SYNTHESIS AND SOLVOLYSIS OF COMPOUNDS CONTAINING THE CYCLOPROPYLCARBINYL SYSTEM

By

Joseph Mario Sandri

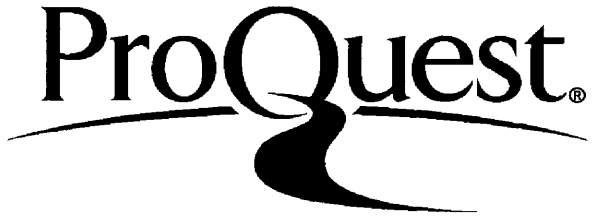
A THESIS

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

DOCTOR OF PHILOSOPHY

Department of Chemistry

1956



ACKNOWLEDGMENT

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AN ABSTRACT

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ABSTRACT

The purpose of this investigation was to obtain more information concerning the role of the cyclopropyl group in solvolysis reactions. In order to do this, p-nitrobenzoates of certain alcohols containing the cyclopropylcarbinyl system were synthesized, and their solvolysis examined.

Cyclopropyllithium was prepared for the first time from the chloride and finely divided lithium in refluxing pentane. Using cyclopropyllithium, dicyclopropyl ketone and di-(2-methylcyclopropyl) ketone as sources of cyclopropyl groups, the following tertiary carbinols were prepared: tricyclopropyl, dicyclopropylisopropyl, di-(2-methylcyclopropyl)isopropyl, dicyclopropylmethyl, and diisopropylcyclopropyl.

The attempted conversion of tricyclopropylcarbinol to the p-nitrobenzoate under a variety of conditions failed; the lithium salt with p-nitrobenzoyl chloride gave 1,1-dicyclopropyl-4-chloro-1-butene, which was also obtained from the carbinol and concentrated hydrochloric acid. This chloroolefin was converted back to tricyclopropylcarbinol when treated with aqueous potassium carbonate.

The other carbinols (except dicyclopropylmethyl) as well as dicyclopropylcarbinol and triisopropylcarbinol were converted to the p-nitrobenzoates. The rates of solvolysis of these esters in aqueous dioxane followed first-order kinetics, were not affected by hydroxide ion but were markedly increased with increasing ionizing power of the solvent,

and were the fastest recorded for aliphatic p-nitrobenzoates. The products were p-nitrobenzoic acid and the original (unrearranged) carbinols, whereas solvolysis in methanolic dioxane gave the methyl ethers of the original carbinol; formation of ethers demonstrated that the solvolyses proceeded via alkyl-oxygen fission.

The order of decreasing reactivity was di-(2-methylcyclopropyl)-isopropylcarbinyl > dicyclopropylisopropylcarbinyl >> diisopropylcyclopropylcarbinyl > dicyclopropylcarbinyl >> triisopropylcarbinyl p-nitrobenzoate. One cyclopropyl group on the carbinol carbon atom was superior to an isopropyl or t-butyl group in facilitating solvolysis, and two cyclopropyl groups were still more effective. The similarity in effect of cyclopropyl and phenyl groups was pointed out.

In certain cases, solvolysis to carbinol and p-nitrobenzoic acid was incomplete, but was accompanied by rearrangement involving opening of the cyclopropane ring. The products were allylcarbinyl esters which were not solvolysed under the reaction conditions; for example, di-isopropylcyclopropylcarbinyl p-nitrobenzoate gave 4-isopropyl-5-methyl-3-hexenyl p-nitrobenzoate as the rearrangement product.

The rates, solvent effects, enthalpies and entropies of activation, and products are all consistent with a mechanism involving ionization to ion-pairs or dissociated ions, rearranged ester being formed via internal return from the former and solvolysis products being formed from the latter or both.

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FIGURE

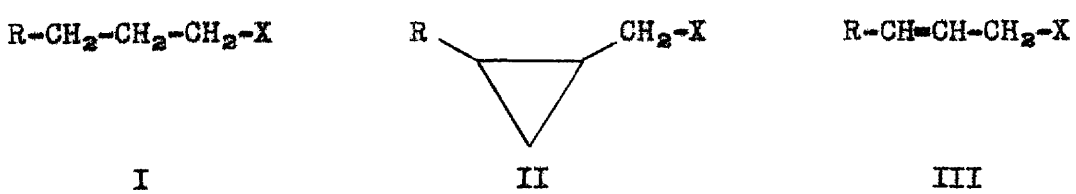
INTRODUCTION

INTRODUCTION

Chemical evidence supports the contention that the cyclopropyl group shows characteristics of unsaturation (1,2). For example, cyclopropane and its derivatives readily undergo addition reactions with halogens (3) and hydrogen halides (4). In general, addition reactions of cyclopropane derivatives occur more slowly than corresponding reactions of similarly substituted alkenes (2).

Extensive studies of physical properties, such as absorption spectra and dipole moments, also demonstrate that the cyclopropane ring is unsaturated in the sense that electrons are available to conjugate with an adjacent unsaturated group (5). In these studies, the degree with which cyclopropyl groups interact with unsaturated groups is intermediate between the activity shown by a saturated group and a vinyl group (5,6).

The type of chemical and physical behavior discussed above indicates that the degree of unsaturation of cyclopropyl groups is somewhat less than that of the alkene linkage. On this basis, it would be expected that the reactivity of the cyclopropylcarbinyl system (II) would be intermediate between that of the corresponding saturated system (I) and the highly reactive allylic (vinylcarbinyl) system (III).

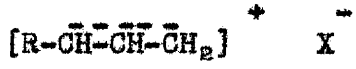


I II III

The enhanced chemical reactivity of the allylic system toward displacement reactions is ascribed to the delocalization of the pi electrons of the double bond in the transition state. For example, a unimolecular displacement in III is facilitated by resonance contributions from structures such as IVa and IVb, which may be summarized as IVc.

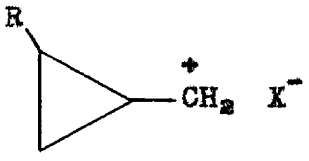
IVa

IVb

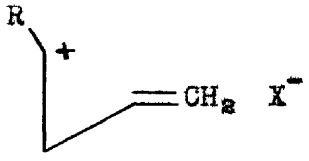


IVc

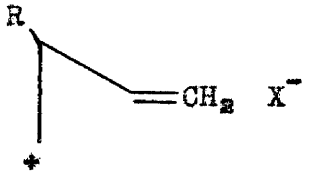
In a similar manner, the reactivity of cyclopropylcarbinyl systems in unimolecular displacement reactions should be enhanced by contributing structures such as Va, Vb and Vc which may be summarized as Vd and Ve; but judging from dipole moment and spectral data (5,6) such stabilization should be less important than in allylic systems.



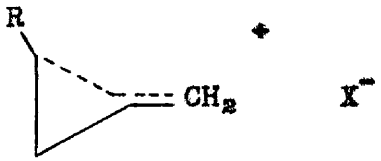
Va



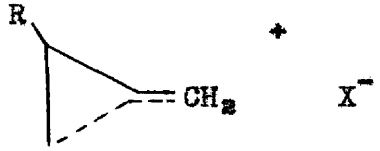
Vb



Vc

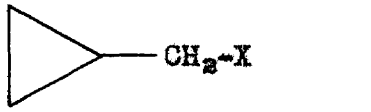


Vd

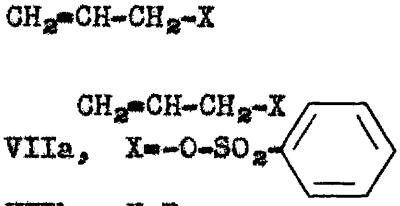


Ve

Although cyclopropylcarbinyl systems have not been extensively investigated, what information is available shows that this system is unusually reactive. Thus, the ethanolysis of cyclopropylcarbinyl benzenesulfonate (VIa) at 20° was 14 times as rapid as that of allyl benzenesulfonate (VIIa) and 1000 times as reactive as allylcarbinyl benzenesulfonate (VIII) (7).



CH_2-X



CH_2=CH-CH_2-X

VIa, X=-O-SO_2-

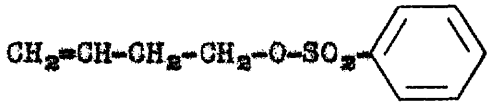
VIb, X=Cl

VIc, X=Br

CH_2=CH-CH_2-X

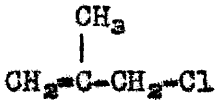
VIIa, X=-O-SO_2-

VIIb, X=Br



CH_2=CH-CH_2-CH_2-O-SO_2-

VIII



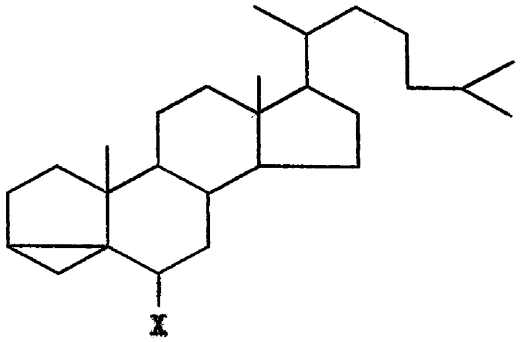
CH_2=C(-CH_3)-CH_2-Cl

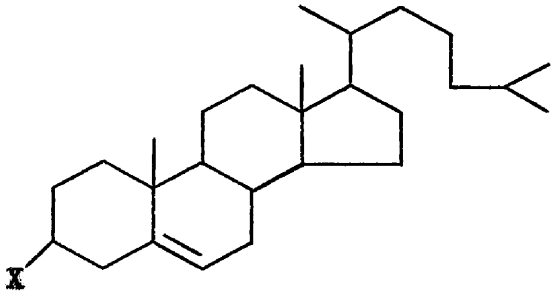
IX

The rate of solvolysis of cyclopropylcarbinyl chloride (VIb) in aqueous ethanol was 40 times faster than β-methylallyl chloride (IX) and cyclopropylcarbinyl bromide (VIc) solvolyzed 26 times faster than allyl bromide (VIIb) (8).

Polycyclic systems which contain a three-membered ring also show remarkable reactivity in solvolytic reactions. In aqueous dioxane, the rate of hydrolysis of 3,5-cyclocholestan-6-yl chloride (Xa) is about 10^8 times as rapid as cholesteryl chloride (XIa) (9a,10). Solvolysis of 3,5-cyclocholestan-6-yl trichloroacetate (Xb) yields cholesteryl

trichloroacetate (XIb) as one of the products (11). Furthermore, Xb solvolyses with alkyl-oxygen fission, whereas XIb solvolyses with acyl-oxygen fission.





Xa, X=Cl

Xb, X=CCl_3COO

XIa, X=Cl

XIb, X=CCl_3COO

The remarkable reactivity of the cyclopropylcarbinyl system certainly cannot be explained by considering the cyclopropyl group a simple but less polarizable analog of the vinyl group.

It was the purpose of the present investigation to obtain more information concerning the role of the cyclopropyl group in solvolysis reactions. In order to do this, compounds containing the cyclopropylcarbinyl system, especially those containing several cyclopropyl groups, were synthesized. The solvolysis rates of these compounds were then studied in detail.

The synthetic methods will be discussed first, followed by an experimental section containing details of the syntheses, the kinetic procedure and the structure proof for the solvolysis products.

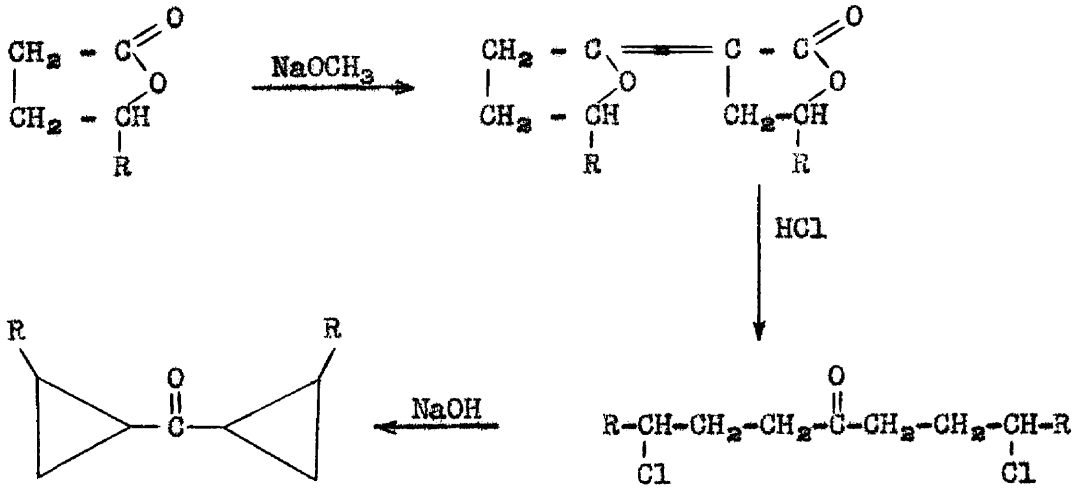
The methods for calculating rate constants, a summary of the values obtained, and a discussion of the solvolysis products follows in a section on results. The detailed kinetic data is presented in an Appendix. Following the section on results, the present solvolysis data are discussed in terms of current concepts of unimolecular solvolyses, and the role of the cyclopropyl group in solvolysis reactions is examined in detail.

DISCUSSION OF SYNTHETIC PROCEDURES

DISCUSSION OF THE SYNTHETIC PROCEDURES

A route to secondary and tertiary alcohols containing one or more cyclopropyl groups on the alcoholic carbon atom was desired, for these alcohols could then be converted to derivatives whose solvolysis behavior might be studied. Important intermediates in making these alcohols would be aldehydes or ketones containing cyclopropyl groups, and/or a cyclopropylorganometallic compound.

Dicyclopropyl ketone (Ia), which afforded an entry, via reaction with organometallics, to polycyclopropylated alcohols, has recently been made readily available (12). The procedure has been modified in the present work, so that it is not necessary to isolate any intermediates (13). The over-all yield from γ-butyrolactone is about 60%. The homologous ketone, di-(2-methylcyclopropyl) ketone (Ib) was prepared by an analogous method.



Ia, R=H

Ib, R=CH_3

The infrared spectrum of Ib appears in Figure 1.

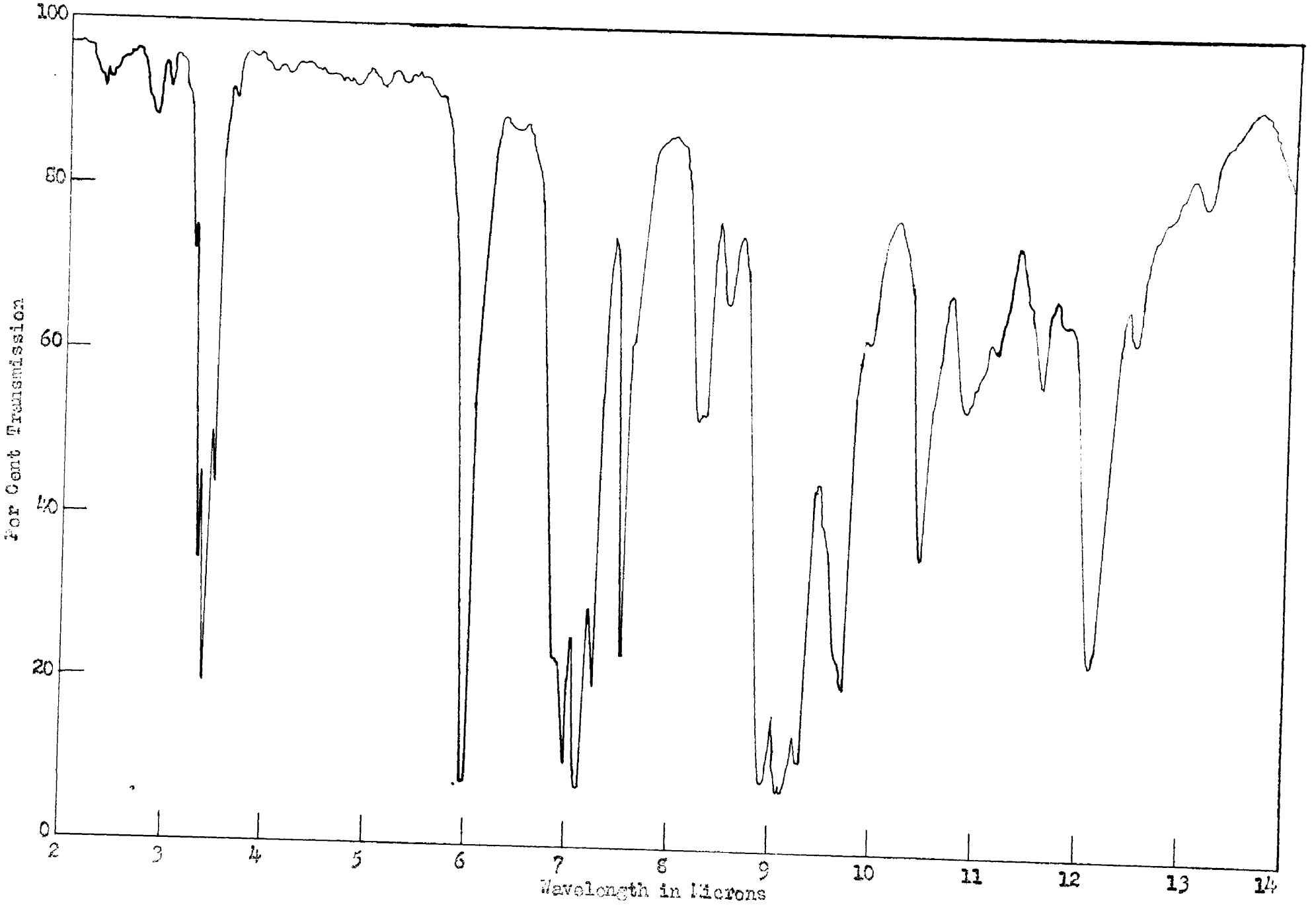


Figure 1. Infrared Spectrum of Di-(2-methylcyclopropyl) ketone (neat)

A readily available cyclopropylorganometallic would greatly facilitate the synthesis of compounds containing the cyclopropyl group. It had been reported that cyclopropyl bromide reacted readily with magnesium, whereas the chloride reacted only very slowly and incompletely (14). The only method found in the literature for the preparation of cyclopropyl bromide involved bromination of silver cyclopropanecarboxylate at -70° in a Freon solvent (14). This method is tedious and limited to small quantities because of the explosiveness of the bromine-silver salt complex. Cyclopropyl chloride, on the other hand, was more easily obtained by a method suitable to preparation in quantity. The procedure described by Roberts (15), involving the vapor phase photochemical chlorination of cyclopropane, was used.

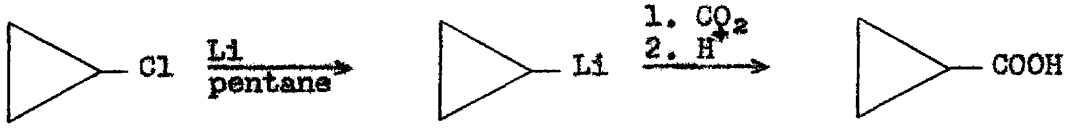
Because of the unreactivity of cyclopropyl chloride, the preparation and use of cyclopropylmagnesium chloride did not appear practical. There was, however, some reason to believe that cyclopropyl chloride would react more readily and more completely with lithium than with magnesium.

It had been reported that cyclopropyl chloride reacted with an ether suspension of lithium so vigorously that external cooling with dry ice was necessary to contain the mixture (16). The major product was cyclopropane, 32% of the chloride being reduced during the reaction and an additional 10% of cyclopropane being formed on hydrolysis. Other products were recovered chloride (21%), dicyclopropyl (10-12%), olefins, acetylenes and tar. It seemed likely that cyclopropyllithium was an intermediate in the formation of certain of these products, but

its presence was not established. It was also reported that no reaction occurred between cyclopropyl chloride and lithium in methylcyclohexane.

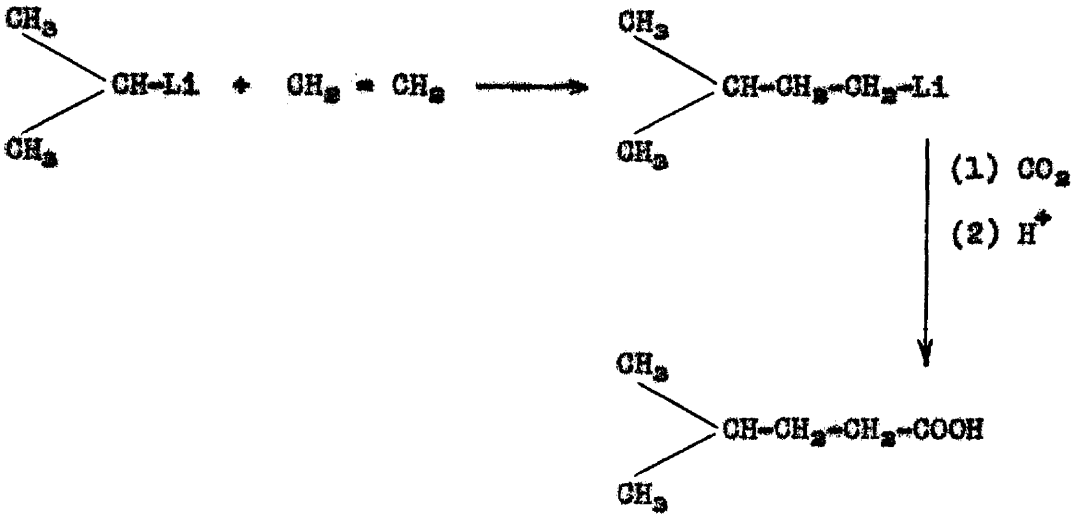
Synthesis of cyclopropyllithium by the normal method for preparing organolithium compounds was not considered practical. Ether could not be used as solvent because secondary and tertiary organolithiums cleave ether at ordinary temperatures. Although some secondary and tertiary organolithiums have been prepared in ether at low temperatures (-70 to -40°) (17,18), this was not considered feasible for the relatively unreactive cyclopropyl chloride. However, low boiling hydrocarbon solvents such as petroleum ether have been used to prepare lithium alkyls (19). This suggested the use of pentane as a solvent. In order to speed up what was anticipated would be a sluggish reaction, lithium in a high state of subdivision was used.

When cyclopropyl chloride and finely powdered lithium metal were refluxed in pentane under a helium atmosphere, the lithium was consumed and replaced by a suspension of cyclopropyllithium and lithium chloride. The structure was proved by carbonation to cyclopropanecarboxylic acid (II), identified by its physical properties and infrared spectrum. Helium was used in place of nitrogen because lithium forms the nitride when exposed to nitrogen, especially warm nitrogen (20). It was feared that with finely divided lithium, this problem might be even more than ordinarily serious, although no critical experiments bearing on this point were performed.



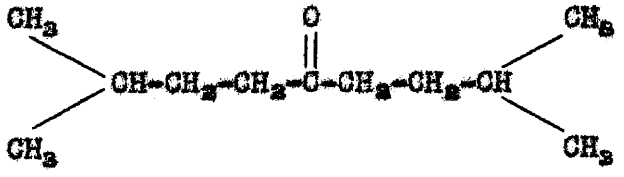
II

Cyclopropyllithium could not be induced to react with ethylene, whereas under similar conditions the addition of isopropyllithium to ethylene, followed by carbonation, gave isocaproic acid (III), identified by its physical properties and infrared spectrum.



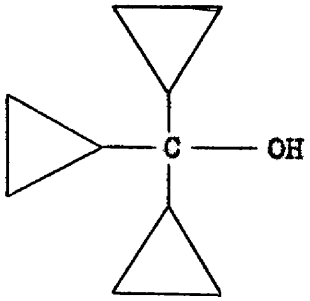
III

No diisoamyl ketone (IV) was isolated (18).

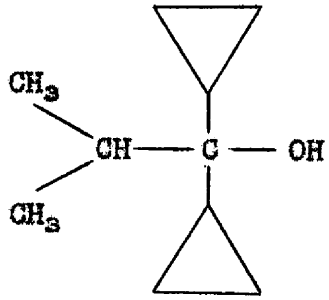


IV

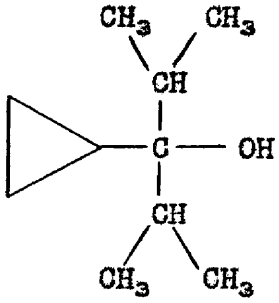
By treatment of either cyclopropyllithium or isopropyllithium with the appropriate ketone, the following carbinols were synthesized in good yield: tricyclopropylcarbinol (V), dicyclopropylisopropylcarbinol (VI), diisopropylcyclopropylcarbinol (VII), triisopropylcarbinol (VIII), and di-(2-methylcyclopropyl) isopropylcarbinol (IX).



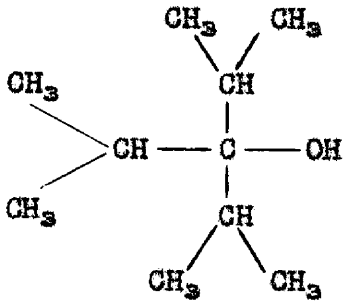
V



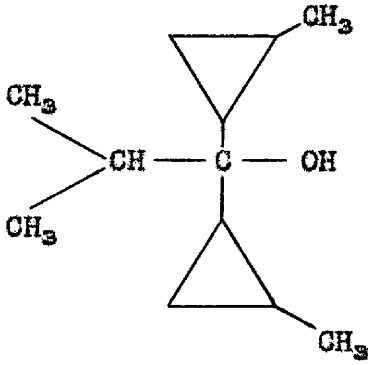
VI



VII



VIII



IX

The infrared spectra of the pure carbinols V, VI, VII and IX appear in Figures 2, 3, 4 and 5.

The lithium salt of each of the carbinols VI, VII, VIII and IX was treated with p-nitrobenzoyl chloride to yield the crystalline p-nitrobenzoates X, XI, XII and XIII respectively. The last of these decomposed to a yellow liquid when allowed to stand, and was quite sensitive to moisture.

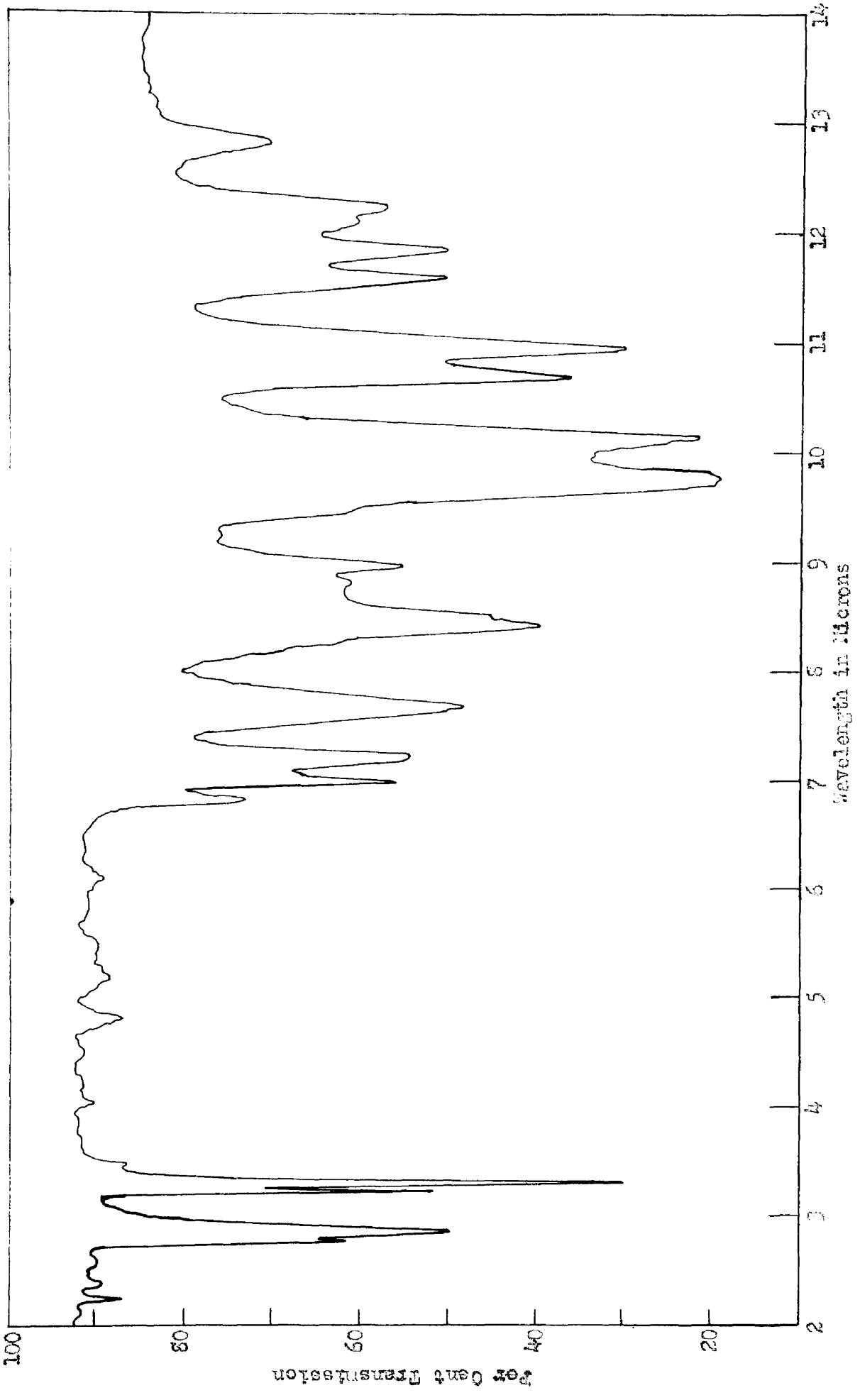


Figure 2. Infrared Spectrum of Tricyclopropylcarbinol (neat).

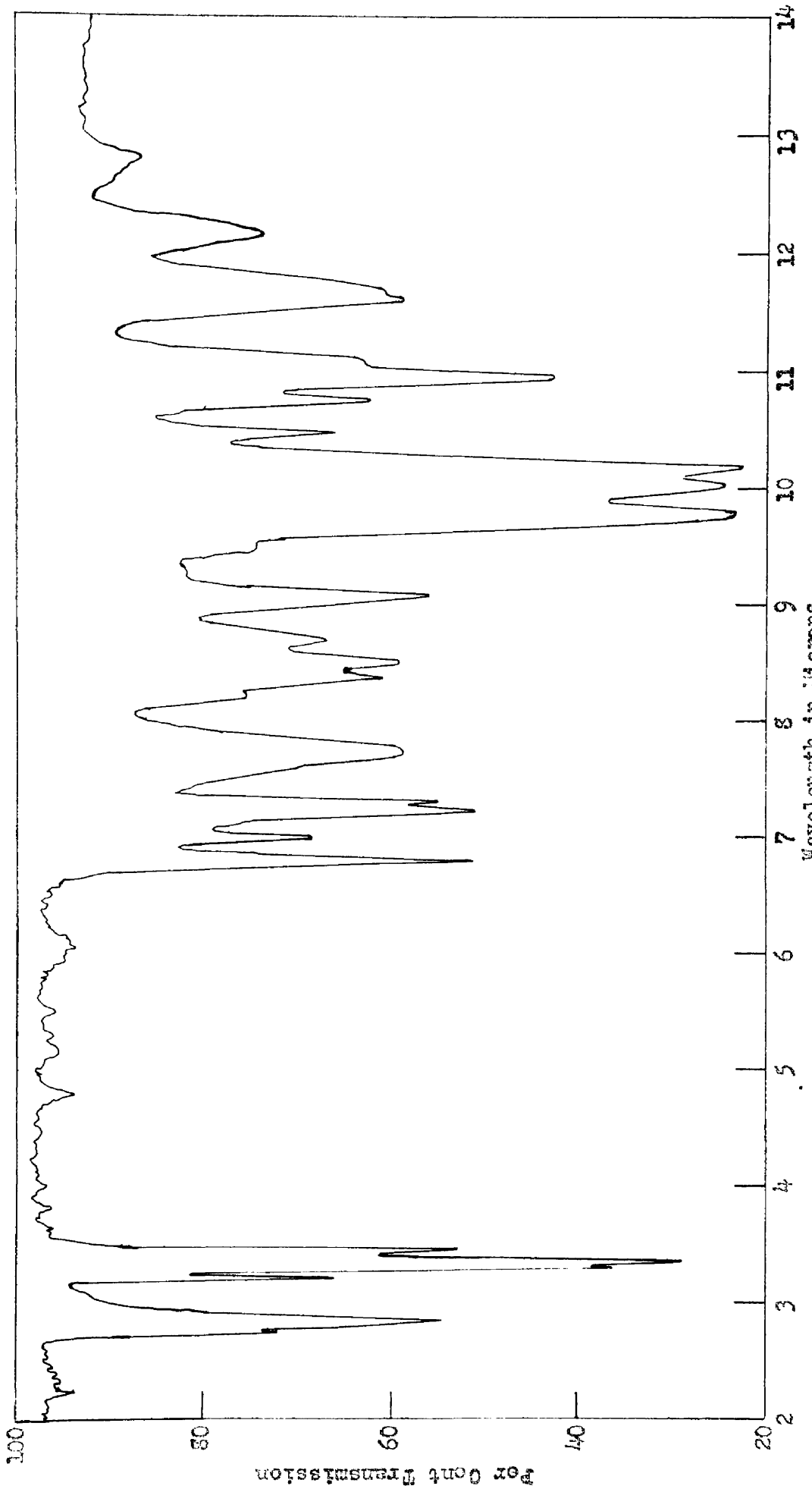


Figure 3. Infrared Spectrum of Dicyclopropylisopropylcarbinol (neat).

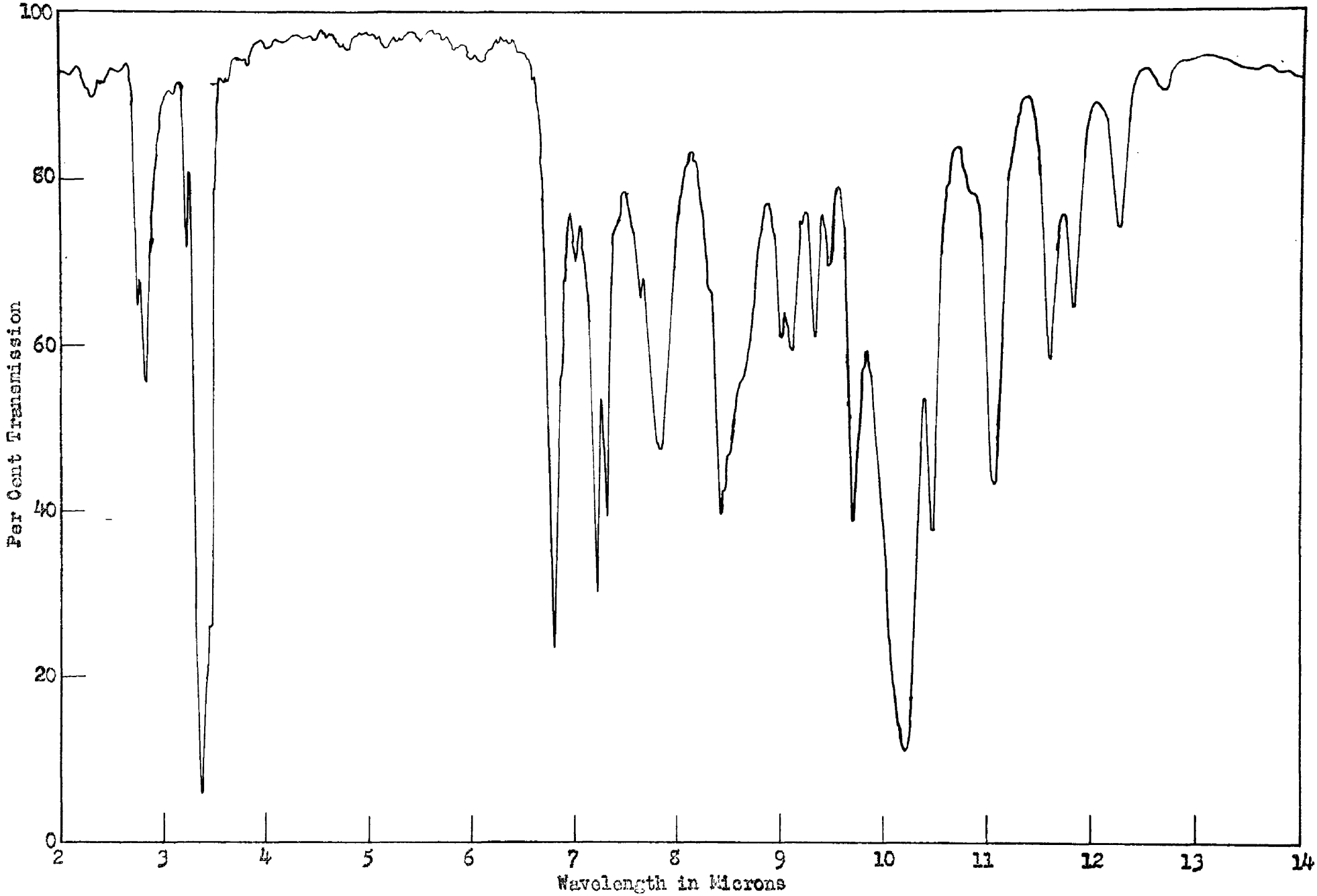


Figure 4. Infrared Spectrum of Diisopropylcyclopropylcarbinol (neat).

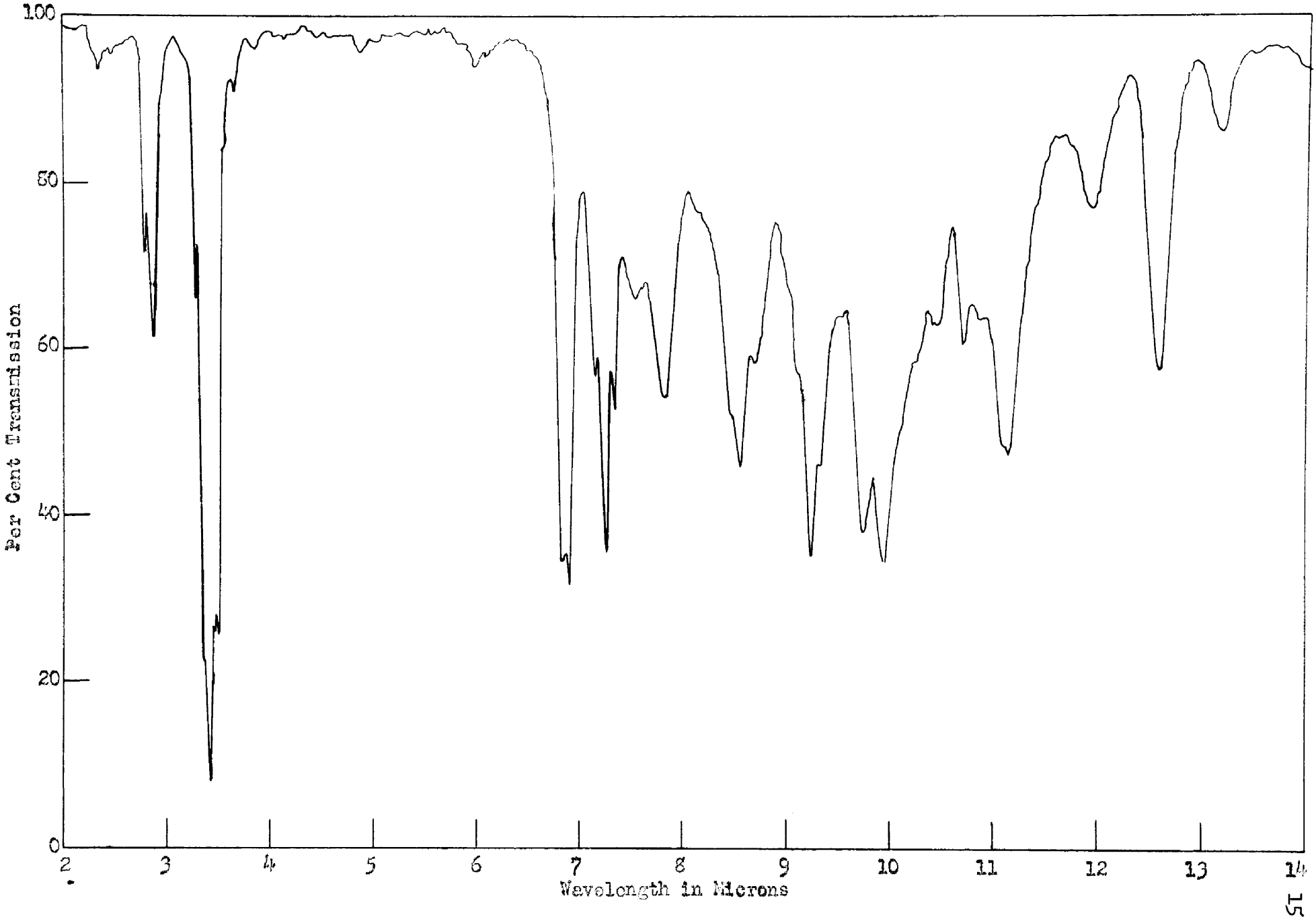
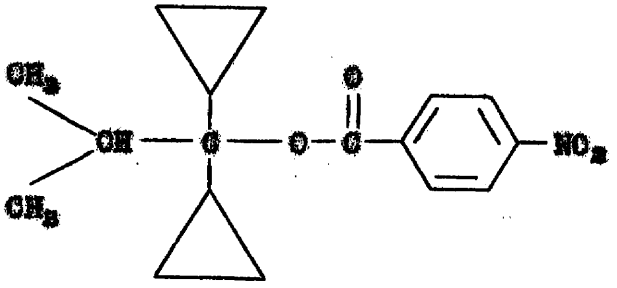
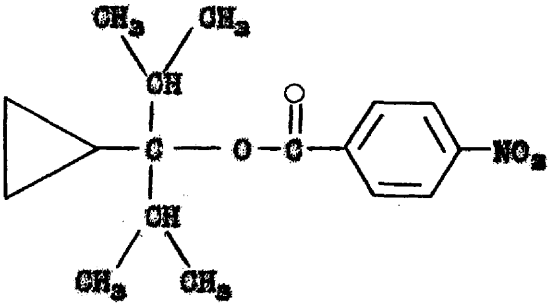


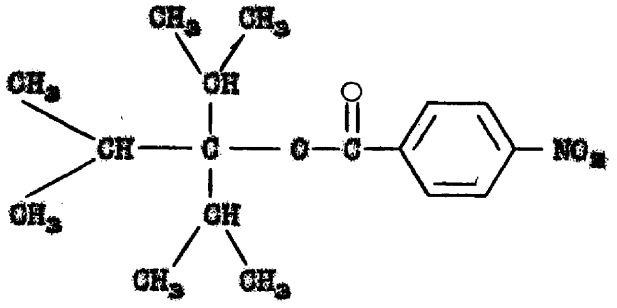
Figure 5. Infrared Spectrum of Di-(2-methylcyclopropyl)isopropylcarbinol (neat).



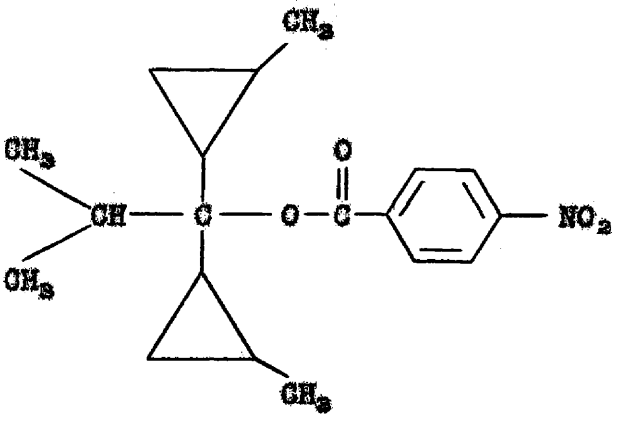
X



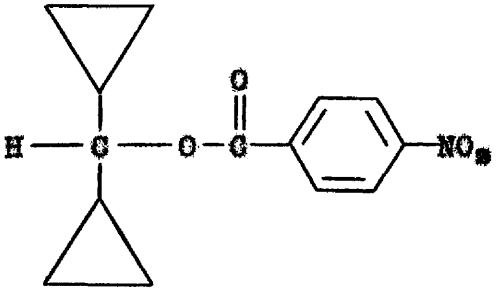
XI



XII



XIII



XIV

Dicyclopropylcarbinyl p-nitrobenzoate (XIV) was obtained from dicyclopropylcarbinol and p-nitrobenzoic acid in the presence of benzenesulfonyl chloride in pyridine solution, using a procedure patterned after Brewster (21).

The infrared spectra of mineral oil mulls of these esters appear in Figures 6, 7, 8, 9, and 10.

Attempts to prepare tricyclopropylcarbinyl p-nitrobenzoate from the lithium salt of tricyclopropylcarbinol and p-nitrobenzoyl chloride or p-nitrobenzoic anhydride were unsuccessful. Treatment of the potassium salt of tricyclopropylcarbinol with p-nitrobenzoyl chloride did not yield the desired ester. The method used for the preparation of dicyclopropylcarbinyl p-nitrobenzoate also failed when applied to tricyclopropylcarbinol. The reasons for the failure to synthesize tricyclopropylcarbinyl p-nitrobenzoate will be more profitably discussed in a subsequent portion of this dissertation.

The product obtained from the reaction of the lithium salt of tricyclopropylcarbinol with p-nitrobenzoyl chloride was 1,1-dicyclopropyl-4-chloro-1-butene (XV), identical with the product formed when tricyclopropylcarbinol was treated with concentrated hydrochloric acid.

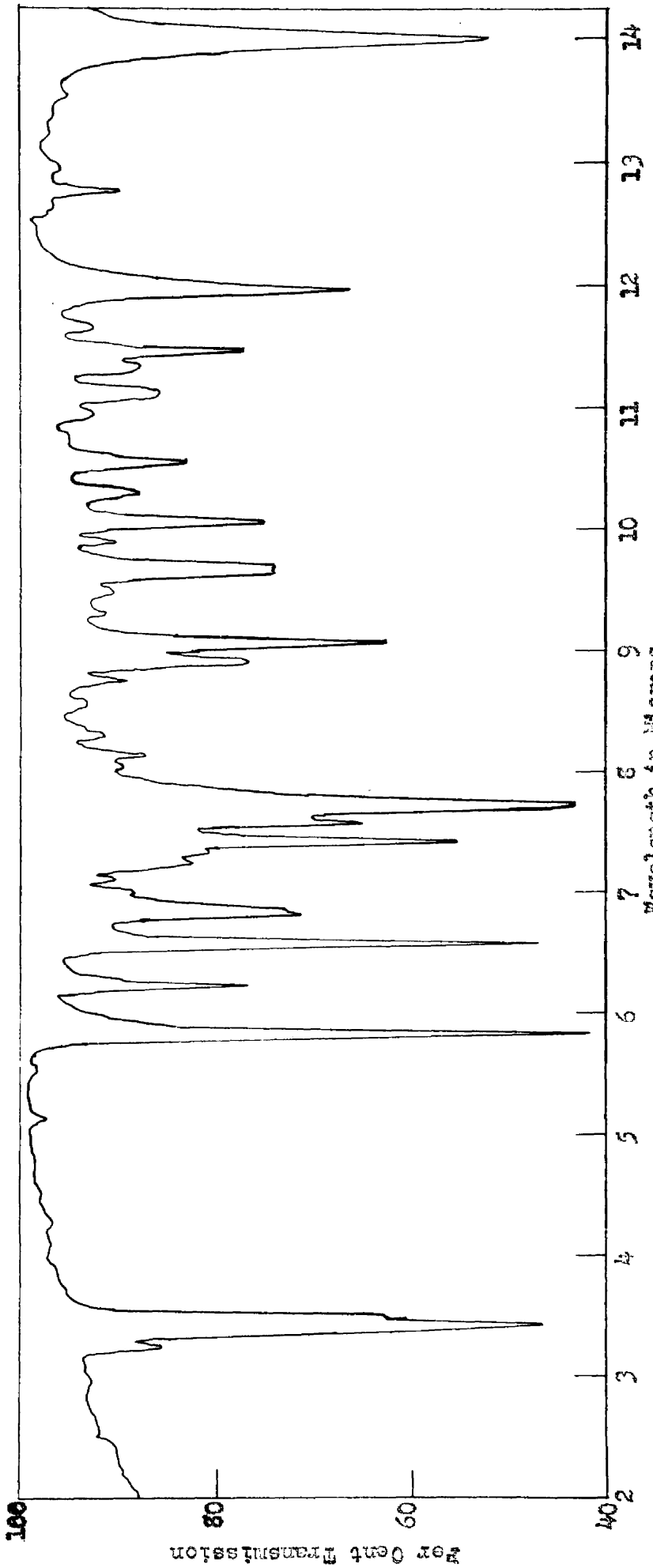


Figure 6. Infrared Spectrum of Dicyclopropylisopropylcarbinyl p-Nitrobenzoate (mineral oil mull).

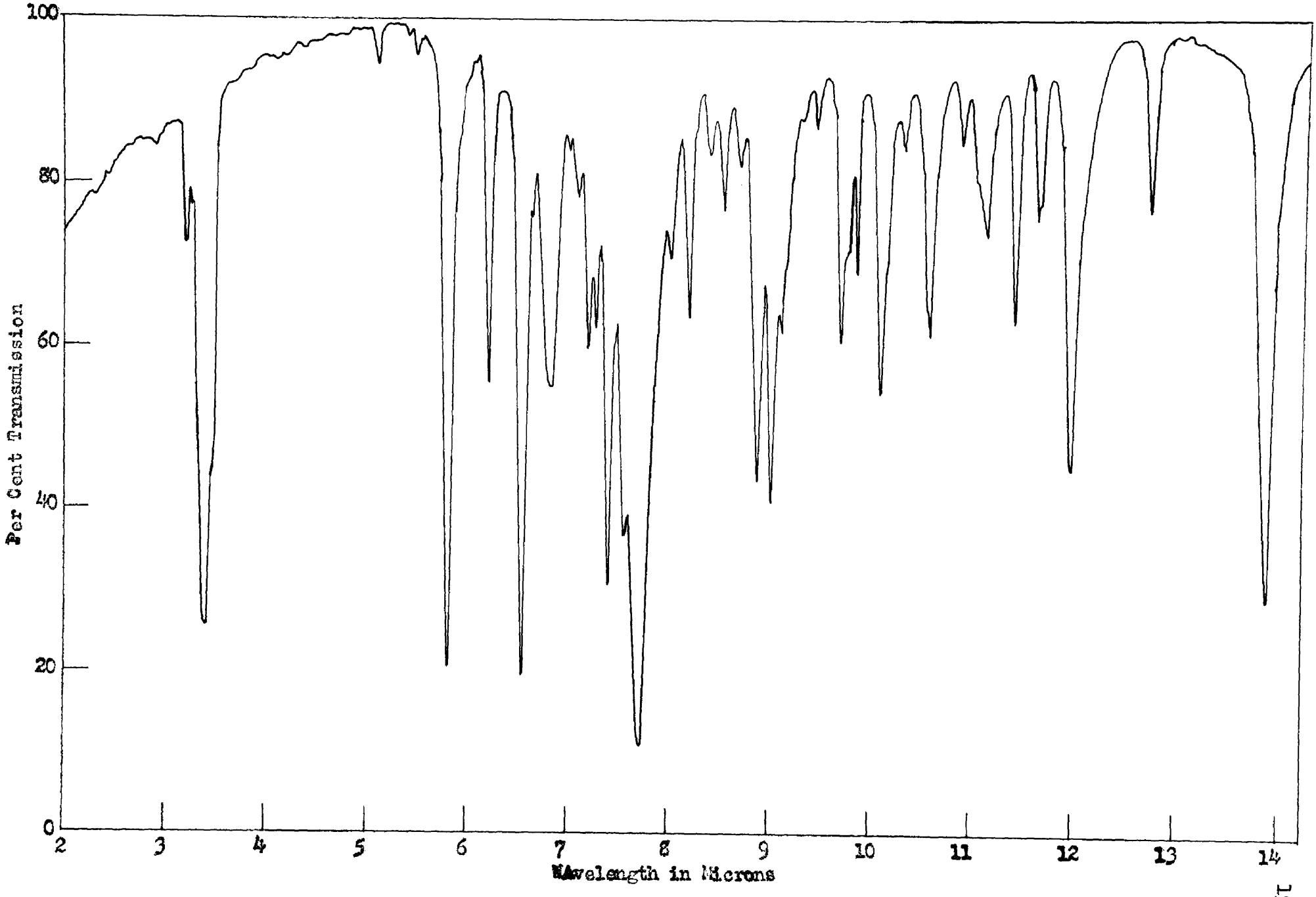


Figure 7. Infrared Spectrum of Diisopropylcyclopropylcarbinyl p-Nitrobenzoate (mineral oil mull).

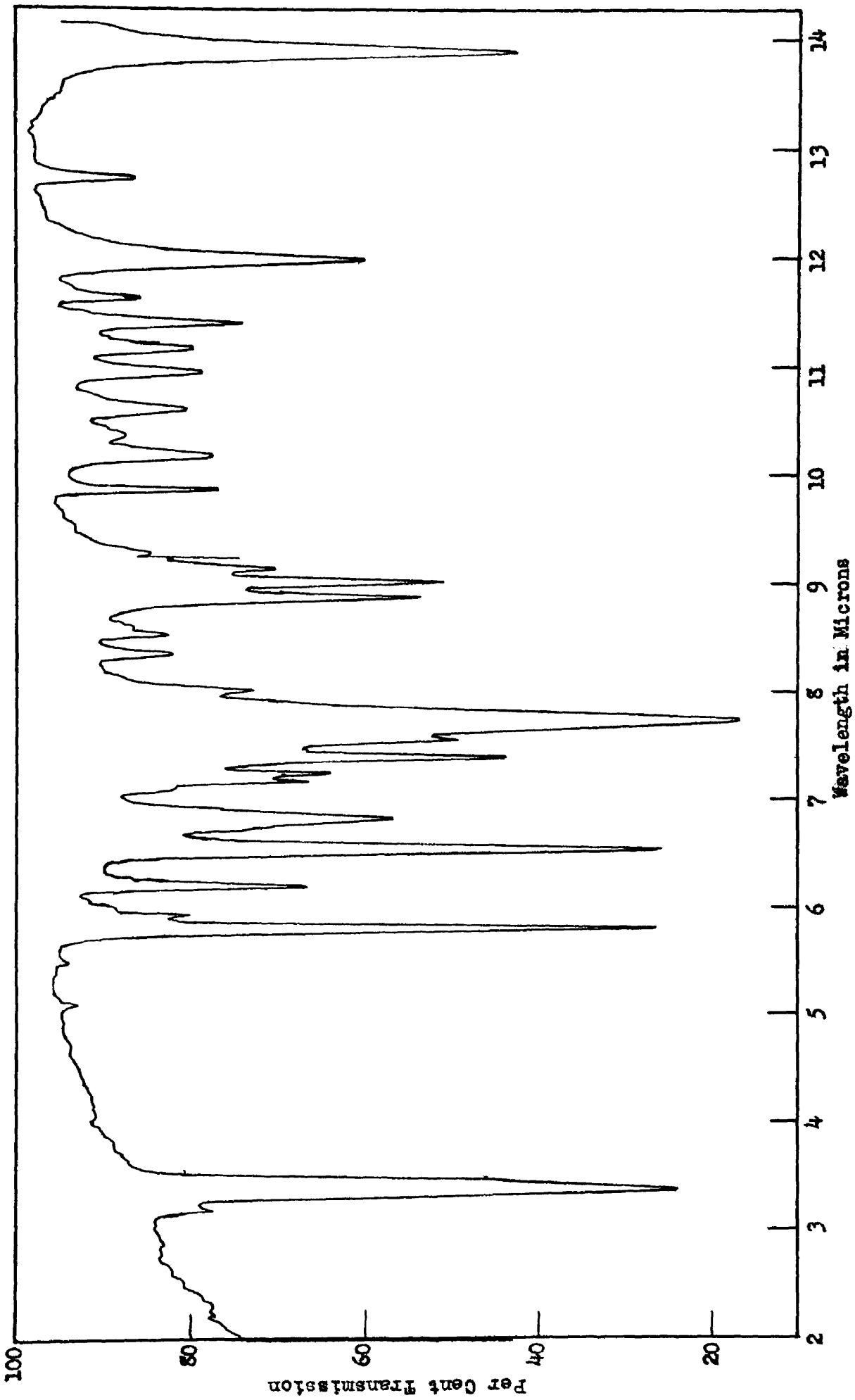


Figure 8. Infrared Spectrum of Triisopropylcarbinyl p-Nitrobenzoate (mineral oil mull).

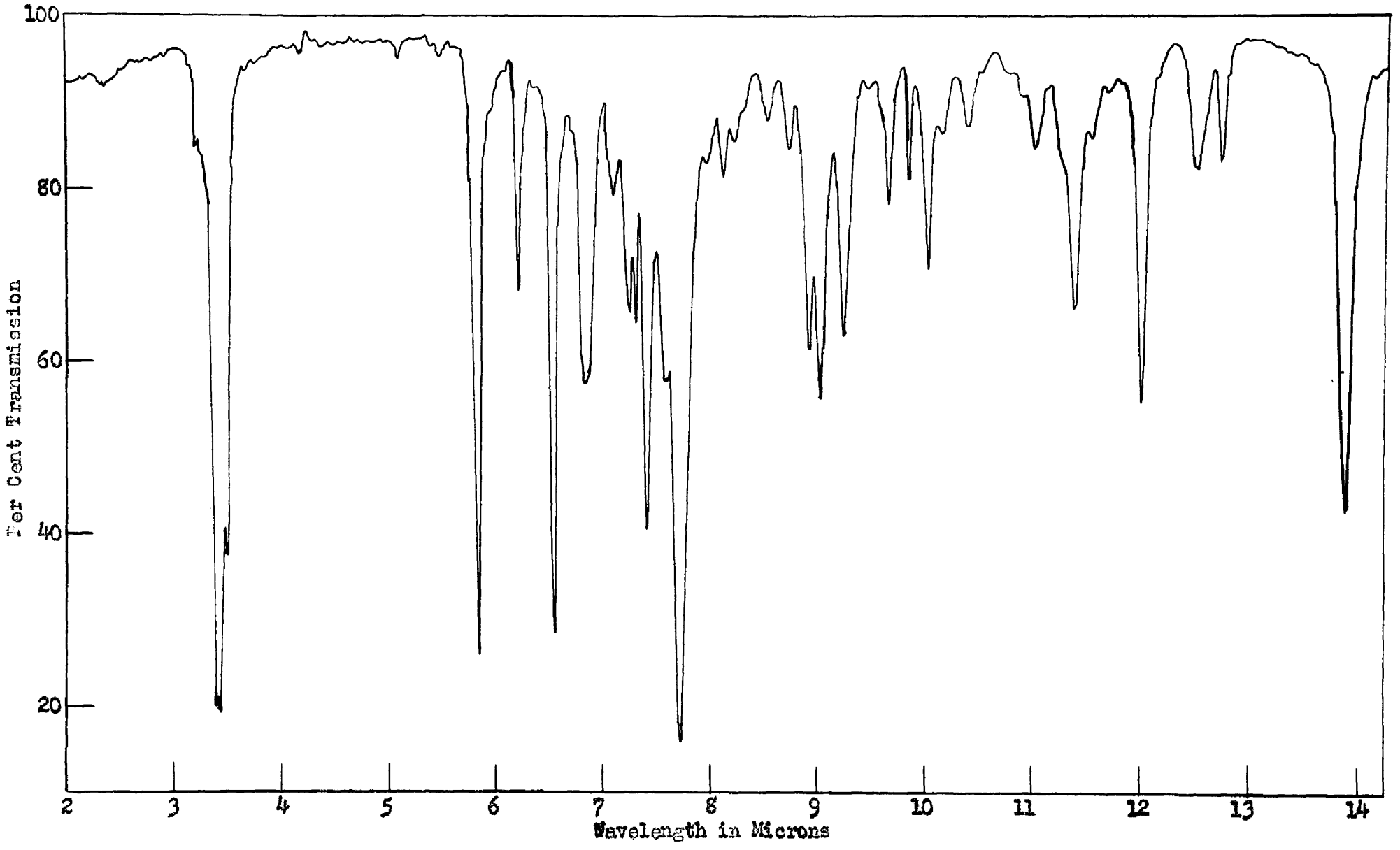


Figure 9. Infrared Spectrum of Di-(2-methylcyclopropyl)isopropylcarbinyl p-Nitrobenzoate (mineral oil mull).

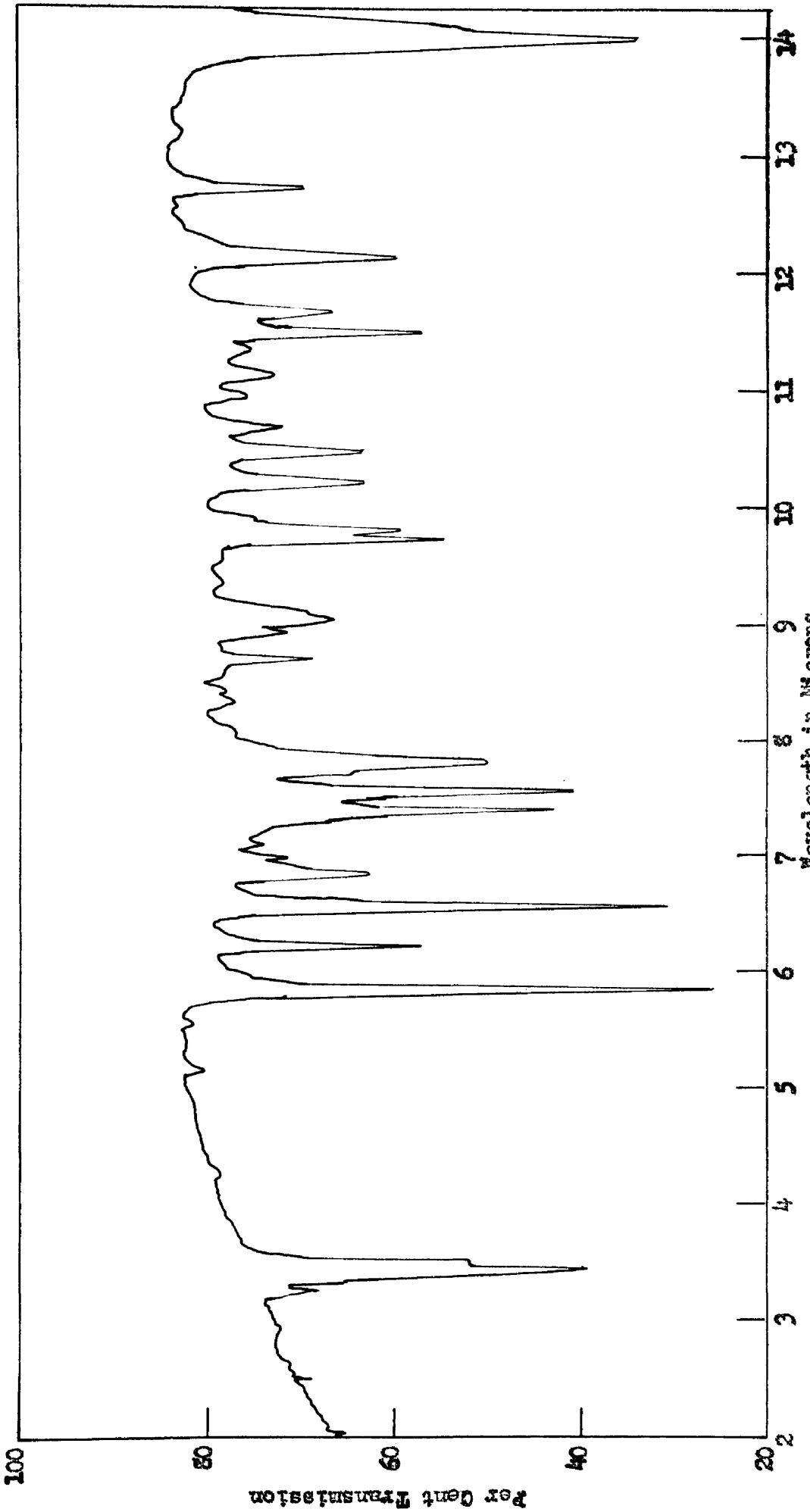
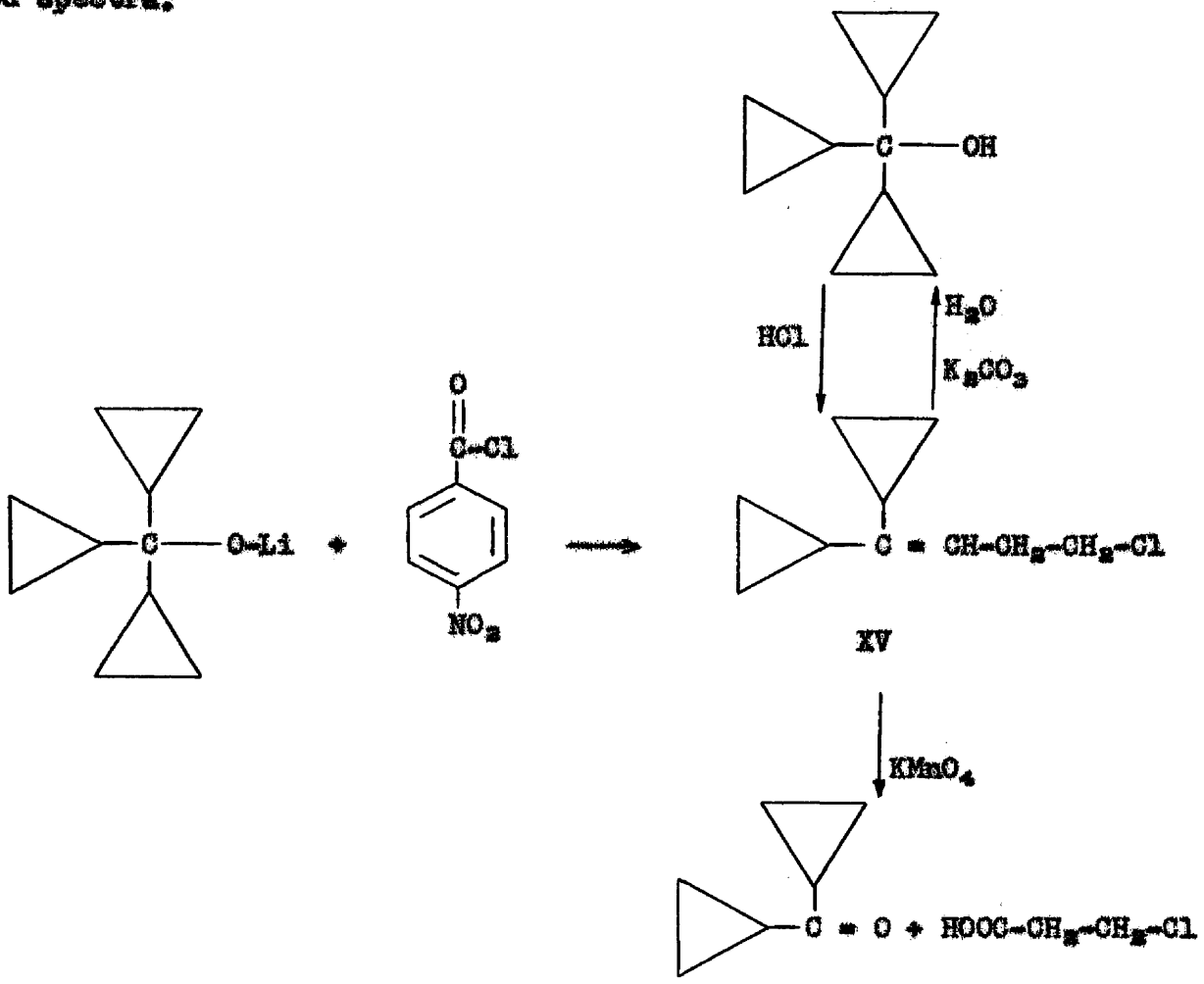


Figure 10. Infrared Spectrum of Diacyclopropylcarbinyl p-Nitrobenzoate (mull in mineral oil).

The structure of 1,1-dicyclopropyl-4-chloro-1-butene was proved by oxidation with potassium permanganate to dicyclopropyl ketone and β-chloropropionic acid. Both products were identified by their infrared spectra.



Furthermore, when 1,1-dicyclopropyl-4-chloro-1-butene was refluxed with aqueous potassium carbonate, it was reconverted to tricyclopropylcarbinol, identified by its infrared spectrum. This reaction will also be discussed in more detail in a subsequent section. The infrared spectrum of 1,1-dicyclopropyl-4-chloro-1-butene appears in Figure 11.

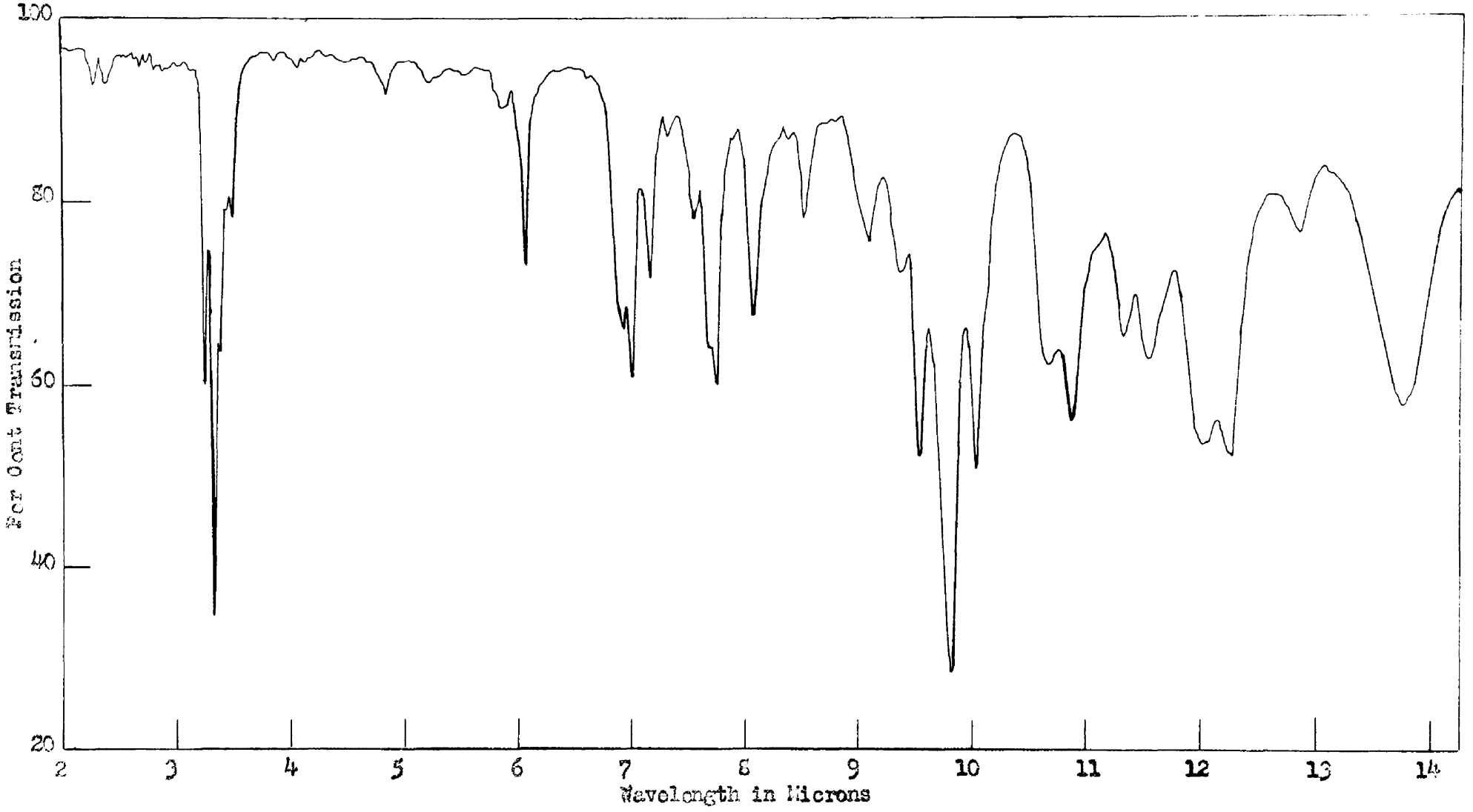


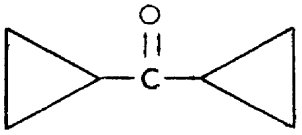
Figure 11. Infrared Spectrum of 1,1-Dicyclopropyl-4-chloro-1-butene (neat).

EXPERIMENTAL

EXPERIMENTAL

A. Syntheses

Dicyclopropyl Ketone (13)

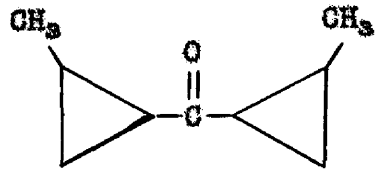


A 5-l. three-necked round-bottomed flask was equipped with a Hershberg stirrer, a dropping funnel and a reflux condenser. In this flask 69 g. (3 g. atoms) of metallic sodium was dissolved in 900 ml. absolute methanol. When all the sodium had dissolved, the solution was maintained at a gentle reflux and 516 g. (6 moles) of γ-butyrolactone (commercial grade) was added dropwise with stirring over a period of 30 minutes. The solution was refluxed for three hours, after which time the flask was equipped for distillation and the methanol removed in vacuo leaving a highly viscous residue. The flask was again fitted with a reflux condenser and dropping funnel, and cooled in an ice bath. Before the viscous residue solidified, concentrated hydrochloric acid was cautiously added with vigorous stirring until the mixture became more mobile. At this time the rate of addition was increased. After 1200 ml. of hydrochloric acid had been added, the mixture was refluxed with vigorous stirring for one hour. The flask was again cooled in an ice bath and a solution of 720 g. of sodium hydroxide in 1 l. of water was cautiously added. The mixture was then

refluxed with vigorous stirring for one hour. The flask was then equipped for distillation and a water-ketone mixture was distilled until the strong characteristic odor of dicyclopropyl ketone was no longer detected in the distillate. The aqueous layer of the distillate was saturated with potassium carbonate and the upper layer of dicyclopropyl ketone was separated. The aqueous layer was extracted with three 100-ml. portions of ether. The combined extracts and the ketone layer were dried over anhydrous magnesium sulfate and distilled through an efficient column. The yield of dicyclopropyl ketone, b.p. 58° at 14 mm., n_D^{25} 1.4654, was 200 g. (60%). This preparation was equally successful when 3 moles of commercial sodium methoxide was used in place of 3 g. atoms of metallic sodium.

Alternatively, immediately after all the γ-butyrolactone had been added, the methanol was removed by slow distillation at atmospheric pressure and the last traces removed *in vacuo*. This variation shortened the time required for the synthesis and did not affect the yield.

Di-(2-methylcyclopropyl) ketone



The procedure was essentially the same as that described in detail for the preparation of dicyclopropyl ketone. The best results were obtained when the methanolic solution was refluxed for three hours and the methanol removed by distillation *in vacuo*. From 600 g. (6 moles)

of γ -valerolactone (Eastman Kodak's practical grade) and 180 g. (3 moles + 5% inert material) of commercial sodium methoxide (Matheson, Coleman and Bell) in 900 ml. of methanol, there was obtained a 50% yield of (di-(2-methylcyclopropyl) ketone, b.p. 66° at 7 mm., n_D^{25} 1.4600-1.4604.

Anal. Calc'd. for $C_9H_{14}O$: C, 78.21; H, 10.21

Found: C, 78.08, 78.11; H, 10.39, 10.44

(Analyses in this thesis were performed by either Clark Microanalytical Laboratory, Urbana, Illinois, Micro-Tech Laboratories, Skokie, Illinois, or Spang Microanalytical Laboratory, Ann Arbor, Michigan)

The 2,4-dinitrophenylhydrazone was prepared (22) and after recrystallization from 95% ethanol melted at 101-102°.

Anal. Calc'd. for $C_{15}H_{18}N_4O_4$: C, 56.59; H, 5.70; N, 17.60

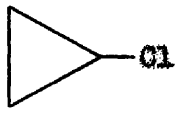
Found: C, 56.88, 56.94; H, 5.56, 5.51; N, 17.49, 17.53

Finely Divided Lithium

A 1-l. three-necked flask equipped with a Labline Stir-O-Vac high-speed stirrer (obtained from the Arthur S. LaPine Co., Chicago, Ill.), thermometer, condenser, and gas inlet tube, was charged with 14 g. (2 moles) of lithium and 100 ml. of mineral oil (previously dried over sodium). The mineral oil was heated (helium atmosphere) to 230°, the source of heat was removed and the molten lithium was whipped into a fine powder with the stirrer. After the suspension had cooled, the stirrer was stopped and a gas dispersion tube was inserted into the flask so that the sintered glass portion touched the bottom of the flask (the lithium particles float on top of the mineral oil). The system was closed and a vacuum was applied to the open end of the gas dispersion tube, the mineral oil being collected in a trap. The lithium powder was then washed with several portions of n-pentane

(previously dried over sodium). Although very fine shiny particles of lithium resulted, this method of removing the mineral oil was somewhat long and tedious. Alternatively, the lithium powder was filtered with suction through a sintered glass funnel, washed with pentane, and poured, with pentane rinses, into the reaction flask. When this operation was done rapidly, clean lithium particles were obtained.

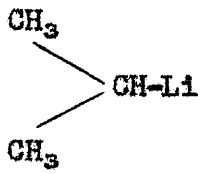
Cyclopropyl Chloride



Cyclopropyl chloride was prepared by the vapor phase photochemical chlorination of cyclopropane. The apparatus was essentially that of Roberts and Dirstine (15), except that the recycling system was eliminated. The reaction chamber consisted of 250 cm. of 0.7 cm. Pyrex tubing bent to form a planar grid which was illuminated by two Ken-Rad RS sunlamps. Gas flow of reactants was regulated to approximately 0.10 mole cyclopropane per minute and 0.033 mole chlorine per minute. The unreacted cyclopropane and the chlorinated products were caught in a cold trap and the excess cyclopropane was recovered and recyclized. In a typical preparation, there was obtained 500 g. (6.5 moles) of cyclopropyl chloride, b.p. 43.5°, n_D^{25} 1.4080 from 14.3 moles of cyclopropane consumed, a yield of 45%. The reported physical properties of cyclopropyl chloride are b.p. 43.43°, n_D^{25} 1.4079. The infra-red spectrum of the product obtained was identical with the spectrum reported by Slabey (16)

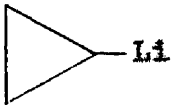
for cyclopropyl chloride. No attempt was made to purify the higher boiling polychlorinated products.

Isopropyllithium



A 1-l. three-necked round-bottomed flask equipped with stirrer, condenser, dropping funnel and gas inlet tube was charged under an atmosphere of helium with a suspension of powdered lithium (14 g., 2 moles) in 300 ml. of pentane. Isopropyl chloride (78.5 g., 1 mole) in 100 ml. of pentane was slowly added with vigorous stirring over a period of about two hours at a rate sufficient to maintain reflux. The mixture was refluxed with stirring for an additional hour. An approximate acidimetric analysis of an aliquot indicated that about 0.6 moles (60%) of isopropyllithium was present.

Cyclopropyllithium (23)

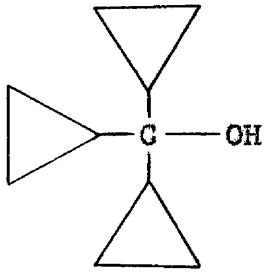


A 1-l. three-necked round-bottomed flask equipped with high-speed stirrer, condenser, dropping funnel and helium gas inlet tube was charged with a suspension of powdered lithium (9.8 g., 1.4 moles) in 300 ml. of pentane. Cyclopropyl chloride (54 g., 0.7 mole) was added in one portion and the mixture was refluxed with vigorous stirring for

ten hours, at which time essentially all the lithium had reacted resulting in a suspension of cyclopropyllithium and lithium chloride. Acidimetric analysis of the solution was not reliable because of the low solubility of cyclopropyllithium in pentane. The reaction between cyclopropyl chloride and lithium was, on occasion, hastened by adding a few drops of ethyl bromide to help initiate the reaction.

When carbon dioxide gas was passed into a solution of cyclopropyllithium at -70° and the resulting mixture acidified, cyclopropanecarboxylic acid, identified by its infra-red spectrum, was obtained. No dicyclopropyl ketone was isolated.

Tricyclopropylcarbinol



To a solution of cyclopropyllithium in pentane, prepared from 9.8 g. (1.4 moles) of powdered lithium and 54 g. (0.7 mole) of cyclopropyl chloride, was slowly added a solution of dicyclopropyl ketone (77 g., 0.7 mole) in 30 ml. of pentane. The mixture was refluxed with stirring for 8 hours. The flask was then cooled in an ice bath and 300 ml. of cold water was slowly added. The upper organic layer was separated and the aqueous layer was extracted with three 70-ml. portions of ether. The extracts were combined with the organic layer and dried over anhydrous magnesium sulfate. After removal of the solvent, there

was obtained 20 g. of unchanged dicyclopropyl ketone and 74 g. of tricyclopropylcarbinol, b.p. 88.5° at 10 mm., n_D^{20} 1.4825, n_D^{25} 1.4802. The yield was 70% based on the amount of cyclopropyl chloride used or 94% based on the amount of ketone consumed.

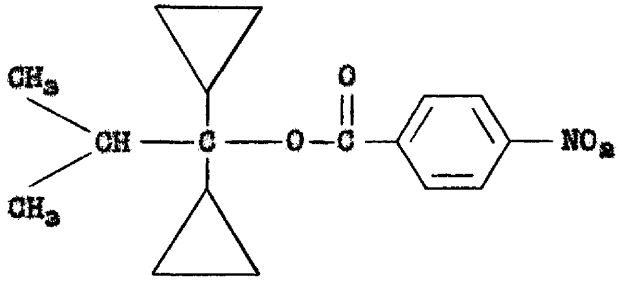
Anal. Calc'd. for $C_{10}H_{16}O$: C, 78.89; H, 10.59

Found: C, 78.52, 78.60; H, 10.49, 10.65

Other Carbinols Containing the Cyclopropyl Group

Using procedures analogous to that described for the preparation of tricyclopropylcarbinol, the carbinols in Table 1, were prepared from the indicated ketones and organometallics. The physical properties, yields and analyses of the carbinols are given in Table 2.

Dicyclopropylisopropylcarbinyl p-nitrobenzoate



The lithium salt of dicyclopropylisopropylcarbinol was prepared in pentane solvent as previously described from 28 g. (4 g. atoms) of lithium, 157 g. (2 moles) of isopropyl chloride, and 220 g. (2 moles) of dicyclopropyl ketone. The flask was cooled in an ice-salt bath and a solution of p-nitrobenzoyl chloride (223 g., 1.2 moles) in 1800 ml. of dry ethyl ether was slowly added, and the temperature maintained

Table 1

Preparation of Certain Carbinols Containing the Cyclopropyl Group

Carbinol	Ketone	Organometallic
Tricyclopropyl	Dicyclopropyl	Cyclopropyllithium
Dicyclopropylisopropyl	Dicyclopropyl	Isopropyllithium Isopropylmagnesium chloride
Di-(2-methylcyclopropyl) isopropyl	Di-(2-methylcyclopropyl)	Isopropyllithium
Dicyclopropylmethyl	Dicyclopropyl	Methylmagnesium iodide
Diisopropylcyclopropyl	Diisopropyl	Cyclopropyllithium
Triisopropyl*	Diisopropyl	Isopropyllithium

*Although this carbinol does not contain the cyclopropyl group it is included in the table because it was prepared and used as a reference compound in subsequent studies.

Table 2

Physical Properties, Yields and Analyses of Several Tertiary Carbinols Containing the Cyclopropyl Group

Carbinol	Boiling Point °C	Boiling Point mm.	n_D^{25}	Yield	Percent Carbon Calc'd.	Percent Carbon Found	Percent Hydrogen Calc'd.	Percent Hydrogen Found
Tricyclopropyl	88.5	10	1.4802	94%	78.89	78.52 78.60	10.59	10.49 10.65
Dicyclopropylisopropyl	81	10	1.4648	69 67[a]	77.87	77.72	11.76	11.56
Di-(2-methylcyclopropyl)isopropyl	67	3	1.4570	83	79.06	79.12 79.18	12.17	12.22 12.08
Dicyclopropylmethyl	45	4	1.4618	70	76.14	75.93	11.18	10.89
Diisopropylcyclopropyl	75	10	1.4518	75	76.86	77.08	12.90	13.12
Triisopropyl[b]	74	10	1.4460	58	a known compound			

[a] From isopropylmagnesium chloride.

[b] Although this carbinol does not contain the cyclopropyl group, it is included in this table because it was prepared and used as a reference compound in subsequent studies.

between -5 and 0°. The flask was packed in ice and allowed to stand with stirring for eight hours. The mixture was filtered and the precipitate extracted with hot ligroin (b.p. 66-75°). The extracts were combined with the filtrate which was evaporated *in vacuo*. The residue, which contained unreacted ketone and dicyclopropylisopropylcarbinol as well as the ester, was taken up in ligroin and recrystallized yielding 80 g. (22%) of the ester. Small amounts of p-nitrobenzoic acid were removed by stirring a warm ligroin solution of the ester with activated alumina. The ester was then recrystallized several times from ligroin. There was obtained 66 g. of dicyclopropylisopropylcarbinyl p-nitrobenzoate, m.p. 114-115° with decomposition.

Anal. Calc'd. for $C_{17}H_{21}NO_4$: C, 67.30; H, 6.98; N, 4.62

Found: C, 67.27; H, 6.81; N, 4.49

The p-Nitrobenzoates of Several Tertiary Carbinols

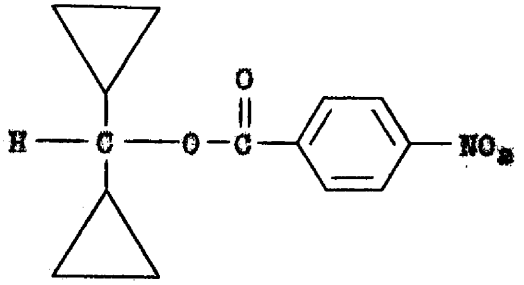
Using procedures analogous to that described for the preparation of dicyclopropylisopropylcarbinyl p-nitrobenzoate, the p-nitrobenzoates of several of the tertiary carbinols listed in Table 2 were prepared. The p-nitrobenzoate of the secondary alcohol dicyclopropylcarbinol was also prepared, by a procedure described below. The esters were recrystallized from petroleum ether (b.p. 30-60°) or from ligroin (b.p. 66-75°). Crystallization was sometimes induced by cooling the solution in crushed dry ice. Melting points, yields and analyses are given in Table 3.

Table 3

Melting Points, Yields and Analyses of Several p-Nitrobenzoates

p-Nitrobenzoate	Melting Point °C	Yield	Percent Carbon		Percent Hydrogen		Percent Nitrogen	
			Calc'd.	Found	Calc'd.	Found	Calc'd.	Found
Dicyclopropylisopropylcarbinyl	114-115 dec.	22%	67.30	67.27	6.98	6.81	4.62	4.49
Di-(2-methylcyclopropyl)isopropylcarbinyl	73-74 dec.	20	68.86	68.75 68.81	7.60	7.57 7.55	4.23	4.22 4.25
Diisopropylcyclopropylcarbinyl	91-92	22	66.86	66.84	7.59	7.63	4.59	4.65
Dicyclopropylcarbinyl	74-75	15	64.35	64.62 64.59	5.79	5.79 5.67	5.36	5.48 5.48
Triisopropylcarbinyl	74-75	20	66.42	66.58 66.69	8.20	8.11 8.34	4.56	4.60 4.56

Dicyclopropylcarbinyl p-nitrobenzoate



The method is essentially that described by Brewster and Ciotti (21). Para-nitrobenzoic acid (16.7 g., 0.1 mole) was dissolved in 800 ml. of warm pyridine. The solution was cooled and benzenesulfonyl chloride (17.7 g., 0.1 mole) was added. The flask was cooled in an ice bath and dicyclopropylcarbinol (11.2 g., 0.1 mole) (prepared by O. E. Curtis, Jr.) was added in one portion. The mixture was kept at 0° for two hours with frequent shaking. The solution was poured into 1500 ml. of a mixture of ice and water and was filtered immediately, yielding 4 g. (15%) of ester. The product was recrystallized several times from petroleum ether to yield white granular crystals of dicyclopropylcarbinyl p-nitrobenzoate, m.p. 74-75°.

Attempted Preparation of Tricyclopropylcarbinyl p-nitrobenzoate

(a) From the lithium salt of tricyclopropylcarbinol and p-nitrobenzoyl chloride.

The procedure was similar to that described in detail for the preparation of dicyclopropylisopropylcarbinyl p-nitrobenzoate. To the lithium salt of tricyclopropylcarbinol prepared in pentane from lithium (7 g., 1 mole), cyclopropyl chloride (0.5 mole, 38.3 g.), and

dicyclopropyl ketone (0.5 mole, 55 g.) at -70° was slowly added with stirring a solution of p-nitrobenzoyl chloride (0.4 mole, 75 g.) in 400 ml. of ether, the temperature being maintained between -70 and -60°. The mixture was stirred for 24 hours at -70°, and then filtered. The filtrate was evaporated in vacuo and the residue taken up in petroleum ether and filtered. The solid, which had m.p. 185-190° (lit. value 193° (24)), was p-nitrobenzoic anhydride, identified by its infrared spectrum.

Other experiments in which the p-nitrobenzoyl chloride was added at the reflux temperature of pentane (twice), at 0° (twice), at -20°, at -40°, and at -70° (twice) all failed to give the desired ester.

The combined residues from four attempts to make the ester, in which a total of 2.9 moles of cyclopropyl chloride had been used, were distilled through a Vigreux column. There was obtained about 60 ml. of dicyclopropyl ketone, b.p. 56° at 16 mm., and 212 g. of a liquid boiling from 90-98° at 5 mm. This material was redistilled through an efficient column in a nitrogen atmosphere, b.p. 82° at 3 mm., n_D^{25} 1.4998.

The infrared spectrum of the product had bands characteristic of the carbon-carbon double bond (6.06μ), the cyclopropyl carbon-hydrogen bond (3.24μ), and the carbon-chlorine bond (13.75μ). The compound was subsequently shown to be 1,1-dicyclopropyl-4-chloro-1-butene, identical with the product formed when tricyclopropylcarbinol was treated with concentrated hydrochloric acid.

Anal. Calc'd. for $C_{10}H_{15}Cl$: C, 70.37; H, 8.86; Cl, 20.77

Found: C, 70.28, 70.31; H, 8.90, 8.81; Cl, 20.86, 20.79

b) From the potassium salt of tricyclopropylcarbinol and p-nitrobenzoyl chloride.

A 1-l. three-necked round-bottomed flask equipped with a high-speed stirrer, condenser, dropping funnel and gas inlet tube, was charged with 5.9 g. (0.15 mole) of potassium metal and 80 ml. of benzene. The flask was heated (nitrogen atmosphere) until the potassium melted. The source of heat was removed and the molten potassium was whipped into a fine powder with the stirrer. The potassium suspension was cooled to room temperature and a solution of tricyclopropylcarbinol (22.8 g., 0.15 mole) in 60 ml. benzene was slowly added with vigorous stirring over a period of one hour, during which time the temperature rose to 40°. After all the carbinol had been added, practically all of the potassium had been consumed and a clear yellow solution resulted. The solution was refluxed for 30 minutes to cause the last few particles of potassium which had adhered to the sides of the flask to react. A solution of p-nitrobenzoyl chloride (29 g., 0.15 mole) in 250 ml. of benzene was slowly added with vigorous stirring while the temperature was maintained between 10° and 20°. Stirring was continued for an additional five hours. The mixture was then filtered and the benzene was removed <u>in vacuo</u>. No ester could be isolated but p-nitrobenzoic acid and p-nitrobenzoic anhydride were identified by infra-red spectra.

c) From the lithium salt of tricyclopropylcarbinol and p-nitrobenzoic anhydride.

The lithium salt of tricyclopropylcarbinol was prepared as previously described from cyclopropyl chloride (38.3 g., 0.5 mole), lithium (7 g.,

1 mole), and dicyclopropyl ketone (55 g., 0.5 mole). A suspension of 158 g. (0.5 mole) of p-nitrobenzoic anhydride (24) in 400 ml. of ether was slowly added with stirring and allowed to stand, with stirring, for twelve hours. The mixture was filtered and the filtrate evaporated in vacuo. No ester could be obtained from the viscous residue.

d) By the method of Brewster and Ciotti (21).

Para-nitrobenzoic acid (2.5 g., 0.05 mole) was dissolved in 50 ml. of warm pyridine. The solution was cooled and benzenesulfonyl chloride (5.3 g., 0.03 mole) was added. The solution was cooled to 0° in an ice bath and tricyclopropylcarbinol (2.3 g., 0.015 mole) was added. The solution was stored at 0° with frequent shaking for four hours. A fairly large amount of crystals had formed which was collected on a filter and was recrystallized by dissolving in acetone and then adding petroleum ether to precipitate the solid. A sharp melting point could not be obtained because of "sintering", but the solid melted at around 180°. The infra-red spectrum (mull in mineral oil) was identical with that of p-nitrobenzoic anhydride. The original filtrate was poured into a mixture of ice and water and was filtered yielding a small amount of p-nitrobenzoic acid, m.p. 240° (lit. value 238° (25)).

The experiment was repeated with the same results. In another experiment, 0.015 mole instead of 0.03 mole of benzenesulfonyl chloride was used but only p-nitrobenzoic acid was isolated.

Structure proof of 1,1-dicyclopropyl-4-chloro-1-butene; oxidation with neutral potassium permanganate.

A mixture of 31.6 g. (0.2 mole) of potassium permanganate, 400 ml. of water, and 17 g. (0.1 mole) of 1,1-dicyclopropyl-4-chloro-1-butene

(obtained from the reaction of the lithium salt of tricyclopropylcarbinol with p-nitrobenzoyl chloride) was stirred for two hours at 0° and for 28 hours at room temperature. The mixture was filtered and the filtrate extracted with five 70-ml. portions of ether. The extracts were combined, dried over anhydrous magnesium sulfate and the solvent removed. There remained 4 g. (40%) of dicyclopropyl ketone, b.p. 65° at 18 mm., the infrared spectrum of which was identical with that of authentic material.

The aqueous solution which remained after the ether extraction was acidified with dilute hydrochloric acid and extracted with five 70-ml. portions of ether. The combined extracts were dried over anhydrous magnesium sulfate and the ether removed in vacuo. The oil which remained was taken up in ligroin (b.p. 66-75°), filtered while hot and then cooled in crushed dry ice. The solid which separated was collected on a filter. There was obtained 3 g. (30%) of β-chloropropionic acid, m.p. 38-39° (lit. value 39° (25)). Its infrared spectrum was identical with that of an authentic sample.

The Reaction of Tricyclopropylcarbinol with Concentrated Hydrochloric Acid.

A test tube containing 10 ml. of concentrated hydrochloric acid was cooled in an ice bath and 5 g. (0.033 mole) of tricyclopropylcarbinol was added. The test tube was shaken frequently over a period of 30 minutes, the temperature being maintained at 0°. The organic layer was separated and the aqueous layer extracted with three 5-ml. portions of ether. The organic layer and the extracts were combined and dried over

anhydrous potassium carbonate. After the solvent was removed there was obtained 4.5 g. (80%) of 1,1-dicyclopropyl-4-chloro-1-butene, b.p. 115-125° at 14 mm., n_D^{25} 1.4990. The infrared spectrum was identical with that of the 1,1-dicyclopropyl-4-chloro-1-butene obtained from the reaction of the lithium salt of tricyclopropylcarbinol with p-nitrobenzoyl chloride.

The Reaction of 1,1-Dicyclopropyl-4-chloro-1-butene with Aqueous Potassium Carbonate

1,1-Dicyclopropyl-4-chloro-1-butene (34 g., 0.2 mole) and 200 ml. of 10% aqueous potassium carbonate solution were refluxed with stirring for 24 hours. After cooling, the organic layer was separated and the aqueous layer extracted with four 50-ml. portions of ether. The combined organic layer and ether extracts were dried over anhydrous magnesium sulfate. After the solvent was removed, there was obtained 27 g. (89%) of tricyclopropylcarbinol, b.p. 71° at 4 mm., the infrared spectrum of which was identical with that of authentic carbinol.

The Addition of Isopropyllithium to Ethylene

The procedure was similar to that used by Bartlett, Friedman and Stiles (18). A solution of 0.3 mole of isopropyllithium in 200 ml. of pentane was cooled to -70° and 400 ml. of precooled ethyl ether was added to the mixture. The helium source was removed and ethylene gas was bubbled into the mixture over a period of six hours, the temperature being maintained between -70° and -60°. The mixture was then stirred for two hours at -60°. Without allowing the temperature to rise above -60°, carbon dioxide gas was bubbled into the mixture for three hours

and the mixture was allowed to stand over night at -60°. The temperature was then allowed to rise to 0° and 300 ml. of 4N hydrochloric acid was slowly added. The organic phase was separated and the aqueous layer extracted with four 70-ml. portions of ether which were combined with the organic phase and extracted with 500 ml. of 2N sodium hydroxide. The remaining ethereal solution was dried over anhydrous magnesium sulfate. The alkaline extract was acidified with hydrochloric acid and the resulting organic phase was separated. The aqueous phase was extracted with ether and the combined extracts and organic phase were dried over magnesium sulfate. After removal of the solvent there was obtained 12 g. (35%) of isocaproic acid, b.p. 93° at 8 mm. n_D^{20} 1.4143 (Literature values: b.p. 91-92° at 9 mm., n_D^{20} 1.4144 (25)). The infrared spectrum was identical with that of authentic isocaproic acid. The ethereal solution which remained after the alkali extraction was distilled, but no diisoamyl ketone could be isolated (18).

Attempts to bring about the addition of isopropyllithium to ethylene in pure pentane solvent were unsuccessful.

The Attempted Addition of Cyclopropyllithium to Ethylene

The procedure was analogous to that described for the addition of isopropyllithium to ethylene. The only product isolated was cyclopropanecarboxylic acid. In another experiment, the ethylene was passed into the solution at -40° instead of -60° but again the only substance isolated was cyclopropanecarboxylic acid, identified by its infrared spectrum.

B. Solvolysis Studies

Solvents

The dioxane used was purified by Fieser's procedure (26).

Carbon dioxide-free distilled water was employed for making up solvent mixtures and reagents.

The methanol was purified by distillation over magnesium methoxide.

The kinetic studies and product analyses were carried out in water-dioxane solvents of several weight per cent compositions. Product analyses for several kinetic conditions were also carried out in methanol-dioxane solvents of several weight per cent compositions.

Standardization of Reagents

The sodium hydroxide was made up in aqueous dioxane solution to approximately 0.01 normal concentration and was standardized immediately before each run against Bureau of Standards benzoic acid in an aqueous dioxane solution using phenolphthalein indicator. If a run lasted longer than one day, the base was standardized each day.

Kinetic Procedure

Approximately 0.01 molar solutions of ester were employed and the reaction was followed by titrating the liberated p-nitrobenzoic acid with standard sodium hydroxide. The reactions were conducted in a constant temperature bath maintained at $\pm$ 0.1° of the desired temperature.

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. At various time intervals, a 5-ml. aliquot was removed, quenched by freezing in an ice-salt bath and immediately titrated 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.

Another method involved the addition of excess base in small increments and recording the time at which the phenolphthalein indicator changed color. This method was only used for a few runs and was abandoned in favor of the aliquot method in which the end points were easier to observe. The two methods agreed when applied to the same compound under the same conditions (compare the rate constants in Tables 56 and 57 with those in Tables 50 to 55).

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

Product Analysis

(a) Solvolysis of dicyclopropylisopropylcarbinyl p-nitrobenzoate in 80% dioxane-20% water at 25°.

Dicyclopropylisopropylcarbinyl p-nitrobenzoate (12.4 g., 0.0409 mole) was dissolved in 300 ml. of 80% dioxane-20% water and maintained at 25° for 48 hours. The solution was poured into 700 ml. of water,

made slightly alkaline with sodium hydroxide, and extracted with eight 100-ml. portions of petroleum ether. The combined extracts were washed with ten 500-ml. portions of water to remove dioxane and were dried over Drierite. After the solvent was removed, there was obtained 6.0 g. (95%) of dicyclopropylisopropylcarbinol, b.p. 64° at 4 mm., $n_D^{25°}$ 1.4645. (cf. Table 2). The infrared spectrum of the liquid was identical with that of authentic dicyclopropylisopropylcarbinol.

In another experiment, 3.72 g. (0.0122 mole) of dicyclopropylisopropylcarbinyl p-nitrobenzoate was dissolved in 100 ml. of 80% dioxane-20% water and stored at 25° for six hours. The mixture was worked up as described above except that the liquid remaining after the petroleum ether was removed was not distilled. An infrared spectrum of the liquid (1.54 g., 81% yield) was identical with that of authentic dicyclopropylisopropylcarbimol.

b) Solvolysis of Dicyclopropylisopropylcarbinyl p-nitrobenzoate in 80% Dioxane-20% Methanol at 25°.

In a preliminary experiment, 0.3481 g. (0.001147 mole) of the ester was weighed into a 100 ml. volumetric flask and brought up to volume with 80% dioxane-20% methanol solvent. At various intervals, a 5-ml. aliquot was titrated with 0.009137N sodium hydroxide in 80% dioxane-20% methanol. After 17 hours, the theoretical acid titer was obtained indicating that the solvolysis had gone to completion.

In another experiment, dicyclopropylisopropylcarbinyl p-nitrobenzoate (10.0 g., 0.033 mole) was dissolved in 100 ml. of 80% dioxane-20% methanol solvent and the solution was maintained at 25° for 18 hours.

The solution was poured into 500 ml. of water, made slightly alkaline with sodium hydroxide, and extracted with seven 100-ml. portions of petroleum ether. The combined extracts were washed with eight 100-ml. portions of water and dried over Drierite. After the solvent was removed there was obtained 4.5 g. (81%) of 1,1-dicyclopropyl-1-methoxy-2-methylpropane, b.p. 61° at 4 mm., n_D^{25} 1.4566. The infrared spectrum contained a very intense ether band (9.2μ). The regions characteristic of hydroxyl absorption (2.7-3.0μ) and of carbon-carbon double bond absorption (5.9-6.3μ) were devoid of bands.

Anal. Calc'd. for $C_{11}H_{20}O$: C, 78.51; H, 11.98

Found: C, 78.55, 78.44; H, 11.98, 11.97

c) Solvolysis of Diisopropylcyclopropylcarbinyl p-nitrobenzoate in 70% Dioxane-30% Water at 60°.

Diisopropylcyclopropylcarbinyl p-nitrobenzoate (6.42 g., 0.0210 mole) was dissolved in 200 ml. of 70% dioxane-30% water and the solution maintained at 60° for 12 hours. After cooling, the solution was poured into 300 ml. of water, made slightly alkaline with sodium hydroxide and extracted with eight 70-ml. portions of petroleum ether. The combined extracts were washed with eight 500-ml. portions of water and dried over Drierite. After the solvent was removed, there remained 3.0 g. of a liquid, the infra-red spectrum of which showed a hydroxyl peak (2.85μ) and a carbonyl peak (5.8μ). Five ml. of petroleum ether was added and the solution placed in crushed dry ice, whereupon crystallization occurred. The crystals (about 50-100 mg.) which were removed by filtration, melted at 46-48°. The infra-red spectrum indicated that the

substance was a p-nitrobenzoate but distinctly different from the starting ester. It was subsequently shown to be 4-isopropyl-5-methyl-3-hexenyl p-nitrobenzoate.

The filtrate from which the solid was separated was distilled and 2.3 g. (70%) of diisopropylcyclopropylcarbinol, b.p. 60-61° at 4 mm., n_D^{25} 1.4516, was obtained. The liquid was identified through its infrared spectrum.

d) Solvolysis of Diisopropylcyclopropylcarbinyl p-nitrobenzoate in Boiling 70% Dioxane-30% Water.

Diisopropylcyclopropylcarbinyl p-nitrobenzoate (0.2971 g., 0.000973 mole) was weighed into a 200-ml. round-bottomed flask. Exactly 100 ml. of 70% dioxane-30% water was pipetted into the flask at 25°. The flask was fitted with a reflux condenser and the solution was refluxed for 26 hours. The solution was cooled to 25° and several aliquots were titrated with standard sodium hydroxide. Only 93.5% of the theoretical acid titer was obtained.

e) Solvolysis of diisopropylcyclopropylcarbinyl p-nitrobenzoate in 90% Dioxane-10% Water at 60°.

Diisopropylcyclopropylcarbinyl p-nitrobenzoate (10.43 g., 0.0341 mole) was dissolved in 250 ml. of 90% dioxane-10% water and stored at 60° for 48 hours. After cooling, the solution was poured into one liter of water, made slightly alkaline with sodium hydroxide, and extracted with eight 150-ml. portions of petroleum ether. The combined extracts were washed with fourteen 500-ml. portions of water and dried over Drierite.

The dried solution was concentrated to about 100 ml. and cooled in crushed dry ice to induce crystallization. The solid was collected on a filter and there was obtained 6.4 g. (63%) of 4-isopropyl-5-methyl-3-hexenyl p-nitrobenzoate, m.p. 46-48°.

Anal. Calc'd. for $C_{17}H_{23}NO_4$: C, 66.86; H, 7.59; N, 4.58

Found: C, 66.91, 67.04; H, 7.30, 7.22; N, 4.49, 4.45

The filtrate from which the ester had separated was distilled, b.p. 60° at 4 mm., and there was obtained 0.7 g. (13%) of diisopropylcyclopropylcarbinol, identified by its infrared spectrum.

f) Solvolysis of Diisopropylcyclopropylcarbinyl p-nitrobenzoate in Refluxing Methanol.

In a preliminary experiment, a solution 0.009523 molar in ester was prepared by dissolving 0.2908 g. of the ester in 100 ml. of anhydrous methanol. The solution was refluxed for 12 hours, cooled and a 5-ml. aliquot was titrated with 0.009137N sodium hydroxide in 80% dioxane-20% methanol. The theoretical acid titer was obtained indicating that 100% solvolysis had taken place.

In another experiment 6.57 g. (0.0215 mole) of the ester was dissolved in 300 ml. of anhydrous methanol and the solution was refluxed for 12 hours. The cooled solution was poured into one liter of water and made slightly alkaline with sodium hydroxide. The mixture was extracted with eight 100-ml. portions of petroleum ether. The combined extracts were washed with eight 500-ml. portions of water and dried over Drierite. After the solvent was removed, there was obtained 3.2 g. (81%) of 3-cyclopropyl-3-methoxy-2,4-dimethylpentane, b.p. 56° at 4 mm.,

n_D^{25} 1.4338. The infrared spectrum contained a very intense ether band (8.93μ) but no hydroxyl band (2.7-3.0μ) and no carbon-carbon double bond band (5.9-6.3μ).

Anal. Calc'd. for $C_{11}H_{22}O$: C, 77.58; H, 13.02

Found: C, 78.21, 78.29; H, 13.03, 13.06

g) Solvolysis of Diisopropylcyclopropylcarbinyl p-nitrobenzoate in 70% dioxane-30% Methanol at 60°.

In a preliminary experiment, 0.3281 g. (0.001074 mole) of the ester was weighed into a 100-ml. volumetric flask, brought up to volume with 70% dioxane-30% methanol and placed in a 60° bath. At various intervals, a 5-ml. aliquot was titrated with 0.009317N sodium hydroxide in 80% dioxane-20% methanol. After 16.25 hours, 34% of the acid titer was obtained and remained at 34% after 37.5 hours, which indicated that solvolysis had ceased.

In another experiment, 5.71 g. (0.0187 mole) of the ester was dissolved in 100 ml. of 70% dioxane-30% methanol and the solution stored at 60° for 36 hours. The cooled solution was poured into 300 ml. of water and made slightly alkaline with sodium hydroxide. The mixture was extracted with eight 100-ml. portions of petroleum ether. The combined extracts were washed with eight 500-ml. portions of water and dried over Drierite. The solution was concentrated to about 50 ml., cooled in crushed dry ice and filtered. There was obtained 3.5 g. (61%) of 4-isopropyl-5-methyl-3-hexenyl p-nitrobenzoate, m.p. 46-48° which was identified by its infrared spectrum.

The filtrate was distilled and there was obtained 0.7 g. (22%) of 3-cyclopropyl-3-methoxy-2,4-dimethylpentane, b.p. 57° at 4 mm., which was also identified by its infrared spectrum.

Proof of Structure of 4-isopropyl-5-methyl-3-hexenyl p-nitrobenzoate

a) Reduction with Lithium Borohydride.

A 500-ml. three-necked round-bottomed flask equipped with stirrer, condenser, dropping funnel, and a gas inlet tube was charged, in a nitrogen atmosphere, with 2.2 g. (0.1 mole) of lithium borohydride and 100 ml. of tetrahydrofuran (dried by distillation over sodium). A solution of 8.0 g. (0.026 mole) of 4-isopropyl-5-methyl-3-hexenyl p-nitrobenzoate in 50 ml. of tetrahydrofuran was slowly added with stirring to the lithium borohydride solution. No heat was evolved during the addition. The solution was stirred at room temperature for 12 hours. The mixture was cooled in an ice bath and 300 ml. of water was slowly added. The solution was extracted with five 100-ml. portions of ether and the combined extracts dried over Drierite. The solution was evaporated to dryness in vacuo. The residue was taken up in petroleum ether and filtered, yielding 3.2 g. (81%) of p-nitrobenzyl alcohol, m.p. 91-93° (lit. value 93° (25)).

The filtrate was distilled and there was obtained 3.0 g. (74%) of 4-isopropyl-5-methyl-3-hexenol, b.p. 83° at 5 mm., n_D^{25} 1.4505. The infrared spectrum contained a broad intense hydroxyl band (3.0μ) and a weak carbon-carbon double bond band (6.0μ) characteristic of trisubstituted ethylenes.

Anal. Calc'd. for $C_{10}H_{20}O$: C, 76.86; H, 12.90

Found: C, 76.96, 76.91; H, 12.87, 12.74

b) Oxidation of 4-isopropyl-5-methyl-3-hexenol With Neutral Potassium Permanganate.

A mixture of 1 g. (0.0064 mole) of the unsaturated alcohol, 4 g. (0.025 mole) of potassium permanganate and 100 ml. of water was stirred for four hours at room temperature. The mixture had the strong characteristic odor of diisopropyl ketone. The mixture was filtered, the filtrate extracted with five 20-ml. portions of ether and the combined extracts dried over Drierite. The ether was removed and an infrared spectrum of the residual liquid (about 0.7 ml.) showed a strong carbonyl band (5.85μ) but also a hydroxyl band (2.80μ). Comparison of this spectrum with that of authentic diisopropyl ketone showed that the wavelength of each carbonyl band was identical.

In an attempt to distil the mixture, decomposition took place.

In another experiment, about 50 mg. of the unsaturated alcohol was shaken with 20 ml. of aqueous potassium permanganate for one hour. The mixture was filtered and the filtrate was extracted with four 5-ml. portions of ether. The combined extracts were dried over Drierite. The dried ether solution was concentrated to about 1 ml. The presence of diisopropyl ketone in the solution was then ascertained by vapor phase chromatography. This was accomplished by passing an ethereal solution of authentic diisopropyl ketone through the Vapor Fractometer and obtaining a record of the band due to diisopropyl ketone. Then a sample of the unknown solution was passed through the Vapor Fractometer and the identical band corresponding to diisopropyl ketone was obtained.

SOLVOLYSIS RESULTS

SOLVOLYSIS RESULTS

A. The Rates

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 p-nitrobenzoic acid with standard sodium hydroxide. The rates were unaffected by added hydroxide ion (Compare the rate constants in Tables 25 and 26 with those in Tables 27 and 28, and compare the k values in Tables 64 and 65 with those in Tables 66 and 67).

In most cases the ester was completely solvolyzed to an alcohol and p-nitrobenzoic acid, but in certain instances, solvolysis appeared to be incomplete; that is, the theoretical amount of p-nitrobenzoic acid was not liberated. Each of these two alternatives required separate kinetic treatment.

For the case of complete solvolysis, the reaction may be expressed by the general equation

$$\underset{(a-x)}{\text{Ester}} \xrightarrow{k} \underset{(x)}{\text{Alcohol}} + \underset{(x)}{\text{Acid}} \qquad (1)$$

where

a = initial ester concentration in moles/liter

x = concentration of alcohol or acid at time t

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

According to the usual treatment of a first-order reaction,

$$\log (a-x) = -\frac{k}{2.3} t + \log a \qquad (2)$$

The measured quantity was

V = volume (ml.) of standard sodium hydroxide required to neutralize the p-nitrobenzoic acid found at time t (in a 5 ml. aliquot).

If V_f = volume (ml.) of standard sodium hydroxide required to neutralize the theoretical quantity of p-nitrobenzoic acid (in a 5 ml. aliquot),

then

$(a-x)$ is proportional to (V_f-V)

and (a) is proportional to V_f

whence

$$\log (V_f-V) = -\frac{k}{2.3} t + \log V_f \qquad (3)$$

Note that

$$V_f = \frac{.005a}{N}$$

where N = normality of the sodium hydroxide.

From equation (3) we see that a plot of log (V_f-V) vs. t should be linear, and the slope of this line allows one to calculate the specific first order rate constant k (for a typical plot, see Figure 12).

In some cases it was observed that the reaction did not follow the first order rate law described by equation (3). Furthermore, the calculated value of V_f was always significantly greater than the observed value of V_f. A typical plot of log (V_f-V) versus t for one of these reactions is shown in Figure 13. It was found that if the observed value of V_f, called V'_f, was used in place of the calculated value of V_f, a plot of log $(V_f'-V)$ versus t gave a straight line (Figure 14).

Figure 12. Plot of log $(V_f - V)$ versus t for the Solvolysis of 0.00977M Molar Dicyclopropylisopropylcarbinyl p-Nitrobenzoate in 80% Dioxane - 20% Water.

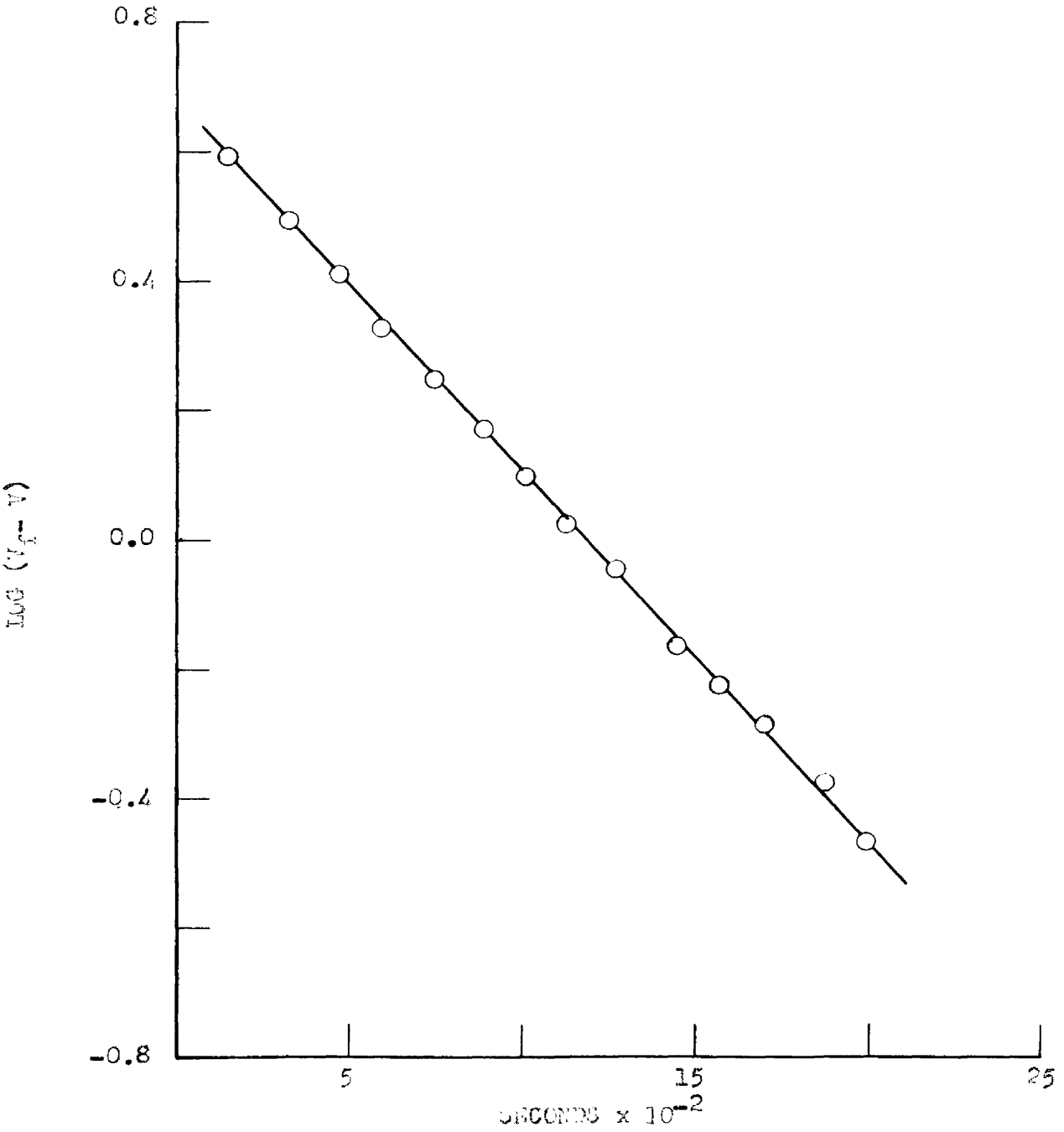


Figure 13. Plot of log $(V_f - V)$ versus t for the Solvolysis of 0.01158 Molar Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 80% Dioxane-20% Water.

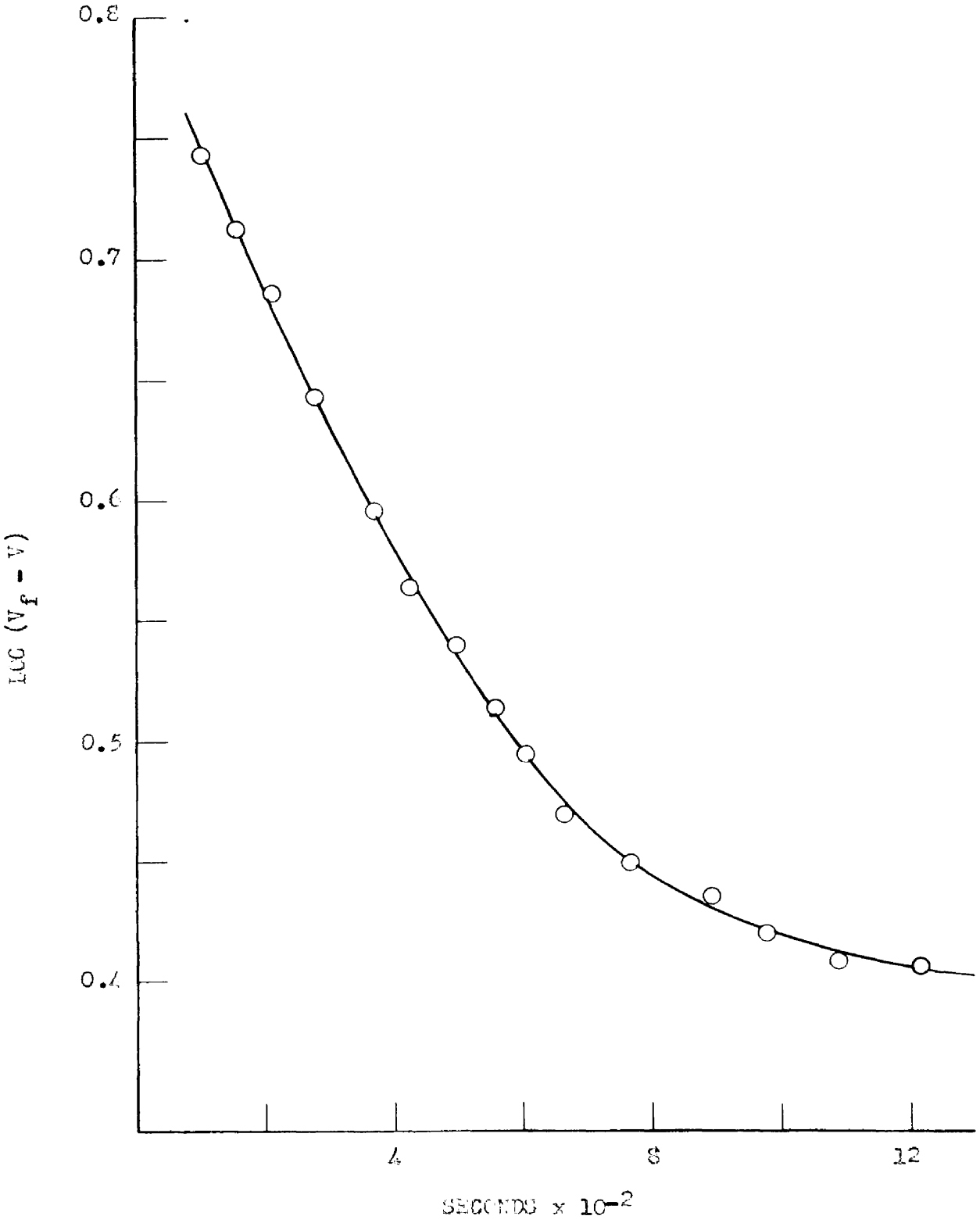
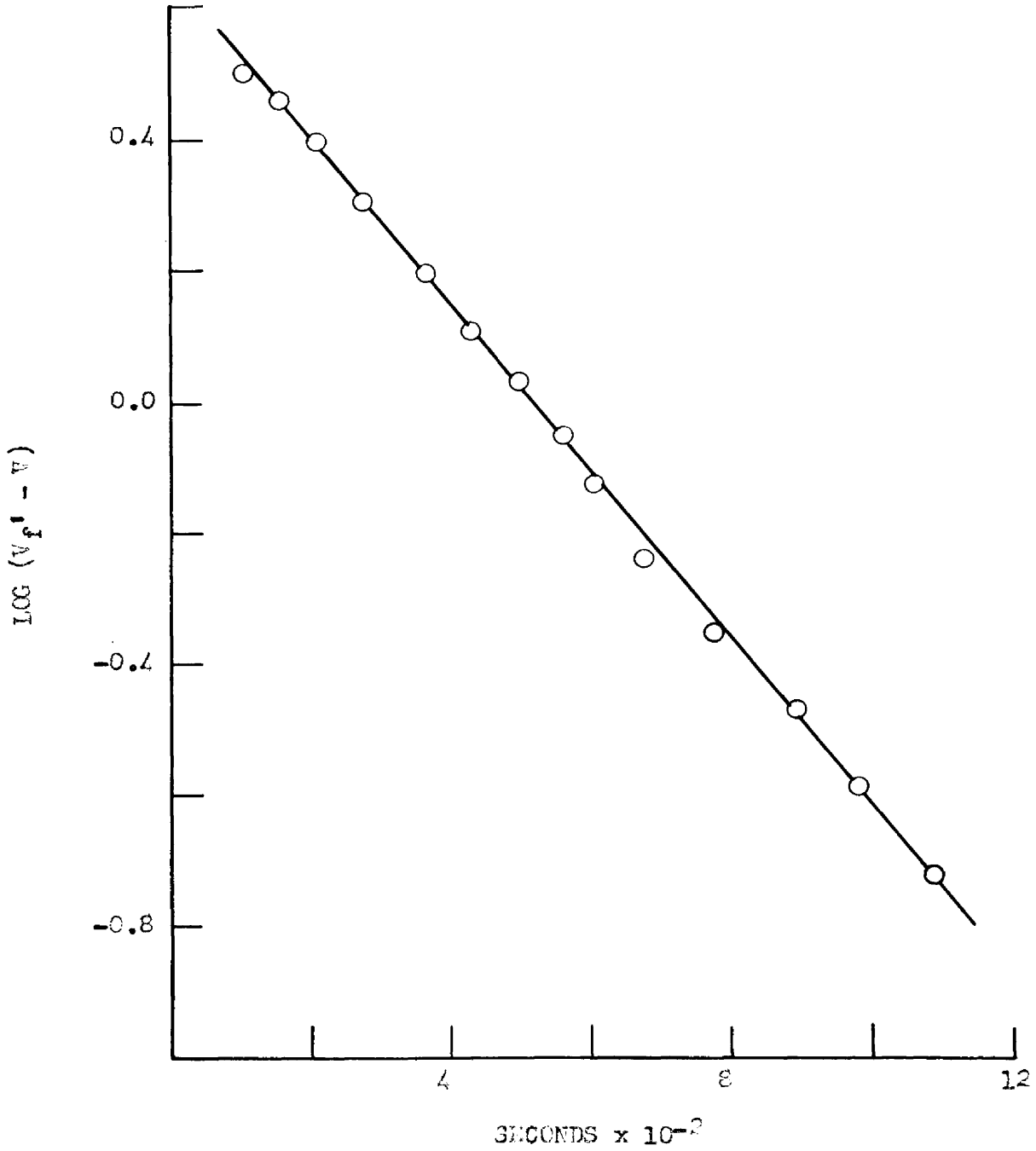


Figure 14. Plot of log $(V_f' - V)$ versus t for the Solvolysis of 0.01158 Molar Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 80% Dioxane-20% Water.



This indicated that the amount of ester represented by V_f' solvolyzed to give p-nitrobenzoic acid by a first order process. The quantity of ester represented by (V_f-V_f') must have been converted to some product which did not liberate p-nitrobenzoic acid. The conclusion, later verified by product analysis, was that the original ester had undergone solvolysis to alcohol and acid and rearrangement to a new ester. Since the total theoretical acid titer was never obtained, neither under the kinetic reaction conditions nor under forcing conditions (i.e., refluxing solvent for an extended period of time), it was obvious that the rearranged ester was quite unreactive. The process may be represented by

$$\underset{E}{\text{Ester}} \xrightarrow{k} \underset{A}{\text{Alcohol}} + \underset{A}{\text{Acid}} + \underset{E'}{\text{New ester}} \qquad (4)$$

A somewhat more detailed representation is

$$\text{Ester}\ (E) \xrightarrow{k_s} \underset{A}{\text{Acid}} + \underset{A}{\text{Alcohol}} \qquad (5)$$

$$\text{Ester}\ (E) \xrightarrow{k_r} \underset{E'}{\text{New Ester}}$$

where

$$k = k_s + k_r \qquad (5a)$$

and

k_s = specific rate constant for solvolysis
k_r = specific rate constant for rearrangement
E = concentration of original ester at time t
A = concentration of alcohol or acid at time t
E' = concentration of new ester at time t.

If E_o = initial concentration of original ester
A_f = final concentration of alcohol or acid
E'_f = final concentration of new ester

then

$$E_o = E + A + E' \tag{6}$$

and $$E'_f = E_o - A_f \tag{7}$$

The rate of disappearance of ester is given by

$$-\frac{dE}{dt} = k_s (E) + k_r (E) \tag{8}$$

$$= k (E) \tag{9}$$

and $$\log E = -\frac{k}{2.3} t + \log E_o \tag{10}$$

Since

$$\frac{E'}{A} = \frac{E'_f}{A_f} = \frac{k_r}{k_s} \tag{11}$$

it is easily shown that

$$E = E_o - \frac{A}{A_f} E_o \tag{12}$$

whereupon equation (10) becomes

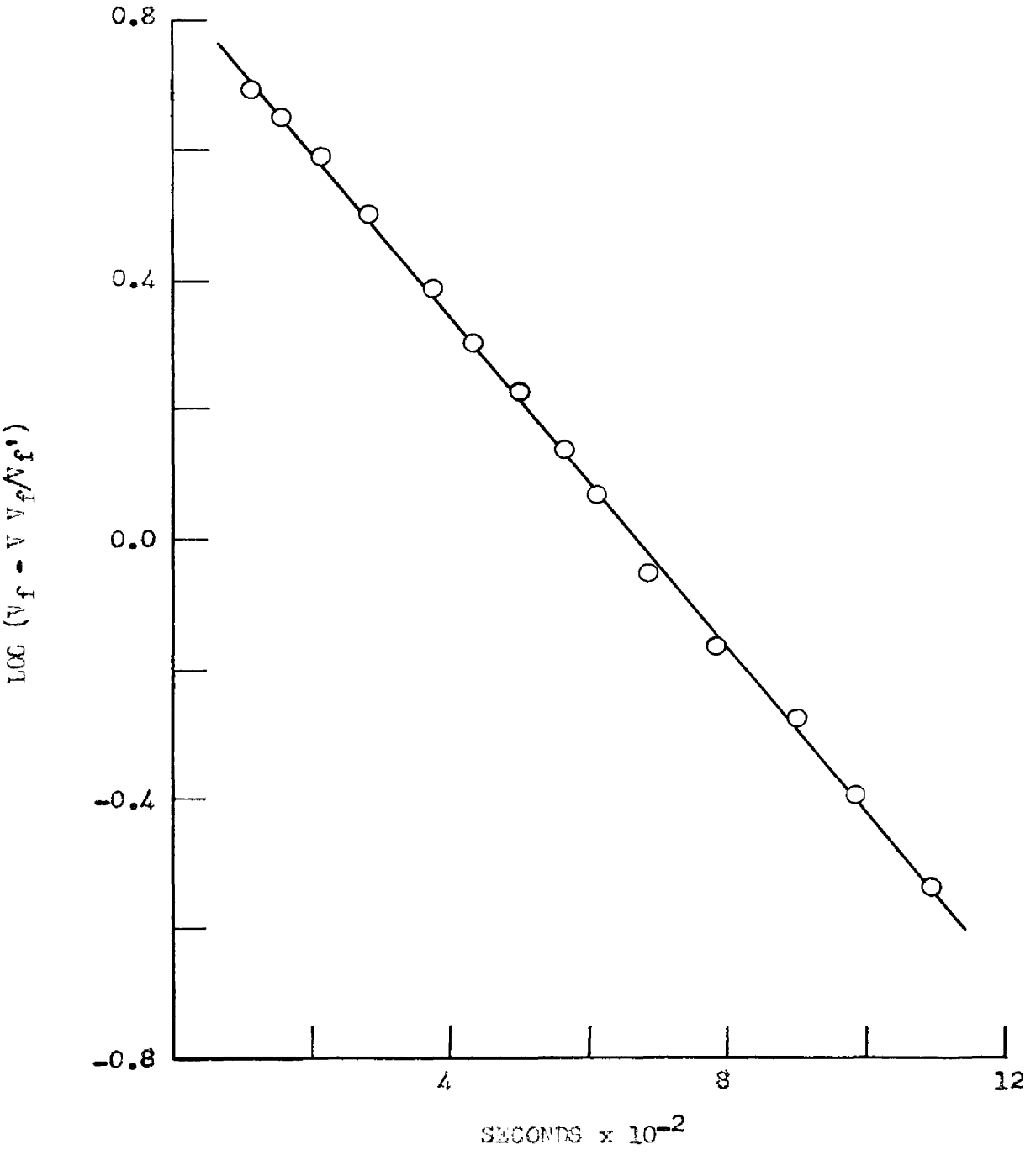
$$\log (E_o - \frac{A}{A_f} E_o) = -\frac{k}{2.3} t + \log E_o \tag{13}$$

Using the previous definitions of V, V_f and V'_f, equation (13) reduces to

$$\log (V_f - \frac{V}{V'_f} V_f) = -\frac{k}{2.3} t + \log V_f \tag{14}$$

where V and V_f' are experimentally determined and V_f is calculated from the original amount of ester taken. A plot of $\log (V_f - \frac{V}{V_f'} V_f)$ vs. t gave straight lines (see Figure 15 for a typical plot) from the slope of which k was calculated.

Figure 15. Plot of log ($V_f - V\ V_f/V_f'$) versus t for the Solvolysis of 0.01158 Molar Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 80% Dioxane-20% Water .



Since

$$k_s = \frac{A_f}{E_o} k = \frac{V'_f}{V_f} k \qquad (15)$$

and

$$k_r = (1 - \frac{V'_f}{V_f}) k \qquad (16)$$

k_r and k_s can be evaluated from k and the ratio of solvolysis to rearrangement product.

The values of k, k_s, and k_r obtained for the reactions of the esters under various conditions are listed in Tables 4, 5, 6, 7, and 8. The value of the specific rate constant listed at a given temperature is the arithmetic mean of all the rate constants obtained at that temperature. The standard deviation (56) from each mean value is also given.

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

$$\log k = -\frac{E_a}{2.3R} \frac{1}{T} + Z \qquad (17)$$

The linear plots of log K versus $\frac{1}{T}$ for the various reactions appear in Figures 22 to 38 in the Appendix. In each case, the slope was obtained by the method of least squares (27,56) and E_a was obtained from the equation

$$E_a = 2.3R (- \text{slope}) \qquad (18)$$

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

The enthalpy of activation, $\triangle H^*$, was calculated from the equation

Table 4

Specific Rate Constants for the Solvolysis of Dicyclopropylisopropylcarbinyl p-Nitrobenzoate in Aqueous Dioxane

°C		10^4 k, sec.$^{-1}$ Weight Per Cent Dioxane		
	95	90	85	80
7				1.53±0.01
16				4.90±0.11
25		1.60±0.01	5.49±0.05	13.3 ±0.2
40		6.69±0.09		
50		16.8 ±0.1		
60	k 5.69±0.16	38.9*		448*
	k_s 5.24±0.12			
	k_r 0.450±0.045			
	k_s/k_r 11.6			

*Calculated from the Arrhenius equation

Table 5

Specific Rate Constants for the Solvolysis of Di-(2-methylcyclopropyl)-isopropylcarbinyl p-Nitrobenzoate in Aqueous Dioxane

°C	10^4 k, sec.$^{-1}$				
	Weight Per Cent Dioxane				
	90				80
	k	k_s	k_r	k_s/k_r	k
7					8.05±0.04
16	2.80±0.09	2.58±0.07	0.217±0.017	11.9	
25	7.09±0.07	6.53±0.06	0.567±0.020	11.5	
35	18.3±0.3	16.5±0.03	1.84±0.11	9.0	
60	156*	136*	21.4*	6.31	

*Calculated from the Arrhenius equation.

Table 6

Specific Rate Constants for the Solvolysis of Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in Aqueous Dioxane

°C	$10^4 k$, sec.$^{-1}$ Weight Per Cent Dioxane			
	90	85	80	70
40				
k_t				1.61±0.03
k_s				1.54±0.03
k_r				0.0654±0.0065
k_s/k_r				23.5
50				
k_t				5.12±0.09
k_s				4.89±0.10
k_r				0.229±0.001
k_s/k_r				21.4
60				
k_t	0.739±0.06	2.09±0.04	4.69±0.28	14.7±0.2
k_s	0.208±0.001	0.838±0.012	3.04±0.16	13.9±0.3
k_r	0.532±0.006	1.25±0.02	1.65±0.15	0.831±0.016
k_s/k_r	0.391	0.670	1.84	16.7
70				
k_t		5.74±0.05	11.9±0.2	
k_s		2.33±0.01	7.69±0.12	
k_r		3.42±0.05	4.13±0.04	
k_s/k_r		0.681	1.86	
80				
k_t		14.8±0.1	29.6±0.5	
k_s		5.62±0.19	19.0±0.4	
k_r		9.10±0.04	10.5±0.2	
k_s/k_r		0.618	1.81	

Table 7

Specific Rate Constants for the Solvolysis of Dicyclopropylcarbinyl p-Nitrobenzoate in Aqueous Dioxane

	$10^4 k$, sec.$^{-1}$	
°C.	Weight Per Cent Dioxane	
	85	80
60		1.16±0.06
70		2.92±0.06
80	2.68±0.06	7.06±0.01

Table 8

Specific Rate Constants for the Solvolysis of Triisopropylcarbinyl p-Nitrobenzoate in Aqueous Dioxane

°C.	$10^6 k$, sec.$^{-1}$ Weight Per Cent Dioxane	
	80	70
60	1.91±0.09	7.52±0.03
70	6.82±0.01	25.5 ±0.5
80	27.1 ±0.6	81.5 ±1.7

$$\Delta H^{*} = E_a - RT \qquad (19)$$

The entropy of activation, ΔS^{*}, was calculated from the Eyring (28) equation

$$k = \frac{k_B T}{h} e^{\Delta S^{*}/R} e^{-\Delta H^{*}/RT} \qquad (20)$$

or

$$\Delta S^{*} = 2.3R \log \left(\frac{k\,h}{k_B T}\right) + \frac{\Delta H^{*}}{T} \qquad (21)$$

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}

The values of ΔH^{*} and ΔS^{*} obtained for the various reactions are listed in Table 9. The value of ΔS^{*} listed for a given compound is the arithmetic mean of all the ΔS^{*} values calculated from equation (21) for each k obtained for that compound. The standard deviation from each mean value is also given.

B. The Products

Solvolysis of dicyclopropylisopropylcarbinyl p-nitrobenzoate in 80% dioxane-20% water at 25° yielded dicyclopropylisopropylcarbinol which was identified by its physical properties and infrared spectrum. The yield of isolated product was as high as 95%, and there was no evidence of olefin-formation. Replacement of the water with methanol gave 1,1-dicyclopropyl-1-methoxy-2-methylpropane. Although the structure of this product was not conclusively demonstrated, the elemental analysis and infrared spectrum (Figure 16) were consistent with this assignment.

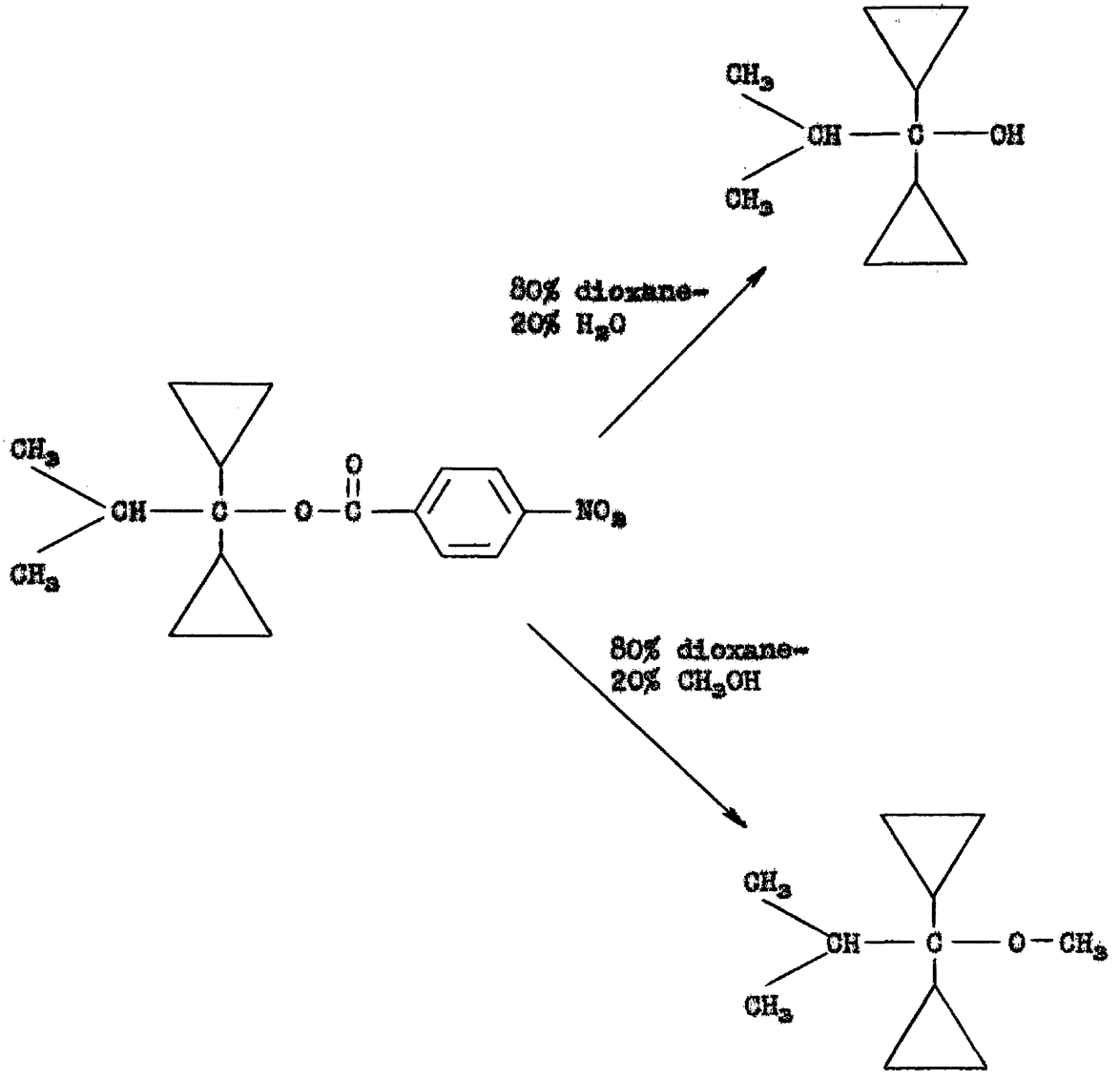
Table 9

Molar Enthalpies and Entropies of Activation for the Solvolysis of Several p-Nitrobenzoates in Aqueous Dioxane

p-Nitrobenzoate	Weight Per Cent Dioxane							
	90		85		80		70	
	ΔH^* Kcal.	ΔS^* e.u.	ΔH^* Kcal.	ΔS^* e.u.	ΔH^* Kcal.	ΔS^* e.u.	ΔH^* Kcal.	ΔS^* e.u.
Dicyclopropylisopropylcarbinyl	17.3	-17.8±0.1			19.3	-7.09±0.08		
Di-(2-methylcyclopropyl)-isopropylcarbinyl[a]	16.9	-16.3±0.1						
	16.7	-17.3±0.1						
	19.4	-12.6±0.2						
Diisopropylcyclopropylcarbinyl[a]			22.2	- 9.06±0.05	20.8	-11.6±0.1	20.7	-9.73±0.08
			21.6	-12.7±0.1	20.8	-12.5±0.1	20.5	-10.3±0.1
			22.5	-8.97±0.07	21.7	-11.1±0.2	24.0	-5.66±0.16
Dicyclopropylcarbinyl					20.5	-15.4±0.1		
Triisopropylcarbinyl					30.4	+6.17±0.12	27.2	-0.601±0.068

[a] The three values listed are for the over-all reaction, the solvolysis, and the rearrangement, respectively.

The formation of the ether from methanol demonstrates that solvolysis of dicyclopropylisopropylcarbinyl p-nitrobenzoate proceeded by alkyl-oxygen fission. This criterion has been employed in numerous other cases (29a).



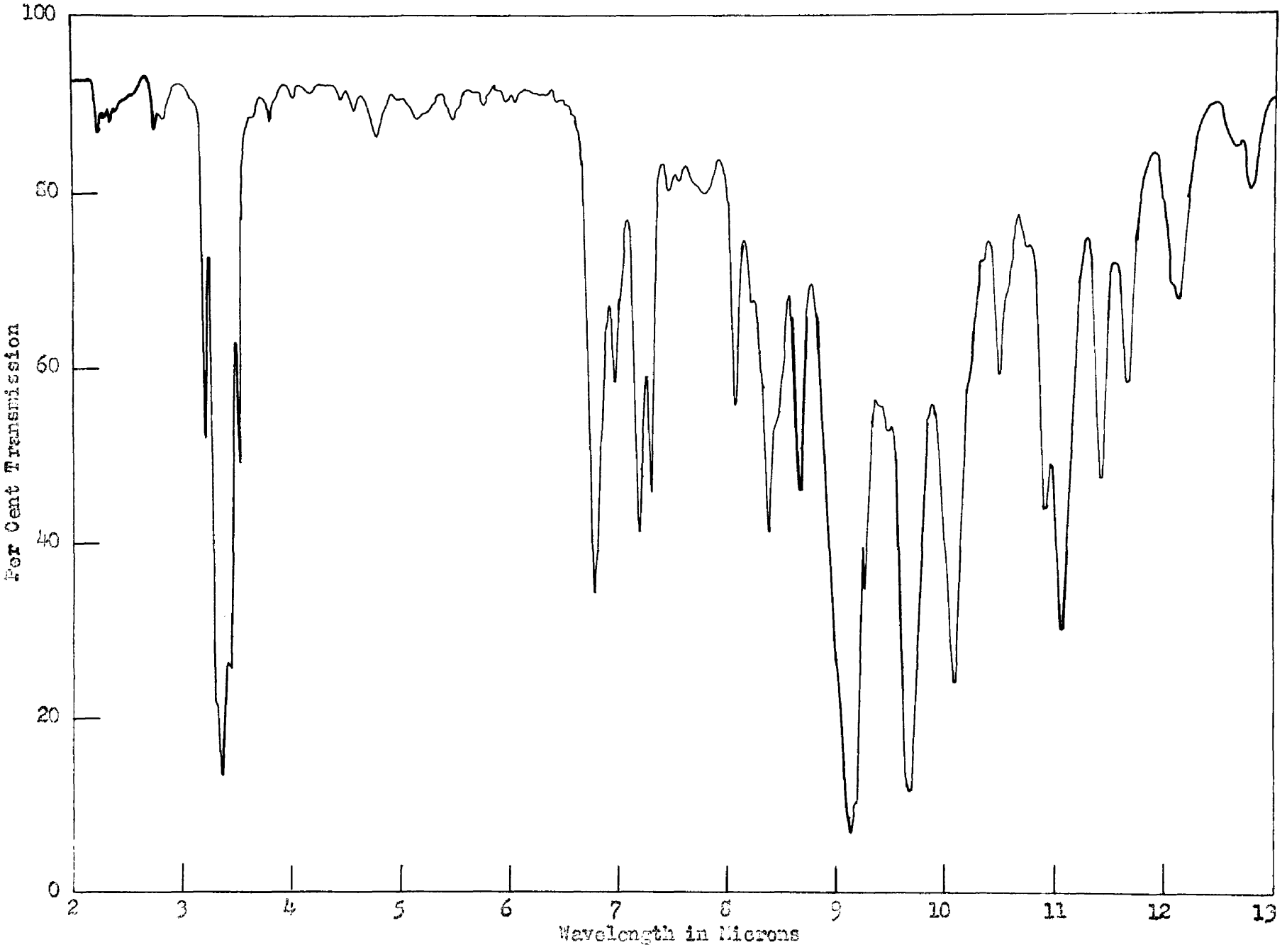
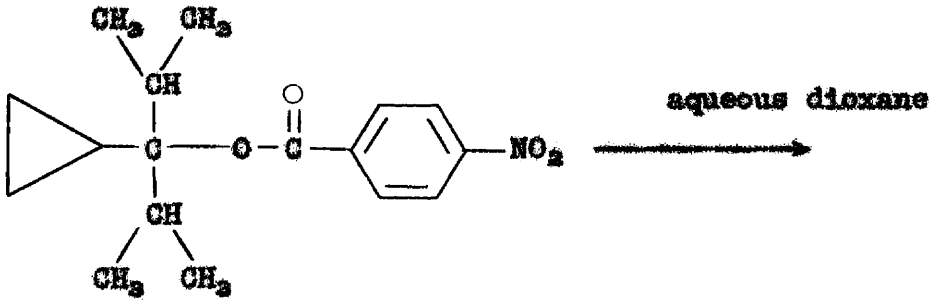
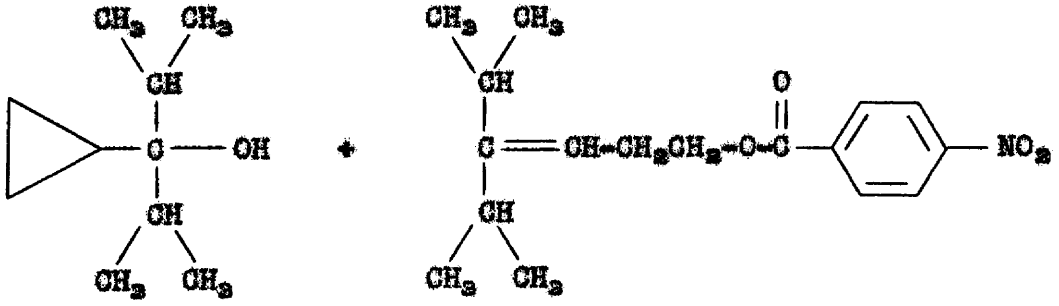


Figure 16. Infrared Spectrum of 1,1-Dicyclopropyl-1-methoxy-2-methylpropane (neat).

Diisopropylcyclopropylcarbinyl p-nitrobenzoate in 70% dioxane-30% water at 60° gave 96% diisopropylcyclopropylcarbinol and 4% 4-isopropyl-5-methyl-3-hexenyl p-nitrobenzoate. In 90% dioxane-10% water, also at 60°, the yields of these same products were 28% and 72%, respectively. These yields are not based on isolated product, but rather on the kinetic results. However, the products were isolated, and there was no evidence for any other products.





70% dioxane-30% H_2O:	96%	4%
90% dioxane-10% H_2O:	28%	72%

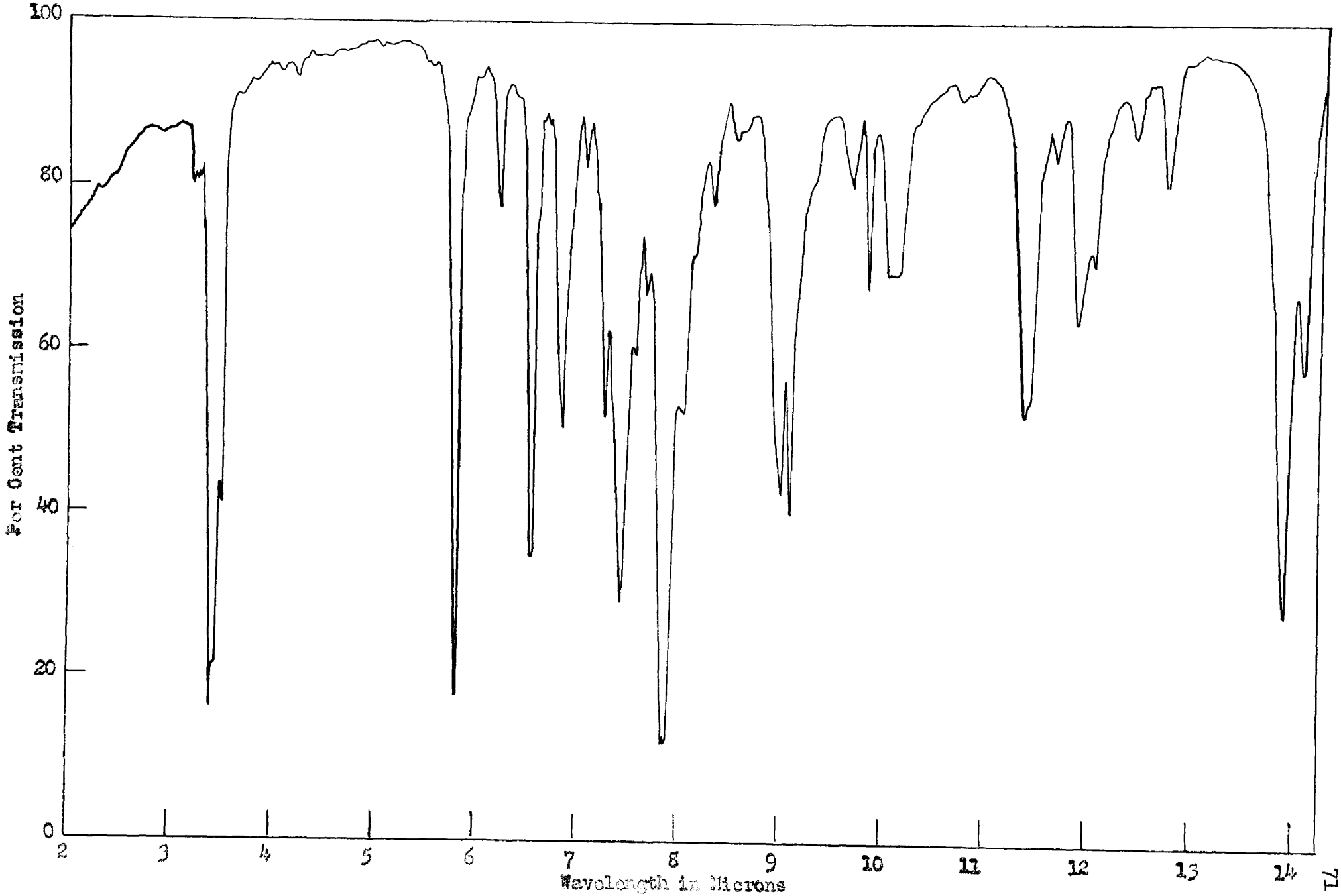
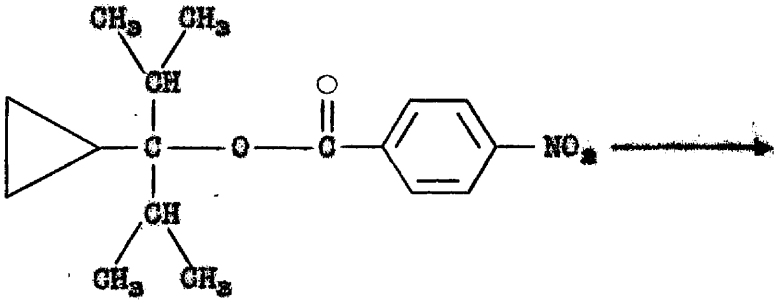
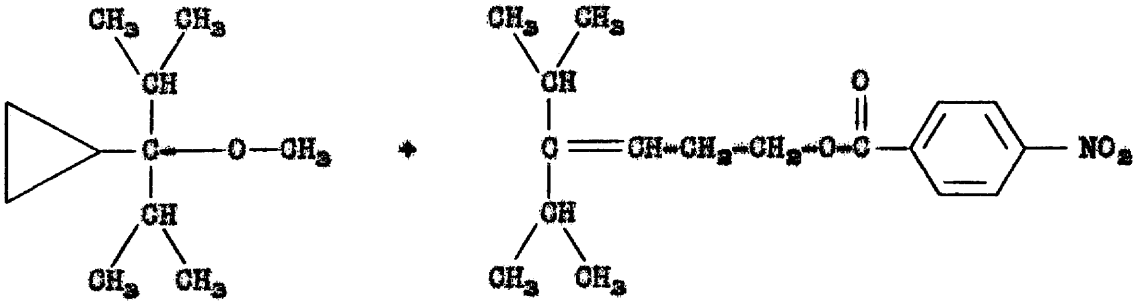


Figure 17. Infrared Spectrum of 4-Isopropyl-5-methyl-3-hexenyl p-Nitrobenzoate (mineral oil mull).

The same ester, in refluxing methanol yielded exclusively 3-cyclopropyl-3-methoxy-2,4-dimethylpentane; but in 70% dioxane-30% methanol at 60°, only a 34% yield of the ether was obtained, and 66% of the ester had isomerized to 4-isopropyl-5-methyl-3-hexenyl p-nitrobenzoate. The infrared spectrum (Figure 18) and elemental analysis of the ether were consistent with the assigned structure. It is again clear that solvolysis involved alkyl-oxygen fission.





CH_3OH 100%

70% dioxane-30% CH_3OH 34% 66%

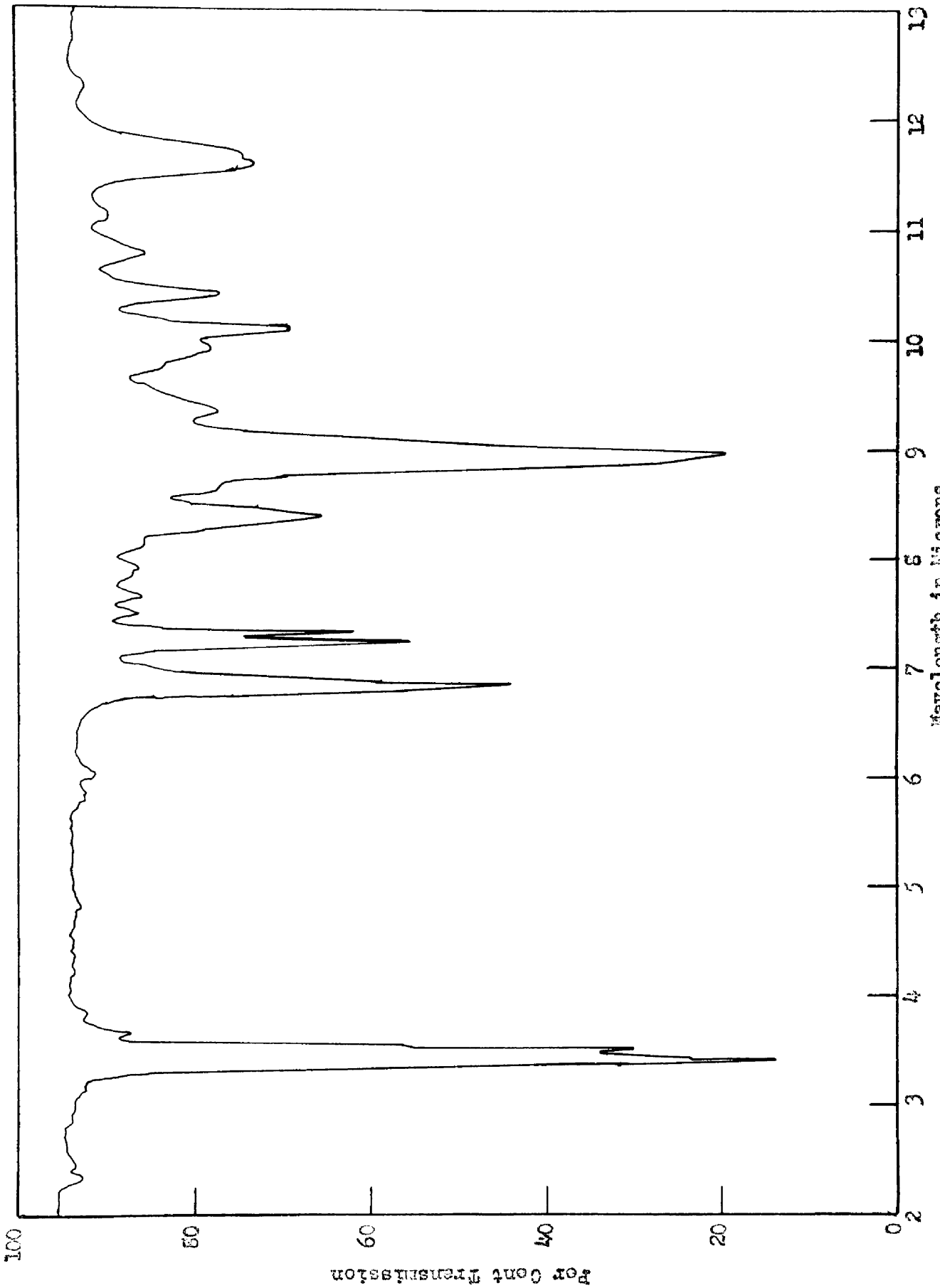
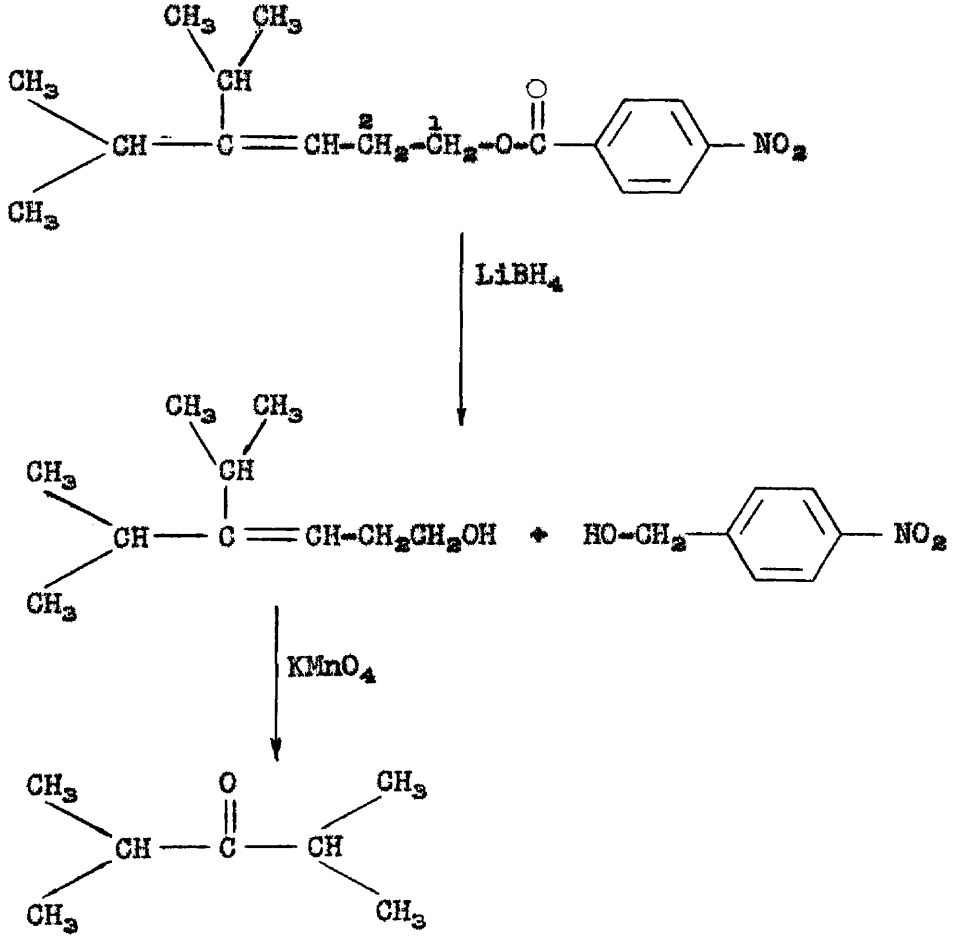


Figure **18.** Infrared Spectrum of 3-Cyclopropyl-3-methoxy-2,4-dimethylpentane (neat).

The unreactivity of the rearranged ester, 4-isopropyl-5-methyl-3-hexenyl p-nitrobenzoate, was demonstrated by the fact that even after prolonged boiling (26 hours) of the original ester in 70% dioxane-30% water, the theoretical titer of p-nitrobenzoic acid was not obtained, nor was it increased from that obtained in the kinetic experiments.

The structure of 4-isopropyl-5-methyl-3-hexenyl p-nitrobenzoate was proved by reduction with lithium borohydride to 4-isopropyl-5-methyl-3-hexenol and p-nitrobenzyl alcohol. The 4-isopropyl-5-methyl-3-hexenol gave diisopropyl ketone when oxidized with neutral potassium permanganate.



This fixes the position of the double bond as shown, but the ester function might have been at C_1 or C_2. Carbon atom 2 is eliminated on the basis that the ester would then have been allylic, and easily solvolyzed under the reaction conditions.

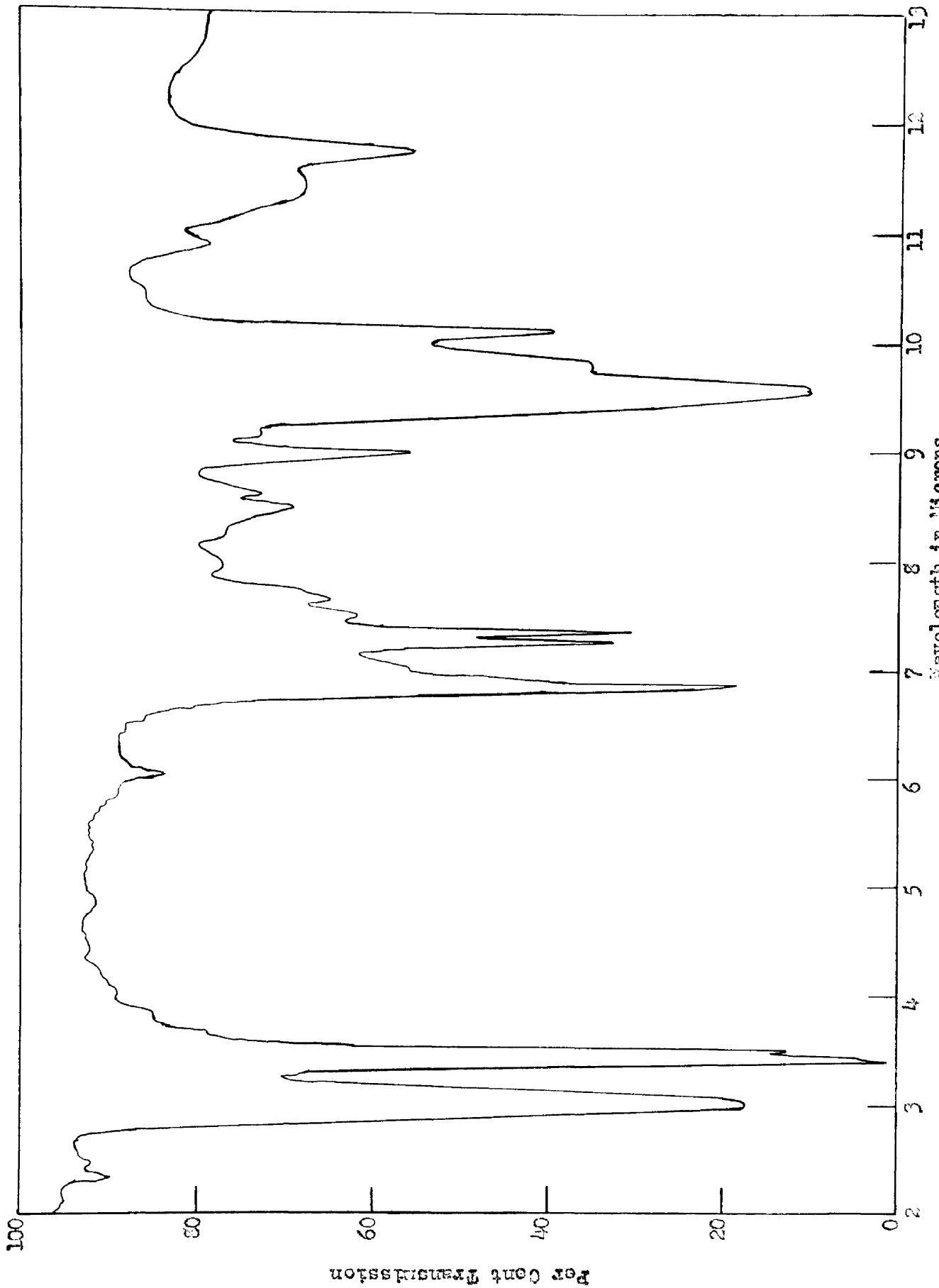


Figure **19.** Infrared Spectrum of 4-Isopropyl-5-methyl-3-hexenol (neat).

DISCUSSION OF THE SOLVOLYSIS STUDIES

DISCUSSION OF THE SOLVOLYSIS STUDIES

In order to place the results of the present investigation in proper perspective, it will be necessary first to discuss certain applicable phenomena in the general area of solvolysis mechanisms. This will be followed by a brief review of previous studies on cyclopropylcarbinyl systems, after which the present results will be examined in some detail.

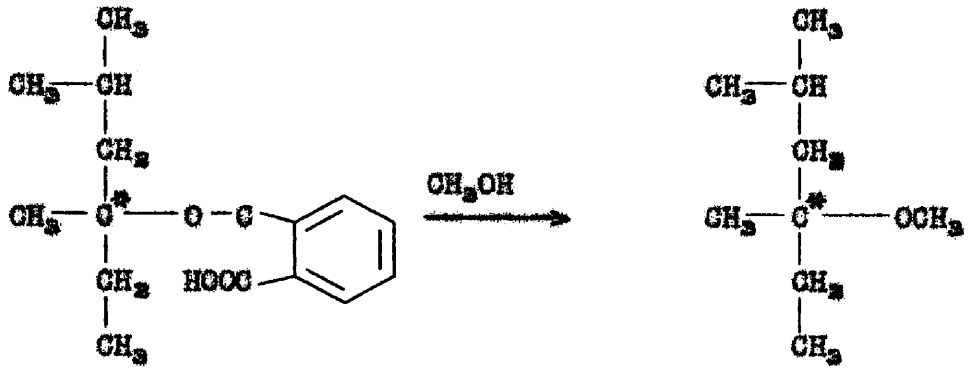
A. Recent Concepts in Solvolysis Mechanisms

A comprehensive and elegant review article on solvolytic displacement reactions at saturated carbon atoms by Streitwieser (9) considers at length and in detail the various nuances in solvolysis mechanisms. For this reason, a detailed review will not be attempted here. Since the ester solvolyses reported in this thesis are all of the S_N1 (9,29b) type, discussion is limited to this type of mechanism.

By the term S_N1 is meant a unimolecular nucleophilic substitution which usually occurs by a rate-determining ionization to a carbonium ion, followed by rapid reaction of this ion with a nucleophilic species. This general definition describes the gross features of the process, but omits many of the details; in particular, one is concerned with the mechanism of the ionization process itself, and also with the ultimate combination of species to form covalent product. Details about the ionization step were derived from stereochemical and kinetic studies.

The usual stereochemical consequence of an S_N1 reaction would be racemization at the carbonium carbon atom, because a completely solvated

planar carbonium ion can not be asymmetric. In certain systems, this is found to be the case (solvolysis of esters of p-methoxybenzhydrol (30) and of certain arylmethylcarbinols (31)). But in most instances, racemization is accompanied by a small amount of inversion (9b). Particularly remarkable is the 60% inversion observed in the methanolysis of hydrogen 2,4-dimethylhexyl-4 phthalate (32).



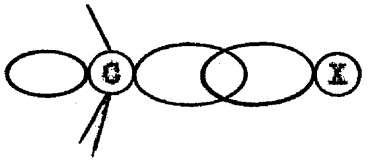
60% inversion

In order to account for the small amount of inversion in many S_N1 solvolyses, Hughes and Ingold (33,34) suggested preferential "shielding" of the carbonium ion during solvolysis; in order to account for varying amounts of inversion depending on the structure of the substrate, the concept of "lifetime" of the carbonium ion was introduced. Judicious combination of "shielding" and "lifetime" could qualitatively explain differing degrees of stereochemical inversion, but a quantitative treatment was impossible. Furthermore, the concept was confusing (35).

Shielding by the leaving group was placed on a sounder conceptual basis by Hammett who suggested that the product of the ionization step is an ion-pair (36). He implied that reaction with solvent before

dissociation of the ion pair would occur with inversion. Hammett's interpretation requires but little modification to account for several recently observed phenomena discussed below.

Doering and Zeiss (32) were led to a somewhat different, and structurally more detailed hypothesis, from their observation of considerable inversion in the methanolysis of hydrogen 2,4-dimethylhexyl-4 phthalate. Their argument has been amplified by Streitwieser (9). The transition state in the ionization process is represented by

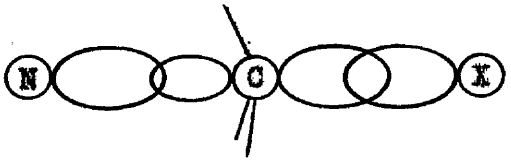


or

I

in which the C-X bond is intermediate between sp^3 (in the original molecule) and p (as it would be if X were associated with a planar carbonium ion). The central carbon will be electronically deficient to an extent which depends upon the degree of solvation of X and the nature of the groups attached to C. The greater the ability of the system to internally disperse this positive charge, the closer to tetrahedral will the structure of the transition state be.

A nucleophilic reagent N can help accommodate the developing positive charge by overlapping with the 'tail' of the reaction orbital as in

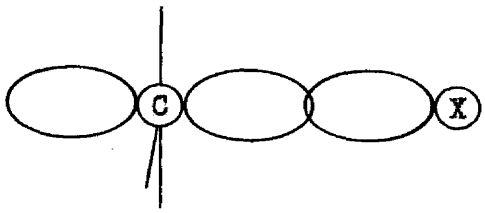


or

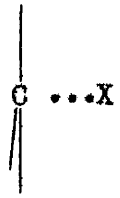
II

the better the internal compensation, the less the need for rearward participation; the greater the nucleophilicity of N the greater the importance of such participation.

In the tertiary carbinyl system in a highly ionizing medium the transition state I will lead directly to an intermediate

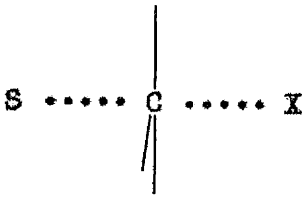


or



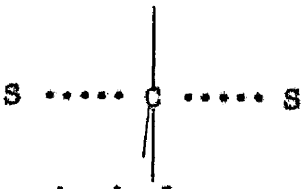
III

which, if X is an anion, can be referred to as an ion-pair (or more precisely, an intimate ion-pair (37,38)). Reaction with solvent to form



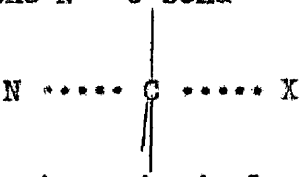
IV

and subsequently



V

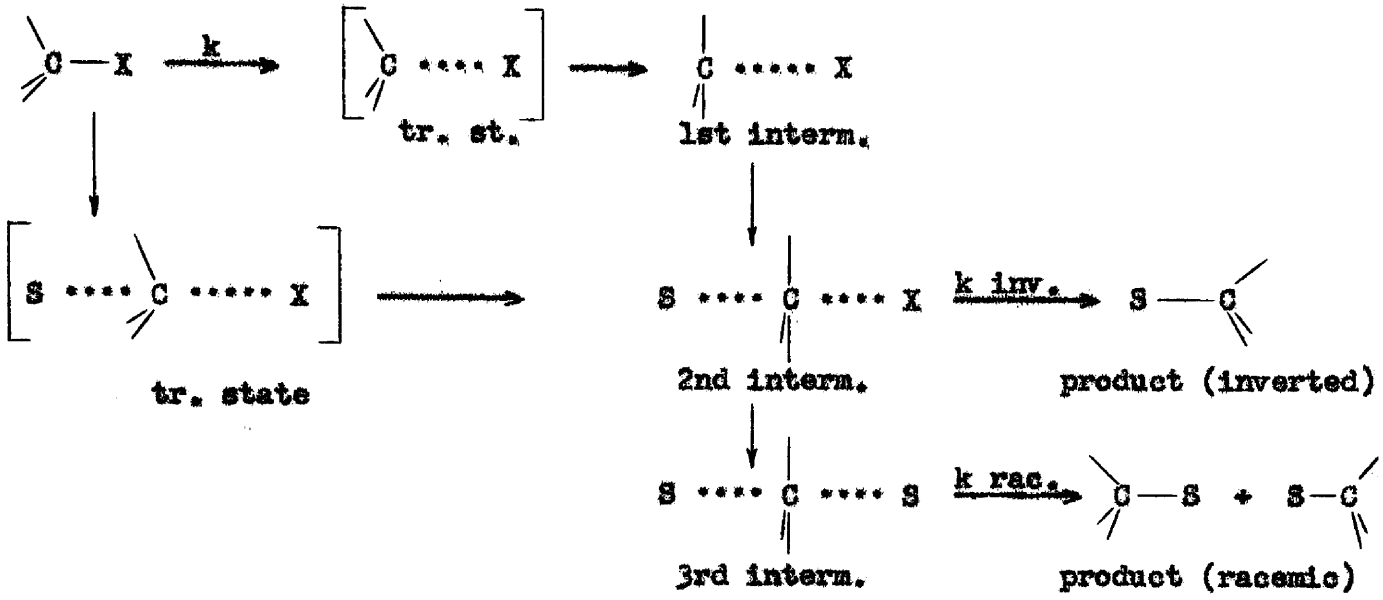
will be rapid; the stereochemical consequence will be racemization. If the solvent is strongly nucleophilic, the transition state is best represented by II, leading to an intermediate which has a good deal of covalent character to the N - C bond



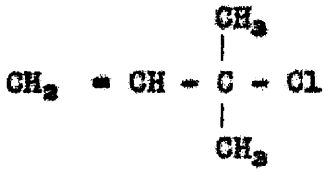
VI

X then departs, the net stereochemical result being inversion.

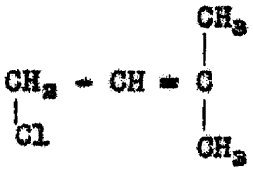
One notable virtue of this mechanistic picture is that it can accommodate the broad spectrum of displacement results, from classical S_N1 to classical S_N2. The stereochemical outcome will be determined by the relative rate constants in the following summarizing scheme:



The mechanism depicted thus far does not allow for reversibility which had to be introduced to explain certain results in allyl, norbornyl and other systems. The acetolysis of α,α-dimethylallyl chloride (VII) was accompanied by a first order isomerization

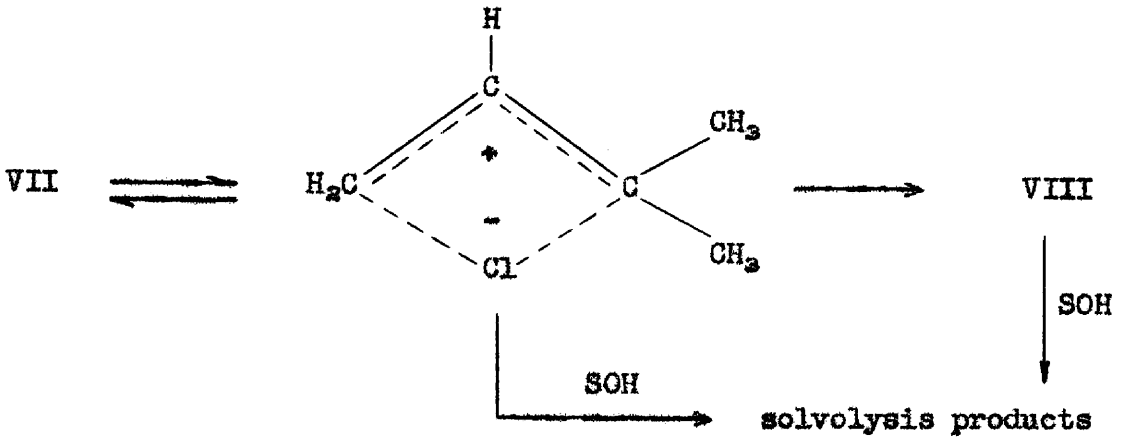


VII



VIII

to γ,γ-dimethylallyl chloride (VIII) (39). The rate of isomerisation was independent of added chloride ion, but sensitive to the ionising power of the medium, being favored by polar solvents. The results were interpreted in terms of an ion-pair which could go on to solvolysis products or return to original or isomerized halide. The phenomenon is



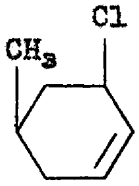
known as "internal return." The partition of the intermediate between 'return' and further solvolytic reactions will be a function of solvent nucleophilicity and ionizing power; this is shown in Table 10.

Table 10

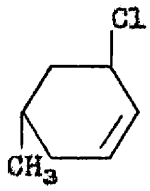
Solvolysis of α,α- and γ,γ-Dimethylallyl Chloride

	10^5 k, sec.$^{-1}$		
Rate Constant	Acetic Acid	75% Ethanol	Ethanol
k_i	4.0	180	0.
k_t	1.5	380	1.8
k_p	0.22	115	0.65

A stereochemical consequence of internal return in halides showed up in the investigations of Goering, et al., (4)) on the 3-chloro-5-methylcyclohexene system.

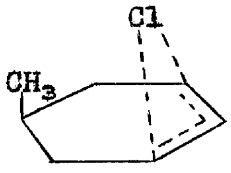


IX

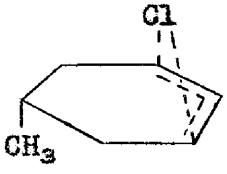


X

In the acetolysis and ethanolysis of optically active IX and X the rate of racemization (formation of ion-pair) was greater in acetic acid than in absolute ethanol, whereas the rate of solvolysis was actually less in acetic acid than in ethanol. For both geometric isomers in either acetic acid or ethanol, the rate of racemization was greater than the rate of solvolysis and was unaffected by added chloride ion. Racemisation occurred without cis-trans isomerization. Racemized chloride recovered before solvolysis was complete, was not geometrically isomerized. The first ion-pair intermediates involved in each case, XI and XII are symmetrical; they are incapable of sustaining optical activity.



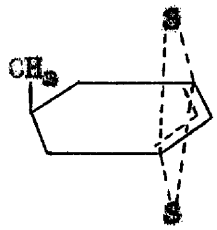
XI



XII

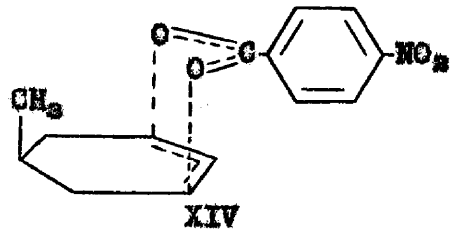
These structures represent ion-pairs which are different from the classical Debye-Hückel type of ion-pair. Their structure is geometrically more precise; the ions are not separately solvated and free to rotate with respect to one another. This allows retention of geometrical purity, yet permits racemization. In a more detailed analysis of ionic intermediates, Winstein and co-workers (37,38) have been able to distinguish kinetically between an 'intimate' ion-pair, a 'solvent-separated' ion-pair, classical ion-pairs and free ions.

The ethanolysis and acetolysis products from IX and X contained the same ratio of cis/trans isomers. Presumably these products arose from a di-solvated intermediate XIII:



XIII

In a very similar study, internal return was investigated in the reactions of optically active cis and trans-5-methylcyclohexen-3-yl p-nitrobenzoate (41). Solvolysis in 80% aqueous acetone proceeded by alkyl-oxygen cleavage. For each isomer, the rate of racemization was greater than the rate of solvolysis. Each ester racemized without cis-trans isomerization. The intermediate (for the cis compound) is probably best formulated as XIV:



XIV

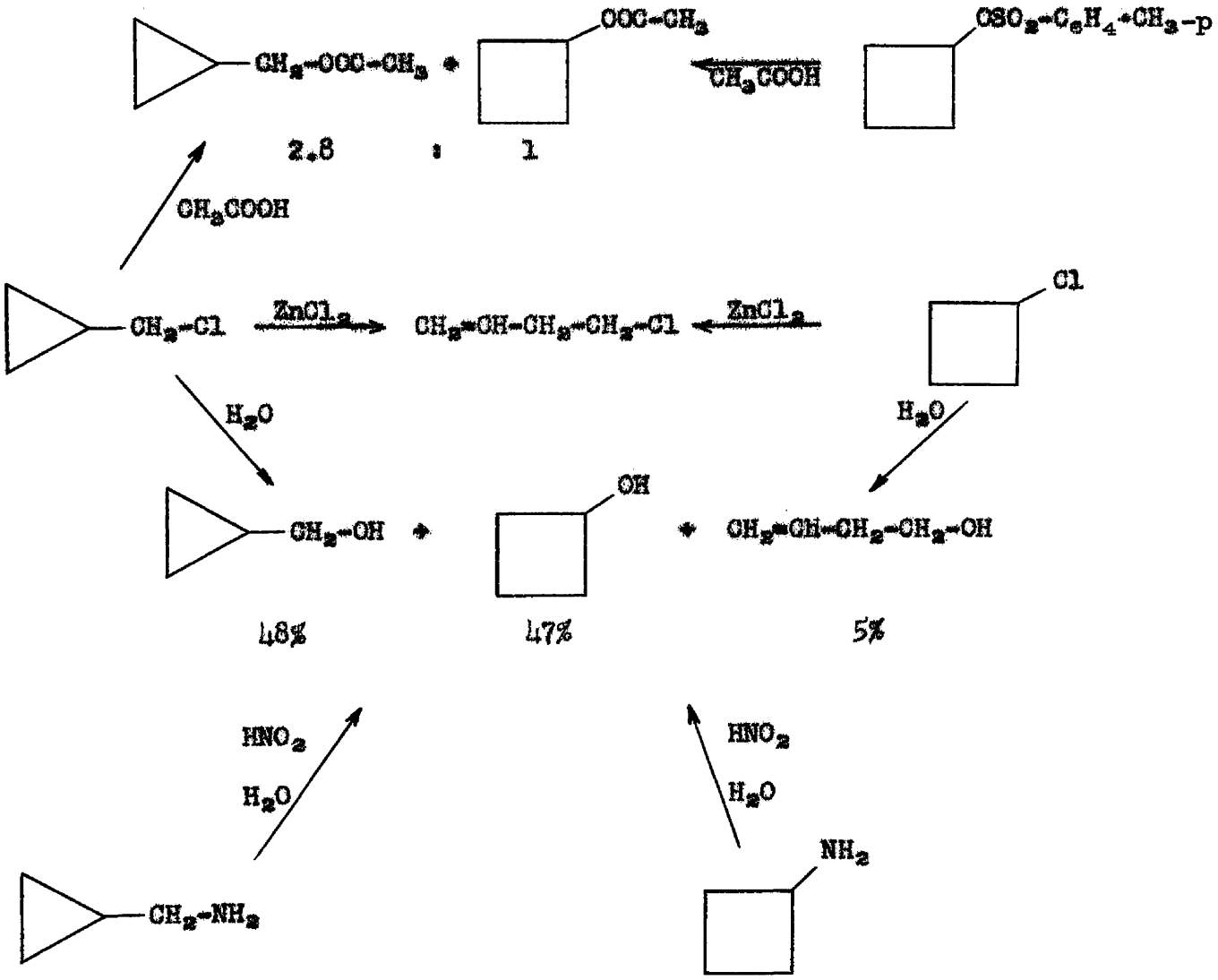
B. Previous Investigations of the Cyclopropylcarbinyl Systems

Although some very careful and elegant investigations of the cyclopropylcarbinyl system have been performed, a completely consistent mechanistic picture of the reactions has not yet evolved. In certain instances, rearrangement products predominate, whereas in others, no rearrangement of the carbon skeleton is observed; some rationalisations are possible, but they are not always consistent, and it is still difficult to predict what products might be expected under a given set of experimental conditions. Previous work was concerned with primary and secondary cyclopropylcarbinyl systems, whereas the work described in this thesis deals mainly with tertiary systems.

The unusual reactivity of the cyclopropylcarbinyl system in solvolysis reactions has already been referred to in the introduction to this thesis. This section will focus attention on the solvolysis products. Partial hydrolysis of cyclopropylcarbinyl chloride yielded a mixture of carbinols consisting of 48% cyclopropylcarbinol, 47% cyclobutanol and 5% allylcarbinol and a mixture of unreacted chlorides which contained both cyclobutyl chloride and allylcarbinyl chloride (8). Under the conditions used, the isomeric chlorides would not have solvolyzed significantly. The rearranged carbinols are, therefore, derived from cyclopropylcarbinyl chloride. Hydrolysis of cyclobutyl

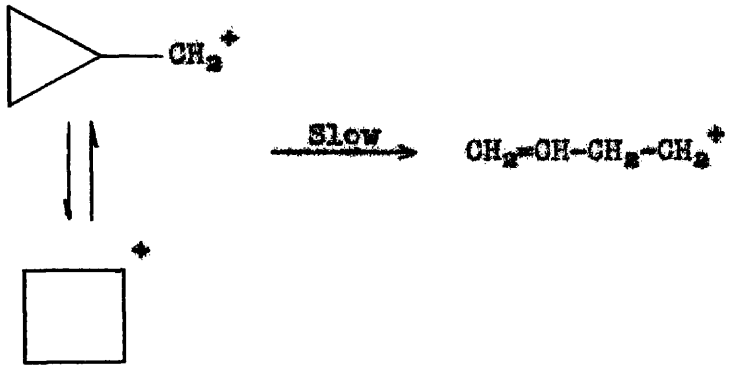
chloride yielded an identical mixture of carbinols (8). Furthermore, the diazotization of cyclopropylcarbinylamine or cyclobutylamine also gave the same carbinol mixture (8).

On the other hand, acetolysis of cyclobutyl p-toluenesulfonate (42) or cyclopropylcarbinyl chloride (8) resulted in a different ratio of solvolysis products; cyclopropylcarbinyl and cyclobutyl acetates were formed in a ratio of about 2.8 to 1. As above,

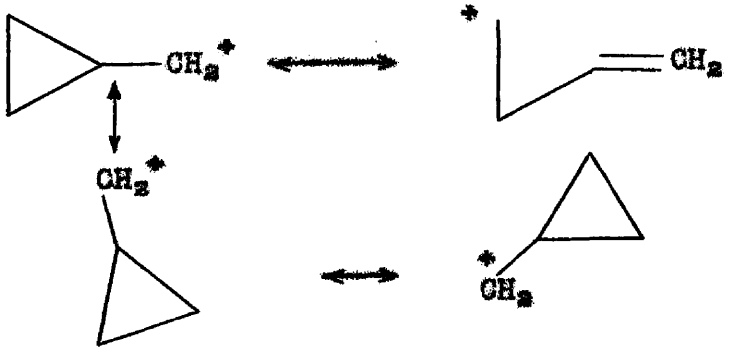


rearranged starting material was also found which implies internal return from ion-pair intermediates.

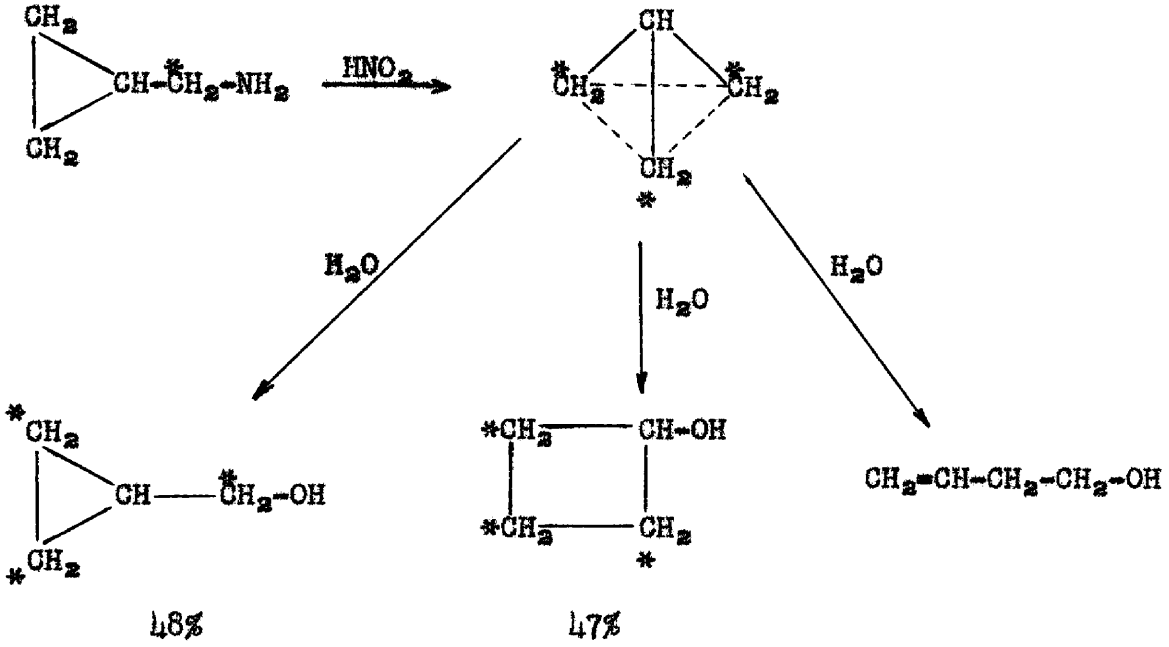
The reactions were interpreted (8) by assuming an interconversion of the cyclopropylcarbinyl carbonium ion and the cyclobutyl carbonium ion with a slow and essentially irreversible reaction to allylcarbinyl derivatives. For example, treatment of cyclopropylcarbinyl, cyclobutyl or allylcarbinyl chlorides with zinc chloride and hydrochloric acid gave essentially pure allylcarbinyl chloride (8). The following scheme was proposed (8) for explaining the various reactions:



The stability of the cyclopropylcarbinyl carbonium ion has been attributed (7,8) to resonance of the following type:



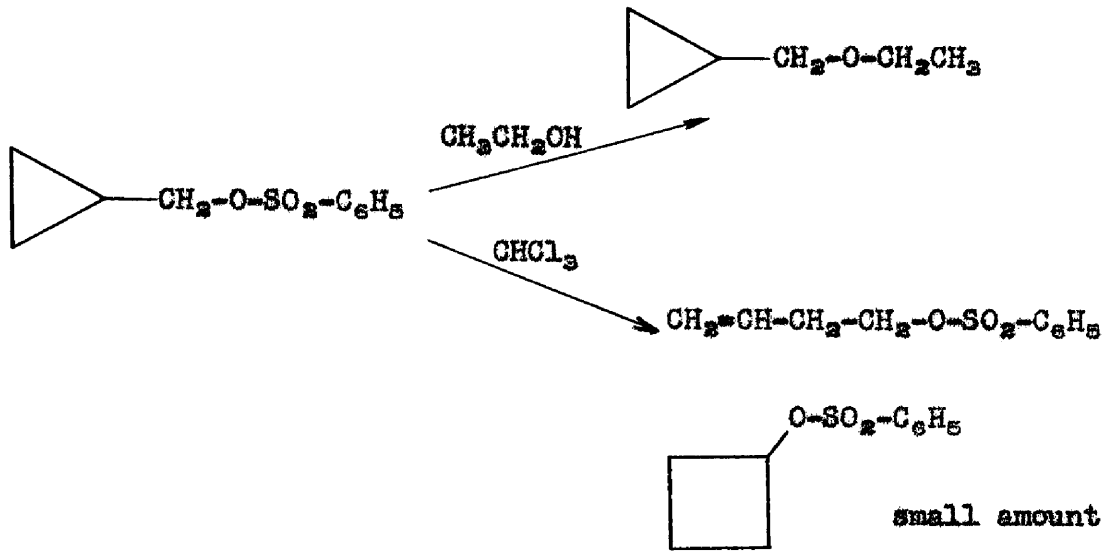
An alternative explanation, involving a "non-classical" carbonium ion, was suggested by Roberts and Mazur (43) to account for the results obtained when cyclopropylcarbinylamine-1-C^{14} was treated with nitrous acid.



The C^{14} was distributed statistically between the three methylene carbon atoms in the cyclobutanol. A carbonium ion of the type shown in the scheme would explain this result, the two methylene groups of the cyclopropane ring becoming equivalent with the exocyclic methylene group. However, in the cyclopropylcarbinol formed, an excess of the C^{14} (45% rather than 33.3%) over that predicted by the non-classical intermediate was found at the carbinol carbon atom, and only 54% (rather than 66.7%) was found in the ring. This implies that more than one mechanism is operative. The results can also be explained by assuming facile interconversion of the cations

It is perhaps worth noting that although the cyclobutane ring and especially the cyclopropane ring are "strained," in terms of tetrahedral (sp^3) bonding, these rings do not always relieve this strain when the opportunity arises (i.e., by exclusively forming open-chain allylcarbinyl product). This suggests that the bonding in these rings is somewhat different than sp^3. Furthermore, although secondary carbonium ions are generally more stable than primary carbonium ions (29b), the primary cyclopropylcarbinyl carbonium ion is apparently at least as stable as the secondary cyclobutyl carbonium ion. The situation is somewhat analogous to the comparable stability of benzyl ions.

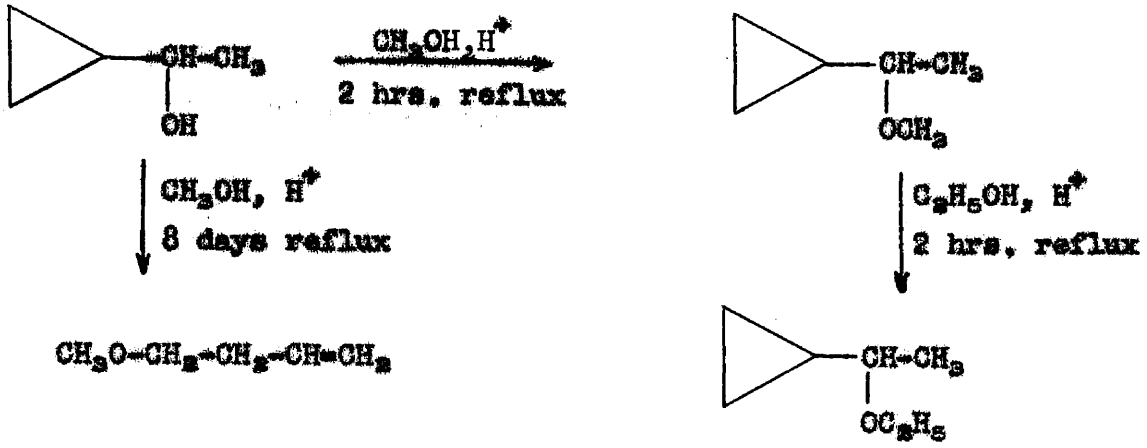
Two striking cases have been reported, one primary and the other secondary, in which no ring opening or rearrangement occurs during solvolysis. Bergstrom and Siegel (7) found that cyclopropylcarbinyl benzenesulfonate in absolute ethanol gave cyclopropylcarbinyl ethyl ether in a first order process. It was also observed that the benzenesulfonate rearranged rapidly in chloroform to allylcarbinyl benzenesulfonate and a small amount of the cyclobutyl isomer.



The absence of any significant amount of cyclobutyl ethyl ether in the solvolysis product is striking, especially since cyclopropylcarbinyl chloride in 50% aqueous ethanol yielded equal amounts of cyclobutanol and cyclopropylcarbinol. The results may be explained in terms of the structural concept for S_N1 mechanisms of Doering, Zeiss, and Streitwieser; the transition state has a structure close to sp^2 in which the "tail" of the reaction orbital is fairly large. This, combined with the small degree of steric hindrance, makes orbital overlap with the highly nucleophilic ethanol important and ether is irreversibly produced without rearrangement. The situation is reminiscent of the lack of internal return in the solvolysis of α,α-dimethylallyl chloride in absolute ethanol.

Pearson and Langer (44) found that in the presence of toluenesulfonic acid, cyclopropylmethylcarbinol in methanol gave the methyl ether without rearrangement. The methyl ether, in ethanol under similar conditions, was solvolyzed to the ethyl ether, also without rearrangement. Only on

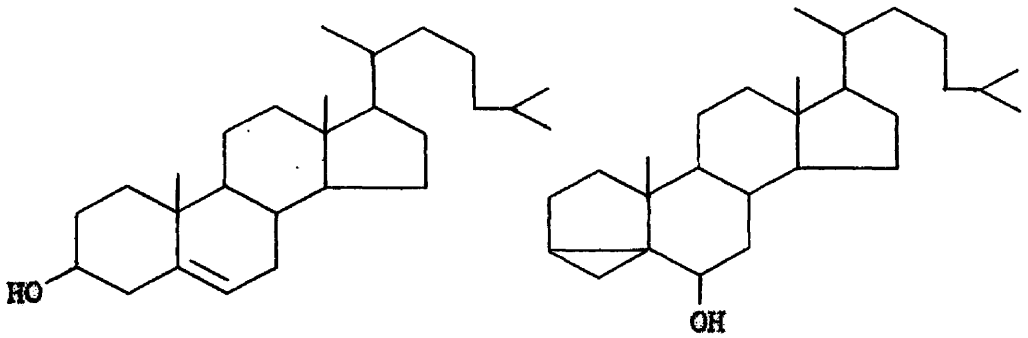
prolonged (8 days) reflux, was any allylcarbinyl methyl ether formed.



These results are similar to those of Winstein and Adams (45) with the i-steroids.

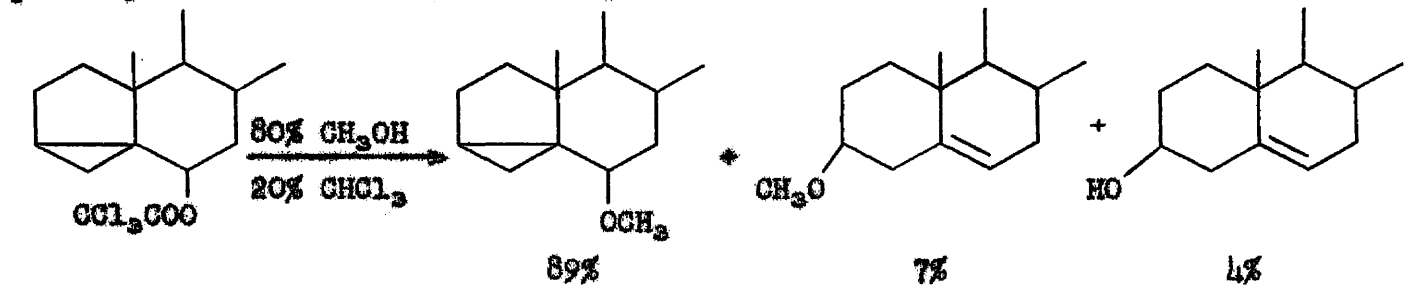
Results very closely related to the present work were reported by Kosower and Winstein (11) after the experimental work described in this thesis was completed. Because of direct bearing on the present results, their work will be outlined in some detail.

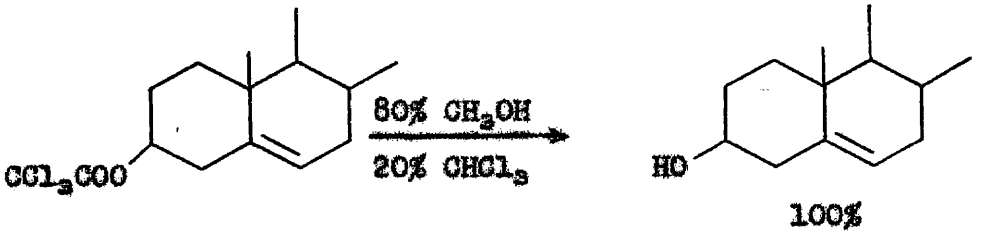
For the sake of brevity, derivatives of 3,5-cyclocholestan-6-ol (XVI) will be referred to as C (cyclo) and those of cholesterol (XV) will be referred to as A (allylcarbinyl). Although this will not always lead to precise names, the meaning will be clear, and extensive repetition of lengthy names will be avoided.

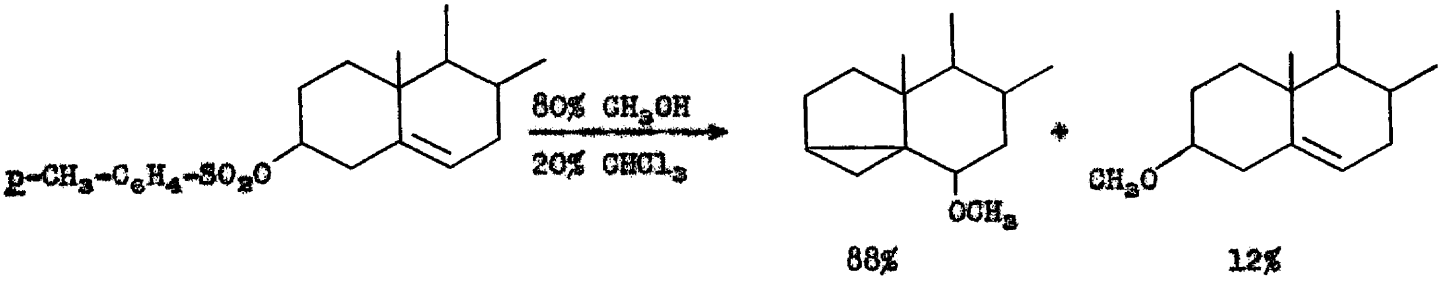


XV XVI

Solvolysis of C trichloroacetate in 80% methanol-20% chloroform gave 89% of C methyl ether, 7% of A methyl ether and 4% of A (cholesterol); but A trichloroacetate under the same conditions gave 100% A. In the same solvent, A p-toluenesulfonate, instead of the trichloroacetate, gave 88% of C methyl ether and 12% of A methyl ether, products almost identical to those obtained from C trichloroacetate, except that the small quantity of cholesterol was absent.

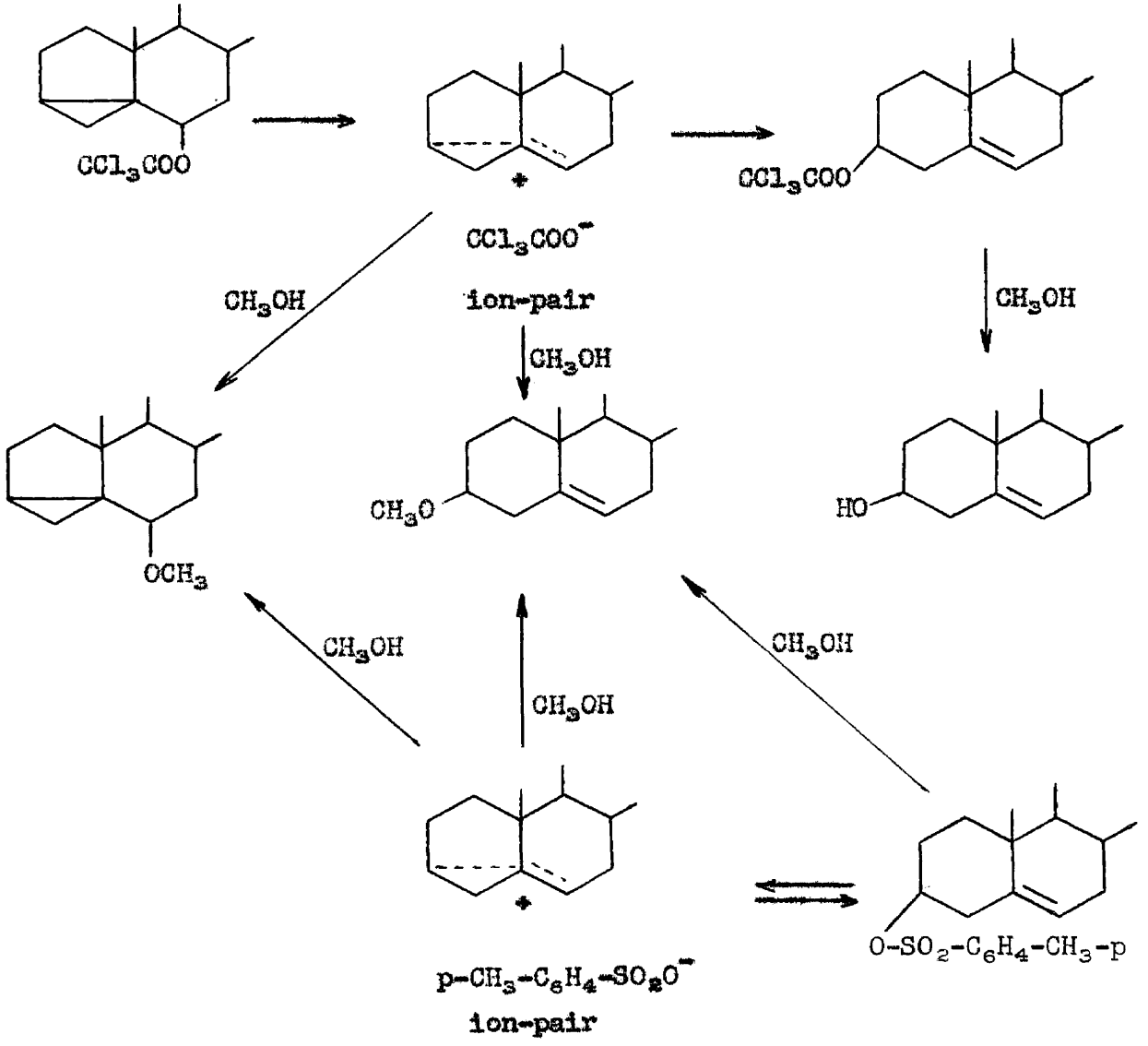




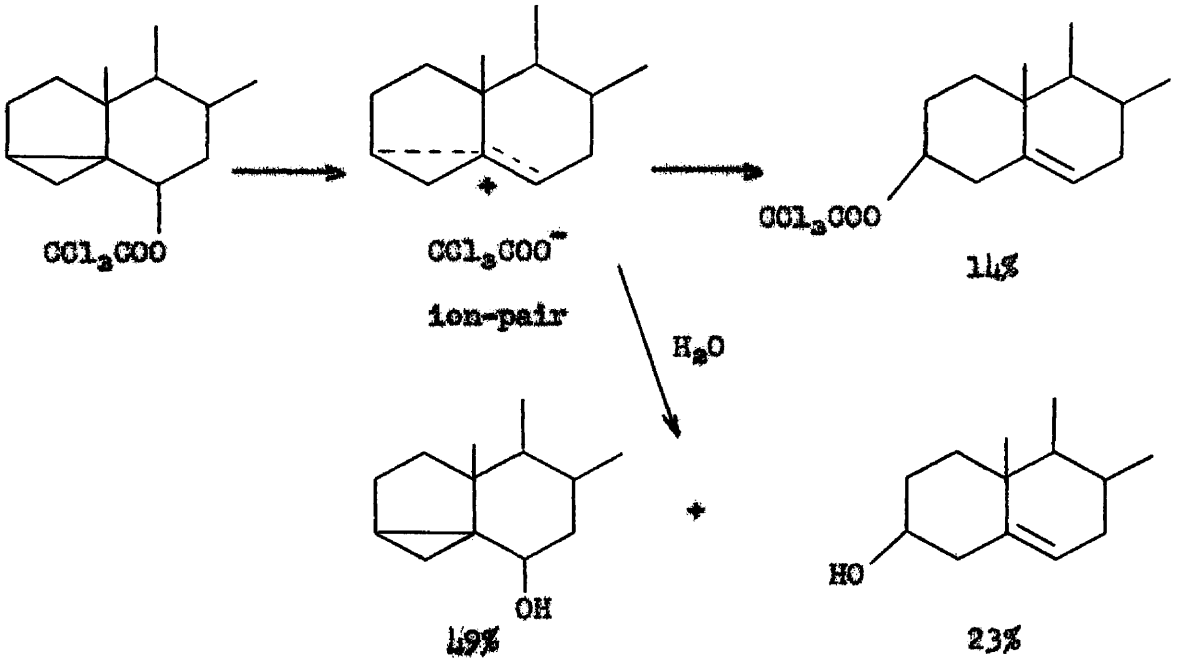


It is therefore clear that A trichloroacetate solvolyzed with acyl-oxygen fission, whereas C trichloroacetate and A p-toluenesulfonate solvolyzed with alkyl-oxygen cleavage. The small amount of cholesterol formed during the methanolysis of C trichloroacetate indicates internal

return to A trichloroacetate, followed by acyl-oxygen cleavage of the latter to yield cholesterol. Since both C trichloroacetate and A p-toluenesulfonate yielded identical ethers in about the same proportions, the solvolysis of these compounds must have proceeded through a common intermediate. The formation of more A methyl ether from A p-toluenesulfonate than from C trichloroacetate indicates that the p-toluenesulfonate returned internally to the cholesteryl derivative which further solvolysed to the ether. The results may be depicted as follows:

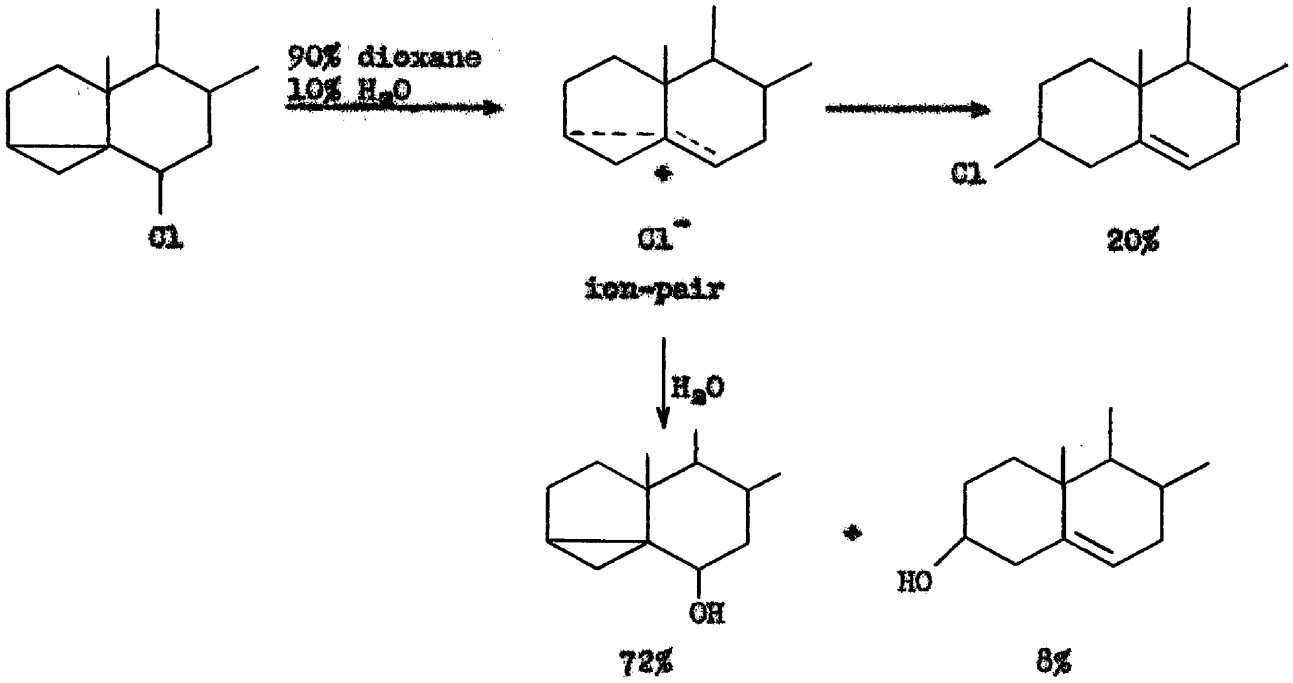


Solvolysis of C trichloroacetate in 90% aqueous dioxane yielded 49% of C (3,5-cyclocholestan-6-ol), 23% of A, and 14% of A trichloroacetate. Cholesterol did not react appreciably with trichloroacetic acid under the solvolysis conditions; hence the A trichloroacetate isolated from the solvolytic reaction represented a direct solvolysis product. Addition of lithium trichloroacetate to the solvolysis mixture did not effect the composition of the alcohol product but markedly decreased the amount of A trichloroacetate produced. The results strongly indicate an ion-pair mechanism:



Solvolysis of C chloride (10) in 90% aqueous dioxane (containing excess lithium acetate) yielded 72% of C, 20% of A chloride, and 8% of A. The lithium acetate, which was used to prevent the solution from becoming acid, did not react with the A chloride under the

solvolysis conditions. Apparently, internal return was more important during solvolysis of the chloride than the trichloroacetate. C chloride is reported to solvolyze about 10^8 times faster than A chloride in 90% aqueous dioxane (9a,10).



Winstein's results with the 3,5-cyclocholestan-6-yl derivatives demonstrate again the remarkable reactivity of the cyclopropylcarbinyl system. The secondary cyclopropylcarbinyl carbonium ion is apparently the major contributing form to the resonance hybrid, since predominantly cyclopropylcarbinyl, rather than allylcarbinyl derivatives were the major solvolysis products.

C. The Present Investigation

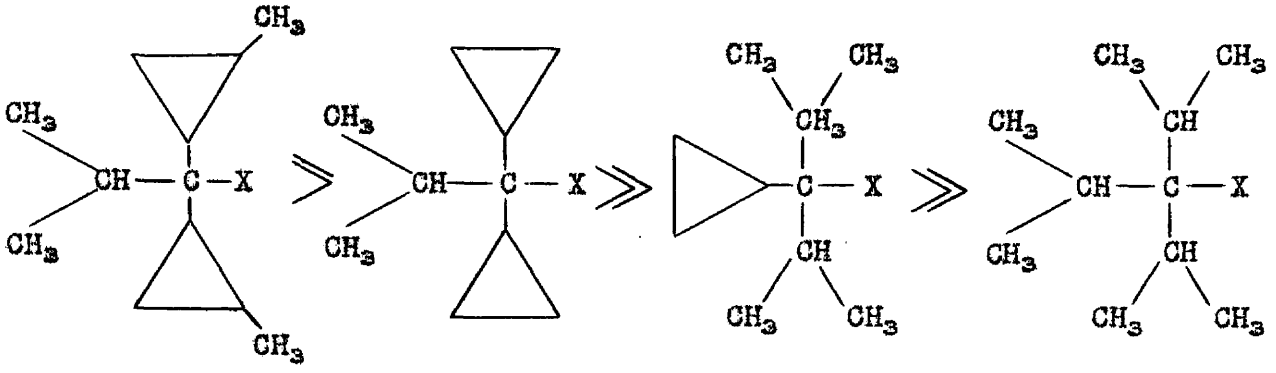
1. The Nature of the Reaction

Carboxylic esters may solvolyze by acyl-oxygen or by alkyl-oxygen

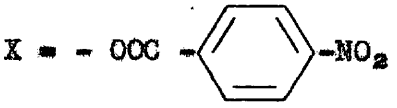
fission (29c), and this solvolysis may be catalyzed by acids or bases. All the evidence accumulated in the present work is consistent with unimolecular alkyl-oxygen fission of the cyclopropylcarbinyl p-nitrobenzoates. This conclusion is supported by the observations that the kinetics were first order and independent of added hydroxide ion; furthermore, there was no catalytic effect of the p-nitrobenzoic acid produced during the solvolysis. The product of methanolysis in methanolic dioxane was the alkyl methyl ether; since there is no evidence for the existence of a methyl carbonium ion in solution (46), this constitutes support for alkyl-oxygen fission of the ester. Finally, the rate of solvolysis was greatly increased by increasing the ionizing power of the solvent. For example, the rate constants for hydrolysis of dicyclopropylisopropylcarbinyl p-nitrobenzoate at 25° were found to be 1.60, 5.49 and 13.3 x 10^{-4} $sec.^{-1}$ in 90, 85 and 80 percent aqueous dioxane respectively. This behavior is precisely what would be expected from a reaction in which the rate-determining step involves ionization of a neutral molecule (29d).

2. Effect of Structure on the Rates

The rates of solvolysis reported here are truly remarkable for carboxylic esters. For example, the half-life of dicyclopropylisopropylcarbinyl p-nitrobenzoate at 25° in 80% dioxane-20% water was only nine minutes, and this was not the fastest ester studied. That the cyclopropyl groups must be responsible for this unusual behavior is clear from the following observed decreasing order of reactivity:



XVII XVIII XIX XX



That each additional cyclopropyl group helps to stabilize the carbonium ion formed in solvolysis is apparent from a detailed examination of the data in Table 11.

Replacement of one isopropyl group of triisopropylcarbinyl p-nitrobenzoate with a cyclopropyl group increased the rate of reaction by a factor of 246. Replacement of a second isopropyl group with a cyclopropyl group further increased the rate 96-fold. When the rates are compared in terms of solvolysis only (i.e. neglecting rearrangement) these factors become 159 and 147 respectively. It is highly likely that a third cyclopropyl group would increase the rate by several more powers of ten. This may well be the reason why the numerous attempts to prepare tricyclopropylcarbinyl p-nitrobenzoate failed.

Steric acceleration of S_N1 solvolyses is now reasonably well established (47). The cyclopropyl group probably has a smaller steric requirement than an isopropyl group, and certainly than a t-butyl group.

Table II

Relative Rates[a] of Solvolysis of Several p-Nitrobenzoates in Aqueous Dioxane

p-Nitrobenzoate	Weight Per Cent Dioxane						
	80				90		
	60°		7°		60°		25°
Di-(2-methylcyclopropyl)-isopropylcarbinyl (XVII)	124000[b]	2030[b]	505[b]	5.26	211 (654)	4.01 (3.50)	4.43 (4.08)
Dicyclopropylisopropyl-carbinyl (XVIII)	23500	386	96 (147)	1.00	52.6 (187)	1.00	1.00
Diisopropylcyclopropyl-carbinyl (XIX)	246 (159)	4.04 (2.62)	1.00 (1.00)		1.00 (1.00)		
Dicyclopropylcarbinyl (XXI)	60.7	1.00					
Triisopropylcarbinyl (XX)	1.00						

[a]The values were evaluated from the over-all rate constant (k) except for the values in parentheses; these were derived from k_s for those cases in which simultaneous solvolysis and rearrangement occurred.

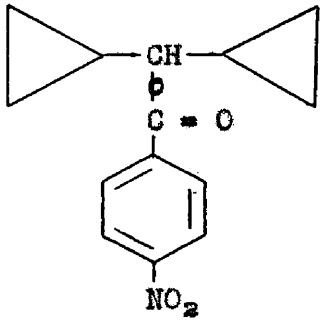
[b]From data at 7°.

Clearly then, the electron-releasing effect of the cyclopropyl group must override any steric plus electronic effect of the isopropyl group. From the unusually fast rate observed for the p-nitrobenzoate of the secondary alcohol, dicyclopropylcarbinol, one can say that one cyclopropyl group is about equivalent to two isopropyl groups. (On this basis, one would predict that cyclopropylisopropylcarbinyl p-nitrobenzoate should solvolyze at about the same rate as the triisopropylcarbinyl ester).

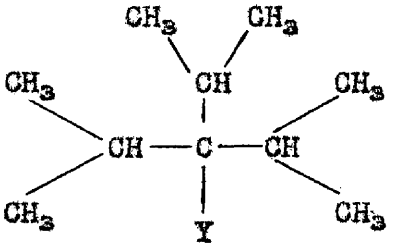
The solvolysis in aqueous dioxane of the p-nitrobenzoates of all the possible tertiary carbinols with alkyls either isopropyl or t-butyl was studied by Bartlett and Stiles (48). Acceleration by t-butyl was marked (9-fold for replacement of two isopropyl groups by t-butyl groups), but relatively small when compared with the 23,500-fold increase for a similar substitution of cyclopropyl groups. The electronic influence of the cyclopropyl group is of tremendous magnitude when compared with steric effects, or with electronic effects of simple alkyl groups.

The similarity between the cyclopropyl group and the phenyl group in electronic influence on reaction rates is striking. Although not enough data are available to make extensive quantitative comparisons, the indications are that the cyclopropyl group is at least as effective as the phenyl group towards stabilization of carbonium ions. Cyclopropylcarbinyl chloride in 50% aqueous ethanol at 50° solvolyzed ten times faster than benzyl chloride (8,49) and both of these are several powers of ten faster than a primary saturated chloride. This is the only case where a direct comparison is possible. The rates of solvolysis of

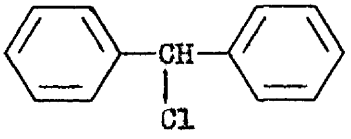
cyclopropylcarbinyl and benzyl p-toluenesulfonates are 7.6×10^{-5} sec.$^{-1}$ (calculated from the benzenesulfonate (7)) and 5.33×10^{-5} sec.$^{-1}$ (44) respectively in absolute ethanol at 25°. Again, this is many powers of ten faster than similar esters of primary aliphatic alcohols. Somewhat more indirect comparisons are possible which admittedly are not quantitative, but indicate strongly that the cyclopropyl and phenyl groups are similar, and that the cyclopropyl group is very different from a saturated alkyl or larger cycloalkyl group. Some data of this type is given in the chart.



XXI

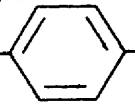


XXII



XXIII

When Y = Cl, the relative rate of XXII/XXIII is 11 in 90% aqueous acetone at 25° (50,33).

When Y =  , the relative rate of XXI/XXII is 61 in 80% aqueous dioxane at 60° (see Table 11).

3. The Driving Force

The unsaturated character of cyclopropane was explained by Walsh (51) in the following way. He considers each of the three carbon atoms

to be in a state of sp^2 hybridization analogous to ethylenic carbon atoms. The three carbon atoms are at the corners of an equilateral triangle with two hydrogen atoms lying in the plane bisecting each angle. The hydrogen-carbon-hydrogen bond angle is 116° (52) which is practically the same as in ethylene. The bonds between the three carbon atoms are formed by overlap of the three p orbitals whose axes lie in the plane of the ring and by overlap of the three sp^2 orbitals (whose axes also lie in the plane of the ring) to form a three-center bond. The overlap is shown in Figure 20. The six sp^2 carbon hydrogen bond orbitals have been omitted for clarity and are merely represented by lines. Walsh offers physical and chemical evidence for this structure. The disposition of the electrons in the cyclopropane ring is somewhat similar to that in the benzene ring. In the latter, the overlap of two sp^2 bonds for each carbon atom results in strong carbon-carbon bonds and the six p electrons are completely delocalized. The sp^2 three-center bond in cyclopropane renders this carbon skeleton much less stable than that of benzene, and even somewhat less stable than sp^3 carbon-carbon bonds in acyclic compounds. Although the p electrons are not completely delocalized, a cyclopropylcarbinyl carbonium ion should be stabilized to a considerable extent through overlap of p orbitals to form a non-localized π orbital (see Figure 21). This stabilization of the carbonium ion should provide a driving force for solvolysis reactions of the cyclopropylcarbinyl system. Since four p-orbitals are involved in the delocalization of the cyclopropylcarbinyl carbonium ion, it should be more stable than the allyl carbonium ion in which only three p orbitals are involved.

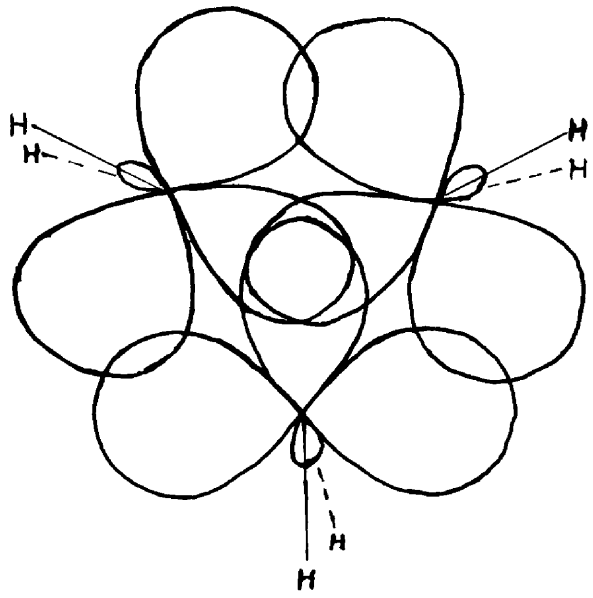


Figure 20. Molecular Orbital Structure for Cyclopropane.

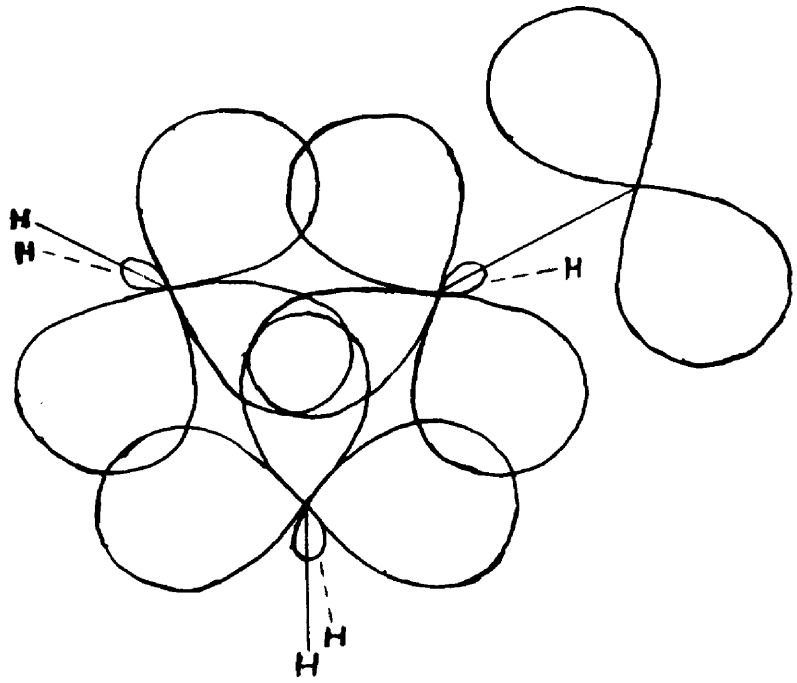
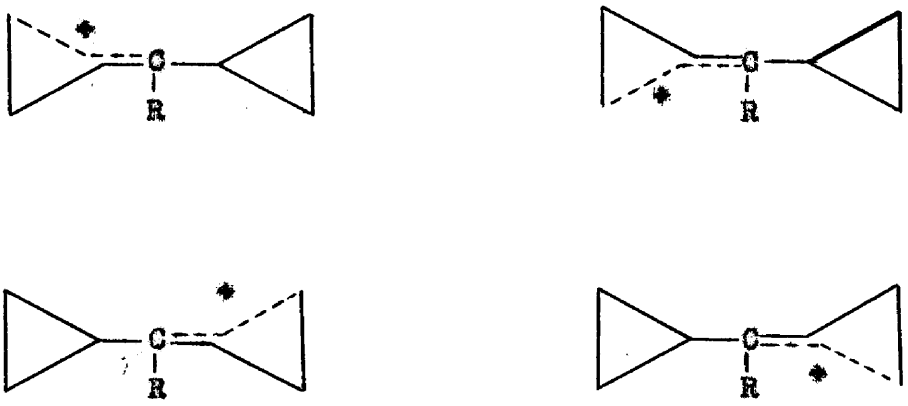
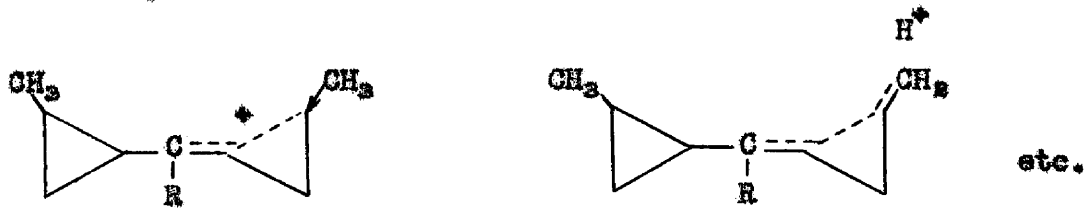


Figure 21. Molecular Orbital Structure for Cyclopropylcarbinyl Carbonium Ion.

It was observed in the present investigation that a second cyclopropyl group further enhanced the reactivity of the cyclopropylcarbinyl system toward solvolysis to a considerable degree (note the similarity of benzyl versus benzhydryl). This may be ascribed to the additional contributing structures which a second cyclopropyl group can provide.



The increase in reactivity observed when a methyl group is at the 2-position of the ring might be due to its ability to transmit its electrical effects through the cyclopropane ring as well as the steric acceleration it may afford.



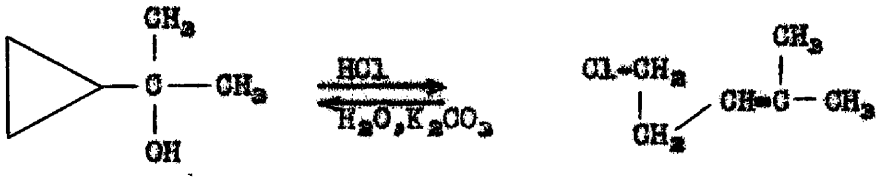
etc.

The driving force for reactions of cyclopropyl systems has sometimes been ascribed to a need for releasing the strain energy in the three-membered ring (53,45,8). The situation, however, does not seem to be entirely clear. For example, in the present cases (as will be

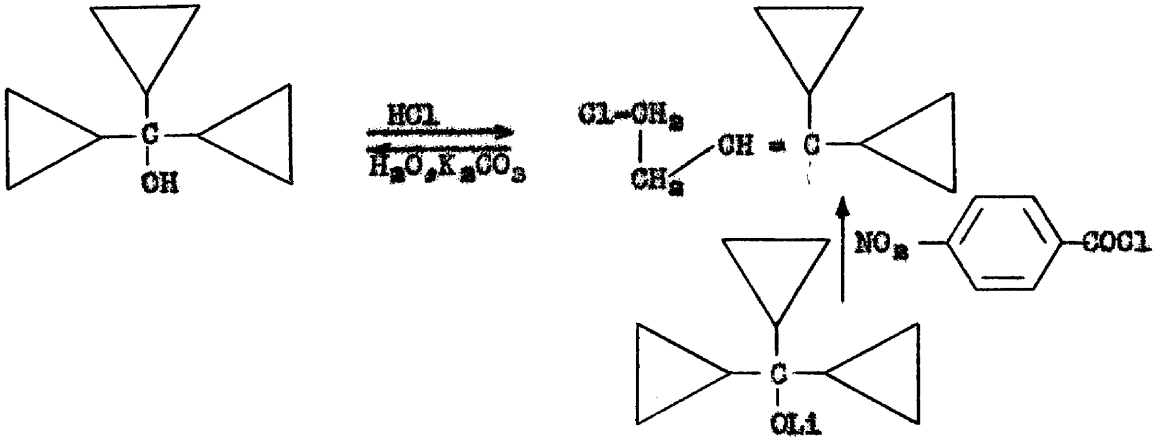
discussed below in detail) the fastest rates were not necessarily associated with ring opening.

Facile ring closure under what might be considered surprising conditions further support the contention that ring-opening is not a necessary feature in the driving force.

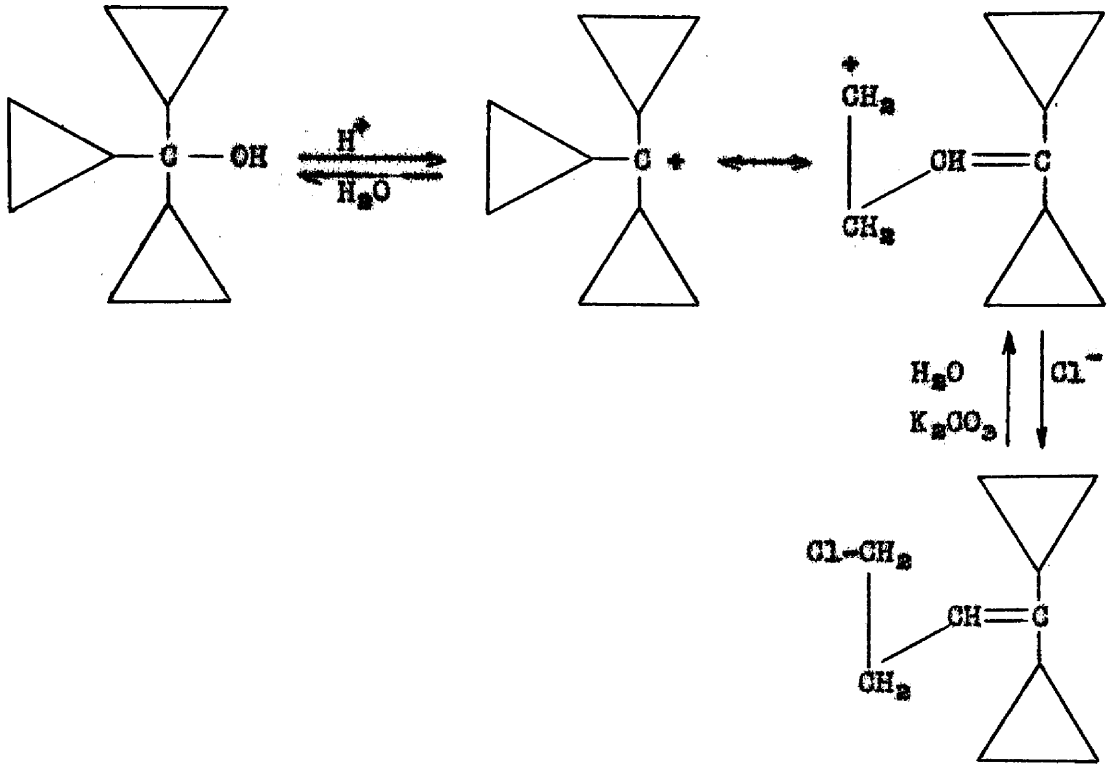
Dimethylcyclopropylcarbinol, with hydrochloric acid, gave 5-chloro-2-methyl-2-pentene which upon treatment with aqueous potassium carbonate reversed the process (54).



Similarly, it was observed in the present investigation that treatment of tricyclopropylcarbinol with concentrated hydrochloric acid or treatment of the lithium salt of tricyclopropylcarbinol with p-nitrobenzoyl chloride yielded 1,1-dicyclopropyl-4-chloro-1-butene which, upon treatment with aqueous potassium carbonate again yielded tricyclopropylcarbinol.



The interconversion between carbinol and unsaturated chloride most likely proceeds through a common carbonium ion intermediate:



The controlling and conflicting factors appear to be the stability of the carbonium ion (tertiary > secondary > primary), the stability of the product (allylcarbinyl > cyclopropylcarbinyl) and the reaction medium (nucleophilicity of the reagent).

4. The Internal Rearrangement

Diisopropylcyclopropylcarbinyl, di-(2-methylcyclopropyl)isopropyl-carbinyl, and dicyclopropylisopropylcarbinyl p-nitrobenzoates rearranged simultaneously with solvolysis. Rearrangement was a function of the water content of the solvent, as shown in Table 12.

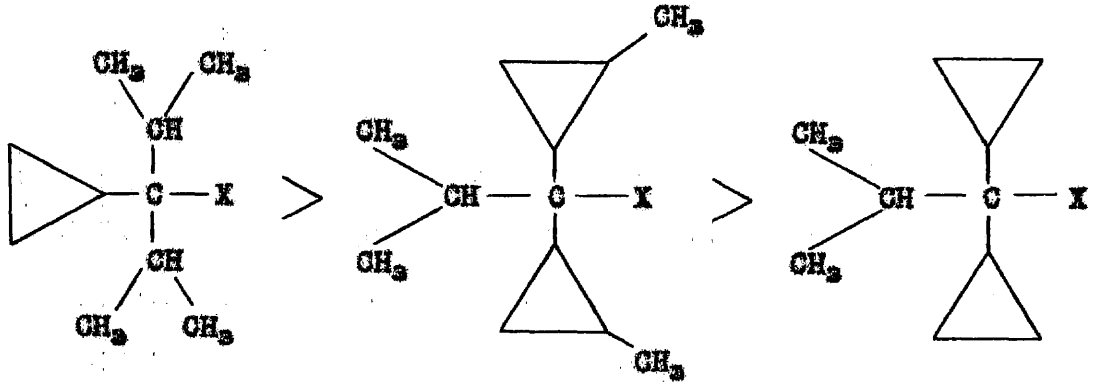
Table 12

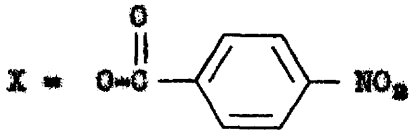
Rearrangement of Several p-Nitrobenzoates in Aqueous Dioxane
As a Function of the Water Content of the Solvent

p-Nitrobenzoate	Weight Per Cent Water									
	5		10		15		20		30	
	%S	%R	%S	%R	%S	%R	%S	%R	%S	%R
Dicyclopropylisopropyl-carbinyl	92	8	100		100		100			
Di-(2-methylcyclopropyl)-isopropylcarbinyl			91	9			100			
Diisopropylcyclopropyl-carbinyl			28	72	40	60	65	35	96	4
Dicyclopropylcarbinyl					100		100			
Triisopropylcarbinyl							100		100	

S = Solvolysis
R = Rearrangement

The facility with which rearrangement occurred decreased in the order





which is quite different from the order of solvolysis rates (see Table 11).

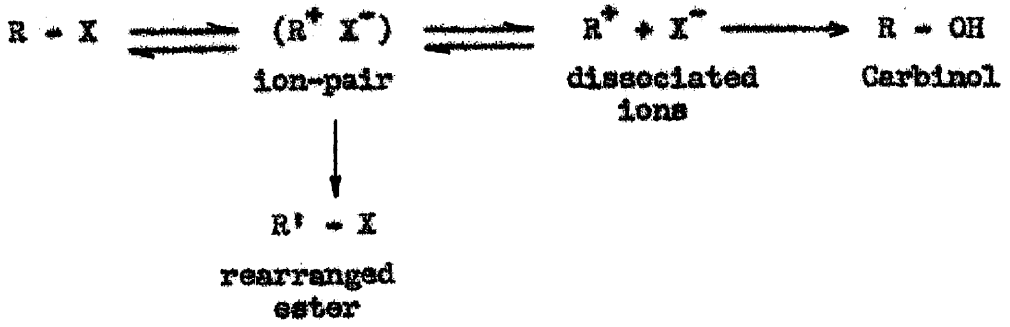
There seems to be no direct correlation between the reactivity of the esters and their tendency to rearrange. On the other hand, rearrangement appears to be favored in those compounds which contained bulky groups attached to the reactive center. Methyl substituents on the cyclopropane rings favored rearrangement, as did replacement of a cyclopropyl with an isopropyl group.

That water (and presumably ionization) is essential to rearrangement is shown by an experiment in which diisopropylcyclopropylcarbinyl p-nitrobenzoate did not rearrange in anhydrous dioxane even after five days at 60° (Compare the rate constants in Tables 52 and 53 with those in Tables 50, 51, 54, 55, 56 and 57). The conclusion was that the rearrangement was not a separate reaction but was intimately involved with the solvolysis.

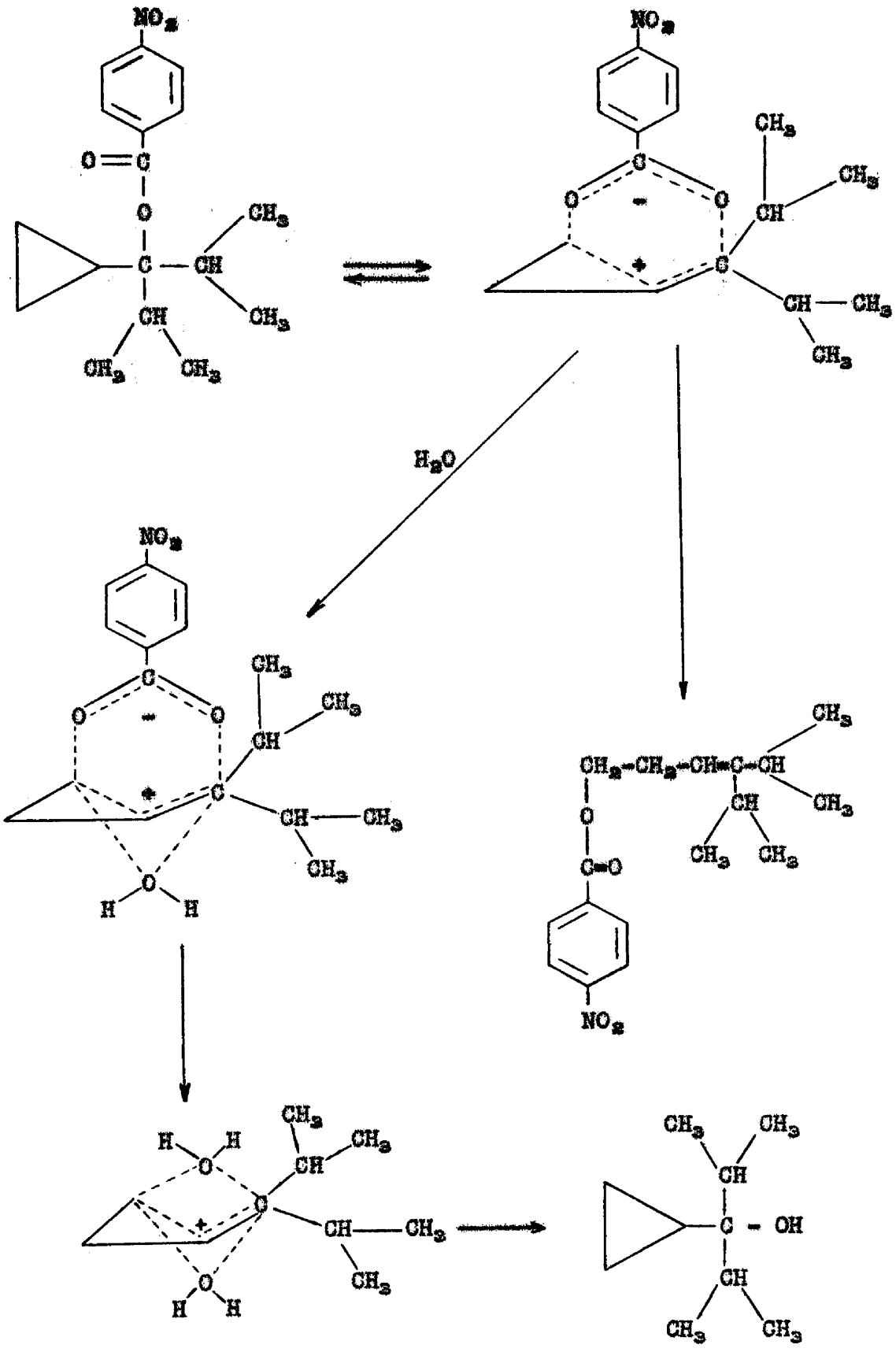
These observations, together with the fact that an increase in water content decreased the amount of rearrangement, strongly indicated an ion-pair internal return phenomenon. It was also observed that for the reaction of diisopropylcyclopropylcarbinyl p-nitrobenzoate in various aqueous dioxane mixtures, both k and k_s increased uniformly as the per cent of water increased whereas k_r increased as the percentage of water was raised from 10 to 15 to 20%, but decreased again in dioxane containing 30% water (see Table 6). This phenomenon can best be explained in terms of an ion-pair intermediate which can either solvolyze or revert to rearranged ester. This phenomenon cannot be readily interpreted in terms of two non-related reaction paths.

5. Mechanism

All of the evidence presented thus far suggests that the cyclopropylcarbinyl esters studied solvolyze <u>via</u> an ion-pair intermediate. This may be summarized by the kinetic scheme



or for the solvolysis of diisopropylcyclopropylcarbinyl p-nitrobenzoate in aqueous dioxane,



Increasing the water content of the solvent facilitates ionization and hence increases the over-all rate of reaction (k). Since both the rate of solvolysis (k_s) and rate of rearrangement (k_r) depend on the concentration of the ion-pair, the observed rate constants, k, k_s and k_r, will be increased as the water content increases (see Table 6). Furthermore, a higher water content will shift the equilibrium away from ion-pairs toward dissociated ions making replacement of the p-nitrobenzoate ion with water (to yield the carbinol) the favored reaction path. The rate of rearrangement to new ester will be enhanced as the concentration of ion-pairs becomes larger, but if the water content is made too great, the rearrangement cannot compete with dissociation, and complete solvolysis occurs. The result is that as the ionizing power of the solvent is increased, k, k_s, and k_r all increase; but k_s increases more rapidly than k_r, the consequence being that ultimately no rearrangement occurs, and carbinol is the only reaction product.

Methanol is not as good an ionizing solvent as water (55). It would be expected, then, if the proposed ion-pair mechanism is correct, that substitution of methanol for water would favor internal rearrangement over solvolysis. This was indeed found to be the case. When diisopropylcyclopropylcarbinyl p-nitrobenzoate was solvolyzed in 70% methanolic dioxane, 66% of rearranged ester was formed. This is to be contrasted with only 4% of rearrangement in 70% aqueous dioxane.

The observation that bulky groups appear to favor the rearrangement is also consistent with the proposed mechanism. Such groups would decrease the susceptibility of the ion-pair to attack by solvent and

also decrease the amount of dissociation to free ions.

The proposed mechanism gives only the broad outline of the reaction path. For example, k_s represents the sum of all rate constants leading to carbinol and p-nitrobenzoic acid; it includes ionization to ion-pairs, dissociation of the latter (possibly in several discrete steps (37,38)), and reaction with the solvent. Similarly, k_r includes ionization to ion-pairs (of varying degrees of solvation) followed by some unspecified rearrangement mechanism. Additional kinetic work, including a study of salt effects, would be required to better define these mechanistic details. Other experiments which might further elaborate the mechanism could involve the stereochemistry (using an optically active tertiary ester) and the disposition of the oxygen in the rearranged ester (using, say, carbonyl O^{18}-labelled p-nitrobenzoates).

6. The Energetics

The enthalpies and entropies of activation obtained in the present investigation are listed in Table 9. Several generalizations can be made from the data, and interpreted in a fashion consistent with the proposed mechanism.

In a given solvent (say 80% dioxane) the energies of activation are relatively insensitive to variations in the structure of the cyclopropylcarbinyl esters. The observed differences in rate can be ascribed largely to entropy differences.

In each case (triisopropylcarbinyl p-nitrobenzoate excepted; there is no evidence that ion-pairs are important here (48)) the entropy of

activation is negative. This is consistent with an ionization mechanism, since ionic or ion-pair intermediates will require greater orientation of surrounding solvent molecules than would the original neutral ester. Several cases permit a detailed interpretation.

The important structural change in going from the dicyclopropylcarbinyl to the dicyclopropylisopropylcarbinyl ester is a change from a secondary to a tertiary carbinyl group. In the latter, because of steric requirements of the group, the number of degrees of freedom is less than in the secondary ester. But in the ion-pairs derived from each ester, charge would be approximately equally dispersed (each ester has two cyclopropyl groups), requiring similar orientation of the solvent. Therefore, in going from reactant to transition state, the tertiary ester would require less change in degrees of freedom than the secondary ester and would have the more positive $\triangle S^*$.

On the other hand, dicyclopropylisopropylcarbinyl and diisopropylcyclopropylcarbinyl p-nitrobenzoates have roughly equivalent steric requirements restricting atomic motions in the ester. But in the former, the presence of two cyclopropyl groups permits a greater dispersion of charge (because of more contributing structures to the resonance hybrid) in the transition state. This greater charge dispersion will not only result in a lower $\triangle H^*$ (about 1.5 kcal. difference was observed) but will also require less restriction of solvent orientation; hence $\triangle S^*$ will be more positive for the ester with two cyclopropyl groups.

For each case in which simultaneous solvolysis and rearrangement occurred, $\triangle S^*$ for rearrangement was more positive than $\triangle S^*$ for

solvolysis. This is consistent with the proposed mechanism; the intermediate which furnishes the rearranged ester is not as polar as that which proceeds to yield the carbinol and p-nitrobenzoic acid. This less polar intermediate will therefore not require as constrained an orientation of solvent molecules in the transition state and will have a more positive entropy of activation.

The decrease in $\triangle S^{*}$ with decreasing water content that becomes apparent in 90% aqueous dioxane reflects the increased restriction in degrees of freedom in the transition state required for solvent orientation in this relatively poorly ionizing solvent.

It was also observed that $\triangle H^{*}$ for rearrangement was greater than $\triangle H^{*}$ for solvolysis for each case in which simultaneous rearrangement and solvolysis occurred. This is consistent with the mechanism because rearrangement of the original ester to a new ester requires more bonds to be broken than does solvolysis of the original ester to the original carbinol.

SUMMARY

SUMMARY

1. Cyclopropyllithium was prepared in good yield from the chloride and finely divided lithium in refluxing pentane. Cyclopropyllithium, and certain cyclopropyl-containing ketones were used as the sources of cyclopropyl groups to prepare the following new carbinols: tricyclopropyl, dicyclopropylisopropyl, di-(2-methylcyclopropyl)-isopropyl, dicyclopropylmethyl, and diisopropylcyclopropyl.

2. Tricyclopropylcarbinol failed to give a p-nitrobenzoate by a variety of methods; the lithium salt, with p-nitrobenzoyl chloride (and the carbinol with concentrated hydrochloric acid) gave 1,1-dicyclopropyl-4-chloro-1-butene, the structure of which was proved by oxidation to dicyclopropyl ketone and 3-chloropropionic acid. The chlorooolefin, with aqueous carbonate, was converted back to the carbinol.

3. The p-nitrobenzoates of the remaining carbinols (except dicyclopropylmethyl) were prepared, as were those of dicyclopropylcarbinol and triisopropylcarbinol. Their rates of solvolysis in aqueous dioxane were studied, variants being the per cent of water and the temperature. All the esters solvolyzed with first-order kinetics and alkyl-oxygen fission; the rates were the fastest recorded for carboxylic esters of aliphatic alcohols. Hydroxide ion was without effect on the rates. The products from solvolysis in aqueous dioxane were the original carbinols from which the esters had been prepared; i.e., there was no opening of the cyclopropane rings. Similarly, solvolysis in methanolic dioxane

gave methyl ethers of the original carbinols. Two cyclopropyl groups on the carbinol carbon atom were appreciably more effective than one such cyclopropyl group in facilitating solvolysis. The parallel effects of cyclopropyl and phenyl groups on reaction rates were noted.

In certain cases, solvolysis to carbinol and p-nitrobenzoic acid was incomplete; examination showed that solvolysis was accompanied by rearrangement involving opening of a cyclopropane ring. The rearrangement products were allylcarbinyl esters; for example, diisopropylcyclopropylcarbinyl p-nitrobenzoate gave 4-isopropyl-5-methyl-3-hexenyl p-nitrobenzoate.

4. The rates, solvent effects, entropies and energies of activation, and products are all consistent with a mechanism involving ionization of the ester to ion-pairs or dissociated ions, rearranged ester being formed via internal return from the former and solvolysis products being formed from the latter or both.

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APPENDIX

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 p-nitrobenzoic acid in a 5-ml. aliquot obtainable from the weight of ester used in the run.

V'_f = volume (ml.) of standard sodium hydroxide required to neutralize the total amount of p-nitrobenzoic 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 13

Solvolysis of 0.007005 Molar Dicyclopropylisopropylcarbinyl p-Nitrobenzoate in 95% Dioxane - 5% Water at 60°

t sec.	V ml.	V V_f/V_f' ml.	V_f - V V_f/V_f' ml.
156	0.44	0.48	3.54
388	0.86	0.94	3.08
528	1.02	1.11	2.91
701	1.28	1.40	2.62
854	1.44	1.57	2.45
1060	1.70	1.86	2.16
1350	2.05	2.24	1.78
1507	2.20	2.40	1.62
1708	2.34	2.56	1.46
1973	2.50	2.73	1.29
2354	2.75	3.00	1.02
2807	3.00	3.28	0.74
3241	3.14	3.43	0.59
3761	3.28	3.58	0.44
4834	3.46	3.78	0.24
5834	3.56	3.89	0.13
6832	3.62	3.95	0.07
10189	3.64	3.98	0.04
54275	3.68	4.02	0.0

Titrant: 0.008716N NaOH
V_f/V_f' = 4.02 ml./3.68 ml. = 1.09
k = 5.84 x 10^{-4} $sec.^{-1}$
k_s = 5.35 x 10^{-4} $sec.^{-1}$
k_r = 0.494 x 10^{-4} $sec.^{-1}$

Table 14

Solvolysis of 0.006185 Molar Dicyclopropylisopropylcarbinyl p-Nitrobenzoate in 95% Dioxane - 5% Water at 60°

t sec.	V ml.	$V \frac{V_f}{V_f'}$ ml.	$V_f - V \frac{V_f}{V_f'}$ ml.
212	0.49	0.53	3.02
401	0.76	0.82	2.73
621	1.04	1.12	2.43
791	1.22	1.32	2.23
978	1.44	1.55	2.00
1133	1.60	1.73	1.82
1320	1.77	1.91	1.64
1603	1.98	2.14	1.41
1788	2.12	2.29	1.26
1973	2.21	2.38	1.17
2146	2.32	2.50	1.05
2392	2.41	2.60	0.95
2558	2.50	2.70	0.85
3015	2.68	2.89	0.66
3814	2.90	3.13	0.42
4902	3.06	3.30	0.25
6949	3.22	3.47	0.08
20103	3.23	3.44	0.06
63593	3.29	3.55	0.0

Titrant: 0.008715N NaOH

$V_f/V_f' = 3.55$ ml./3.29 ml. = 1.08

$k = 5.53 \times 10^{-4}$ sec.$^{-1}$

$k_s = 5.12 \times 10^{-4}$ sec.$^{-1}$

$k_r = 0.405 \times 10^{-4}$ sec.$^{-1}$

Table 15

Solvolysis of 0.01124 Molar Dicyclopropylisopropylcarbinyl p-Nitrobenzoate in 90% Dioxane - 10% Water at 25°

t sec.	V ml.	$V_f - V$ ml.
230	0.51	5.29
740	0.80	5.00
980	1.02	4.78
1180	1.18	4.62
1390	1.32	4.48
2280	1.89	3.91
3973	2.85	2.95
4820	3.18	2.62
6090	3.70	2.10
7800	4.28	1.52
8730	4.50	1.30
11782	5.38	0.68

Titrant: 0.009686N NaOH
V_f = 5.80 ml.
$k = 1.61 \times 10^{-4}$ sec.$^{-1}$

Table 16

Solvolysis of 0.01808 Molar Dicyclopropylisopropylcarbinyl p-Nitrobenzoate in 90% Dioxane - 10% Water at 25°C

t sec.	V ml.	$V_f - V$ ml.
146	0.42	8.91
519	0.95	8.38
830	1.30	8.03
1155	1.61	7.72
1850	2.45	6.88
3570	4.00	5.33
3952	4.28	5.05
4725	4.84	4.49
5650	5.47	3.86
6835	6.20	3.13
8190	6.88	2.45
10450	7.60	1.73
12745	8.25	1.08

Titrant: 0.009686N NaOH
V_f = 9.33 ml.
$k = 1.59 \times 10^{-4}$ sec.$^{-1}$

Table 17

Solvolysis of 0.009549 Molar Dicyclopropylisopropylcarbinyl p-Nitrobenzoate in 90% Dioxane - 10% Water at 40°C

t sec.	V ml.	$V_f - V$ ml.
99	0.64	4.47
345	1.22	3.89
552	1.68	3.43
729	2.05	3.06
919	2.36	2.75
1107	2.73	2.38
1267	2.94	2.17
1415	3.16	1.95
1682	3.50	1.61
1914	3.74	1.37
2234	3.94	1.17
2683	4.25	0.86
3244	4.50	0.61
4085	4.70	0.41
6091	4.96	0.15
7416	5.10	0.01
64800	5.11	0.0

Titrant: 0.009349N NaOH
V_f = 5.11 ml.
k = 6.60 x 10^{-4} $sec.^{-1}$

Table 18

Solvolysis of 0.008258 Molar Dicyclopropylisopropylcarbinyl p-Nitrobenzoate in 90% Dioxane - 10% Water at 40°C

t sec.	V ml.	V_f-V ml.
141	0.60	3.82
474	1.33	3.09
641	1.65	2.77
805	1.92	2.50
972	2.20	2.22
1426	2.78	1.64
1672	3.02	1.40
1856	3.20	1.22
2028	3.35	1.07
2661	3.68	0.74
3234	3.94	0.48
4132	4.14	0.28
5259	4.22	0.20
6310	4.30	0.12
7903	4.36	0.06
12095	4.40	0.02
61200	4.42	0.0

Titrant: 0.009349N NaOH
V_f = 4.42 ml.
k = 6.77×10^{-4} $sec.^{-1}$

Table 19

Solvolysis of 0.008175 Molar Dicyclopropylisopropylcarbinyl p-Nitrobenzoate in 90% Dioxane - 10% Water at 50°C

t sec.	V ml.	V_f-V ml.
79	0.75	3.64
236	1.52	2.87
403	2.16	2.23
544	2.66	1.73
689	3.00	1.39
822	3.28	1.11
951	3.51	0.88
1108	3.72	0.67
1300	3.92	0.47
1458	3.98	0.41
1608	4.03	0.36
2178	4.24	0.15
2471	4.26	0.13
3515	4.32	0.07
4821	4.33	0.06

Titrant: 0.009311N NaOH
V_f = 4.39 ml.
k^1 = 16.7 x 10^{-4} $sec.^{-1}$

Table 20

Solvolysis of 0.008159 Molar Dicyclopropylisopropylcarbinyl p-Nitrobenzoate in 90% Dioxane - 10% Water at 50°C

t sec.	V ml.	V_f-V ml.
72	0.65	3.73
279	1.60	2.78
429	2.25	2.13
591	2.76	1.62
790	3.25	1.13
969	3.52	0.86
1169	3.76	0.62
1360	3.89	0.49
1539	4.03	0.35
1729	4.12	0.26
1898	4.19	0.19
2117	4.23	0.15
2373	4.25	0.13
2868	4.25	0.13
9343	4.28	0.0

Titrant: 0.009311N NaOH
V_f = 4.38 ml.
k = 16.8 x 10^{-4} $sec.^{-1}$

Table 21

Solvolysis of 0.01255 Molar Dicyclopropylisopropylcarbinyl p-Nitrobenzoate in 85% Dioxane - 15% Water at 25°C

t sec.	V ml.	V_f-V ml.
240	0.91	5.73
414	1.40	5.24
605	1.92	4.72
785	2.33	4.31
955	2.74	3.90
1115	3.01	3.63
1295	3.38	3.26
1560	3.80	2.84
1700	4.06	2.58
1895	4.28	2.36
2175	4.60	2.04
2350	4.76	1.88
2570	4.98	1.66
2895	5.38	1.26
3220	5.66	0.98
5300	6.42	0.22

Titrant: 0.009456N NaOH
V_f = 6.64 ml.
k^1 = 5.44 x 10^{-4} $sec.^{-1}$

Table 22

Solvolysis of 0.007038 Molar Dicyclopropylisopropylcarbinyl p-Nitrobenzoate in 85% Dioxane - 15% Water at 25°C

t sec.	V ml.	V_f-V ml.
404	0.84	2.88
640	1.16	2.56
840	1.40	2.32
1040	1.68	2.04
1225	1.86	1.86
1410	2.04	1.68
1612	2.18	1.54
1870	2.38	1.34
2025	2.48	1.24
2255	2.62	1.10
2470	2.77	0.95
2742	2.92	0.80
4415	3.38	0.34

Titrant: 0.009456N NaOH
V_f = 3.72 ml.
k = 5.47 x 10^{-4} sec.$^{-1}$

Table 23

Solvolysis of 0.008264 Molar Dicyclopropylisopropylcarbinyl p-Nitrobenzoate in 80% Dioxane - 20% Water at 7°C

t sec.	V ml.	V_f-V ml.
948	0.92	3.53
1506	1.24	3.21
2117	1.52	2.93
2682	1.72	2.73
3302	2.02	2.43
4430	2.36	2.09
5501	2.71	1.74
6197	2.92	1.53
7253	3.12	1.33
7995	3.22	1.23
9211	3.43	1.02
10386	3.58	0.87
11431	3.74	0.71
12873	3.86	0.59

Titrant: 0.009290N NaOH
V_f = 4.45 ml.
k^f = 1.52 x 10^{-4} $sec.^{-1}$

Table 24

Solvolysis of 0.01012 Molar Dicyclopropylisopropylcarbinyl p-Nitrobenzoate in 80% Dioxane - 20% Water at 7°C

t sec.	V ml.	V_f-V ml.
916	1.22	4.23
1483	1.48	3.97
2103	1.87	3.58
2713	2.20	3.25
3479	2.52	2.93
4381	2.95	2.50
5518	3.34	2.11
6205	3.55	1.90
7227	3.80	1.65
7962	3.97	1.48
9200	4.22	1.23
10445	4.42	1.03
11445	4.63	0.82
12973	4.78	0.67

Titrant: 0.009290N NaOH
V_f = 5.45 ml.
k' = 1.54 x 10^{-4} $sec.^{-1}$

Table 25

Solvolysis of 0.009522 Molar Dicyclopropylisopropylcarbinyl p-Nitrobenzoate in 80% Dioxane - 20% Water at 16°C

t sec.	V ml.	V_f-V ml.
264	0.98	4.00
513	1.44	3.54
694	1.74	3.24
897	2.06	2.92
1115	2.36	2.62
1467	2.78	2.20
1675	3.02	1.96
1877	3.20	1.78
2154	3.44	1.54
2388	3.59	1.39
2595	3.76	1.22
2978	3.98	1.00
3426	4.14	0.84
3945	4.34	0.64
4446	4.48	0.50

Titrant: 0.009561N NaOH
V_f = 4.98 ml.
k = 5.01 x 10^{-4} $sec.^{-1}$

Table 26

Solvolysis of 0.01019 Molar Dicyclopropylisopropylcarbinyl p-Nitrobenzoate in 80% Dioxane - 20% Water at 16°C

t sec.	V ml.	V_f-V ml.
314	1.14	4.19
504	1.45	3.88
681	1.80	3.53
846	2.06	3.27
1012	2.34	2.99
1201	2.53	2.80
1413	2.82	2.51
1605	3.06	2.27
1778	3.20	2.13
1944	3.38	1.95
2139	3.55	1.78
2348	3.74	1.59
2631	3.93	1.40
3036	4.15	1.18
3470	4.40	0.93
3962	4.54	0.79
4460	4.65	0.68
10000	5.30	0.03

Titrant: 0.009561N NaOH
V_f = 5.33 ml.
k = 4.78 x 10^{-4} $sec.^{-1}$

Table 27

Solvolysis of 0.009368 Molar Dicyclopropylisopropylcarbinyl p-Nitrobenzoate in 80% Dioxane - 20% Water 0.009525 Normal in Sodium Hydroxide at 16°C

t sec.	V ml.	$V - V_f$ ml.
228	4.17	4.09
435	3.87	3.79
720	3.45	3.37
894	3.09	3.01
1130	2.78	2.70
1390	2.54	2.46
1632	2.33	2.25
1924	2.01	1.93
2438	1.61	1.53
2601	1.49	1.41
2989	1.29	1.21
3389	1.09	1.01
3887	0.89	0.81
4383	0.74	0.66
4933	0.58	0.50
5978	0.36	0.28

Titrant: 0.009525N HCl
V_f = 0.08 ml.
k^f = 4.55 x 10^{-4} $sec.^{-1}$

Table 28

Solvolysis of 0.008845 Molar Dicyclopropylisopropylcarbinyl p-Nitrobenzoate in 80% Dioxane - 20% Water 0.009525 Normal in Sodium Hydroxide at 16°C

t sec.	V ml.	$V - V_f$ ml.
381	3.96	3.60
562	3.62	3.26
766	3.30	2.94
972	3.08	2.72
1184	2.77	2.41
1432	2.48	2.12
1680	2.30	1.94
1980	1.96	1.60
2339	1.77	1.41
2831	1.54	1.18
3117	1.40	1.04
4249	0.84	0.48
5267	0.68	0.32
5505	0.63	0.27
6600	0.48	0.12
7637	0.46	0.10

Titrant: 0.009525N HCl
V_f = 0.36 ml.
k = 4.73 x 10^{-4} $sec.^{-1}$

Table 29

Solvolysis of 0.01235 Molar Dicyclopropylisopropylcarbinyl p-Nitrobenzoate in 80% Dioxane - 20% Water at 25°C

t sec.	V ml.	$V_f - V$ ml.
163	1.78	4.90
350	2.78	3.90
501	3.52	3.16
619	3.94	2.74
740	4.40	2.28
848	4.68	2.00
950	4.92	1.76
1105	5.24	1.44
1255	5.45	1.23
1437	5.74	0.94
1610	5.90	0.78
1790	6.02	0.66
2033	6.15	0.53
2355	6.28	0.40
2764	6.40	0.28
6700	6.52	0.16

Titrant: 0.00925ON NaOH
V_f = 6.62 ml.
$k' = 13.2 \times 10^{-4}$ sec.$^{-1}$

Table 30

Solvolysis of 0.00972 Molar Dicycloprepylisopropylcarbinyl p-Nitrobenzoate in 80% Dioxane - 20% Water at 25°C

t sec.	V ml.	V_f-V ml.
143	1.40	3.92
325	2.22	3.10
467	2.72	2.60
595	3.18	2.14
743	3.54	1.78
888	3.82	1.50
1010	4.06	1.26
1133	4.26	1.06
1268	4.42	0.90
1455	4.63	0.69
1577	4.72	0.60
1707	4.80	0.52
1878	4.90	0.42
1999	4.98	0.34
2277	5.11	0.21
2649	5.30	0.02

Titrant: 0.00913ON NaOH
V_f = 5.32 ml.
$k^{'}$ = 13.0 x 10^{-4} $sec.^{-1}$

Table 31

Solvolysis of 0.009305 Molar Dicyclopropylisopropylcarbinyl p-Nitrobenzoate in 80% Dioxane - 20% Water at 25°C

t sec.	V ml.	$V_f - V$ ml.
159	1.30	3.73
283	1.82	3.21
385	2.22	2.81
501	2.63	2.40
625	2.98	2.05
744	3.32	1.71
875	3.56	1.47
992	3.80	1.23
1114	4.00	1.03
1219	4.12	0.91
1328	4.21	0.82
1464	4.38	0.65
1609	4.47	0.56
1776	4.50	0.45
1951	4.71	0.32
2108	4.75	0.28
2450	4.86	0.17

Titrant: 0.009250N NaOH
V_f = 5.03 ml.
k = 13.5 x 10^{-4} $sec.^{-1}$

Table 32

Solvolysis of 0.009022 Molar Dicyclopropylisopropylcarbinyl p-Nitrobenzoate in 80% Dioxane - 20% Water at 25°C

t sec.	V ml.	V_f-V ml.
135	1.53	3.98
205	1.74	3.77
264	2.01	3.50
332	2.42	3.09
427	2.72	2.79
514	2.98	2.53
583	3.22	2.29
637	3.41	2.00
710	3.57	1.94
784	3.83	1.68
875	3.99	1.52
964	4.16	1.35
1027	4.23	1.28
1107	4.40	1.11
7287	5.40	0.11

Titrant: 0.008182N NaOH
V_f = 5.51 ml.
k = 13.5 x 10^{-4} $sec.^{-1}$

Table 33

Solvolysis of 0.005522 Molar Di-(2-methylcyclopropyl)isopropylcarbinyl p-Nitrobenzoate in 90% Dioxane - 10% Water at 16°C

t sec.	V ml.	$V\frac{V_f}{V_f'}$ ml.	$V_f - V\frac{V_f}{V_f'}$ ml.
146	0.40	0.43	3.39
337	0.56	0.60	3.22
678	0.83	0.90	2.92
1098	1.16	1.25	2.57
1586	1.44	1.55	2.27
1981	1.62	1.75	2.07
3198	2.16	2.33	1.49
4809	2.66	2.87	0.95
32344	3.54	3.82	0.0

Titrant: 0.007223N NaOH
V_f/V_f' = 3.82 ml./3.54 ml. = 1.08
k = 2.71×10^{-4} sec.$^{-1}$
k_s = 2.51×10^{-4} sec.$^{-1}$
k_r = 0.199×10^{-4} sec.$^{-1}$

Table 34

Solvolysis of 0.005498 Molar Di-(2-methylcyclopropyl)isopropylcarbinyl p-Nitrobenzoate in 90% Dioxane - 10% Water at 16°C

t sec.	V ml.	$V\frac{V_f}{V_f'}$, ml.	$V_f - V\frac{V_f}{V_f'}$, ml.
376	0.57	0.62	3.19
877	0.95	1.03	2.78
1278	1.23	1.34	2.47
2074	1.72	1.87	1.94
3302	2.24	2.44	1.37
4913	2.68	2.92	0.89
6632	3.04	3.31	0.50
9372	3.26	3.55	0.26
32324	3.50	3.81	0.0

Titrant: 0.007223N NaOH

V_f/V_f' = 3.81 ml./3.50 ml. = 1.09

$k = 2.88 \times 10^{-4}$ sec.$^{-1}$

$k_s = 2.65 \times 10^{-4}$ sec.$^{-1}$

$k_r = 0.234 \times 10^{-4}$ sec.$^{-1}$

Table 35

Solvolysis of 0.006240 Molar Di-(2-methylcyclopropyl)isopropylcarbinyl p-Nitrobenzoate in 90% Dioxane - 10% Water at 25°C

t sec.	V ml.	$V\frac{V_f}{V_f'}$ ml.	$V_f - V\frac{V_f}{V_f'}$ ml.
111	0.64	0.69	3.67
321	1.06	1.15	3.21
662	1.71	1.85	2.51
905	2.06	2.23	2.13
1313	2.57	2.79	1.57
1840	3.04	3.30	1.06
2840	3.51	3.81	0.55
4580	3.84	4.16	0.20
33630	4.02	4.36	0.0

Titrant: 0.007158N NaOH

V_f/V_f' = 4.36 ml./4.02 ml. = 1.09

k = 7.02 x 10^{-4} sec.$^{-1}$

k_s = 6.47 x 10^{-4} sec.$^{-1}$

k_r = 0.547 x 10^{-4} sec.$^{-1}$

Table 36

Solvolysis of 0.006294 Molar Di-(2-methylcyclopropyl)isopropylcarbinyl p-Nitrobenzoate in 90% Dioxane - 10% Water at 25°C

t sec.	V ml.	$V\frac{V_f}{V_f'}$ ml.	$V_f - V\frac{V_f}{V_f'}$ ml.
125	0.61	0.66	3.74
322	1.13	1.23	3.17
601	1.63	1.78	2.62
924	2.14	2.33	2.07
1339	2.58	2.81	1.59
1820	3.02	3.29	1.11
2858	3.52	3.83	0.57
4970	3.88	4.23	0.17
28592	4.04	4.40	0.0

Titrant: 0.007158N NaOH
V_f/V_f' = 4.40 ml./4.04 ml. = 1.09
k = 7.16 x 10^{-4} sec.$^{-1}$
k_s = 6.58 x 10^{-4} sec.$^{-1}$
k_r = 0.586 x 10^{-4} sec.$^{-1}$

Table 37

Solvolysis of 0.005975 Molar Di-(2-methylcyclopropyl)isopropylcarbinyl p-Nitrobenzoate in 90% Dioxane - 10% Water at 35°C

t sec.	V ml.	$V\frac{V_f}{V_f'}$ ml.	$V_f - V\frac{V_f}{V_f'}$ ml.
86	0.87	0.96	3.22
245	1.58	1.74	2.44
505	2.46	2.71	1.47
645	2.72	3.00	1.18
895	3.12	3.44	0.74
1190	3.38	3.73	0.45
1904	3.64	4.01	0.17
86400	3.79	4.18	0.0

Titrant: 0.007146N NaOH
V_f/V_f' = 4.18 ml./3.79 ml. = 1.10
k = 17.8 x 10^{-4} sec.$^{-1}$
k_s = 16.2 x 10^{-4} sec.$^{-1}$
k_r = 1.67 x 10^{-4} sec.$^{-1}$

Table 38

Solvolysis of 0.006258 Molar Di-(2-methylcyclopropyl)isopropylcarbinyl p-Nitrobenzoate in 90% Dioxane - 10% Water at 35°C

t sec.	V ml.	$V\frac{V_f}{V_f'}$ ml.	$V_f - V\frac{V_f}{V_f'}$ ml.
80	0.82	0.92	3.46
261	1.74	1.94	2.44
405	2.21	2.47	1.91
607	2.75	3.07	1.31
879	3.22	3.60	0.78
1182	3.51	3.92	0.46
1744	3.81	4.26	0.12
2411	3.90	4.36	0.02
72000	3.92	4.38	0.0

Titrant: 0.007146N NaOH
V_f/V_f' = 4.38 ml./3.92 ml. = 1.12
$k = 18.4 \times 10^{-4}$ sec.$^{-1}$
$k_s = 16.5 \times 10^{-4}$ sec.$^{-1}$
$k_r = 1.94 \times 10^{-4}$ sec.$^{-1}$

Table 39

Solvolysis of 0.006952 Molar Di-(2-methylcyclopropyl)isopropylcarbinyl p-Nitrobenzoate in 90% Dioxane - 10% Water at 35°C

t sec.	V ml.	$V\frac{V_f}{V_f'}$ ml.	$V_f - V\frac{V_f}{V_f'}$ ml.
82	0.88	0.98	3.88
220	1.68	1.87	2.99
356	2.28	2.54	2.32
553	2.92	3.25	1.61
778	3.46	3.86	1.00
958	3.67	4.09	0.77
1580	4.12	4.59	0.27
2467	4.28	4.77	0.09
93600	4.36	4.86	0.0

Titrant: 0.007146N NaOH
V_f/V_f' = 4.86 ml./4.36 ml. = 1.12
k = 18.6 x 10^{-4} sec.$^{-1}$
k_s = 16.7 x 10^{-4} sec.$^{-1}$
k_r = 1.91 x 10^{-4} sec.$^{-1}$

Table 40

Solvolysis of 0.005625 Molar Di-(2-methylcyclopropyl)isopropylcarbinyl p-Nitrobenzoate in 80% Dioxane - 20% Water at 7°C

t sec.	V ml.	V_f-V ml.
159	1.22	2.61
320	1.54	2.29
506	1.90	1.93
683	2.13	1.70
890	2.40	1.43
1204	2.72	1.11
1608	3.00	0.83
2608	3.38	0.45
79200	3.83	0.02

Titrant: 0.007306N NaOH
V_f = 3.85 ml.
k^1 = 8.01 x 10^{-4} sec.$^{-1}$

Table 41

Solvolysis of 0.006059 Molar Di-(2-methylcyclopropyl)isopropylcarbinyl p-Nitrobenzoate in 80% Dioxane - 20% Water at 7°C

t sec.	V ml.	$V_f - V$ ml.
149	1.06	3.08
298	1.52	2.62
459	1.88	2.26
688	2.24	1.90
994	2.64	1.50
1394	3.04	1.10
2007	3.40	0.74
3005	3.80	0.34
75600	4.14	0.01

Titrant: 0.007306N NaOH
V_f = 4.15 ml.
$k = 8.09 \times 10^{-4}$ sec.$^{-1}$

Table 42

Solvolysis of 0.008950 Molar Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 90% Dioxane - 10% Water at 60°C

t sec.	V ml.	$V\frac{V_f}{V_f'}$ ml.	$V_f - V\frac{V_f}{V_f'}$ ml.
395	0.20	0.71	4.38
910	0.24	0.85	4.24
2762	0.44	1.56	3.53
8678	0.76	2.69	2.40
13964	0.96	3.39	1.70
20353	1.18	4.17	0.92
28221	1.28	4.52	0.57
33538	1.33	4.70	0.39
73002	1.44	5.09	0.0
84813	1.44	5.09	0.0
99617	1.44	5.09	0.0
129974	1.44	5.09	0.0

Titrant: 0.008791N NaOH
V_f/V_f' = 5.09 ml./1.44 ml. = 3.53
k = 0.733 x 10^{-4} sec.$^{-1}$
k_s = 0.207 x 10^{-4} sec.$^{-1}$
k_r = 0.526 x 10^{-4} sec.$^{-1}$

Table 43

Solvolysis of 0.009317 Molar Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 90% Dioxane - 10% Water at 60°C

t sec.	V ml.	$V\frac{V_f}{V_f'}$ ml.	$V_f - V\frac{V_f}{V_f'}$ ml.
346	0.22	0.79	4.51
825	0.26	0.93	4.37
2498	0.37	1.32	3.98
8583	0.82	2.94	2.36
13718	0.98	3.51	1.79
20185	1.18	4.23	1.07
28108	1.34	4.80	0.50
33303	1.40	5.01	0.29
72319	1.48	5.30	0.0
84595	1.48	5.30	0.0
99310	1.48	5.30	0.0
130015	1.48	5.30	0.0

Titrant: 0.008791N NaOH

$V_f/V_f' = 5.30$ ml./1.48 ml. = 3.58

$k = 0.745 \times 10^{-4}$ sec.$^{-1}$

$k_s = 0.208 \times 10^{-4}$ sec.$^{-1}$

$k_r = 0.537 \times 10^{-4}$ sec.$^{-1}$

Table 44

Solvolysis of 0.01024 Molar Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 85% Dioxane - 15% Water at 60°C

t sec.	V ml.	$V\frac{V_f}{V_f'}$ ml.	$V_f - V\frac{V_f}{V_f'}$ ml.
284	0.35	0.87	5.00
748	0.50	1.25	4.62
1359	0.67	1.67	4.20
2519	1.03	2.57	3.30
2907	1.15	2.87	3.00
3453	1.30	3.25	2.62
4223	1.44	3.60	2.27
4867	1.53	3.82	2.05
5533	1.67	4.17	1.70
6751	1.82	4.55	1.32
8025	1.94	4.85	1.02
10243	2.08	5.20	0.67
13794	2.26	5.65	0.22
19483	2.35	5.87	0.0
28741	2.35	5.87	0.0

Titrant: 0.008716N NaOH
V_f/V_f' = 5.87 ml./2.35 ml. = 2.50
k = 2.12 x 10^{-4} sec.$^{-1}$
k_s = 0.850 x 10^{-4} sec.$^{-1}$
k_r = 1.27 x 10^{-4} sec.$^{-1}$

Table 45

Solvolysis of 0.008655 Molar Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 85% Dioxane - 15% Water at 60°C

t sec.	V ml.	$V\frac{V_f}{V_f'}$ ml.	$V_f - V\frac{V_f}{V_f'}$ ml.
277	0.25	0.62	4.35
681	0.41	1.02	3.95
1229	0.58	1.44	3.53
2482	0.89	2.21	2.76
2891	0.94	2.34	2.63
3389	1.05	2.61	2.36
4244	1.24	3.08	1.89
4840	1.32	3.28	1.69
5460	1.43	3.55	1.42
6645	1.52	3.78	1.19
7701	1.61	4.00	0.97
10194	1.80	4.47	0.50
13761	1.90	4.72	0.25
19440	2.00	4.97	0.0
28666	2.00	4.97	0.0

Titrant: 0.008716N NaOH

V_f/V_f' = 4.97 ml./2.00 ml. = 2.49

$k = 2.05 \times 10^{-4}$ sec.$^{-1}$

$k_s = 0.826 \times 10^{-4}$ sec.$^{-1}$

$k_r = 1.23 \times 10^{-4}$ sec.$^{-1}$

Table 46

Solvolysis of 0.009242 Molar Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 85% Dioxane - 15% Water at 70°C

t sec.	V ml.	$V\frac{V_f}{V_f'}$, ml.	$V_f - V\frac{V_f}{V_f'}$, ml.
286	0.36	0.88	4.02
449	0.50	1.23	3.67
710	0.70	1.72	3.18
853	0.82	2.01	2.89
1125	0.98	2.40	2.50
1267	1.06	2.60	2.30
1390	1.13	2.77	2.13
1672	1.28	3.14	1.76
1889	1.36	3.33	1.57
2185	1.43	3.50	1.40
2450	1.52	3.72	1.18
2825	1.64	4.02	0.88
3320	1.70	4.17	0.73
4430	1.82	4.46	0.44
5803	1.89	4.63	0.27
7818	1.91	4.68	0.22
11753	1.92	4.70	0.20
50443	1.98	4.85	0.05
89334	2.00	4.90	0.0

Titrant: 0.009442N NaOH

V_f/V_f' = 4.90 ml./2.00 ml. = 2.45

k = 5.69 x 10^{-4} sec.$^{-1}$

k_s = 2.32 x 10^{-4} sec.$^{-1}$

k_r = 3.37 x 10^{-4} sec.$^{-1}$

Table 47

Solvolysis of 0.01096 Molar Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 85% Dioxane - 15% Water at 70°C

t sec.	V ml.	$V\frac{V_f}{V_f'}$ ml.	$V_f - V\frac{V_f}{V_f'}$ ml.
105	0.24	0.60	5.21
297	0.46	1.14	4.67
467	0.58	1.44	4.37
961	1.02	2.53	3.27
1115	1.15	2.86	2.95
1365	1.27	3.15	2.66
1758	1.50	3.72	2.09
2167	1.70	4.22	1.59
2573	1.82	4.52	1.29
3114	1.96	4.87	0.94
3641	2.02	5.02	0.79
4702	2.18	5.41	0.40
5823	2.22	5.51	0.30
7166	2.22	5.51	0.30
13037	2.28	5.66	0.15
51693	2.34	5.81	0.0
87372	2.34	5.81	0.0

Titrant: 0.009442N NaOH
V_f/V_f' = 5.81 ml./2.34 ml. = 2.48
k = 5.79 x 10^{-4} sec.$^{-1}$
k_s = 2.33 x 10^{-4} sec.$^{-1}$
k_r = 3.46 x 10^{-4} sec.$^{-1}$

Table 48

Solvolysis of 0.008783 Molar Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 85% Dioxane - 15% Water at 80°C

t sec.	V ml.	$V\frac{V_f}{V_f'}$ ml.	$V_f - V\frac{V_f}{V_f'}$ ml.
102	0.40	1.07	3.60
232	0.56	1.50	3.17
343	0.73	1.96	2.71
464	0.99	2.66	2.01
614	1.10	2.95	1.72
736	1.21	3.25	1.42
863	1.28	3.44	1.23
1033	1.37	3.68	0.99
1197	1.44	3.86	0.81
1363	1.46	3.92	0.75
2183	1.61	4.32	0.35
2956	1.72	4.62	0.05
3775	1.74	4.67	0.0
72221	1.74	4.67	0.0

Titrant: 0.009397N NaOH

V_f/V_f' = 4.67 ml./1.74 ml. = 2.68

k = 14.6 x 10^{-4} sec.$^{-1}$

k_s = 5.43 x 10^{-4} sec.$^{-1}$

k_r = 9.14 x 10^{-4} sec.$^{-1}$

Table 49

Solvolysis of 0.008482 Molar Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 85% Dioxane - 15% Water at 80°C

t sec.	V ml.	$V\frac{V_f}{V_f'}$ ml.	$V_f - V\frac{V_f}{V_f}$ ml.
118	0.39	1.00	3.51
268	0.62	1.59	2.92
392	0.80	2.05	2.46
537	0.99	2.54	1.97
659	1.10	2.82	1.69
792	1.26	3.23	1.28
915	1.33	3.41	1.10
1058	1.40	3.59	0.92
1250	1.48	3.79	0.72
1562	1.64	4.20	0.31
2072	1.66	4.25	0.26
3184	1.68	4.31	0.20
5334	1.73	4.43	0.08
7742	1.75	4.48	0.03
75719	1.76	4.51	0.0

Titrant: 0.009397N NaOH
V_f/V_f' = 4.51 ml./1.75 ml. = 2.56
k = 14.9 x 10^{-4} sec.$^{-1}$
k_s = 5.80 x 10^{-4} sec.$^{-1}$
k_r = 9.06 x 10^{-4} sec.$^{-1}$

Table 50

Solvolysis of 0.007015 Molar Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 80% Dioxane - 20% Water at 60°C

t sec.	V ml.	$V\frac{V_f}{V_f'}$ ml.	$V_f - V\frac{V_f}{V_f'}$ ml.
172	0.26	0.40	3.43
419	0.47	0.73	3.10
652	0.66	1.02	2.81
874	0.90	1.39	2.44
1582	1.31	2.02	1.81
2016	1.53	2.37	1.46
2562	1.79	2.77	1.06
2823	1.85	2.86	0.97
3051	1.96	3.03	0.80
3259	2.00	3.09	0.74
3653	2.08	3.22	0.61
4325	2.24	3.46	0.37
4617	2.27	3.51	0.32
4945	2.33	3.60	0.23
6844	2.48	3.83	0.0

Titrant: 0.009151N NaOH
V_f/V_f' = 3.83 ml./2.48 ml. = 1.54
k = 5.00 x 10^{-4} sec.$^{-1}$
k_s = 3.24 x 10^{-4} sec.$^{-1}$
k_r = 1.76 x 10^{-4} sec.$^{-1}$

Table 51

Solvolysis of 0.006933 Molar Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 80% Dioxane - 20% Water at 60°C

t sec.	V ml.	$V\frac{V_f}{V_f'}$ ml.	$V_f - V\frac{V_f}{V_f'}$ ml.
187	0.29	0.45	3.49
420	0.53	0.82	3.12
604	0.69	1.07	2.87
788	0.83	1.29	2.65
1230	1.15	1.78	2.16
1482	1.32	2.03	1.91
1757	1.46	2.26	1.68
2580	1.83	2.84	1.10
2817	1.89	2.93	1.01
3060	1.95	3.02	0.92
3323	2.01	3.11	0.83
3855	2.16	3.35	0.59
5225	2.38	3.69	0.25
7475	2.54	3.94	0.0

Titrant: 0.008805N NaOH
V_f/V_f' = 3.94 ml./2.54 ml. = 1.55
k = 4.65 x 10^{-4} sec.$^{-1}$
k_s = 3.00 x 10^{-4} sec.$^{-1}$
k_r = 1.65 x 10^{-4} sec.$^{-1}$

Table 52

Solvolysis of 0.007637 Molar Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 80% Dioxane - 20% Water at 60°C*

t sec.	V ml.	$V\frac{V_f}{V_f'}$ ml.	$V_f - V\frac{V_f}{V_f'}$ ml.
102	0.31	0.46	3.97
332	0.58	0.86	3.57
619	0.83	1.23	3.20
841	0.98	1.45	2.98
1032	1.17	1.73	2.70
1235	1.33	1.97	2.46
1740	1.66	2.46	1.97
2327	2.05	3.03	1.40
3264	2.32	3.44	0.99
4640	2.62	3.88	0.55
6102	2.77	4.10	0.33
8220	2.94	4.35	0.09
16527	3.00	4.43	0.00

Titrant: 0.00862ON NaOH
V_f/V_f' = 4.43 ml./3.00 ml. = 1.48
k = 4.47 x 10^{-4} sec.$^{-1}$
k_s = 3.03 x 10^{-4} sec.$^{-1}$
k_r = 1.44 x 10^{-4} sec.$^{-1}$

*The ester was dissolved in anhydrous dioxane and stored at 60° for three days after which time sufficient water was added to make the solution 80% dioxane - 20% water and measurement of the rate was begun immediately.

Table 53

Solvolysis of 0.01194 Molar Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 80% Dioxane - 20% Water at 60°C*

t sec.	V ml.	$V\frac{V_f}{V_f'}$ ml.	$V_f - V\frac{V_f}{V_f'}$ ml.
245	0.65	1.04	5.88
479	1.00	1.60	5.32
731	1.35	2.16	4.76
1004	1.72	2.75	4.17
1255	2.01	3.22	3.70
1598	2.36	3.78	3.14
2267	2.90	4.64	2.28
2640	3.11	4.98	1.94
2986	3.31	5.30	1.62
3425	3.48	5.57	1.35
3765	3.60	5.76	1.16
4117	3.70	5.92	1.00
5514	4.02	6.44	0.48
7027	4.12	6.60	0.32
12200	4.33	6.92	0.00
26267	4.33	6.92	

Titrant: 0.008620N NaOH
$V_f/V_f' = 6.92$ ml./4.33 ml. = 1.60
$k = 4.65 \times 10^{-4}$ sec.$^{-1}$
$k_s = 2.91 \times 10^{-4}$ sec.$^{-1}$
$k_r = 1.74 \times 10^{-4}$ sec.$^{-1}$

* The ester was dissolved in anhydrous dioxane and stored at 60° for five days after which time sufficient water was added to make the solution 80% dioxane - 20% water and measurement of the rate was begun immediately.

Table 54

Solvolysis of 0.009481 Molar Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 80% Dioxane - 20% Water at 60°C

t sec.	V ml.	$V\frac{V_f}{V_f'}$ ml.	$V_f - V\frac{V_f}{V_f'}$ ml.
127	0.30	0.47	5.03
456	0.69	1.08	4.42
831	1.14	1.79	3.71
1163	1.49	2.34	3.16
1597	1.83	2.98	2.52
1943	2.12	3.33	2.17
2333	2.30	3.61	1.89
3251	2.79	4.38	1.12
3912	2.99	4.70	0.80
4840	3.19	5.01	0.49
9840	3.51	5.50	0.0
11373	3.51	5.50	0.0

Titrant: 0.00862ON NaOH
V_f/V_f' = 5.50 ml./3.51 ml. = 1.57
k = 5.09 x 10^{-4} sec.$^{-1}$
k_s = 3.25 x 10^{-4} sec.$^{-1}$
k_p = 1.84 x 10^{-4} sec.$^{-1}$

Table 55

Solvolysis of 0.01123 Molar Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 80% Dioxane - 20% Water at 60°C

t sec.	V ml.	$V\frac{V_f}{V_f'}$ ml.	$V_f - V\frac{V_f}{V_f'}$ ml.
138	0.27	0.41	5.89
313	0.59	0.90	5.40
550	0.94	1.44	4.86
767	1.24	1.89	4.41
1027	1.48	2.29	4.01
1470	1.98	3.02	3.28
2100	2.48	3.78	2.52
2900	2.95	4.50	1.80
3240	3.10	4.73	1.57
3916	3.37	5.15	1.15
4742	3.55	5.42	0.88
5548	3.72	5.67	0.63
7247	3.94	6.01	0.29
11150	4.13	6.30	0.0

Titrant: 0.008918N NaOH
$V_f/V_f' = 6.30$ ml./4.13 ml. = 1.53
$k = 4.27 \times 10^{-4}$ sec.$^{-1}$
$k_s = 2.80 \times 10^{-4}$ sec.$^{-1}$
$k_r = 1.47 \times 10^{-4}$ sec.$^{-1}$

Table 56

Solvolysis of 0.004067 Molar Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 80% Dioxane - 20% Water at 60°C*

t sec.	V ml.	$V\frac{V_f}{V_f'}$ ml.	$V_f - V\frac{V_f}{V_f'}$ ml.
394	0.40	0.61	3.54
600	0.62	0.95	3.20
830	0.82	1.25	2.90
1350	1.22	1.86	2.29
1830	1.52	2.32	1.83
2270	1.72	2.62	1.53
2754	1.92	2.93	1.22
3385	2.12	3.23	0.92
4278	2.32	3.54	0.61
5500	2.52	3.84	0.31
55275	2.72	4.15	0.0

Titrant: 0.09810N NaOH
V_f/V_f' = 4.15 ml./2.72 ml. = 1.53
k = 4.49 x 10^{-4} sec.$^{-1}$
k_s = 2.93 x 10^{-4} sec.$^{-1}$
k_r = 1.56 x 10^{-4} sec.$^{-1}$

*The rate in this run was followed by adding excess standard NaOH in small increments and recording the times at which the phenolphthalein indicator changed color.

Table 57

Solvolysis of 0.00579 Molar Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 80% Dioxane - 20% Water at 60°C*

t sec.	V ml.	$V\frac{V_f}{V_f'}$ ml.	$V_f - V\frac{V_f}{V_f'}$ ml.
332	0.61	0.96	4.91
638	1.01	1.59	4.28
938	1.41	2.21	3.66
1368	1.83	2.87	3.00
1800	2.13	3.34	2.53
2325	2.53	3.97	1.90
3025	2.93	4.60	1.27
3970	3.33	5.23	0.64
5435	3.74	5.87	0.0

Titrant: 0.09869N NaOH
V_f/V_f' = 5.87 ml./3.74 ml. = 1.57
$k = 4.90 \times 10^{-4}$ sec.$^{-1}$
$k_s = 3.12 \times 10^{-4}$ sec.$^{-1}$
$k_r = 1.78 \times 10^{-4}$ sec.$^{-1}$

*The rate in this run was followed by adding excess standard NaOH in small increments and recording the times at which the phenolphthalein indicator changed color.

Table 58

Solvolysis of 0.008570 Molar Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 80% Dioxane - 20% Water at 70°C

t sec.	V ml.	$V\frac{V_f}{V_f'}$ ml.	$V_f - V\frac{V_f}{V_f'}$ ml.
132	0.39	0.60	3.54
293	0.75	1.15	2.99
485	1.14	1.75	2.39
676	1.45	2.22	1.92
833	1.67	2.56	1.58
1001	1.88	2.88	1.26
1179	2.04	3.13	1.01
1377	2.15	3.30	0.84
1731	2.36	3.62	0.52
2319	2.53	3.88	0.26
2910	2.57	3.94	0.20
5295	2.67	4.09	0.05
48720	2.70	4.14	0.0

Titrant: 0.01034N NaOH
V_f/V_f' = 4.14 ml./2.70 ml. = 1.53
k = 12.0 x 10^{-4} sec.$^{-1}$
k_s = 7.80 x 10^{-4} sec.$^{-1}$
k_r = 4.20 x 10^{-4} sec.$^{-1}$

Table 59

Solvolysis of 0.008626 Molar Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 80% Dioxane - 20% Water at 70°C

t sec.	V ml.	$V\frac{V_f}{V_f'}$ ml.	$V_f - V\frac{V_f}{V_f'}$ ml.
84	0.32	0.49	3.59
370	0.92	1.42	2.66
551	1.27	1.96	2.12
831	1.65	2.54	1.54
984	1.82	2.80	1.28
1111	1.95	3.00	1.08
1311	2.10	3.23	0.85
1427	2.20	3.39	0.69
1591	2.25	3.46	0.62
1949	2.38	3.66	0.42
2456	2.50	3.85	0.23
3177	2.59	3.99	0.09
5452	2.65	4.08	0.0
87390	2.65	4.08	0.0

Titrant: 0.01057N NaOH

V_f/V_f' = 4.08 ml./2.65 ml. = 1.54

$k = 11.7 \times 10^{-4}$ sec.$^{-1}$

$k_s = 7.57 \times 10^{-4}$ sec.$^{-1}$

$k_r = 4.13 \times 10^{-4}$ sec.$^{-1}$

Table 60

Solvolysis of 0.01015 Molar Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 80% Dioxane - 20% Water at 80°C

t sec.	V ml.	$V\frac{V_f}{V_f'}$ ml.	$V_f - V\frac{V_f}{V_f'}$ ml.
85	0.86	1.33	4.35
120	1.09	1.69	3.99
191	1.49	2.31	3.37
255	1.79	2.78	2.90
311	2.15	3.34	2.34
367	2.41	3.74	1.94
423	2.60	4.03	1.65
485	2.82	4.38	1.30
564	2.99	4.64	1.04
632	3.13	4.86	0.82
723	3.30	5.12	0.56
818	3.35	5.20	0.48
920	3.44	5.34	0.34
1083	3.57	5.54	0.14
1264	3.61	5.60	0.08
4479	3.66	5.68	0.0

Titrant: 0.008932N NaOH

$V_f/V_f' = 5.68$ ml./3.66 ml. = 1.55

$k = 30.2 \times 10^{-4}$ sec.$^{-1}$

$k_s = 19.4 \times 10^{-4}$ sec.$^{-1}$

$k_r = 10.8 \times 10^{-4}$ sec.$^{-1}$

Table 61

Solvolysis of 0.01158 Molar Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 80% Dioxane - 20% Water at 60°C

t sec.	V ml.	$V\frac{V_f}{V_f'}$, ml.	$V_f - V\frac{V_f}{V_f'}$, ml.
102	1.14	1.76	4.91
152	1.42	2.20	4.47
210	1.79	2.78	3.89
276	2.28	3.54	3.13
368	2.74	4.25	2.42
426	3.01	4.67	2.00
494	3.21	4.98	1.69
558	3.41	5.29	1.38
601	3.55	5.51	1.16
663	3.73	5.79	0.88
767	3.86	5.99	0.68
895	3.96	6.14	0.53
981	4.04	6.27	0.40
1088	4.11	6.38	0.29
1222	4.12	6.39	0.28
7924	4.30	6.67	0.0

Titrant: 0.008689N NaOH

$V_f/V_f' = 6.67$ ml./4.30 ml. = 1.55

$k = 28.9 \times 10^{-4}$ sec.$^{-1}$

$k_s = 18.6 \times 10^{-4}$ sec.$^{-1}$

$k_r = 10.3 \times 10^{-4}$ sec.$^{-1}$

Table 62

Solvolysis of 0.008986 Molar Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 70% Dioxane - 30% Water at 40°C

t sec.	V ml.	$V\frac{V_f}{V_f'}$ ml.	$V_f - V\frac{V_f}{V_f'}$ ml.
319	0.40	0.42	4.39
803	0.68	0.71	4.10
1241	1.01	1.06	3.75
2077	1.43	1.50	3.31
3075	1.94	2.03	2.78
3741	2.20	2.30	2.51
4307	2.40	2.51	2.30
5293	2.73	2.85	1.96
6256	3.01	3.15	1.66
7064	3.18	3.33	1.48
8839	3.54	3.70	1.11
10639	3.82	3.99	0.82
12609	4.04	4.22	0.59
14652	4.22	4.41	0.40
17325	4.30	4.50	0.31
19738	4.40	4.60	0.21
22398	4.44	4.64	0.17
86400	4.60	4.81	0.0

Titrant: 0.009349N NaOH

V_f/V_f' = 4.81 ml./4.60 ml. = 1.05

$k = 1.64 \times 10^{-4}$ sec.$^{-1}$

$k_s = 1.57 \times 10^{-4}$ sec.$^{-1}$

$k_r = 0.0718 \times 10^{-4}$ sec.$^{-1}$

Table 63

Solvolysis of 0.009435 Molar Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 70% Dioxane - 30% Water at 40°C

t sec.	V ml.	$V\frac{V_f}{V_f'}$ ml.	$V_f - V\frac{V_f}{V_f'}$ ml.
144	0.34	0.35	4.70
424	0.52	0.54	4.51
730	0.74	0.77	4.28
1223	1.08	1.12	3.93
1540	1.22	1.27	3.78
2307	1.64	1.70	3.35
2965	1.95	2.03	3.02
3555	2.23	2.32	2.73
4482	2.57	2.67	2.38
5376	2.86	2.97	2.08
6389	3.17	3.29	1.76
7341	3.40	3.53	1.52
8465	3.62	3.76	1.29
9574	3.82	3.97	1.08
11267	4.07	4.23	0.82
13579	4.28	4.45	0.60
19120	4.56	4.74	0.31
26693	4.70	4.88	0.17
86400	4.86	5.05	0.0

Titrant: 0.009349N NaOH
V_f/V_f' = 5.05 ml./4.86 ml. = 1.04
k = 1.57 x 10^{-4} sec.$^{-1}$
k_s = 1.51 x 10^{-4} sec.$^{-1}$
k_r = 0.0589 x 10^{-4} sec.$^{-1}$

Table 64

Solvolysis of 0.008528 Molar Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 70% Dioxane - 30% Water at 50°C

t sec.	V ml.	$V\frac{V_f}{V_f'}$ ml.	$V_f - V\frac{V_f}{V_f'}$ ml.
363	0.88	0.92	3.66
708	1.42	1.48	3.10
1020	1.85	1.93	2.65
1299	2.18	2.28	2.30
1604	2.48	2.59	1.99
1895	2.78	2.91	1.67
2288	3.04	3.18	1.40
2691	3.28	3.43	1.15
3092	3.48	3.64	0.94
3597	3.72	3.89	0.69
4241	3.91	4.09	0.49
4768	4.02	4.20	0.38
5250	4.09	4.28	0.30
6141	4.16	4.35	0.23
6986	4.23	4.42	0.16
8824	4.31	4.51	0.07
16908	4.36	4.56	0.02
79200	4.38	4.58	0.0

Titrant: 0.009311N NaOH
V_f/V_f' = 4.58 ml./4.38 ml. = 1.05
k = 5.21 x 10^{-4} sec.$^{-1}$
k_s = 4.98 x 10^{-4} sec.$^{-1}$
k_r = 0.228 x 10^{-4} sec.$^{-1}$

Table 65

Solvolysis of 0.008940 Molar Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 70% Dioxane - 30% Water at 50°C

t sec.	V ml.	$V\frac{V_f}{V_f'}$ ml.	$V_f - V\frac{V_f}{V_f'}$ ml.
267	0.66	0.69	4.11
673	1.40	1.47	3.33
992	1.92	2.01	2.79
1294	2.24	2.35	2.45
1578	2.62	2.75	2.05
1872	2.88	3.02	1.78
2254	3.19	3.34	1.46
2661	3.45	3.62	1.18
3060	3.64	3.81	0.99
3556	3.83	4.01	0.79
4202	4.02	4.21	0.59
4687	4.18	4.38	0.42
5162	4.28	4.49	0.31
5950	4.34	4.55	0.25
6957	4.42	4.63	0.17
8588	4.50	4.72	0.08
16662	4.56	4.78	0.02
79200	4.58	4.80	0.0

Titrant: 0.009311N NaOH

V_f/V_f' = 4.80 ml./4.58 ml. = 1.05

k = 5.02 x 10^{-4} sec.$^{-1}$

k_s = 4.79 x 10^{-4} sec.$^{-1}$

k_r = 0.230 x 10^{-4} sec.$^{-1}$

Table 66

Solvolysis of 0.009296 Molar Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 70% Dioxane - 30% Water 0.009410 Normal in Sodium Hydroxide at 50°C

t sec.	V ml.	$V - V_f$ ml.
82	4.71	4.59
275	4.42	4.30
433	4.13	4.01
629	3.92	3.80
925	3.30	3.18
1059	3.12	3.00
1292	2.82	2.70
1671	2.33	2.21
1929	2.19	2.07
2115	1.91	1.79
2581	1.60	1.48
3314	1.19	1.07
4493	0.84	0.72
5558	0.62	0.50
6478	0.46	0.34
7582	0.37	0.25
12393	0.26	0.14
72000	0.12	0.0

Titrant: 0.009525N HCl
V_f = 0.12 ml.
k = 4.58 x 10^{-4} sec.$^{-1}$

Table 67

Solvolysis of 0.009068 Molar Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 70% Dioxane - 30% Water 0.009410 Normal in Sodium Hydroxide at 50°C

t sec.	V ml.	$V - V_f$ ml.
150	4.68	4.50
316	4.44	4.26
567	3.93	3.75
745	3.60	3.42
976	3.30	3.12
1170	3.02	2.84
1462	2.65	2.47
1859	2.24	2.06
2301	1.84	1.66
2724	1.59	1.41
3126	1.28	1.10
3578	1.11	0.93
4077	0.95	0.77
5124	0.69	0.51
6251	0.58	0.40
7789	0.37	0.19
43200	0.22	0.04

Titrant: 0.009525N HCl
V_f = 0.18 ml.
k = 4.66 x 10^{-4} sec.$^{-1}$

Table 68

Solvolysis of 0.008832 Molar Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 70% Dioxane - 30% Water at 60°C

t sec.	V ml.	$V\frac{V_f}{V_f'}$ ml.	$V_f - V\frac{V_f}{V_f'}$ ml.
92	0.59	0.63	4.00
233	1.21	1.28	3.35
404	1.92	2.04	2.59
551	2.40	2.55	2.13
683	2.71	2.88	1.75
818	3.04	3.23	1.40
969	3.31	3.51	1.12
1132	3.56	3.78	0.85
1316	3.80	4.04	0.59
1477	3.88	4.12	0.51
1684	4.02	4.27	0.36
1884	4.08	4.33	0.30
2195	4.16	4.42	0.21
2455	4.24	4.50	0.13
2758	4.26	4.52	0.11
3255	4.32	4.59	0.04
4250	4.36	4.63	0.0
13303	4.36	4.63	0.0
97200	4.36	4.63	0.0

Titrant: 0.0095hlN NaOH
V_f/V_f' = 4.63 ml./4.36 ml. = 1.06
k = 14.5 x 10^{-4} $sec.^{-1}$
k_s = 13.7 x 10^{-4} $sec.^{-1}$
k_r = 0.847 x 10^{-4} $sec.^{-1}$

Table 69

Solvolysis of 0.009320 Molar Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 70% Dioxane - 30% Water at 60°C

t sec.	V ml.	$V\frac{V_f}{V_f'}$ ml.	$V_f - V\frac{V_f}{V_f'}$ ml.
90	0.64	0.68	4.21
228	1.23	1.30	3.59
403	1.98	2.10	2.79
545	2.46	2.60	2.29
685	2.94	3.11	1.78
877	3.32	3.51	1.38
1025	3.57	3.78	1.11
1185	3.75	3.97	0.92
1346	4.01	4.24	0.65
1543	4.16	4.40	0.44
1724	4.26	4.51	0.38
1925	4.34	4.59	0.30
2135	4.44	4.70	0.19
2354	4.46	4.72	0.17
2585	4.48	4.74	0.15
3428	4.58	4.85	0.04
7292	4.62	4.89	0.0

Titrant: 0.009541N NaOH
V_f/V_f' = 4.89 ml./4.62 ml. = 1.06
k = 14.8 x 10^{-4} sec.$^{-1}$
k_s = 14.0 x 10^{-4} sec.$^{-1}$
k_r = 0.815 x 10^{-4} sec.$^{-1}$

Table 70

Solvolysis of 0.006235 Molar Dicyclopropylcarbinyl p-Nitrobenzoate in 85% Dioxane - 15% Water at 80°C

t sec.	V ml.	$V_f - V$ ml.
257	0.50	3.35
526	0.65	3.20
816	0.89	2.96
1130	1.09	2.76
1553	1.38	2.47
2017	1.67	2.18
2343	1.80	2.05
2824	2.11	1.74
3273	2.29	1.56
3857	2.50	1.35
4353	2.66	1.19
5127	2.92	0.93
6200	3.22	0.63
6992	3.38	0.47
8082	3.48	0.37
9723	3.72	0.13
13314	3.84	0.01

Titrant: 0.008093N NaOH
V_f = 3.85 ml.
$k^{'}$ = 2.62 x 10^{-4} $sec.^{-1}$

Table 71

Solvolysis of 0.006897 Molar Dicyclopropylcarbinyl p-Nitrobenzoate in 85% Dioxane - 15% Water at 80°C

t sec.	V ml.	V_f-V ml.
330	0.57	3.69
612	0.80	3.46
924	1.02	3.24
1251	1.29	2.97
1704	1.61	2.65
2118	1.89	2.37
2412	2.05	2.21
2926	2.35	1.91
3341	2.52	1.74
3963	2.86	1.40
4445	3.01	1.25
5251	3.25	1.01
6324	3.53	0.73
7090	3.74	0.52
8216	3.91	0.35
9895	4.19	0.07

Titrant: 0.008093N NaOH
V_f = 4.26 ml.
k = 2.73 x 10^{-4} $sec.^{-1}$

Table 72

Solvolysis of 0.007173 Molar Dicyclopropylcarbinyl p-Nitrobenzoate in 80% Dioxane - 20% Water at 60°C

t sec.	V ml.	V_f-V ml.
118	0.24	4.80
350	0.31	4.73
834	0.58	4.46
1370	0.79	4.25
1865	0.99	4.05
2667	1.36	3.68
3451	1.65	3.39
4441	1.96	3.08
5590	2.36	2.68
6964	2.72	2.32
8290	3.03	2.01
9495	3.27	1.77
10670	3.54	1.50
12366	3.78	1.26
14021	3.98	1.06
18959	4.45	0.59

Titrant: 0.007123N NaOH
V_f = 5.04 ml.
k = 1.10 x 10^{-4} $sec.^{-1}$

Table 73

Solvolysis of 0.009806 Molar Dicyclopropylcarbinyl p-Nitrobenzoate in 80% Dioxane - 20% Water at 60°C

t sec.	V ml.	$V_f - V$ ml.
128	0.15	4.94
645	0.40	4.69
906	0.55	4.54
1184	0.64	4.45
2014	1.05	4.04
2914	1.44	3.65
3636	1.80	3.29
5312	2.39	2.70
5717	2.52	2.57
6881	2.84	2.25
8207	3.20	1.89
9561	3.50	1.59
10887	3.80	1.29
12124	4.02	1.07
15426	4.54	0.55

Titrant: 0.009638N NaOH
V_f = 5.09 ml.
k = 1.21 x 10^{-4} $sec.^{-1}$

Table 74

Solvolysis of 0.008038 Molar Dicyclopropylcarbinyl p-Nitrobenzoate in 80% Dioxane - 20% Water at 70°C

t sec.	V ml.	$V_f - V$ ml.
290	0.40	3.52
625	0.67	3.25
1003	1.00	2.92
1432	1.37	2.55
1763	1.60	2.32
2080	1.80	2.12
2435	2.01	1.91
2918	2.25	1.67
3534	2.55	1.37
4409	2.(0	1.02
6140	3.36	0.56
6955	3.52	0.40
11072	3.92	0.0

Titrant: 0.01025N NaOH
V_f = 3.92 ml.
k = 2.86 x 10^{-4} sec.$^{-1}$

Table 75

Solvolysis of 0.007341 Molar Dicyclopropylcarbinyl p-Nitrobenzoate in 80% Dioxane - 20% Water at 70°C

t sec.	V ml.	V_f-V ml.
349	0.45	3.13
744	0.83	2.75
1092	1.13	2.45
1491	1.35	2.23
1807	1.57	2.01
2133	1.71	1.87
2652	1.99	1.59
3247	2.25	1.33
4126	2.62	0.96
5765	3.10	0.48
7067	3.25	0.33
11174	3.58	0.0

Titrant: 0.01025N NaOH
V_f = 3.58 ml.
k = 2.98×10^{-4} sec.$^{-1}$

Table 76

Solvolysis of 0.01063 Molar Dicyclopropylcarbinyl p-Nitrobenzoate in 80% Dioxane - 20% Water at 80°C

t sec.	V ml.	V_f-V ml.
96	0.74	5.48
162	0.86	5.36
256	1.16	5.06
353	1.45	4.77
509	1.93	4.29
602	2.22	4.00
754	2.60	3.62
841	2.81	3.41
1004	3.15	3.07
1133	3.42	2.80
1208	3.58	2.64
1455	3.96	2.26
1723	4.40	1.82
1911	4.78	1.44
2273	5.02	1.20
7750	6.22	0.0

Titrant: 0.008874N NaOH
V_f = 6.22 ml.
k = 7.06×10^{-4} sec.$^{-1}$

Table 77

Solvolysis of 0.007900 Molar Dicyclopropylcarbinyl p-Nitrobenzoate in 80% Dioxane - 20% Water at 80°C

t sec.	V ml.	V_f-V ml.
72	0.63	4.05
140	0.69	3.99
246	0.92	3.76
345	1.14	3.54
505	1.53	3.15
623	1.79	2.89
730	1.98	2.70
902	2.29	2.39
1010	2.50	2.18
1114	2.62	2.06
1274	2.85	1.83
1474	3.12	1.56
1687	3.35	1.33
1921	3.55	1.13
2145	3.72	0.96
4957	4.68	0.0

Titrant: 0.008874N NaOH
V_f = 4.68 ml.
k = 7.04 x 10^{-4} $sec.^{-1}$

Table 78

Solvolysis of 0.008472 Molar Triisopropylcarbinyl p-Nitrobenzoate in 80% Dioxane - 20% Water at 60°C

t sec.	V ml.	V_f-V ml.
100	0.21	4.77
414	0.21	4.77
918	0.25	4.74
1966	0.26	4.73
5162	0.27	4.72
26637	0.47	4.52
79668	0.92	4.06
107345	1.10	3.88
167040	1.46	3.52
197280	1.60	3.38
258480	2.12	2.86

Titrant: 0.008512N NaOH
V_f = 4.98 ml.
k = 1.99 x 10^{-6} $sec.^{-1}$

Table 79

Solvolysis of 0.01056 Molar Triisopropylcarbinyl p-Nitrobenzoate in 80% Dioxane - 20% Water at 60°C

t sec.	V ml.	V_f-V ml.
96	0.26	5.94
848	0.26	5.94
4026	0.28	5.92
25639	0.52	5.62
78752	1.06	5.14
106355	1.25	4.95
164712	1.77	4.43
194952	1.93	4.27
256152	2.54	3.66

Titrant: 0.008512N NaOH
V_f = 6.20 ml.
k = 1.82 x 10^{-6} $sec.^{-1}$

Table 80

Solvolysis of 0.009546 Molar Triisopropylcarbinyl p-Nitrobenzoate in 80% Dioxane - 20% Water at 70°C

t sec.	V ml.	V_f-V ml.
514	0.20	4.46
1538	0.25	4.41
6570	0.34	4.32
22225	0.77	3.89
30901	1.05	3.61
75998	1.94	2.72
82721	2.12	2.54
89253	2.23	2.43
94398	2.29	2.37
116041	2.82	1.84

Titrant: 0.01025N NaOH
V_f = 4.66 ml.
k = 6.82 x 10^{-6} $sec.^{-1}$

Table 81

Solvolysis of 0.01099 Molar Triisopropylcarbinyl p-Nitrobenzoate in 80% Dioxane - 20% Water at 70°C

t sec.	V ml.	V_f-V ml.
688	0.19	5.17
1704	0.24	5.12
6660	0.36	5.00
22384	0.89	4.47
31264	1.15	4.21
76269	2.21	3.15
83007	2.41	2.95
89637	2.56	2.80
94682	2.61	2.75
116227	3.13	2.23

Titrant: 0.01025N NaOH
V_f = 5.36 ml.
$k = 6.81 \times 10^{-6}$ sec.$^{-1}$

Table 82

Solvolysis of 0.008338 Molar Triisopropylcarbinyl p-Nitrobenzoate in 80% Dioxane - 20% Water at 80°C

t sec.	V ml.	$V_f - V$ ml.
335	0.37	4.14
685	0.40	4.11
2359	0.60	3.91
7419	1.08	3.43
9566	1.23	3.28
11655	1.43	3.08
14906	1.72	2.79
18145	1.90	2.61
21715	2.17	2.34
24669	2.36	2.15
28335	2.56	1.95
32812	2.83	1.68
93800	4.41	0.10

Titrant: 0.009251N NaOH
V_f = 4.51 ml.
k = 27.7 x 10^{-6} $sec.^{-1}$

Table 83

Solvolysis of 0.01020 Molar Triisopropylcarbinyl p-Nitrobenzoate in 80% Dioxane - 20% Water at 80°C

t sec.	V ml.	V_f-V ml.
382	0.42	5.10
732	0.45	5.07
2791	0.70	4.82
7507	1.24	4.28
9745	1.43	4.09
11735	1.67	3.85
15075	1.99	3.53
18301	2.28	3.24
21856	2.52	3.00
24776	2.72	2.80
28546	3.05	2.47
32910	3.40	2.12
94087	5.35	0.17

Titrant: 0.009251N NaOH
V_f = 5.52 ml.
$k = 26.5 \times 10^{-6}$ sec.$^{-1}$

Table 84

Solvolysis of 0.009809 Molar Triisopropylcarbinyl p-Nitrobenzoate in 70% Dioxane - 30% Water at 60°C

t sec.	V ml.	V_f-V ml.
347	0.24	5.34
981	0.28	5.30
5109	0.47	5.11
10848	0.62	4.96
16155	0.80	4.78
22495	1.01	4.57
30434	1.26	4.32
35661	1.39	4.19
75212	2.52	3.06
87227	2.81	2.77
97107	2.96	2.62
102147	3.06	2.52
110629	3.24	2.34
131958	3.58	2.00

Titrant: 0.008791N NaOH
V_f = 5.58 ml.
k = 7.55 x 10^{-6} $sec.^{-1}$

Table 85

Solvolysis of 0.008576 Molar Triisopropylcarbinyl p-Nitrobenzoate in 70% Dioxane - 30% Water at 60°C

t sec.	V ml.	V_f-V ml.
363	0.24	4.64
1005	0.26	4.62
5195	0.40	4.48
10975	0.59	4.29
16210	0.73	4.15
22585	0.89	3.99
30475	1.12	3.76
35753	1.28	3.60
75369	2.24	2.64
88180	2.43	2.45
97167	2.64	2.24
102232	2.68	2.20
110731	2.84	2.04
131912	3.13	1.75

Titrant: 0.008791N NaOH
V_f = 4.88 ml.
$k^{'}$ = 7.49 x 10^{-6} $sec.^{-1}$

Table 86

Solvolysis of 0.007870 Molar Triisopropylcarbinyl p-Nitrobenzoate in 70% Dioxane - 30% Water at 70°C

t sec.	V ml.	$V_f - V$ ml.
495	0.28	3.89
1040	0.32	3.85
2376	0.38	3.79
7004	0.78	3.39
9427	1.04	3.13
11390	1.10	3.07
15266	1.42	2.75
52860	3.10	1.07
55948	3.14	1.03
64204	3.36	0.81
69178	3.46	0.71
89985	3.88	0.29

Titrant: 0.009442N NaOH
V_f = 4.17 ml.
k = 25.0 x 10^{-6} sec.$^{-1}$

Table 87

Solvolysis of 0.008670 Molar Triisopropylcarbinyl p-Nitrobenzoate in 70% Dioxane - 30% Water at 70°C

t sec.	V ml.	V_f-V ml.
546	0.26	4.33
1167	0.33	4.26
2400	0.42	4.17
7088	0.88	3.71
9542	1.10	3.49
11468	1.22	3.37
15378	1.52	3.07
53054	3.46	1.13
56053	3.50	1.09
64340	3.74	0.85
69362	3.86	0.73
90118	4.28	0.31

Titrant: 0.009442N NaOH
V_f = 4.59 ml.
$k^{'}$ = 25.9 x 10^{-6} $sec.^{-1}$

Table 88

Solvolysis of 0.007985 Molar Triisopropylcarbinyl p-Nitrobenzoate in 70% Dioxane - 30% Water at 80°C

t sec.	V ml.	V_f-V ml.
242	0.28	3.97
601	0.33	3.92
1192	0.52	3.73
1824	0.72	3.53
3268	1.12	3.13
4373	1.36	2.89
5512	1.66	2.59
6531	1.80	2.45
7614	2.04	2.21
9276	2.36	1.89
10287	2.50	1.75
11276	2.68	1.57
14115	2.94	1.31
25038	3.86	0.39
30929	4.06	0.19

Titrant: 0.009353N NaOH
V_f = 4.25 ml.
k = 83.2 x 10^{-6} $sec.^{-1}$

Table 89

Solvolysis of 0.01079 Molar Triisopropylcarbinyl p-Nitrobenzoate in 70% Dioxane - 30% Water at 80°C

t sec.	V ml.	V_f-V ml,
343	0.34	5.43
720	0.52	5.25
1294	0.72	5.05
1915	0.91	4.86
3486	1.46	4.31
4476	1.78	3.99
5678	2.15	3.62
6671	2.43	3.34
7764	2.76	3.01
9409	3.12	2.65
10428	3.33	2.44
11425	3.52	2.25
14219	4.09	1.68
25229	5.17	0.60
31092	5.44	0.33

Titrant: 0.009353N NaOH
V_f = 5.77 ml.
k = 79.8 x 10^{-6} $sec.^{-1}$

Figure 22. Plot of log k versus 1/T for the Solvolysis of Dicyclopropylisopropylcarbinyl p-Nitrobenzoate in 90% Dioxane-10% Water.

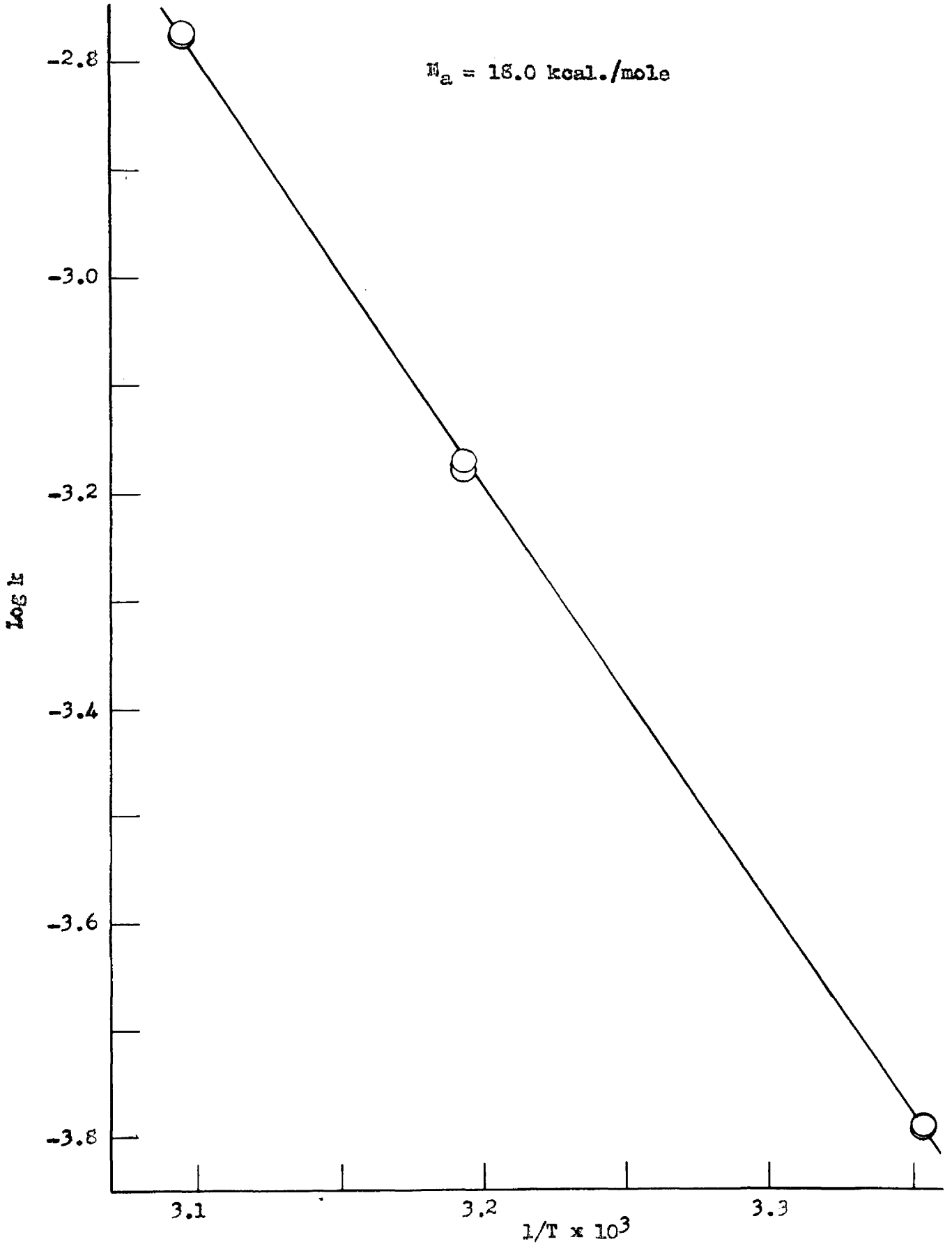

Figure 23. Plot of log k versus 1/T for the Solvolysis of Dicyclopropylisopropylcarbinyl p-Nitrobenzoate in 30% Dioxane-20% Water.

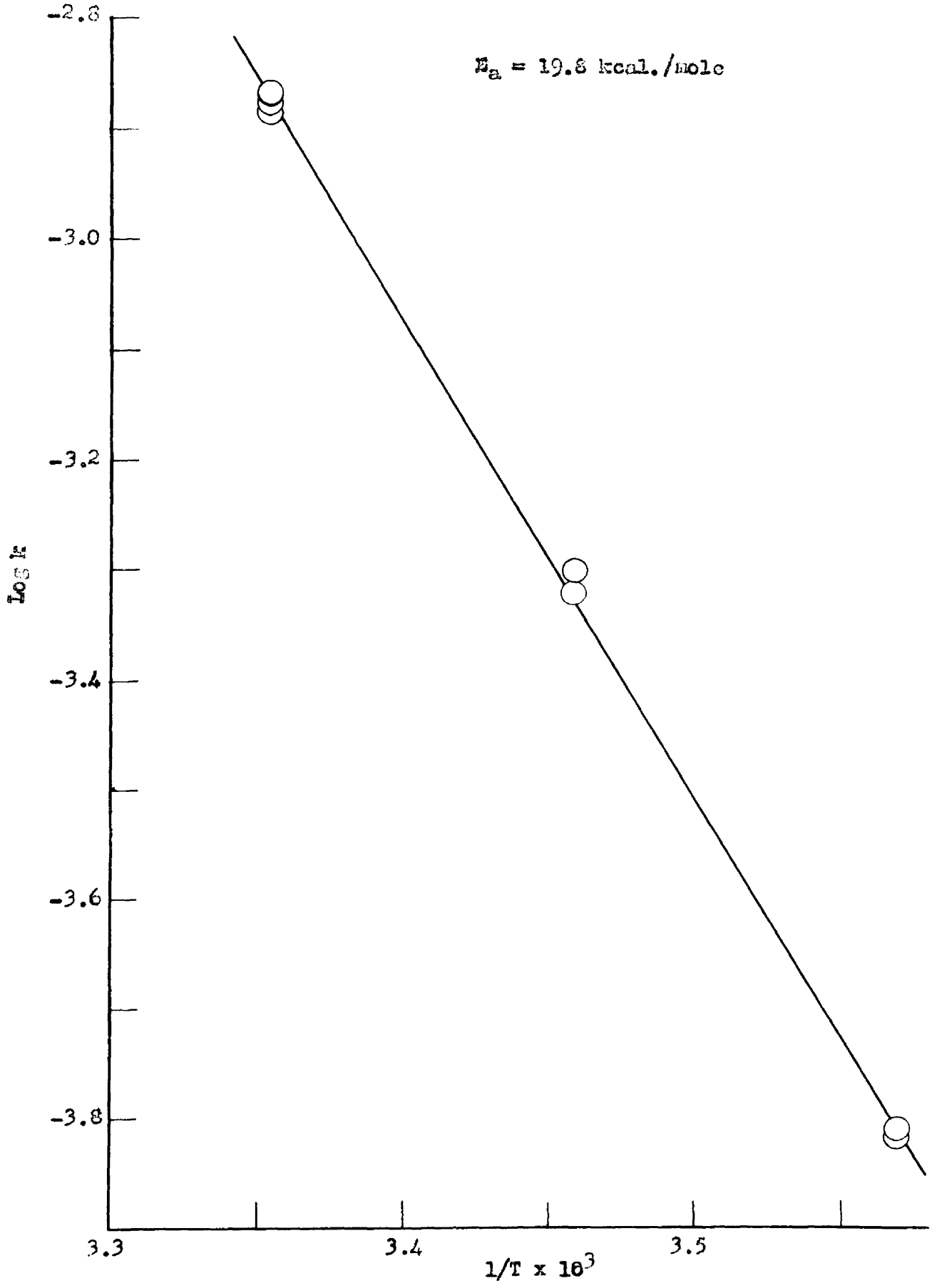

Figure 24. Plot of log k versus 1/T for the Solvolysis of Di-(2-methylcyclopropyl)isopropylcarbinyl p-Nitrobenzoate in 90% Dioxane - 10% Water.

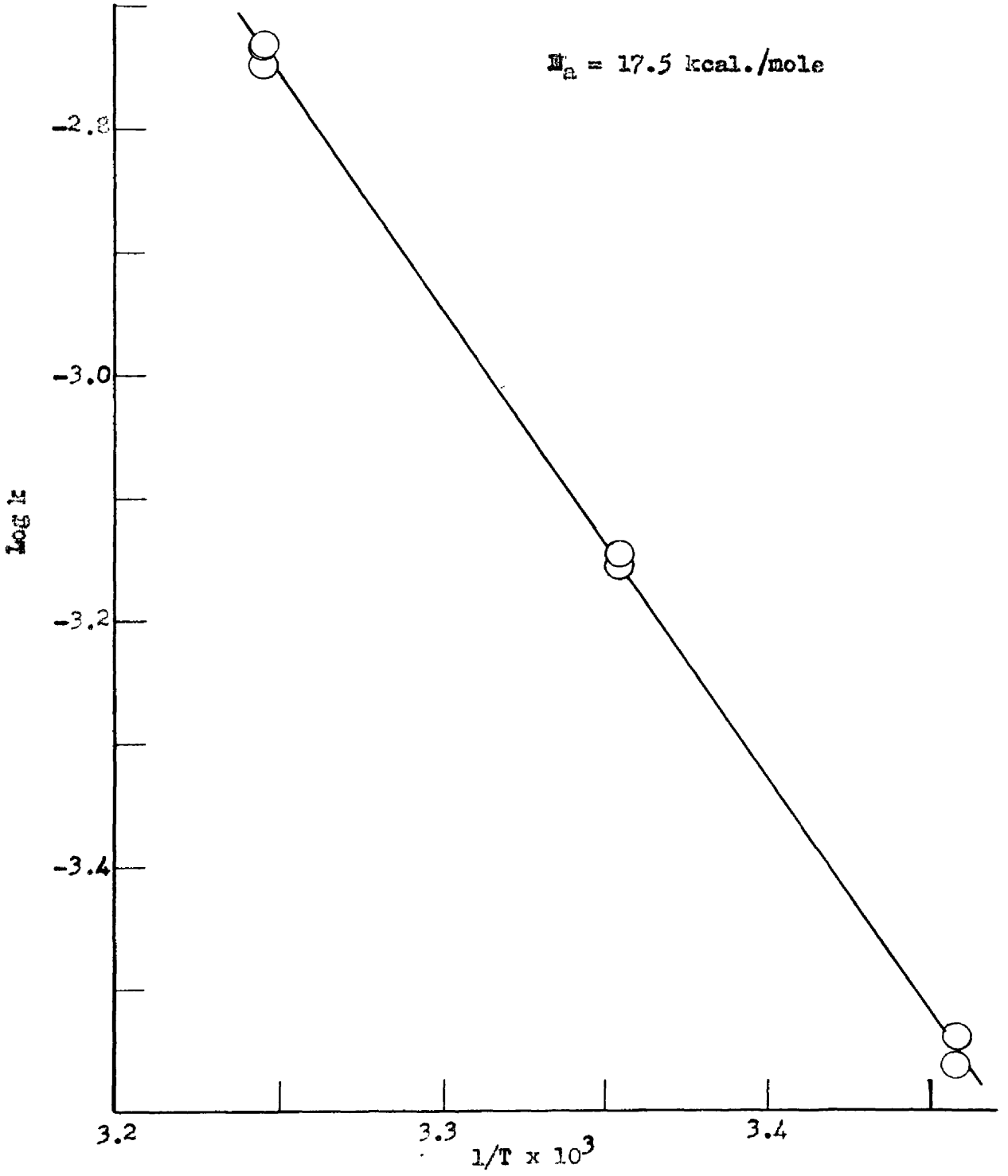

Figure 25. Plot of log k_s versus 1/T for the Solvolysis of Di-(2-methylcyclopropyl)isopropylcarbinyl p-Nitrobenzoate in 90% Dioxane - 10% Water.

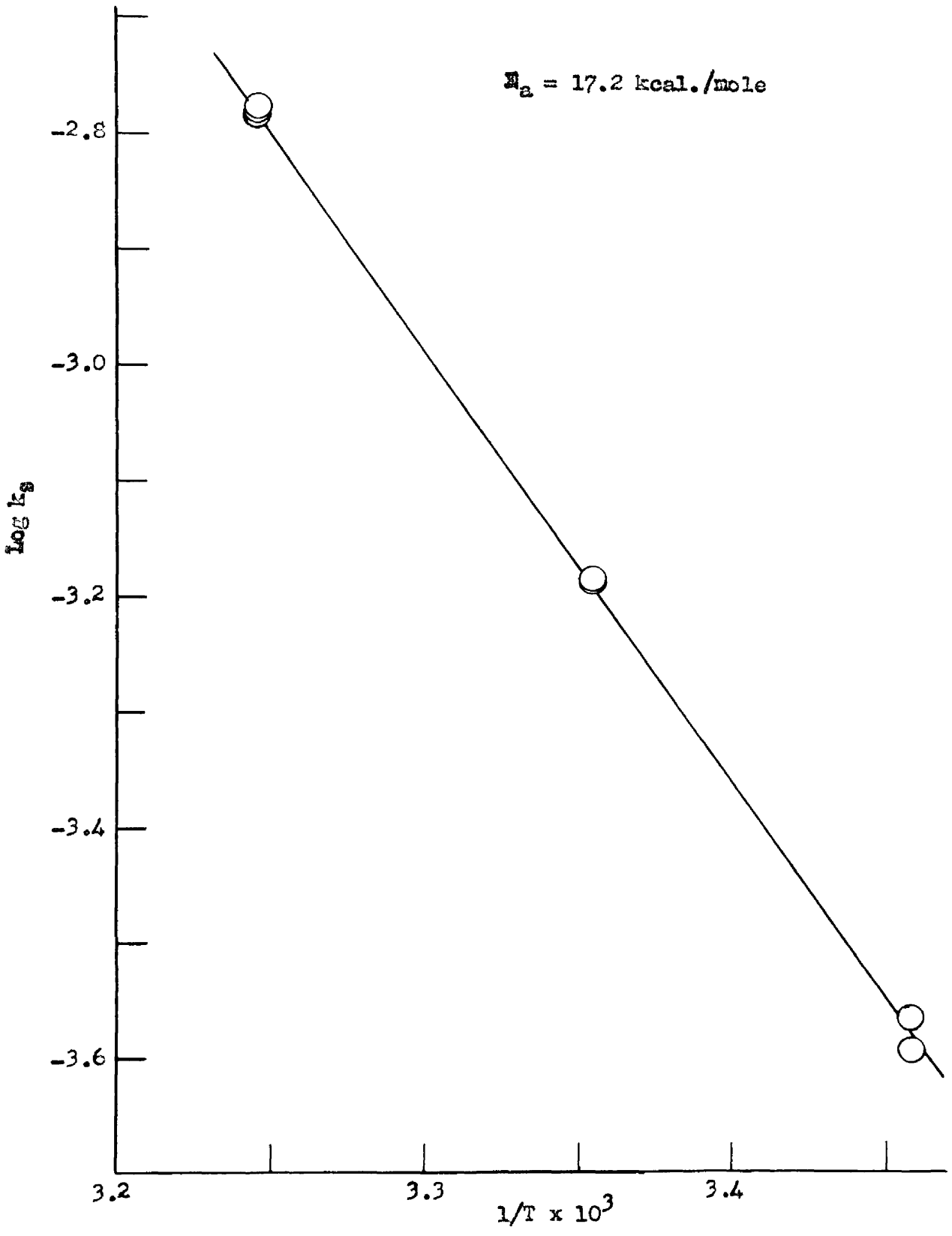

Figure 26. Plot of log k_r versus 1/T for the Rearrangement of Di-(2-methylcyclopropyl)isopropylcarbinyl p-Nitrobenzoate in 90% Dioxane - 10% Water.

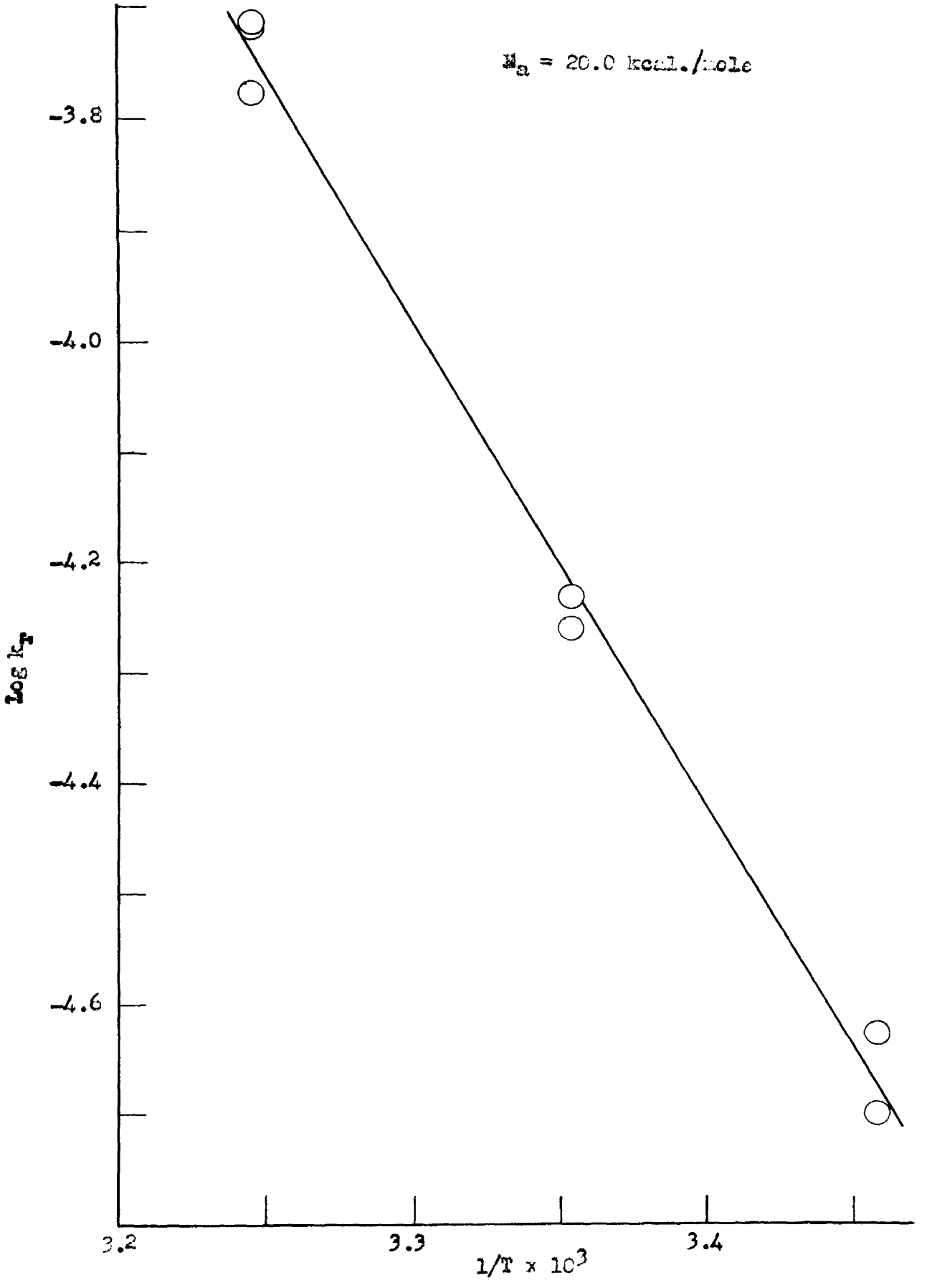

Figure **27.** Plot of log k versus 1/T for the Solvolysis of Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 85% Dioxane-15% Water.

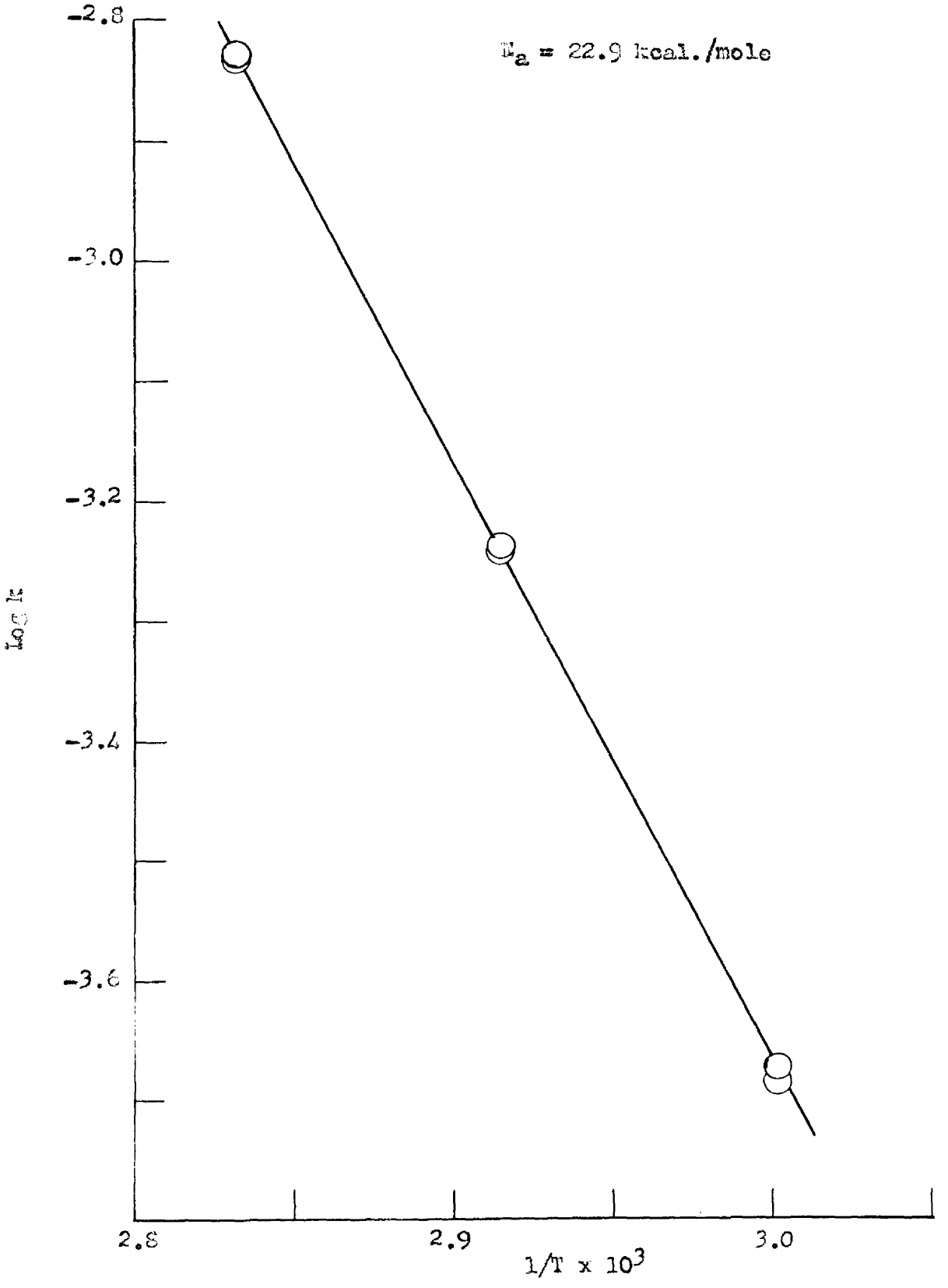

Figure 28. Plot of log k_a versus 1/T for the Solvolysis of Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 85% Dioxane-15% Water.

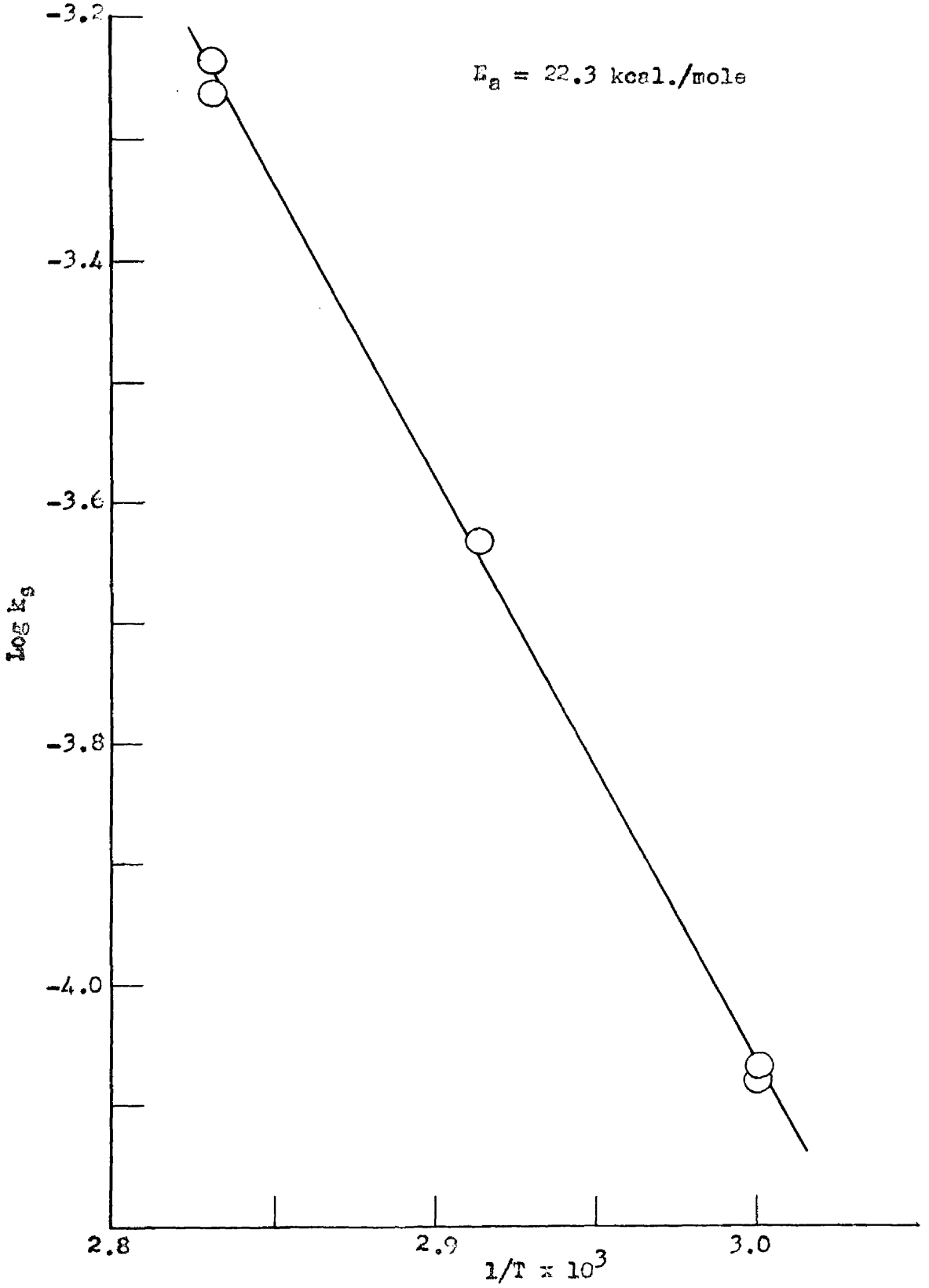

Figure 29. Plot of log k_r versus 1/T for the Rearrangement of Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 85% Dioxane-15% Water.

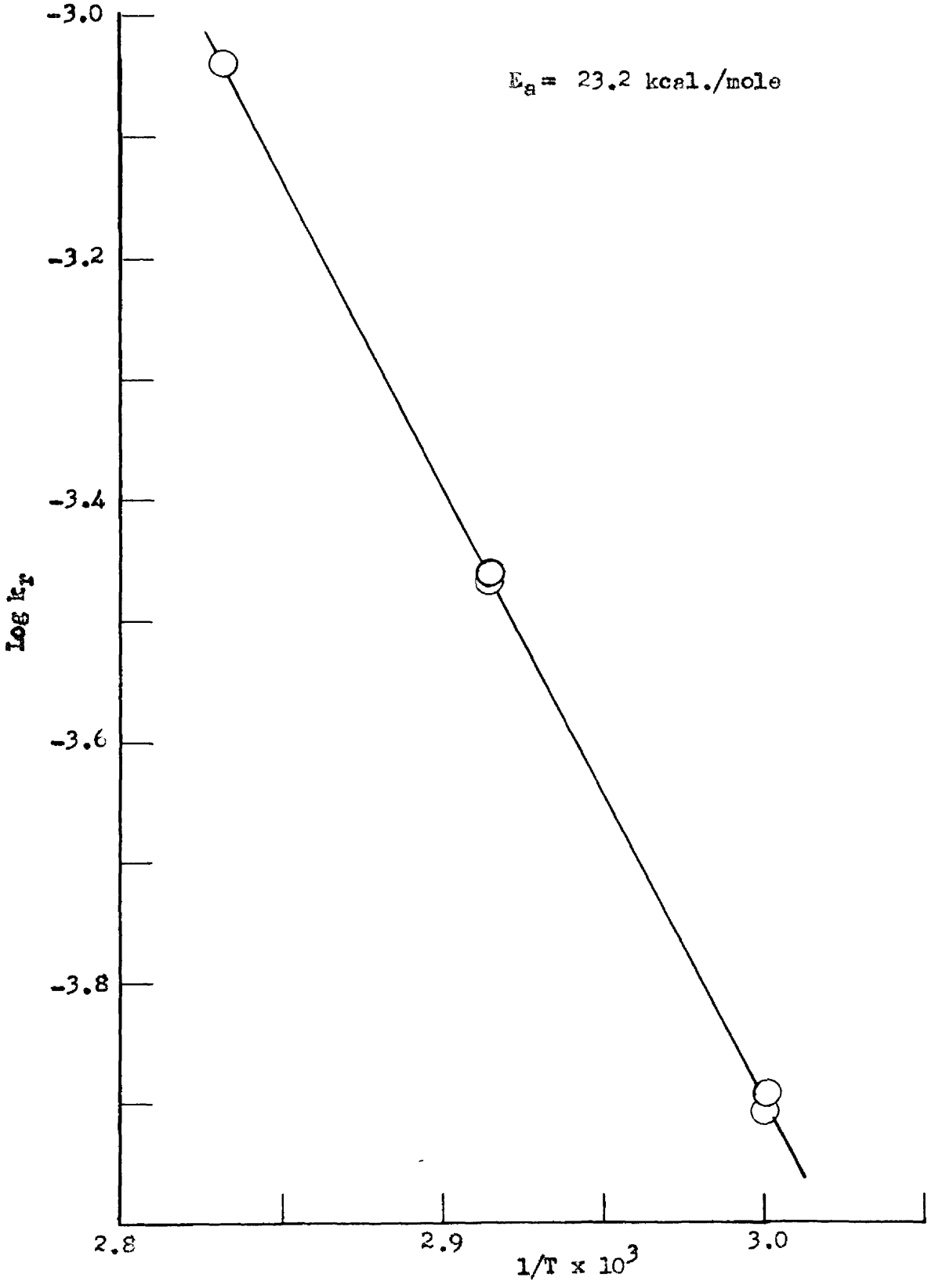

Figure 30. Plot of log k versus 1/T for the Solvolysis of Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 80% Dioxane - 20% Water.

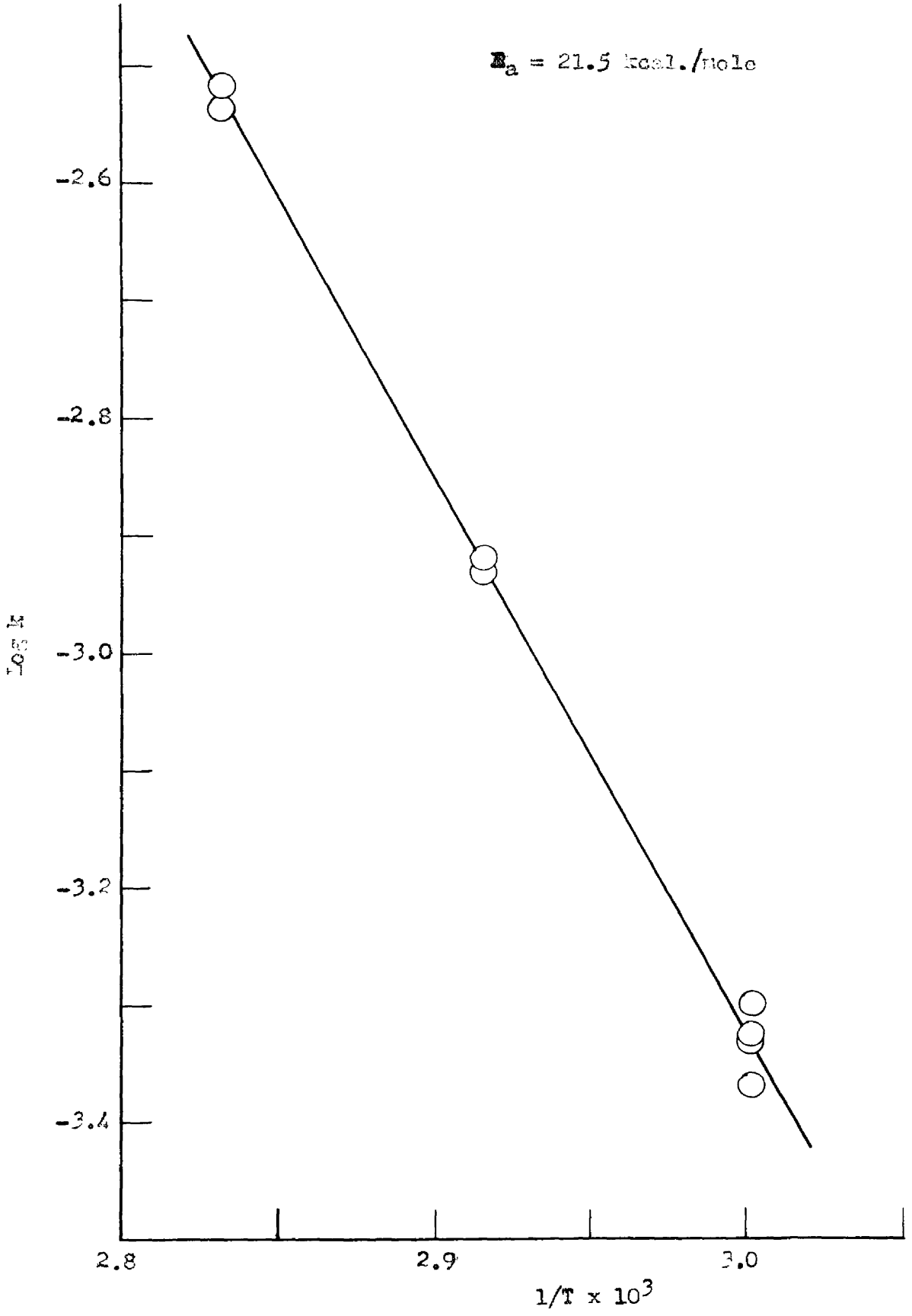

Figure 31. Plot of log k_s versus 1/T for the Solvolysis of Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 80% Dioxane-20% Water.

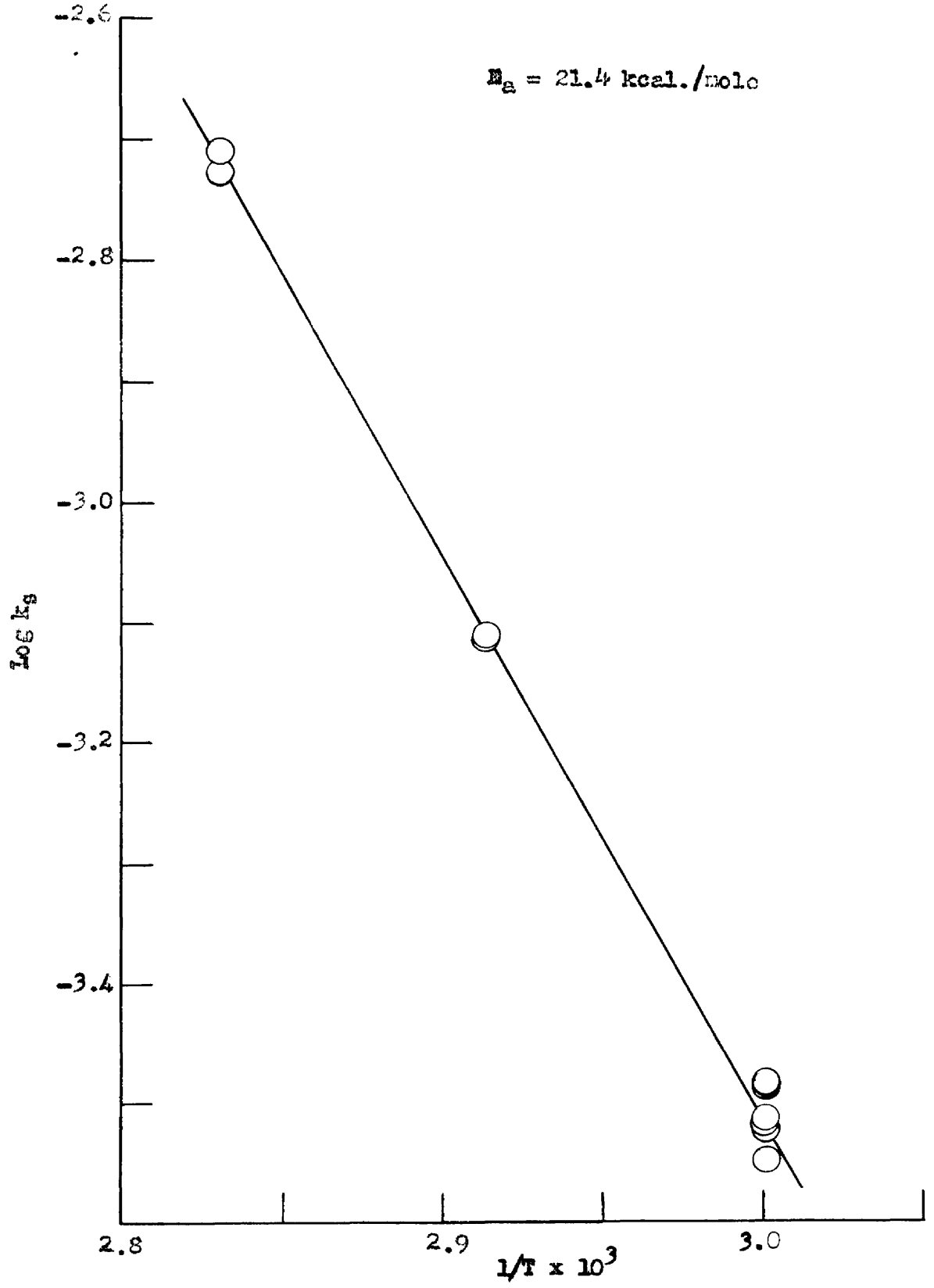

Figure 32. Plot of log k_r versus 1/T for the Rearrangement of Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 80% Dioxane-20% Water.

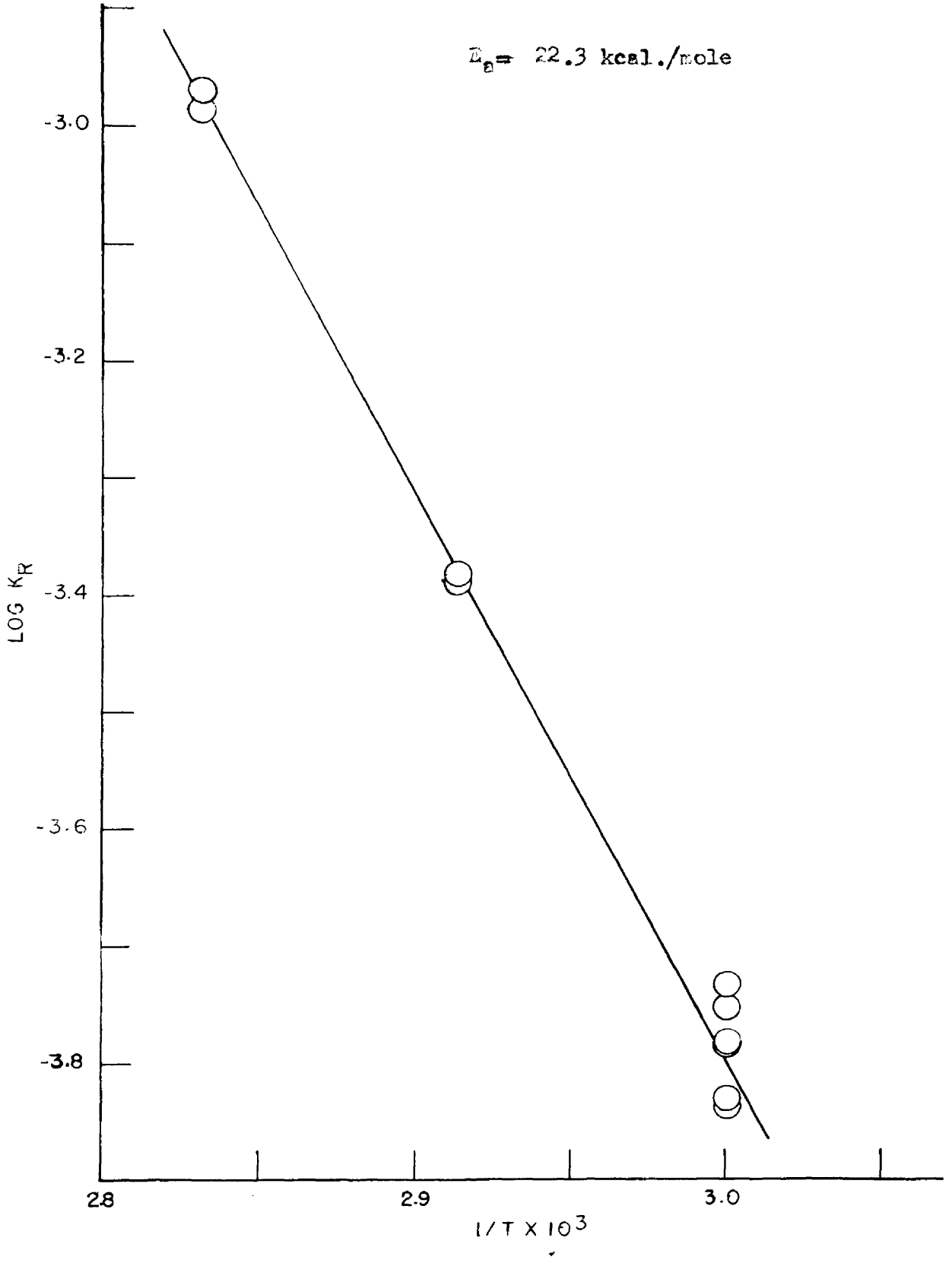

Figure 39. Plot of log k versus 1/T for the Solvolysis of Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 70% Dioxane-30% Water.

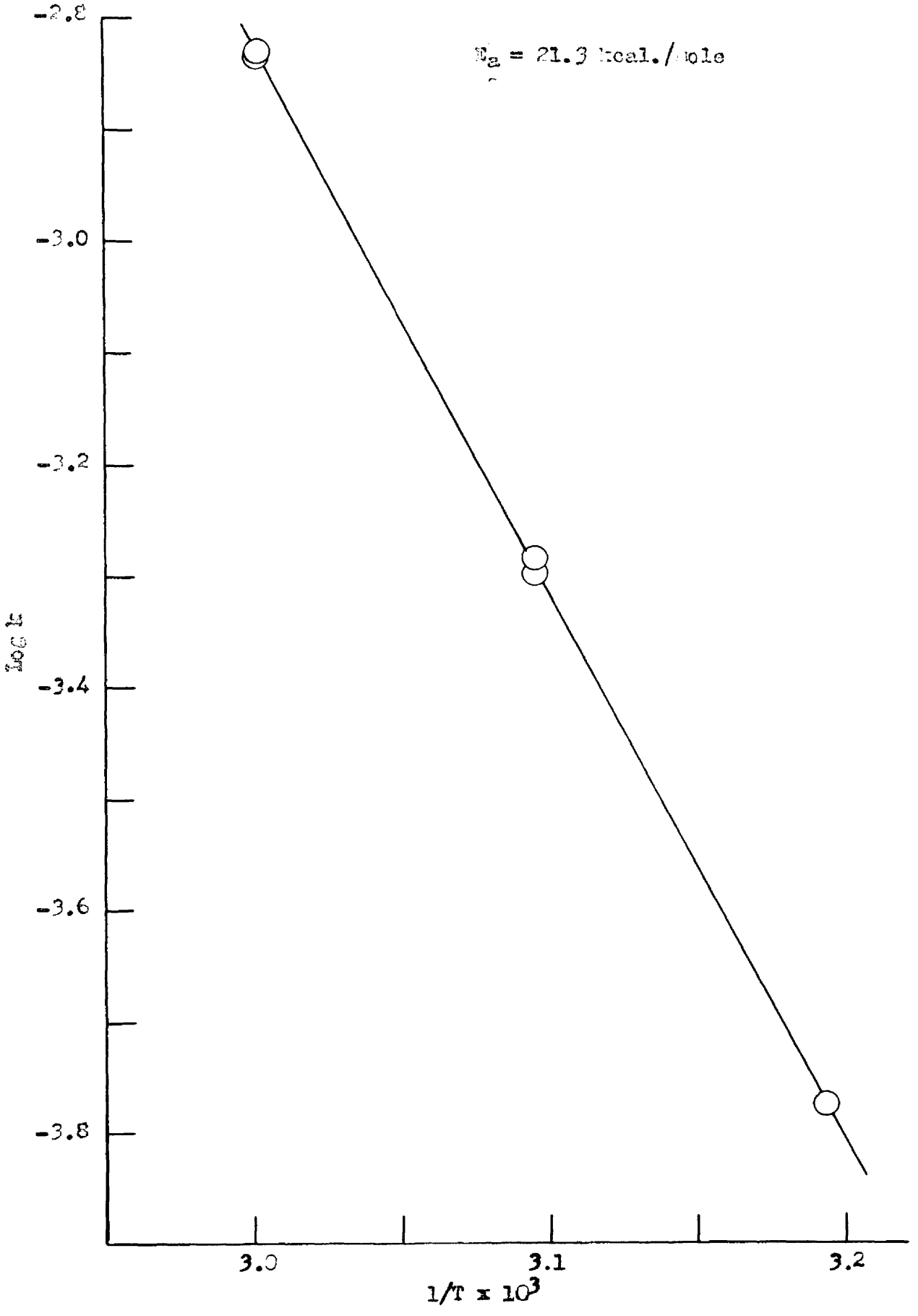

Figure 34. Plot of log k_s versus 1/T for the Solvolysis of Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 70% Dioxane-30% Water.

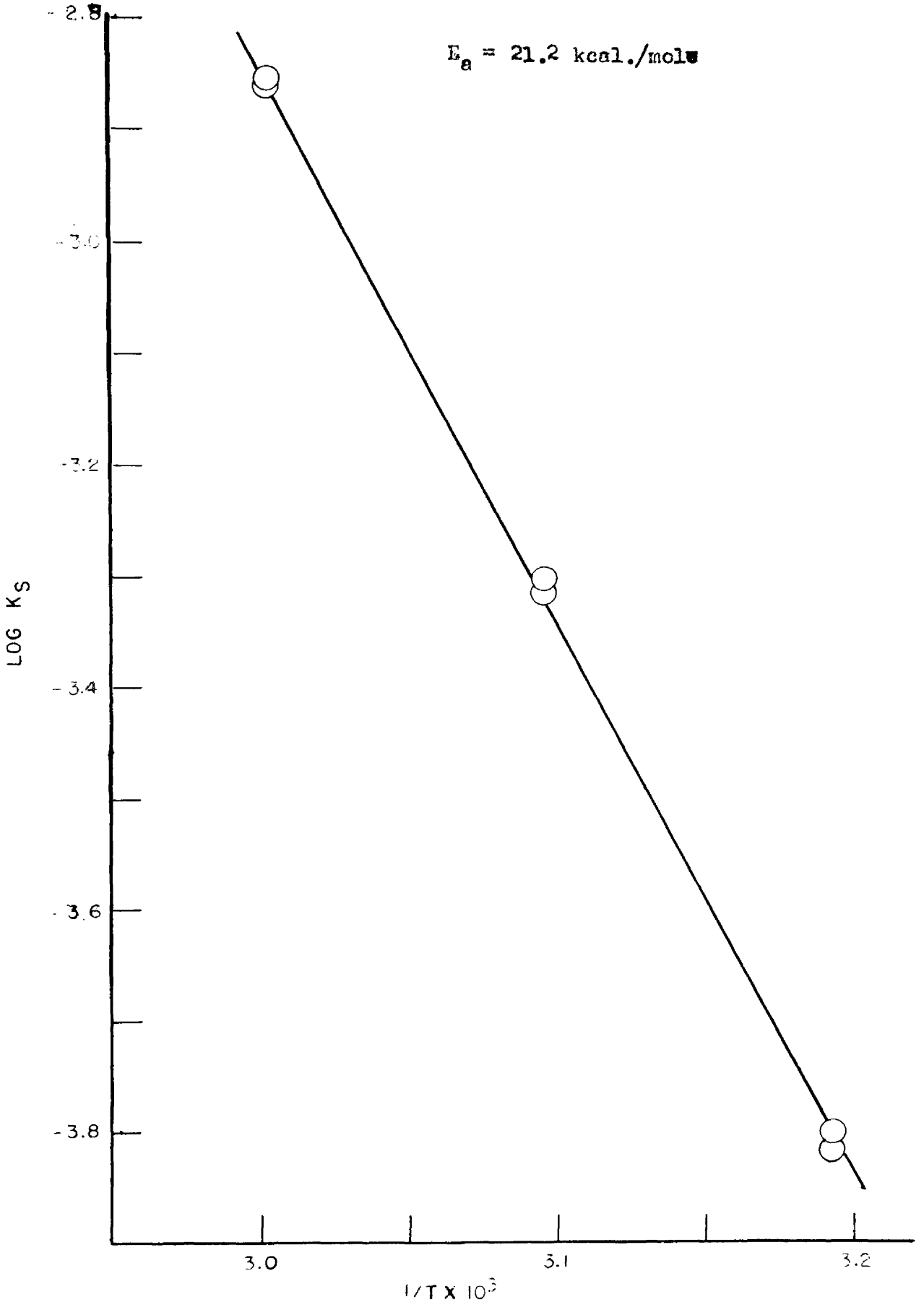

Figure 35. Plot of log k_r versus 1/T for the Rearrangement of Diisopropylcyclopropylcarbinyl p-Nitrobenzoate in 70% Dioxane-30% Water.

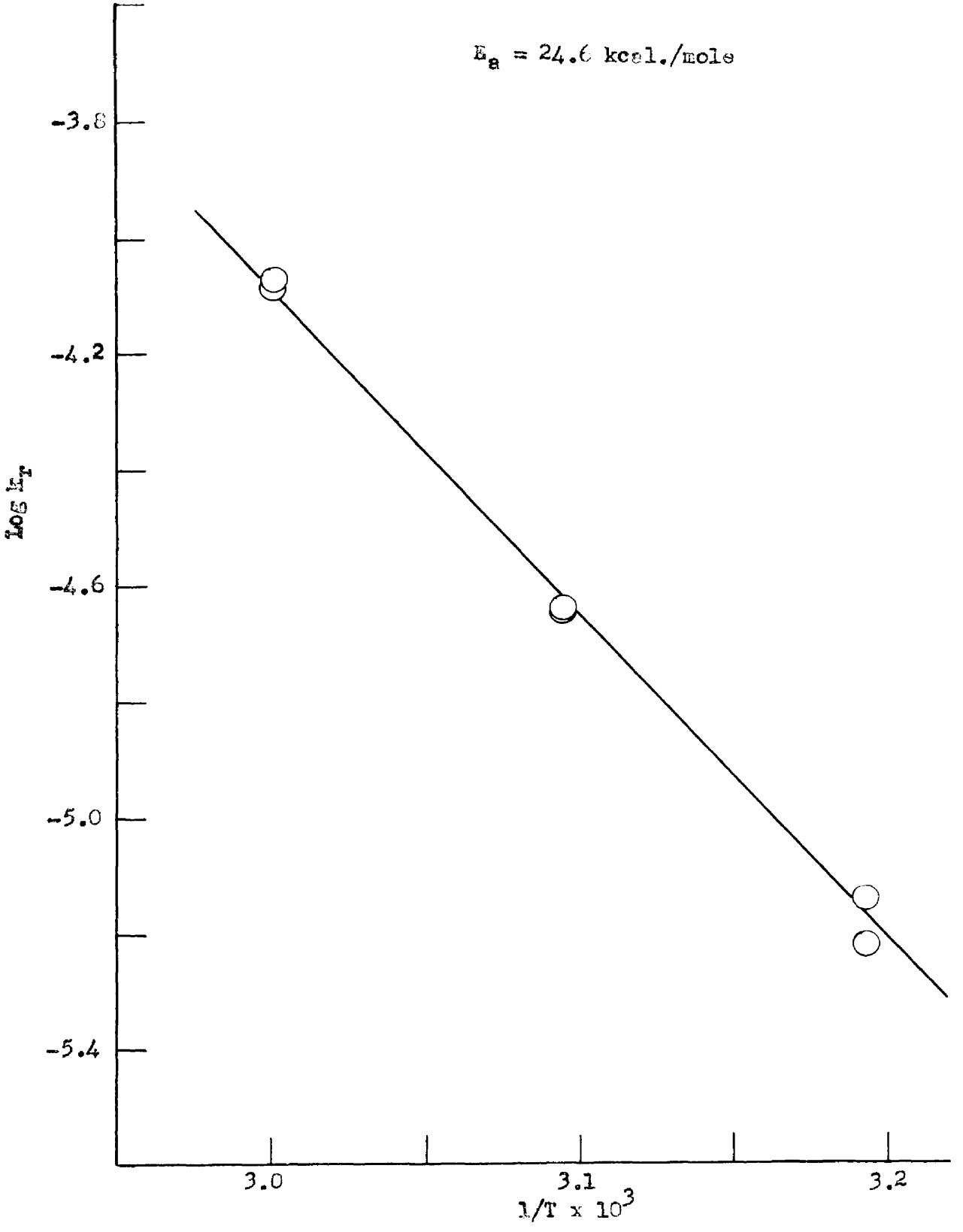

Figure 36. Plot of log k versus 1/T for the Solvolysis of Dicyclopropylcarbinyl p-Nitrobenzoate in 80% Dioxane-20% Water.

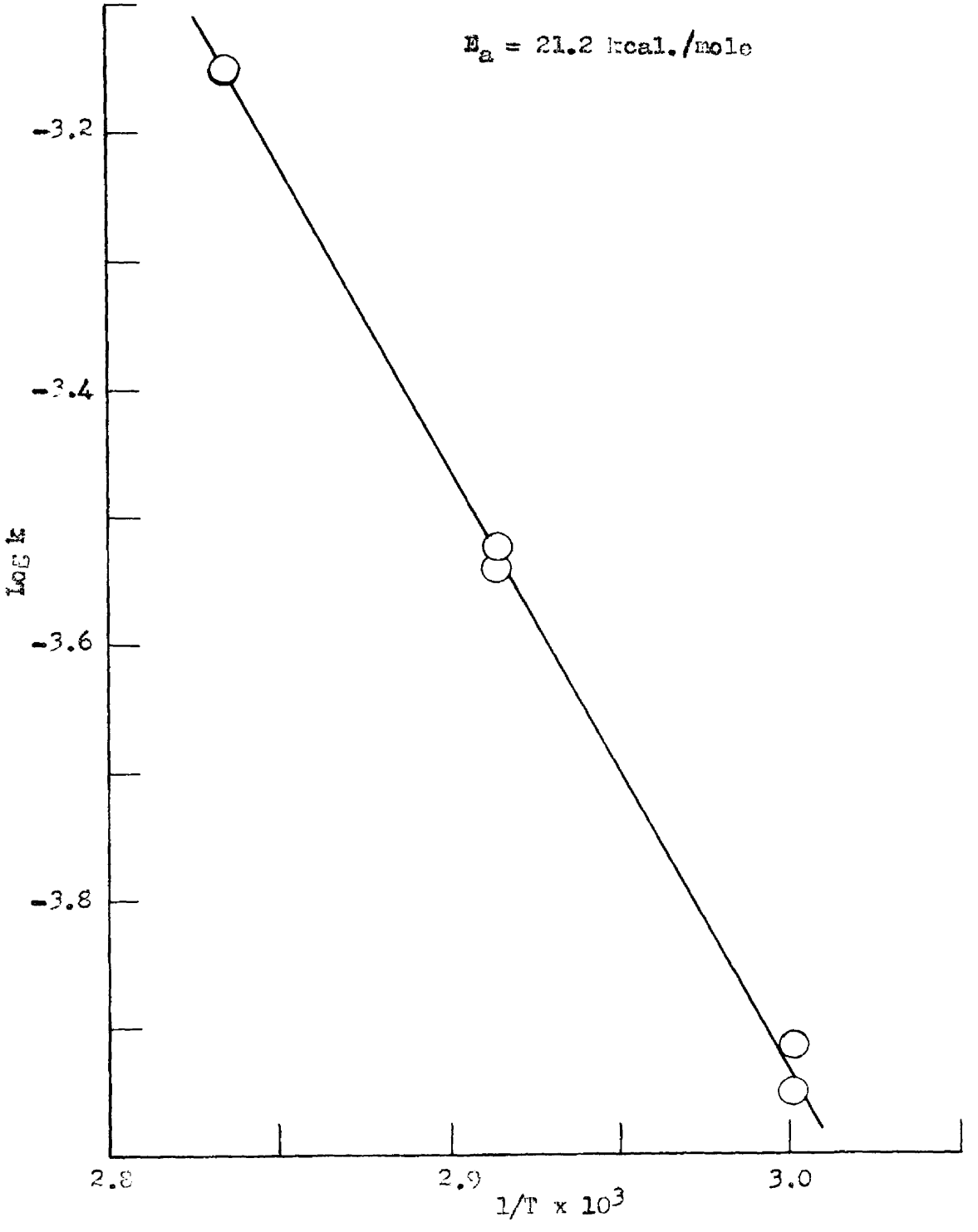

Figure 37. Plot of log k versus 1/T for the Solvolysis of Triisopropylcarbinyl p-Nitrobenzoate in 80% Dioxane - 20% Water.

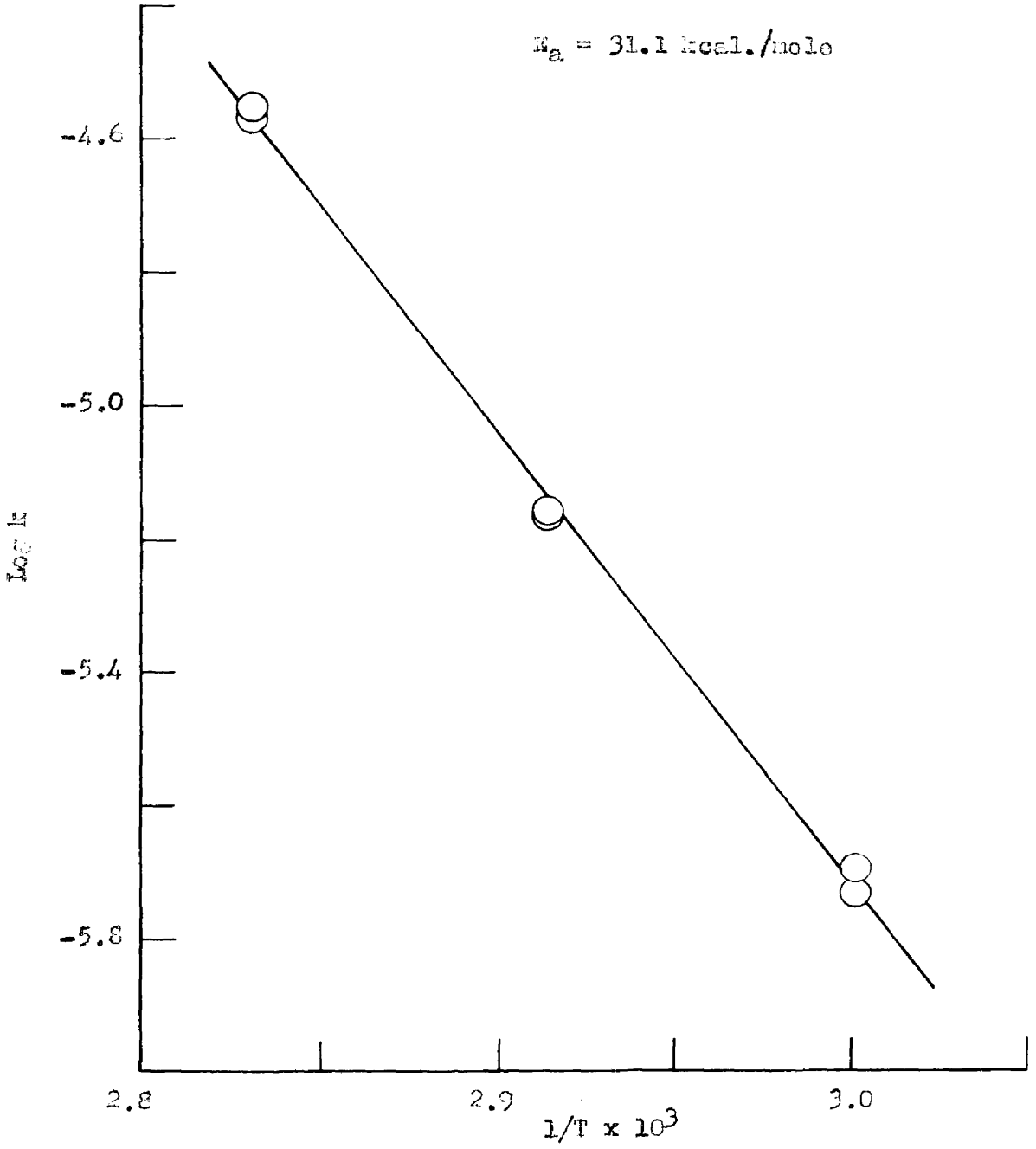

Figure 38. Plot of log k versus 1/T for the Solvolysis of Triisopropylcarbinyl p-Nitrobenzoate in 70% Dioxane - 30% Water.