. The products were 2,2-dicyclopropyltetrahydrofuran (synthesized independently from γ-butyrolactone and cyclopropyl lithium) and bis (4,4-dicyclopropylbut-3-en-1-yl) ether. The alcohol 4,4-dicyclopropylbut-3-en-1-ol may be an intermediate, since it also gave the tetrahydrofuran on treatment with sulfuric acid. When dicyclopropylcarbinol was treated similarly the products were 2-cyclopropyltetrahydrofuran and bis (4-cyclopropylbut-3-en-1-yl) ether.

6. Catalytic reduction of tricyclopropylcarbinol using hydrogen and copper oxide-chromium oxide catalyst produced tricyclopropylmethane in 36% yield. Other products were 1, 1-dicyclopropyl-1-butene, 1, 1-dicyclopropylbutane, 4-cyclopropylheptane and 4-propylheptane. Reduction of dicyclopropylcarbinol yielded only a small amount (8.1%) of dicyclopropylmethane. The major product was 21.5% of 1-cyclopropylbutane. Other products were n-heptane and a dimer, probably 1, 1-dicyclopropyl-2-(cyclopropylmethyl) butane.

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APPENDIX

THE RATES OF SOLVOLYSIS

The rates of solvolysis of the esters were measured in dioxane containing various weight percentages of water at several temperatures; the reactions were followed by titrating the liberated benzoic acid with standard sodium hydroxide.

The reaction may be expressed by the equation:

$$\underset{E - A}{\text{Ester}} \xrightarrow{k} \underset{A}{\text{Alcohol}} + \underset{A}{\text{Acid}}$$

where E = initial ester concentration in moles/liter

A = concentration of alcohol or acid at time t

E - A = concentration of ester at time t.

The treatment for a first order reaction is:

$$\log (E - A) = - \frac{k}{2.3} t + \log E.$$

The measured quantity was:

V = volume (ml.) of standard sodium hydroxide required to neutralize the benzoic acid found at time t (using a 5 ml. aliquot).

If V_f = volume (ml.) of standard sodium hydroxide required to neutralize the theoretical quantity of benzoic acid (using a 5 ml. aliquot)

then (E - A) is proportional to $(V_f - V)$

and E is proportional to V_f

thus $\log (V_f - V) = - \frac{k}{2.3} t + \log V_f$.

From this equation it is seen that a plot of log $(V_f - V)$ vs. t should be linear, and the specific first order rate constant k may be calculated from the slope of this line (for a typical plot, see Figure 12).

For the treatment of the isopropyldicyclopropylcarbinyl benzoate solvolysis, in which case simultaneous rearrangement occurred, see Hart and Sandri (12).

The values of k, k_s and k_r obtained for the reactions of the esters under various conditions are listed in Table 3. The value of the specific rate constant listed at a given temperature is the arithmetic mean of all rate constants obtained at that temperature.

The energy of activation, Ea, was determined in the usual manner from the Arrhenius equation:

$$\log k = -\frac{Ea}{2.3R}\ \frac{1}{T} + Z$$

The linear plot of log k versus $\frac{1}{T}$ for tricyclopropylcarbinyl benzoate is shown in Figure 13. The slope was obtained by the method of least squares (45) and Ea was obtained from the equation:

$$Ea = -2.3R\ m$$

where $R = 1.987$ calories degree^{-1} mole^{-1}

and m = slope

The enthalpy of activation, ΔH^*, was calculated from the equation:

$$\Delta H^* = Ea - RT$$

The entropy of activation, ΔS^*, was calculated from the Eyring equation:

$$k = \frac{k_B T}{h}\ e^{\Delta S^*/R}\ e^{-\Delta H^*/RT}$$

or $$\Delta S^* = 2.3R \log \left(\frac{kh}{k_B T}\right) + \frac{\Delta H^*}{T}$$

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

and k_B = Boltzmann constant, 1.380×10^{-16} erg degree^{-1} molecule^{-1}

Table 3. Specific Rate Constants for the Solvolysis of Tricyclopropylcarbinyl Benzoate and Dicyclopropylisopropylcarbinyl Benzoate in Aqueous Dioxane

Ester	°C		Weight Per Cent Dioxane 95	90
Tricyclopropylcarbinyl Benzoate	25.0	$k \times 10^4$ sec.$^{-1}$	12.3 ± 1.6	
	15.5	$k \times 10^4$ sec.$^{-1}$	4.37 ± .58	
	7.9	$k \times 10^4$ sec.$^{-1}$	2.52 ± .07	
	7.9	$k \times 10^4$ sec.$^{-1}$		22.9 ± 1.6
Dicyclopropylisopropylcarbinyl Benzoate	59.6	$k \times 10^4$ sec.$^{-1}$	0.262 ± .012	
		$k_s \times 10^4$ sec.$^{-1}$	0.232 ± .006	
		$k_r \times 10^4$ sec.$^{-1}$	0.030 ± .008	
	25.0	$k \times 10^4$ sec.$^{-1}$	0.0114 ± .0002	
		$k_s \times 10^4$ sec.$^{-1}$	0.0095 ± .0003	
		$k_r \times 10^4$ sec.$^{-1}$	0.0019 ± .0002	

The Data Obtained from the Solvolysis Rate Measurements

The following tables contain the data obtained from the rate measurements.

t = time in seconds

V = volume (ml.) of standard sodium hydroxide required to neutralize a 5 ml. aliquot of the reacting solution.

V_f = volume (ml.) of standard sodium hydroxide required to neutralize the theoretical amount of benzoic acid in a 5-ml. aliquot obtainable from the saponification equivalent of ester used in the run.

V'_f = volume (ml.) of standard sodium hydroxide required to neutralize the total amount of benzoic acid liberated in a 5-ml. aliquot when this amount was significantly less than the theoretical.

Plots of log $(V_f - V)$ versus t or log $(V_f - V\frac{V_f}{V'_f})$ versus t were linear and the specific rate constants were calculated from the slopes of these lines.

$k = k_s + k_r$

k_s = rate constant for solvolysis

k_r = rate constant for rearrangement

where $\frac{k_s}{k_r} = \frac{V'_f}{V_f - V'_f}$

Table 4. Solvolysis of 1.40×10^{-2} Molar Tricyclopropylcarbinyl Benzoate in 95% Dioxane - 5% Water at 7.9°

t (sec.)	V (ml. corr.)	$V_f - V$
232	0.41	3.75
734	0.93	3.23
1225	1.28	2.88
1739	1.60	2.56
2234	1.93	2.23
2773	2.19	1.97
3258	2.37	1.79
3806	2.62	1.54
4320	2.89	1.27
4840	3.02	1.14
5373	3.06	1.10
5884	3.29	0.87
6445	3.33	0.83
7004	3.42	0.74
7563	3.55	0.61
8040	3.62	0.54
8572	3.76	0.40
9080	3.80	0.36

Titrant: 0.01479 N NaOH

$V_f = 4.16$ ml.

Blank = 0.06 ml.

Purity of ester 87.89% $k = 2.54 \times 10^{-4}$ sec.$^{-1}$

Table 5. Solvolysis of 1.51×10^{-2} Molar Tricyclopropylcarbinyl Benzoate in 95% Dioxane - 5% Water at 7.9°

t (sec.)	V (ml., corr.)	$V_f - V$
288	0.52	3.96
793	1.07	3.41
1333	1.44	3.04
1796	1.98	2.50
2314	1.98	2.50
2828	2.40	2.08
3325	2.49	1.99
3878	2.96	1.52
4407	3.08	1.40
4926	3.03	1.45
5443	3.40	1.08
5947	3.51	0.97
6512	2.59	0.89
7101	3.74	0.74
7643	3.84	0.60
8110	3.93	0.55
8641	4.07	0.41
9175	3.99	0.49
9561	3.96	0.52

Titrant: 0.01479 N NaOH

$V_f = 4.48$ ml.

Blank = 0.06 ml.

Purity of ester 87.89% $k = 2.59 \times 10^{-4}$ sec.$^{-1}$

Table 6. Solvolysis of 1.42×10^{-2} Molar Tricyclopropylcarbinyl Benzoate in 95% Dioxane - 5% Water at 7.9°

t (sec.)	V (ml., corr.)	$V_f - V$
135	0.28	4.12
326	0.47	3.93
578	0.79	3.61
842	0.98	3.42
1118	1.26	3.14
1439	1.52	2.88
1742	1.77	2.63
2100	2.05	2.35
2504	2.33	2.07
2894	2.62	1.78
3391	2.60	1.80
3736	2.75	1.65
4277	3.13	1.27
4837	3.18	1.22
5355	3.29	1.11
5836	3.42	0.98
6375	3.44	0.96
6892	3.63	0.77
7338	3.84	0.56

Titrant: 0.01425 N NaOH

$V_f = 4.40$ ml.

Blank = 0.06 ml.

Purity of ester 87.89% $k = 2.44 \times 10^{-4}$ sec.$^{-1}$

Table 7. Solvolysis of 8.04×10^{-3} Molar Tricyclopropylcarbinyl Benzoate in 95% Dioxane - 5% Water at 15.5°

t (sec.)	V (ml., corr.)	$V_f - V$
183	0.51	4.60
438	1.09	4.02
796	1.87	3.24
1113	2.35	2.76
1502	2.75	2.36
1991	3.26	1.85
2633	3.79	1.32
3357	4.22	0.89
4102	4.55	0.56
4797	4.72	0.39
5664	4.87	0.24
6445	4.99	0.12
7158	4.92	0.19

Titrant: 0.007860 N NaOH

V_f = 5.11 ml.

Blank = 0.51 ml.

Purity of ester 56.5% $k = 5.56 \times 10^{-4}$ sec.$^{-1}$

Table 8. Solvolysis of 6.977×10^{-3} Molar Tricyclopropylcarbinyl Benzoate in 95% Dioxane - 5% Water at 15.5°

t (sec.)	V (ml.)	V_f-V
185	0.58	4.19
489	1.16	3.61
793	1.66	3.11
1143	2.17	2.60
1578	2.55	2.22
1869	2.89	1.88
2270	3.18	1.59
2684	3.38	1.29
3036	3.71	1.06
3393	3.90	0.87
3704	4.05	0.72
4161	4.12	0.65
4579	4.30	0.47
5067	4.41	0.36
5515	4.40	0.37
5979	4.64	0.13

Titrant: 0.007310 N NaOH

V_f = 4.77 ml.

Blank = 0.35 ml.

Purity of ester 50.17% $k = 4.70 \times 10^{-4}$ sec.$^{-1}$

Table 9. Solvolysis of 8.38×10^{-3} Molar Tricyclopropylcarbinyl Benzoate in 95% Dioxane - 5% Water at 15.5°

t (sec.)	V (ml.)	$V_f - V$
162	0.41	3.69
354	0.75	3.35
591	1.12	2.98
816	1.37	2.73
1128	1.75	2.35
1478	2.09	2.01
1857	2.36	1.74
2248	2.66	1.44
2640	2.90	1.20
3080	3.01	1.09
3842	3.41	0.69
4510	3.52	0.58
4975	3.62	0.48
5463	3.75	0.35
5932	3.77	0.33
6436	3.80	0.30

Titrant: 0.01021 N NaOH

V_f = 4.10 ml.

Blank = 0.13 ml.

Purity of ester 85.5% $k = 4.16 \times 10^{-4}$ sec.$^{-1}$

Table 10. Solvolysis of 9.26×10^{-3} Molar Tricyclopropylcarbinyl Benzoate in 95% Dioxane - 5% Water at 15.5°

t (sec.)	V (ml.)	$V_f - V$
215	1.04	6.63
449	1.70	5.97
766	2.54	5.13
1151	3.39	4.28
1551	4.24	3.23
1919	4.80	2.87
2299	5.06	2.61
2582	5.32	2.35
2890	5.55	2.12
3225	5.85	1.82
3604	6.13	1.54
3972	6.20	1.47
4300	6.47	1.20
4660	6.64	1.03
4961	6.78	0.89
5340	6.88	0.79

Titrant: 0.006040 N NaOH

$V_f = 7.67$ ml.

Blank = 0.10 ml.

Purity of ester 87.51% $k = 4.14 \times 10^{-4}$ sec.$^{-1}$

Table 11. Solvolysis of 9.732×10^{-3} Molar Tricyclopropylcarbinyl Benzoate in 95% Dioxane - 5% Water at 15.5°

t (sec.)	V (ml.)	$V_f - V$
144	0.97	7.68
320	1.65	7.00
526	2.27	6.38
874	3.40	5.25
1203	4.16	4.49
1553	4.89	3.76
1874	5.48	3.17
2203	5.84	2.81
2563	6.23	2.42
2911	6.52	2.13
3330	6.92	1.73
3681	7.11	1.54
4042	7.36	1.29
4503	7.51	1.14
4959	7.69	0.96
5379	7.96	0.69
5818	8.14	0.51
6183	8.13	0.52

Titrant: 0.005624 N NaOH

V_f = 8.65 ml.

Blank = 0.11 ml.

Purity of ester 87.51% $k = 4.46 \times 10^{-4}$ sec.$^{-1}$

Table 12. Solvolysis of 1.38×10^{-2} Molar Tricyclopropylcarbinyl Benzoate in 95% Dioxane - 5% Water at 25.0°

t (sec.)	V (ml., corr.)	$V_f - V$
72	0.38	3.65
202	0.76	3.27
349	1.31	2.72
490	1.69	2.34
720	2.22	1.81
910	2.52	1.51
1114	2.87	1.16
1431	3.17	0.86
1608	3.38	0.65
1900	3.50	0.53
2085	3.59	0.44
2291	3.65	0.38
2471	3.75	0.28
2663	3.73	0.30
2960	3.87	0.16
3173	3.91	0.12

Titrant: 0.01475 N NaOH

$V_f = 4.03$ ml.

Blank = 0.08 ml.

Purity of ester 86.16% $k = 1.07 \times 10^{-3}$ sec.$^{-1}$

Table 13. Solvolysis of 1.28×10^{-2} Molar Tricyclopropylcarbinyl Benzoate in 95% Dioxane - 5% Water at 25.0°

t (sec.)	V (ml., corr.)	$V_f - V$
122	0.53	3.18
249	0.91	2.80
386	1.28	2.43
519	1.64	2.07
663	1.97	1.74
817	2.27	1.44
1009	2.51	1.20
1156	2.67	1.04
1297	2.85	0.86
1486	3.06	0.65
1656	3.20	0.51
1867	3.26	0.45
2068	3.37	0.34
2265	3.47	0.24
2428	3.51	0.20
2599	3.52	0.19

Titrant: 0.01484 N NaOH

V_f = 3.71 ml.

Blank = 0.06 ml.

Purity of ester 86.16% $k = 1.18 \times 10^{-3}$ sec.$^{-1}$

Table 14. Solvolysis of 1.42×10^{-2} Molar Tricyclopropylcarbinyl Benzoate in 95% Dioxane - 5% Water at 25.0°

t (sec.)	Vol. (ml., corr.)	$V_f - V$
116	0.55	3.56
240	0.99	3.12
378	1.45	2.66
525	1.74	2.37
697	2.24	1.87
899	2.55	1.56
1042	2.80	1.31
1204	3.14	0.97
1387	3.14	0.97
1543	3.32	0.79
1791	3.50	0.61
1951	3.65	0.46
2132	3.62	0.49
2339	3.74	0.37
2549	3.83	0.28
2722	3.88	0.23
2937	3.87	0.24

Titrant: 0.01484 N NaOH

V_f = 4.11 ml.

Blank = 0.06 ml.

Purity of ester 86.16% $k = 1.45 \times 10^{-3}$ sec.$^{-1}$

Table 15. Solvolysis of 1.33×10^{-2} Molar Tricyclopropylcarbinyl Benzoate in 90% Dioxane - 10% Water at 7.9°

t (sec.)	V (ml., corr.)	$V_f - V$
105	1.34	2.58
241	2.07	1.85
378	2.56	1.36
542	2.94	0.96
672	3.25	0.67
821	3.35	0.57
962	3.53	0.39
1128	3.47	0.45

Titrant: 0.01498 N NaOH

V_f = 3.92 ml.

Blank = 0.24 ml.

Purity of ester 87.89% $k = 2.51 \times 10^{-3}$ sec.$^{-1}$

Table 16. Solvolysis of 1.71×10^{-2} Molar Tricyclopropylcarbinyl Benzoate in 90% Dioxane - 10% Water at 7.9°

t (sec.)	V (ml., corr.)	$V_f - V$
115	1.60	3.41
249	2.59	2.82
387	3.32	1.69
564	3.90	1.21
713	4.21	0.80
914	4.38	0.63
1064	4.59	0.42
1294	4.81	0.30
1476	4.79	0.32
1660	4.84	0.27

Titrant: 0.01498 N NaOH

V_f = 5.01 ml.

Blank = 0.24 ml.

Purity of Ester 87.89% $k = 2.12 \times 10^{-3}$ sec.$^{-1}$

Table 17. Solvolysis of 1.49×10^{-2} Molar Tricyclopropylcarbinyl Benzoate in 90% Dioxane - 10% Water at 7.9°

t (sec.)	V (ml., corr.)	$V_f - V$
112	1.48	2.97
238	2.19	2.26
374	2.83	1.62
566	3.39	1.06
697	3.68	0.77
850	3.83	0.62
1000	4.06	0.39
1190	4.09	0.36
1340	4.18	0.27
1527	4.17	0.28
1799	4.32	0.13
2010	4.25	0.20

Titrant: 0.01498 N NaOH

V_f = 4.45 ml.

Blank = 0.24 ml.

Purity of ester 87.89% $k = 2.25 \times 10^{-3}$ sec.$^{-1}$

Table 18. Solvolysis of 1.050×10^{-2} Molar Dicyclopropylisopropylcarbinyl Benzoate in 95% Dioxane - 5% Water at 59.6°

t (sec.)	V (ml., corr.)	$V_f - V \frac{V_f}{V_f'}$
326	0.49	5.61
1705	0.70	5.37
3223	0.85	5.20
5179	1.28	4.71
6991	1.48	4.48
8978	1.65	4.29
11032	1.85	4.06
12880	2.03	3.86
15154	1.97	3.92
16730	2.15	3.72
18524	2.42	3.41
20528	2.58	3.23
22376	2.78	3.00
23980	2.91	2.85
26513	2.94	2.82
30542	3.16	2.57

Titrant 0.007919 N NaOH

$V_f = 6.17$ ml.

$V_f' = 5.40$ ml.

$V_f/V_f' = 1.14$

$k = 2.59 \times 10^{-5}$ sec.$^{-1}$

$k_s = 2.27 \times 10^{-5}$ sec.$^{-1}$

$k_r = 0.32 \times 10^{-5}$ sec.$^{-1}$

Table 19. Solvolysis of 9.376×10^{-3} Molar Dicyclopropylisopropylcarbinyl Benzoate in 95% Dioxane - 5% Water at 59.6°

t (sec.)	V (ml., corr.)	$V_f - V \frac{V_f}{V_f'}$
377	0.39	6.05
2152	0.79	5.58
3701	0.91	5.44
5346	1.27	5.03
7443	1.43	4.84
9456	1.74	4.48
11519	1.98	4.20
13299	2.05	4.12
15528	2.10	4.06
17198	2.29	3.84
19014	2.47	3.63
20972	2.68	3.39
22857	2.87	3.17
24436	3.00	3.02
26407	3.18	2.81
30944	3.53	2.41
34048	3.55	2.38

Titrant: 0.007919 N NaOH

$V_f = 6.50$ ml.

$V_f' = 5.59$ ml.

$V_f/V_f' = 1.16$

$k = 2.78 \times 10^{-5}$ sec.$^{-1}$

$k_s = 2.40 \times 10^{-5}$ sec.$^{-1}$

$k_r = 0.38 \times 10^{-5}$ sec.$^{-1}$

Table 20. Solvolysis of 9.035×10^{-3} Molar Dicyclopropylisopropylcarbinyl Benzoate in 95% Dioxane - 5% Water at 59.6°

t (sec.)	V (ml., corr.)	$V_f - V\frac{V_f}{V_f'}$
400	0.38	4.90
2022	0.46	4.80
3760	0.76	4.48
5851	0.92	4.31
7880	1.13	4.08
9943	1.36	3.38
11700	1.41	3.77
13926	1.56	3.61
15592	1.73	3.42
17399	1.82	3.33
19295	2.07	3.05
21290	2.13	2.99
22827	2.28	2.92
25295	2.45	2.64
29335	2.68	2.39
31925	2.79	2.27
33239	2.92	2.13

Titrant: 0.007919 N NaOH

$V_f = 5.31$ ml.

$V_f' = 4.89$ ml.

$V_f/V_f' = 1.09$

$k = 2.48 \times 10^{-5}$ sec.$^{-1}$

$k_s = 2.28 \times 10^{-5}$ sec.$^{-1}$

$k_r = 0.20 \times 10^{-5}$ sec.$^{-1}$

Table 21. Solvolysis of 8.30×10^{-3} Molar Dicyclopropylisopropylcarbinyl Benzoate in 95% Dioxane - 5% Water at 25.0°

t (sec.)	V (ml., corr.)	$V_f - V\frac{V_f}{V_f'}$
4406	0.20	5.34
32390	0.39	5.10
96285	0.49	4.98
134242	0.76	4.65
194360	1.07	4.27
226885	1.18	4.14
273560	1.30	3.99
305683	1.45	3.81
343170	1.82	3.36
447445	2.00	3.14
524450	2.13	2.98
569092	2.10	3.02
607788	2.36	2.70
681111	2.78	2.31
762097	2.74	2.24

Titrant: 0.008306 N NaOH

Purity of ester = 86.72%

Blank = 0.34 ml.

V_f = 5.58 ml.

V_f' = 4.56 ml.

V_f/V_f' = 1.22

$k = 1.14 \times 10^{-6}$ sec.$^{-1}$

$k_s = 9.32 \times 10^{-7}$ sec.$^{-1}$

$k_r = 2.05 \times 10^{-7}$ sec.$^{-1}$

Table 22. Solvolysis of 1.02×10^{-2} Molar Dicyclopropylisopropylcarbinyl Benzoate in 95% Dioxane - 5% Water at 25.0°

t (sec.)	V (ml., corr.)	$V_f - V \frac{V_f}{V_f'}$
3932	0.16	5.92
30707	0.35	5.70
95670	0.60	5.40
133735	0.72	5.26
193410	1.15	4.75
226550	1.20	4.69
273218	1.41	4.45
305200	1.52	4.32
342250	1.89	3.88
446810	2.03	3.71
523797	2.33	3.36
568575	2.37	3.31
607012	2.65	2.98
680478	2.75	2.84
761257	3.04	2.52

Titrant: 0.008306 N NaOH

Purity of ester = 86.72%

Blank = 0.34 ml.

V_f = 6.11 ml.

V_f' = 5.18 ml.

V_f/V_f' = 1.18

$k = 1.11 \times 10^{-6}$ sec.$^{-1}$

$k_s = 9.36 \times 10^{-7}$ sec.$^{-1}$

$k_r = 1.69 \times 10^{-7}$ sec.$^{-1}$

Table 23. Solvolysis of 9.15×10^{-3} Molar Dicyclopropylisopropylcarbinyl Benzoate in 95% Dioxane - 5% Water at 25.0°

t (sec.)	V (ml., corr.)	$V_f - V\frac{V_f}{V_f'}$
4146	0.16	5.59
31165	0.38	5.69
96000	0.59	5.44
134015	0.73	5.27
194040	1.07	4.87
226660	1.25	4.65
273445	1.35	4.45
305420	1.53	4.32
342600	1.74	4.07
447065	2.05	3.60
524175	2.37	3.32
568804	2.47	3.20
607344	2.56	3.09
680770	2.87	2.27
761135	3.19	2.34

Titrant: 0.008306 N NaOH

Purity of ester = 86.72%

Blank = 0.34 ml.

V_f = 6.14 ml.

V_f' = 5.16 ml.

V_f/V_f' = 1.19

$k = 1.17 \times 10^{-6}$ sec.$^{-1}$

$k_s = 9.85 \times 10^{-7}$ sec.$^{-1}$

$k_r = 1.87 \times 10^{-7}$ sec.$^{-1}$