FREE RADICAL REACTIONS OF COMPOUNDS CONTAINING THE CYCLOPROPANE AND OTHER ALICYCLIC RINGS

Thesis for the Degree of Ph. D.

MICHIGAN STATE UNIVERSITY

Donald Paul Wyman

1957

thesis
e.2 MICHIGAN STATE UNIVERSITY
OF AGRICULTURE AND APPLIED SCIENCE

EAST LANSING, MICHIGAN

LIBRARY
Michigan State
University

FREE RADICAL REACTIONS OF COMPOUNDS CONTAINING THE CYCLOPROPANE AND OTHER ALICYCLIC RINGS

By

Donald Paul Wyman

A THESIS

Submitted to the School 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

1957

FREE RADICAL REACTIONS OF COMPOUNDS CONTAINING THE CYCLOPROPANE AND OTHER ALICYCLIC RINGS

By

Donald Paul Wyman

AN ABSTRACT

Submitted to the School 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

Year 1957

Approved _____

ABSTRACT

The purpose of this investigation was to obtain more information concerning the behavior of cyclopropyl and cyclopropylcarbinyl free radicals. In order to do this and to be able to point out more fully the usual characteristics encountered, peroxides which would upon decomposition furnish the cyclopropyl, cyclopropylcarbinyl, as well as the cyclobutyl through cycloheptyl and cyclobutylcarbinyl through cycloheptylcarbinyl radicals were prepared and decomposed. Radicals were also generated by the photochemical chlorination of various cyclopropane substituted hydrocarbons, and products resulting determined.

The chlorination of isopropylcyclopropane yielded 2-cyclopropyl-1-chloropropane, rather than the expected dimethylcyclopropylcarbinyl chloride. The chlorination of dicyclopropylmethane resulted in the formation of 1-cyclopropyl-3-chlorobutene-1. Possible explanations of these results are offered.

The products and rates of decomposition for the peroxides were determined. All of the decompositions were performed in dilute solutions in carbon tetrachloride and followed strict first order kinetics. The principal products from $(RCO_2)_2$ in all cases but one were carbon dioxide, alkyl chloride (RCl), and lesser amounts of ester (RCO_2R) and acid (RCO_2H). Traces of phosgene were produced, and hexachloroethane was formed in large but undetermined quantities. When R was $\triangleright$-CH_2, the

ester was the major product (9[illegible]%), and no HCl was detected. In all cases > 9[illegible]% of the peroxide was accounted for and it maintained its structural integrity. Authentic samples of the products were synthesized for comparison.

The relative rates of decomposition of the various peroxides at 70°C in carbon tetrachloride were:

$(RCO_2)_2$		$(RCH_2CO_2)_2$	
R = cyclo	k_1, sec.$^{-1}$	R = cyclo	k_1, sec.$^{-1}$
C_3	0.35	C_3	1100
C_4	7.4	C_4	1.79
C_5	31.[illegible]	C_5	2.73
C_6	60.5	C_6	2.[illegible]
C_7	70.3		

where benzoyl peroxide had a value of 1.0. Rates were determined at several temperatures and on duplicate samples. The activation energies for all the peroxides except biscyclopropaneformyl and biscyclopropaneacetyl peroxides were 25 ± 1 kilocalories per mole. The activation energy for biscyclopropaneformyl peroxide was 29 kilocalories per mole, whereas that for biscyclopropaneacetyl peroxide was only 22 kilocalories per mole.

The rates, products, entropies and enthalpies of activation were all consistent with a mechanism which included the formation of an alkyl radical as one of two rate determining steps. The resonance energy of

the cyclopropylcarbinyl radical appears to be appreciable. I-strain in the cyclopropyl and, to a lesser but still important extent, in the cyclobutyl radical can account for their slow rates of formation.

Cyclopropyl iodide was prepared for the first time from the decomposition of biscyclopropaneformyl peroxide in the presence of iodine. It has not been found possible to prepare this compound by displacement reactions. A new, considerably improved, synthesis of cyclopropylcarboxaldehyde based on catalytic dehydrogenation of the alcohol was achieved. The preparation of 3,3-dicyclopropylpropane-1 was accomplished by a sequence of reactions starting with dicyclopropyl ketone. Dicyclopropyl ketone was also converted to cyclopropyl cyclopropanecarboxylate using trifluoroperoxyacetic acid. Several other new cyclopropane-containing derivatives were prepared.

TABLE OF CONTENTS

TABLE OF CONTENTS - Continued

TABLE OF CONTENTS - Continued

LIST OF TABLES

LIST OF TABLES - Continued

LIST OF TABLES - Continued

LIST OF TABLES - Continued

LIST OF FIGURES

LIST OF FIGURES - Continued

LIST OF FIGURES - Continued

INTRODUCTION

This thesis is concerned principally with a study of reactions which proceed via free radical intermediates possessing cyclopropyl, cyclopropylcarbinyl, or other alicyclic groups. There are several reasons why this study was undertaken.

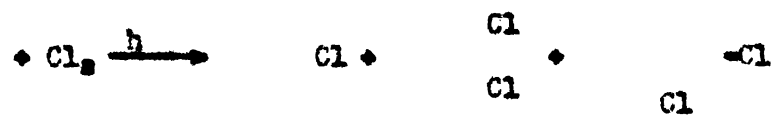
Reactions which proceed via ionic intermediates that contain a cyclopropane ring show several unusual characteristics. For example, when cyclopropyl p-toluenesulfonate was hydrolyzed in acetic acid (1), the reaction proceeded very slowly, and the product was allyl acetate.

The intermediate cyclopropyl carbonium ion, if formed, was produced reluctantly and rearranged readily to the allyl carbonium ion. Cyclopropyl chloride is almost as inert toward both S_N1 and S_N2 displacements as chlorobenzene (2). The difficulty in forming a positive ion with the charge on a cyclopropyl carbon atom has been ascribed to I-strain (3). That is, when bonding is changed from sp^3 (neutral molecule) to sp^2 (carbonium ion), the internal strain is increased. A possible measure of this increase in strain is given by the difference between the bond angles in the two cases; i.e., $(120^\circ-60^\circ)-(109.5^\circ-60^\circ)$ or 10.5°.

Part of this thesis deals with an investigation of this same phenomenon in free radicals. There is conflicting information in the literature about cyclopropyl radicals; under certain circumstances

they seem to maintain their identity, whereas under others they may rearrange to allyl radicals.

The photochemical chlorination of cyclopropane (4) proceeded without rearrangement to yield cyclopropyl chloride as the main product, along with lesser amounts of dichloro compounds.

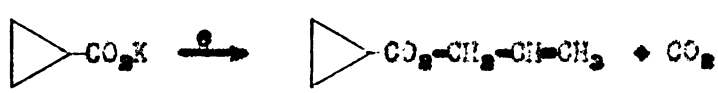


Also, Hass and Schecter (5) found that the vapor phase nitration of cyclopropane gave nitrocyclopropane:

The Hunsdieker reaction on silver cyclopropanecarboxylate (6) yielded cyclopropyl bromide.

Presumably all of these reactions proceed via cyclopropyl free radicals.

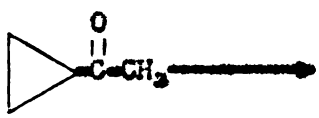
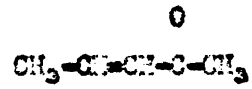
On the other hand, certain reactions which may involve rearrangement of cyclopropyl radicals have been reported. Thus, it is claimed that the Kolbe electrolysis of potassium cyclopropanecarboxylate gave allyl cyclopropanecarboxylate (7):



The photolysis of methyl cyclopropyl ketone (8) also yielded products in which the cyclopropane ring had rearranged.

TABLE 1

PHOTOLYSIS PRODUCTS OF METHYL CYCLOPROPYL KETONE (8)

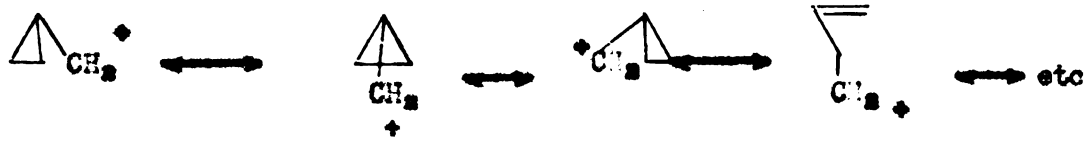
	Product	Quantum Yield 60°
		0.31
	$C{=}O$	0.05
	$CH_3{-}CH_2{-}CH{=}CH_2$	0.021
	$CH_2{=}CH{-}CH_3$	0.05
	$CH_3{-}CH_3$	0.0087
	CH_4	0.0034
	$CH_2{=}CH_2$	0.002
	$CH_2{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2$	0.0006
	Cyclopropane	0.000

Generally ketones when photolysed cleave between the carbonyl carbon atom and one of the alkyl groups. The principal product from methyl cyclopropyl ketone was methyl propenyl ketone, which presumably arose from opening of the cyclopropane ring as the primary process. Some alkyl-carbonyl cleavage did occur, however, giving rise to the minor products shown in the table. Particularly noteworthy is the presence of a number of products which can be ascribed to allyl radicals (i.e., 1-butene, propene and diallyl) and the essential absence of products directly

derived from a cyclopropyl radical (i.e., cyclopropane, methylcyclopropane, dicyclopropyl).

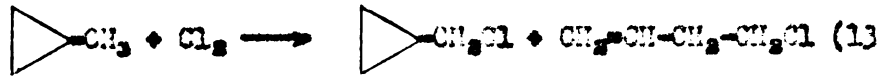
To examine the behavior of cyclopropyl radicals more directly, the diacyl peroxide of cyclopropanecarboxylic acid was prepared, and the kinetics and products of decomposition were studied. For comparison, peroxides which would yield higher cycloalkyl radicals were also prepared and decomposed. The results are reported in this thesis.

In contrast with the reluctance with which cyclopropyl carbonium ions are produced is the remarkable behavior of compounds that furnish cyclopropylcarbinyl carbonium ions. Such cases have been studied extensively by Roberts (9), Winstein (9) and others (11). This type of ion is easily formed, and is stabilized by considerable resonance energy.

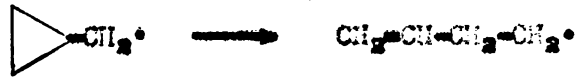


Dicyclopropylcarbinyl carbonium ions are even further stabilized, since Sandri (12) showed that compounds which lead to such ions solvolyse extremely rapidly. Rearrangements occur in certain of these systems. For example, cyclopropylcarbinylamine, with nitrous acid, gives both cyclopropylcarbinol and cyclobutanol.

A few examples of reactions which may proceed via cyclopropylcarbinyl free radicals have been reported. The free radical chlorination of methylcyclopropane yielded a mixture of products which included olefins,



Roberts claimed that the allylcarbinyl chloride was produced by rearrangement of the cyclopropylcarbinyl free radical.



An indication of the unusual stability of a system containing a cyclopropylcarbinyl radical was observed by Overberger and Lebovits (15) in a study of the decomposition rates of several alicyclic substituted azo-bisnitriles.

The ease with which the cyclopropyl compound decomposed has been ascribed (15) to resonance stabilization of the radical produced:

TABLE 2

RATES OF DECOMPOSITION OF $(R-\overset{CH_3}{\underset{CN}{C}}-N)_2$ (15)

R = cyclo	k_1, $sec^{-1} \times 10^4$, 80° C.
C_3	33
C_4	1.51
C_5	1.30
C_6	2.27
Isopropyl	1.03

In this thesis, two approaches to the generation of cyclopropylcarbinyl free radicals were used. The chlorination of certain hydrocarbons (isopropylcyclopropane and dicyclopropylmethane) which would be expected to give intermediates with one or two cyclopropane rings on the carbon bearing the odd electron was investigated. Also, diacyl peroxides which would give the cyclopropylcarbinyl and other cycloalkylcarbinyl radicals were prepared, and the kinetics and products of their decomposition was studied.

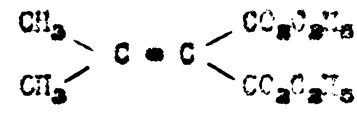
Some miscellaneous reactions involving cyclopropane compounds are also recorded and discussed in the last part of the thesis.

EXPERIMENTAL

A. Chlorination of Hydrocarbons Containing a Cyclopropane Ring

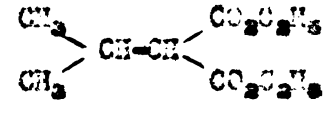
Preparation of Isopropylidenemalonic Ester

(a) Isopropylidenemalonic Ester



Isopropylidenemalonic ester was prepared according to the procedures of Gaind and Guha (16) and Cope and Hancock (17). In a typical preparation, a 3-l. round-bottomed flask equipped with a reflux condenser was charged with 730 g. (4.83 moles) of ethyl malonate, 720 g. (7.15 moles) of acetic anhydride, 60 g. of freshly fused zinc chloride, and 660 g. (11.4 moles) of acetone. The mixture was refluxed for 100 hours, after which it was cooled and poured into three liters of water. The aqueous mixture was extracted with three 350-ml. portions of benzene. The combined benzene extracts were dried over calcium chloride (anhydrous) and the mixture was then distilled *in vacuo* through a 15-inch Vigreux column to remove the benzene. Fractionation of the residual black liquid through a 15-inch glass helice packed jacketed column yielded 620 g. (63.5%) of isopropylidenemalonic ester, b.p. 105-107° at 5 mm., n_D^{25} 1.4470.

(b) Isopropylmalonic Ester



Attempts to hydrogenate isopropylidenemalonic ester at room temperature and three atmospheres of pressure with Raney nickel catalyst proved unsuccessful. However, at a higher temperature and pressure, the uptake of hydrogen proceeded smoothly and rapidly.

In a typical preparation, a 500-ml. high pressure hydrogenation bomb was charged with 300 g. (1.5 moles) of isopropylidenemalonic ester and approximately 20 g. of Raney nickel catalyst. At a temperature of 150° the pressure fell smoothly from an initial value of 800 pounds per square inch to 650 pounds per square inch in a period of 1.5 hours. After removal of the catalyst by filtration, there was obtained 298 g. (98%) of isopropylmalonic ester, b.p. 102° at 15 mm., n_D^{25} 1.4183.

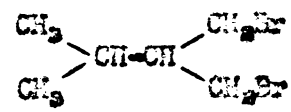
(c) 2-Isopropylpropane-1,3-diol

2-Isopropylpropane-1,3-diol was prepared following the procedure employed by Pines, Huntsman, and Ipatieff (18).

A 2-l. three-necked round-bottomed flask equipped with reflux condenser, mercury-sealed stirrer, and dropping funnel was charged with 31 g. (0.795 mole) of lithium aluminum hydride and 600 ml. of anhydrous ether. There was then added 101 g. (0.5 mole) of isopropylmalonic ester, dropwise, with stirring over a period of three hours. The reaction mixture was allowed to stir for one hour after the addition was complete. At the end of this time, the system was cooled in an ice bath and 125 ml. of water followed by one liter of ice cold 10% sulfuric acid was added

over a period of two hours. Separation of the diol from the reaction mixture by normal extraction procedures proved unsatisfactory due to the formation of emulsions and the appreciable solubility of the diol in water. These difficulties were circumvented by the use of liquid-liquid extraction. The reaction mixture described above was extracted in a single stage liquid-liquid extractor with ether for three hours. After removal of the ether *in vacuo*, distillation yielded 47 g. (70%) of 2-isopropylpropane-1,3-diol, b.p. 130-131° at 14 mm., n_D^{25} 1.4490.

(c) 1,3-Dibromo-2-isopropylpropane



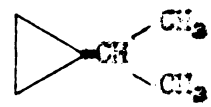
1,3-Dibromo-2-isopropylpropane was prepared by the procedure of Huntsman, Pines, and Ipatieff (10).

In a typical preparation, a 1-l. three-necked round-bottomed flask equipped with a mercury-sealed stirrer, reflux condenser, dropping funnel, and thermometer, was charged with 96 g. (0.915 mole) of 2-isopropylpropane-1,3-diol. This was heated to 70° on the steam bath and 185 g. (0.695 mole) of phosphorous tribromide was added dropwise to the stirred alcohol at a rate sufficient to maintain the reaction temperature between 65-75°. After the addition was complete, the mixture was allowed to heat on the steam bath overnight.

The cooled reaction mixture was then poured into 200 ml. of ice water. The aqueous solution was extracted with three 150-ml. portions of ether. The combined ethereal extracts were washed with three 125-ml.

portions of 10% potassium carbonate solution followed by two 200-ml. portions of water. After drying over anhydrous calcium chloride, the ether was stripped in vacuo. Distillation of the residue yielded 145.5 g. (73%) of 2-isopropyl-1,3-dibromopropane, b.p. 92° at 12 mm., n_D^{25} 1.5055.

(e) Isopropylcyclopropane (3)



A 1-l. three-necked round-bottomed flask equipped with a reflux condenser, mercury-sealed stirrer, and dropping funnel was charged with 80 ml. of 80% ethyl alcohol and 50 g. of zinc dust. The stirred mixture was brought to reflux after which 41 g. (0.178 mole) of 1,3-dibromo-2-isopropylpropane was added dropwise over a period of 3/4 hour. After the addition was complete, stirring and refluxing were continued for 5.5 hours. The apparatus was then fitted for distillation and isopropylcyclopropane was distilled directly from the reaction mixture. Redistillation through a 15-inch glass helice packed column yielded 12.1 g. (83%) of isopropylcyclopropane, b.p. 58.8-59.1°, n_D^{25} 1.3838. See Figure 1 for the infrared spectrum.

Chlorination of Isopropylcyclopropane

A 100-ml. round-bottomed flask equipped with a reflux condenser was charged with 25 g. (0.3 mole) of isopropylcyclopropane, 13.5 g. (0.1 mole) of sulfuryl chloride, 25 ml. of carbon tetrachloride, and 0.1 g. of

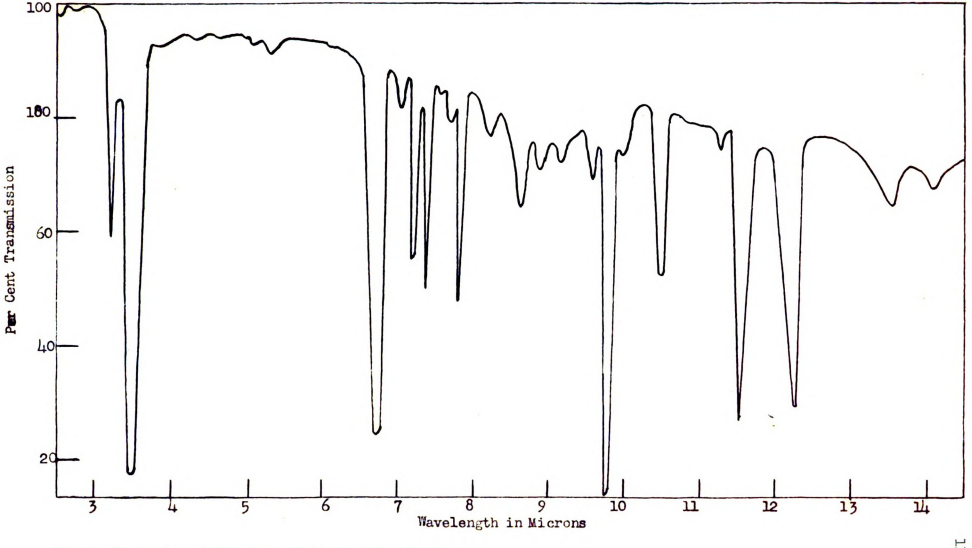


Figure 1. Infrared Spectrum of Isopropylcyclopropane.

benzoyl peroxide. The combined reactants were refluxed for five hours and then fractionated through a 7-plate glass helice packed column. After removing the excess isopropylcyclopropane (19 g.) and carbon tetrachloride, the residue was distilled *in vacuo*. There was obtained 5.4 g. of a material boiling at 55-57° at 55 mm.

The analysis for chlorine was made by the method of Unhoeffer (17).

Calculated for $C_6H_{11}Cl$:	Cl, 29.85%
Found:	Cl, 29.52%
	29.63%

The infrared spectrum (Figure 2) of this compound indicated bands for a cyclopropane ring but not for olefin.

Experiments in which isopropylcyclopropane was chlorinated photochemically with and without carbon tetrachloride as a solvent yielded similar results. However, the yields were very low.

Grignard Reagent from the Product of Chlorination of Isopropylcyclopropane

A 250-ml. three-necked round-bottomed flask equipped with a mercury-sealed stirrer, reflux condenser, and dropping funnel was charged with 1 g. (0.042 g. atom) of magnesium turnings and 20 ml. of anhydrous ether. To this well stirred mixture was added 2 ml. of a solution of 5 g. of the chlorinated isopropylcyclopropane in 5 ml. of ether. Gentle heating initiated the reaction, after which the rest of the chloro compound in ether was added at a rate sufficient to maintain a gentle reflux. After the addition was complete, the solution of Grignard reagent was allowed to stir for an additional two hours.

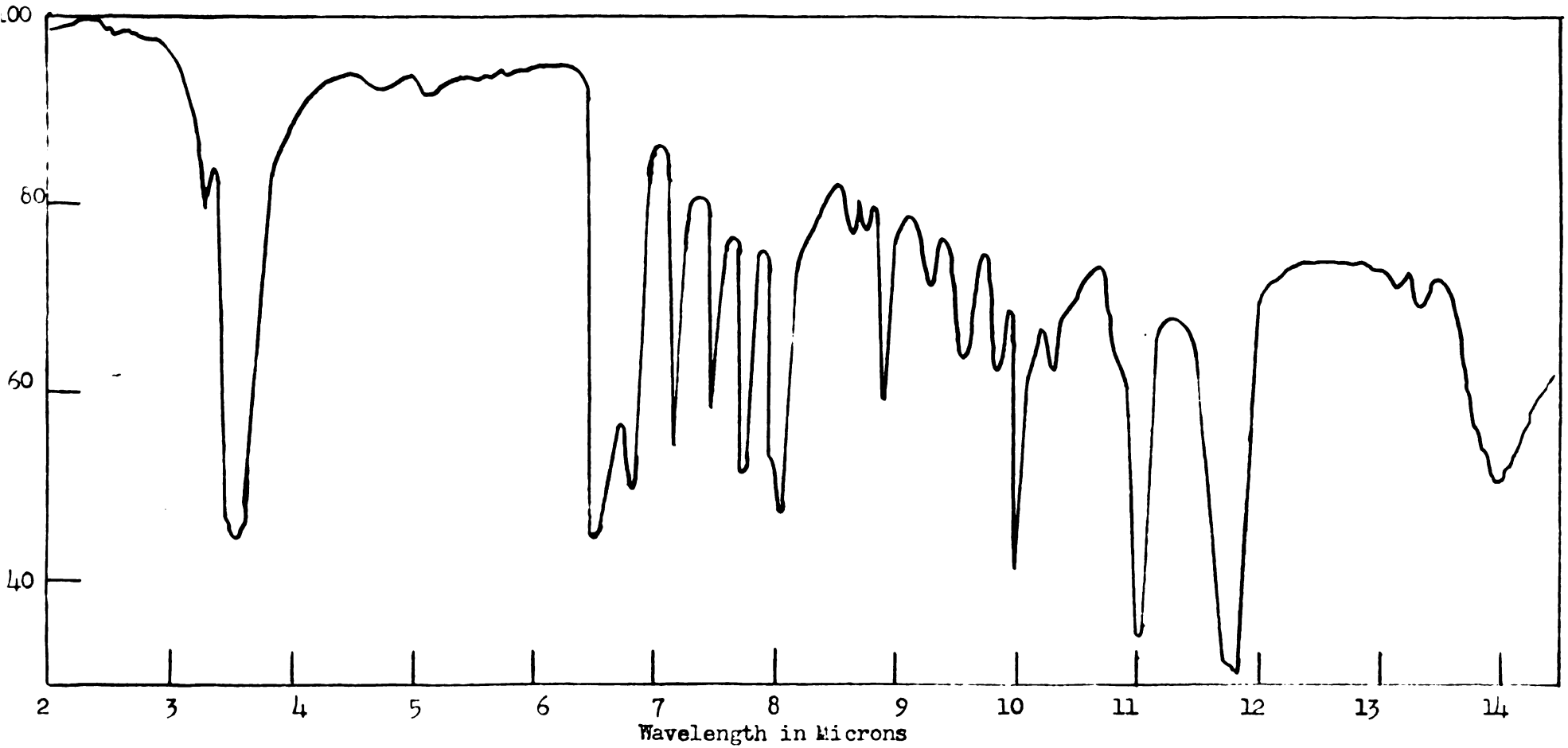


Figure 2. Infrared Spectrum of 2-Cyclopropyl-1-Chloropropane.

The system was then cooled in an ice bath and 25 ml. of water was slowly added to the stirred solution of Grignard reagent. The aqueous and organic layers were separated. The organic layer was dried over anhydrous magnesium sulfate and then distilled. After removal of the ether there was obtained 3 g. (78%) of isopropylcyclopropane, identified by its physical constants and infrared spectrum.

Solvolysis of the Product of Chlorination of Isopropylcyclopropane

One ml. of the chloro compound was pipetted into 100 ml. of 80% ethyl alcohol (by volume) maintained at 25 ± 0.2° in a thermostatted bath. Periodically 5 ml. aliquots were removed, and the solvolysis quenched by immediately inserting the sample into 20 ml. of ice cold absolute ethyl alcohol. Each sample was then titrated without delay with 0.0205 N alcoholic potassium hydroxide. Methyl red was used as the indicator. Preliminary experiments indicated that 25.0 ml. of base were necessary to titrate all the hydrochloric acid obtainable from a 5 ml. aliquot of the solution. The rate constant, k, was calculated from the integrated form of the first order rate equation.

$$k = 2.303/t \log a/a-x$$

t = time (seconds)

a = ml. of base necessary to titrate all of the hydrochloric acid obtainable in a 5 ml. aliquot.

x = amount of base necessary to titrate the hydrochloric acid present at time t.

(a-x) is proportional to the amount of unreacted chloride at time t.

Time (seconds)	Ml. Base	k, Sec.$^{-1}$ x 10^{3}
300	0.034	2.57
600	0.044	1.64
900	0.052	1.32
1200	0.061	1.25
1500	0.067	1.07
1800	0.072	0.86

The inconstancy of k, along with the indicated downward trend of its value was detected throughout an experiment in which the solvolysis was followed for 7500 seconds. At the end of this time, the sample (5 ml. aliquot) required only 0.138 ml. of base for neutralization.

Chlorination of Isooctane

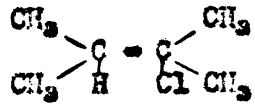
A 100-ml. round-bottomed flask equipped with a reflux condenser was charged with 35 g. (0.3 mole) of isooctane, 13.5 g. (0.1 mole) of sulfuryl chloride, and 0.1 g. of benzoyl peroxide. The resulting solution was refluxed for 2.5 hours. Fractionation through a 15-inch glass helice packed column in vacuo yielded 20 g. of isooctane, b.p. 18.5° at 27 mm., n_D^{25} 1.3902, and 12.4 g. of another substance, b.p. 47.5° at 18 mm., n_D^{24} 1.4284.

The literature values (20) for dimethylneopentylcarbinyl chloride are b.p. 44° at 15 mm., n_D^{24} 1.4284.

The yield of dimethylneopentylcarbinyl chloride was 83% (based on sulfuryl chloride). Experiments in which carbon tetrachloride was employed as a solvent yielded results which were essentially the same as those reported in those cases where carbon tetrachloride was not used.

Experiments in which isooctane was chlorinated photochemically with and without carbon tetrachloride as a solvent yielded similar results.

Dimethylisopropylcarbinyl Chloride (21)



To the Grignard reagent prepared from 24.6 g. (0.185 mole) of isopropyl bromide and 4.8 g. (0.197 mole) of magnesium turnings in a five-hundred ml. three-necked round-bottomed flask equipped with a Hirshberg stirrer, dropping funnel and reflux condenser, acetone (9 g., 0.185 mole) was added dropwise at a rate sufficient to maintain a gentle reflux. After the addition of acetone was completed, the reaction mixture was allowed to stir at room temperature for one hour. The contents of the reaction vessel were then poured into 100 ml. of ice-cold 10% sulfuric acid. The organic and aqueous layers were separated. The aqueous solution was extracted with two 50-ml. portions of ether. The combined ethereal extracts were dried over anhydrous magnesium sulfate, and the ether was then stripped *in vacuo*. The residual dimethylisopropylcarbinol was placed in a 1-l. separatory funnel without further purification. To this was added a 5 molar excess of cold concentrated hydrochloric acid (based on the theoretical yield of carbinol). This mixture was shaken several times over a period of one hour. The lower layer was separated. More hydrochloric acid was added to the separatory funnel,

and the procedure of shaking periodically was repeated during the next hour. Once again the lower layer was separated.

The upper layer from the preceding conversion was dried over anhydrous magnesium sulfate. Distillation through a six-inch Vigreux column yielded 14.7 g. (80%) of dimethylisopropylcarbinyl chloride, b.p. 57.5-58° at 104 mm., n_D^{20} 1.4170.

Chlorination of 2,3-Dimethylbutane

A solution of 26 g. (0.3 mole) of 2,3-dimethylbutane, 13.5 g. (0.1 mole) of sulfuryl chloride, and 0.1 g. of benzoyl peroxide was refluxed for two hours. Distillation of the resulting mixture yielded 13 g. of 2,3-dimethylbutane and 5.3 g. (41%) of dimethylisopropylcarbinyl chloride, b.p. 113-115°, n_D^{20} 1.4170-1.4172.

Dicyclopropylmethane

Dicyclopropylmethane was prepared from dicyclopropyl ketone (12) by the Huang Minlon modification of the Wolff-Kishner reduction (22).

In a typical preparation, a 2-l. two-necked round-bottomed flask equipped with a reflux condenser and thermometer was charged with 66 g. (0.6 mole) of dicyclopropyl ketone, 97.5 g. (1.74 moles) of potassium hydroxide, 600 ml. of diethylene glycol, and 60 ml. of 85% hydrazine hydrate. The reaction mixture was refluxed for one hour. The apparatus was then fitted for distillation and a mixture of water and dicyclopropyl methane was distilled over until the pot temperature reached 175° C.

The apparatus was again arranged for reflux and the solution was further heated under reflux for 2.5 hours. Arrangement was then made for distillation, and distillate boiling up to 115° was collected. All distillates were combined, separated from water, and dried over anhydrous magnesium sulfate. Distillation yielded 33.5 g. (58%) of dicyclopropylmethane, b.p. 103.5-105°, n_D^{25} 1.4224, n_D^{20} 1.4218.

Chlorination of Dicyclopropylmethane

The apparatus consisted of a 500-ml. two-necked round-bottomed flask equipped with a dry ice condenser and, a gas dispersion tube for the admission of chlorine. The flask was immersed to approximately 1/3 its depth in a bath of dry-ice and isopropyl alcohol, and then completely wrapped with aluminum foil except for a small window through which the system was irradiated. Chlorine was conducted from the cylinder through a flow meter into the flask (via the dispersion tube). Irradiation was accomplished by means of a Conco medium pressure mercury arc.

In a typical chlorination, 141 g. (1.75 moles) of dicyclopropylmethane and 150 ml. of carbon tetrachloride were placed in the chlorination flask. The solution was irradiated and chlorine was passed into it at a rate of 0.55 l./minute for 70 minutes.

After removal of carbon tetrachloride and excess dicyclopropylmethane by distillation, there remained 64 g. of residual liquid. Fractional distillation through a 15-inch helice packed column yielded 52 g. of a chlorinated product, b.p. 63-64° at 15 mm. n_D^{20} 1.4770.

The infrared spectrum (Figure 3) of this material had strong olefin bands, and bands attributable to the cyclopropane ring.

Anal.* Calc'd. for $C_7H_{11}Cl$: C, 64.37; H, 8.42; Cl, 27.20

Found: C, 64.52; H, 8.59; Cl, 26.90

Reaction of the Product of Chlorination of Dicyclopropylmethane with Magnesium

A 500-ml. three-necked roundbottomed flask equipped with a Hirshberg stirrer, reflux condenser, and dropping funnel was charged with 0.324 g. (0.0306 mole) of magnesium turnings. To this was added a 5 ml. portion of a solution of 4 g. of the chlorination product of dicyclopropylmethane in 25 ml. of ether. Gentle heating initiated the reaction after which the remaining solution was added dropwise at a rate sufficient to maintain a gentle reflux. After the addition was complete, reflux was continued for eight hours. At the end of this time, essentially all the magnesium had disappeared.

The resulting Grignard reagent was hydrolyzed by cautious addition of 20 ml. of water followed by 20 ml. of ice-cold 10% sulfuric acid. The aqueous and organic layers were separated, and the organic portion was dried over anhydrous magnesium sulfate. After the removal of the ether, distillation yielded 2.5 g. of a hydrocarbon, b.p. 110-111°, n_D^{25} 1.4478. See Figure 4 for the infrared spectrum.

Anal.* Calc'd for $C_{10}H_{14}$: C, 88.43; H, 11.47

Found: C, 88.11; H, 11.55

*Analyses marked with an asterisk were done by a commercial analyst, either Spang Microanalytical Lab., Ann Arbor, Michigan, or Microtech Lab., Skokie, Illinois.

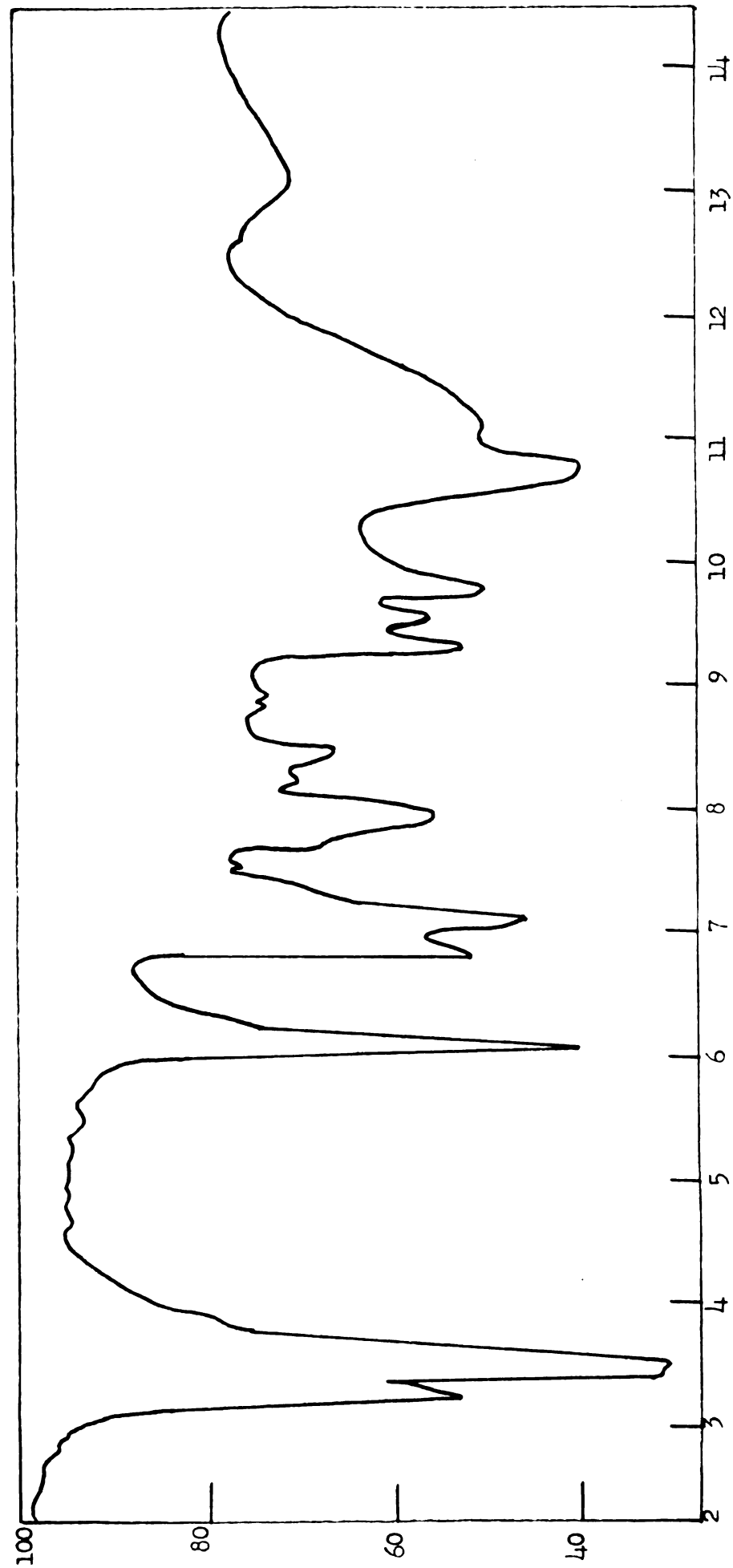


Figure 3. Infrared Spectrum of 1-Cyclopropyl-4-chlorobutene-1.

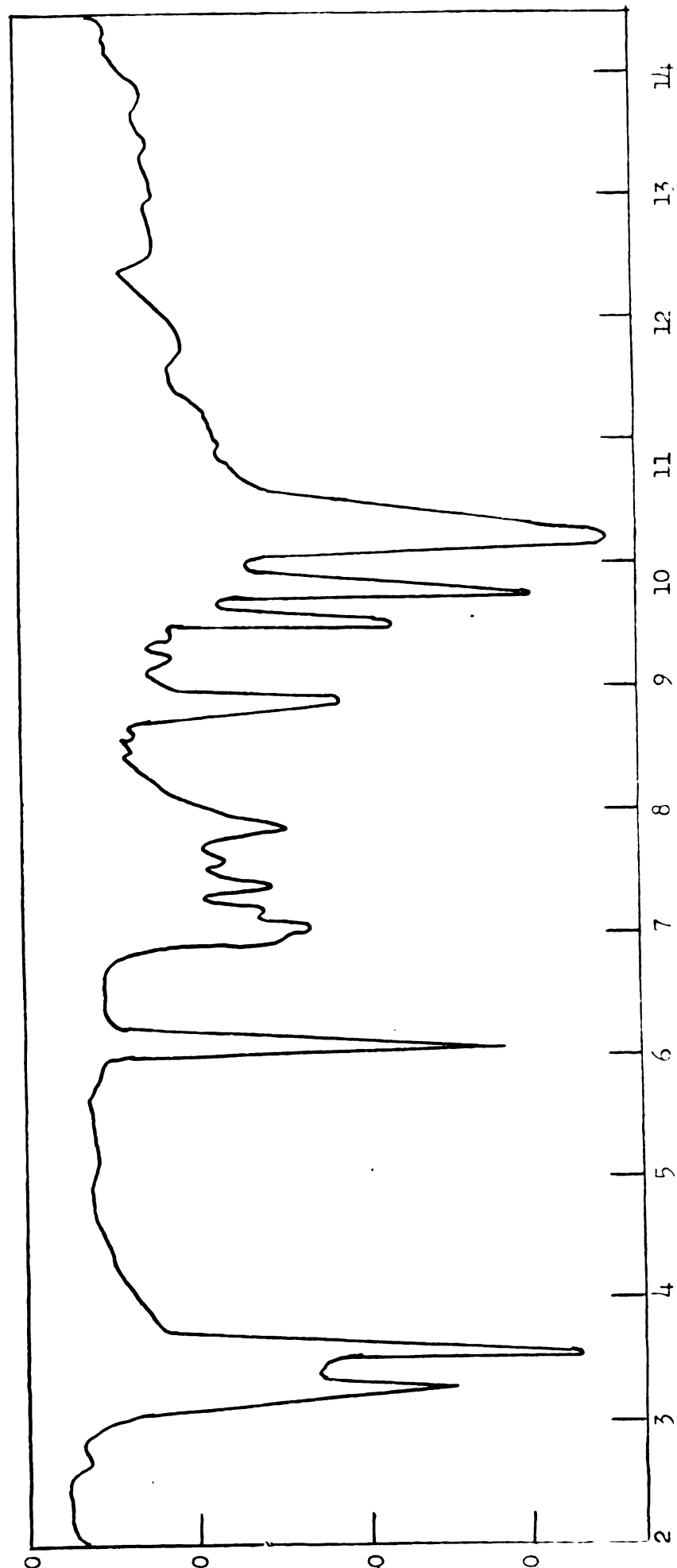


Figure 4. Infrared Spectrum of 1-Cyclopropylbutene-1.

Oxidation of the Product of Chlorination of Methylcyclopropylcarbinol

A 500-ml. Erlenmeyer flask equipped with a Hirshberg stirrer and surrounded by an ice bath was charged with 10 g. (0.085 mole) of the chlorinated hydrocarbon, 50 ml. acetone, 50 ml. water, and 7.3 g. of potassium permanganate. The cooled reaction mixture was stirred vigorously for a period of 60 hours. Excess potassium permanganate was then decomposed by the addition of sodium hydrosulfite. The manganese dioxide was filtered and washed with two 50-ml. portions of boiling water. The acetone was driven off on the steam bath. The remaining aqueous solution was acidified with sulfuric acid, and then extracted with six 200-ml. portions of ether. The combined ethereal extracts were dried over anhydrous calcium chloride, after which the ether was removed *in vacuo*. There remained 7 g. of an acidic residue. Distillation of this residue *in vacuo* through a small seven-plate column yielded 2.8 g. of cyclopropanecarboxylic acid, identified through its infrared spectrum and physical constants. The residue from distillation was taken up in ligroin, filtered while hot, and then cooled in a bath of dry-ice and isopropyl alcohol. The solid which separated was recrystallized once from ligroin and then collected on a filter. There was obtained 2.3 g. of beta-chloropropionic acid, m.p. 38-39°. Its infrared spectrum was identical with that of an authentic sample.

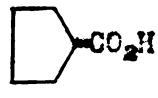
B. Preparation and Decomposition of Certain Alicyclic Acyl Peroxides

Preparation of the Required Carboxylic Acids

Cyclopropanecarboxylic and cyclobutanecarboxylic acids were prepared according to Organic Syntheses (23,24). Cyclohexanecarboxylic acid was obtained from Professor Robert M. Herbst. Cyclopentanecarboxylic acid and cycloheptanecarboxylic acid were prepared from cyclopentyl chloride (Columbia Organic Chemical Co., Columbia, South Carolina) and cycloheptanone (Columbia) respectively, according to the sequences described in detail below.

Cyclopropaneacetic and cyclopentaneacetic acids were prepared from cyclopropyl chloride and cyclopentyl chloride, respectively, as described below. Cyclobutaneacetic acid was available from the organic preparations course; it had been made by H. S. Eleuterio via an Arndt-Eistert synthesis from cyclobutanecarboxylic acid. This procedure is not specifically described in the literature, but is analogous to others which have been described (25). Cyclohexaneacetic acid was also obtained from Professor Herbst.

Cyclopentanecarboxylic Acid

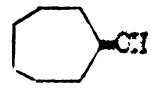


A 500-ml. three-necked round-bottomed flask equipped with a Hirshberg stirrer, reflux condenser, and dropping funnel was charged with 5.7 g. (0.234 g. atom) of magnesium turnings and 100 ml. of dry ethyl ether.

To this was added 5 g. of a 25 g. (0.234 mole) portion of cyclopentyl chloride. Gentle heating initiated the reaction after which the rest of the cyclopentyl chloride was added at a rate sufficient to maintain a gentle reflux. After the addition was complete, the reaction mixture was allowed to stir for an additional 1.5 hours. The cyclopentylmagnesium chloride solution was then poured onto 100 g. of crushed dry ice. The reaction mixture was allowed to warm up until all the dry ice had disappeared, at which time sufficient ice-cold 10% sulfuric acid was added to make the solution acid to congo red. The organic and aqueous layers were separated and the aqueous layer was extracted with three 150-ml. portions of ether. The ethereal solutions were combined and dried over anhydrous calcium chloride. After removal of the ether on the steam bath, distillation of the residue yielded 20 g. (74%) of cyclopentanecarboxylic acid, b.p. 132-133° at 600 mm. n_D^{25} 1.4524. (Literature values b.p. 215° at 760 mm., n_D^{18} 1.4534 (24).)

Cycloheptanecarboxylic Acid

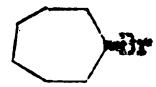
(a) Cycloheptanol



A 500-ml. three-necked round-bottomed flask equipped with a Hirshberg stirrer, dropping funnel, and reflux condenser was charged with 3.25 g. (0.085 mole) of lithium aluminum hydride and 110 ml. of dry ethyl ether. To this was added 25 g. (0.223 mole) of cycloheptanone (Aldrich Chemical Company, Milwaukee, Wisconsin) dropwise with stirring at a rate sufficient

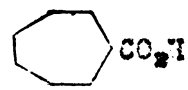
to maintain a gentle reflux. After addition was complete, the mixture was allowed to stir an additional two hours. The system was then cooled in an ice bath and hydrolyzed by the slow addition of enough ice-cold 10% sulfuric acid to make it acid to congo red. The aqueous and organic layers were then separated and the aqueous solution was extracted with two 100-ml. portions of ether. The combined ethereal extracts were dried over anhydrous potassium carbonate. The ether was removed *in vacuo* and distillation yielded 20 g. (80%) of cycloheptanol, b.p. 183-185°, n_D^{25} 1.4744. (Literature value b.p. 183-184°, n_D^{20} 1.4755 (27).)

(b) Cycloheptyl Bromide



Cycloheptyl bromide was prepared from the carbinol and phosphorus tribromide according to the procedure of Ruzicka (28). From 20 g. (0.113 mole) of cycloheptanol and 17.1 g. (0.062 mole) of phosphorus tribromide, there was obtained 20 g. (81.9%) of cycloheptyl bromide, b.p. 80° at 15 mm., n_D^{25} 1.4988. (Literature value b.p. 101.5 at 40 mm., n_D^{22} 1.4996 (28).)

(c) Cycloheptanecarboxylic Acid

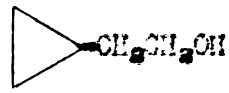


Cycloheptanecarboxylic acid was prepared in a manner analogous to the preparation of cyclopentanecarboxylic acid (page 23). From 2.75 g.

(0.1125 g. atom) of magnesium turnings and 20 g. (0.121 mole) of cycloheptyl bromide there was obtained 7.6 g. ([illegible]) of cycloheptaneacetic acid, b.p. 121° at 10 mm., n_D^{25} 1.4710. (Literature value b.p. 137° at 15 mm., n_D^{20} 1.4753 (29).)

Cyclopropaneacetic Acid

(a) Cyclopropaneethanol

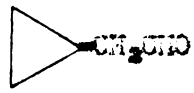


A 1-l. three-necked round-bottomed flask equipped with a high speed stirrer, dry ice condenser, and gas inlet tube was charged with 8 g. (1.13 g. atoms) of lithium powder, 50 g. (0.65 mole) cyclopropyl chloride, and 250 ml. of pentane. Cyclopropyllithium was prepared from this mixture as described by Hart and Sandri (30), and the system was cooled in an ice bath. Gaseous ethylene oxide (57.5 g., 1.3 moles) was introduced into this mixture by means of the gas inlet tube during a period of one-half hour. After the addition was complete, the reaction mixture was allowed to stir in the cold for an additional two hours. Sufficient ice-cold 10% sulfuric acid was then added to make the solution acid to congo red, and the organic and aqueous layers were separated. The aqueous layer was saturated with sodium chloride and then extracted with two 100-ml. portions of ether. The organic fractions were combined and dried over anhydrous potassium carbonate. Distillation yielded 32 g. ([illegible]) of cyclopropaneethanol, b.p. 135° at atmospheric pressure, n_D^{25} 1.4732.

Anal.* Calc'd for $C_5H_{10}O$: C, 69.76; H, 12.51

Found: C, 69.87; H, 12.21

(b) Cyclopropaneacetaldehyde



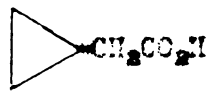
Cyclopropaneethanol was catalytically dehydrogenated to cyclopropaneacetaldehyde over a catalyst of copper and silver suspended on pumice as described by Davies and Hodgson (31). The apparatus consisted of a copper tube 1 meter long and 1 cm. wide, to which was soldered two monel metal 24/40 female joints at the top and bottom. The tube was wrapped with No. 26 nichrome wire for heating and insulated with asbestos. A copper thermocouple well was placed in the middle of the tube in such a fashion that the temperature at the center of the column could be determined. A chromel-alumel thermocouple attached to a Leeds and Northrup model 1316 potentiometer was employed to determine the temperature. In operation, a 250-ml. three-necked round-bottomed flask was attached to the bottom of the copper tube (which was previously packed with catalyst) by means of the steel fitting and a suitable adaptor led from the top of the copper tube to an efficient condenser, which was in turn attached to a receiver holding a second condenser. The receiving flask was usually cooled in an ice bath. The copper tube was preheated to 350°. The oil bath was heated by means of a hot plate to a temperature 40-50° above the boiling point of the alcohol to be dehydrogenated. Air was introduced through the inlet tube at a rate of 0.5 liter per minute. The alcohol was dropped into the heated flask through the dropping funnel at a rate of approximately 5 ml. per minute and the aldehyde was collected in the receiver.

In a typical preparation, 15 g. (0.175 mole) of cyclopropaneethanol yielded 9 g. (61%) cyclopropaneacetaldehyde, b.p. 135-136°, n_D^{25} 1.4382, m.p. of para-nitrophenylhydrazone, 116°.

Anal. Calc'd. for $C_{11}H_{13}N_3O_2$: C, 60.12; H, 5.97; N, 19.13

Found: C, 60.12; H, 5.78; N, 18.85

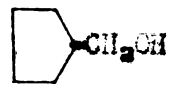
(c) Cyclopropaneacetic Acid



A 125-ml. iodine flask was charged with 6 g. (0.071 mole) of cyclopropaneacetaldehyde, 35 g. (0.152 mole) of silver oxide, and 25 ml. of water. The flask was tightly stoppered and mechanically shaken at room temperature for 12 hours, after which it was removed from the shaker and heated at 60° for one hour. The silver and remaining silver oxide were filtered and washed with several portions of ether. The aqueous portion of the filtrate was extracted with four 150-ml. portions of ether. The ethereal solutions were combined and dried over anhydrous calcium chloride. The ether was removed *in vacuo* leaving a residue, which upon distillation, yielded 5.4 g. (72%) of cyclopropaneacetic acid, b.p. 90° at 15 mm., m.p. of para-bromophenacyl derivative 83-83.5°. (Literature value b.p. 90° at 15 mm., m.p. of para-bromophenacyl derivative 83.5-84 (32).)

Cyclopentaneacetic Acid

(a) Cyclopentylcarbinol



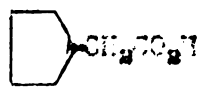
Cyclopentylmagnesium chloride was prepared from 25 g. (0.234 mole) cyclopentyl chloride and 5.7 g. (0.234 g. aton) magnesium turnings. Formaldehyde, generated by the depolymerization of 11.7 g. (0.130 mole) of paraformaldehyde in an oil bath at 200° (33) was introduced in a slow stream of nitrogen through a gas inlet tube. After the paraformaldehyde was completely depolymerized, the reaction mixture was allowed to set overnight. Sufficient ice-cold 10% sulfuric acid was then added to make the solution acid to congo red. The organic and aqueous layers were separated and the aqueous solution was then saturated with sodium chloride and extracted with 100-ml. of ether. The combined organic fractions were dried over anhydrous potassium carbonate. Removal of the ether left a residue which, upon distillation, yielded 15 g. (65%) of cyclopentylcarbinol, b.p. 152°, n_D^{25} 1.4436. (Literature value b.p. 165°, n_D^{20} 1.4453 (34).)

(b) Cyclopentylcarbinyl Bromide

Cyclopentylcarbinyl bromide was prepared from cyclopentylcarbinol and phosphorus tribromide by a method completely analogous to that employed in the preparation of cycloheptyl bromide (page 25).

From 15 g. (0.15 mole) of phosphorus tribromide there was obtained 10.1 g. (38%) cyclopentylcarbinyl bromide, b.p. 110° at 50 mm. n_D^{25} 1.4875. (Literature value b.p. 80° at 30 mm., n_D^{25} 1.4866 (35).)

(c) Cyclopentaneacetic Acid



Cyclopentaneacetic acid was prepared by a method analogous to that used in the formation of cyclopentane carboxylic acid (page 23). From the Grignard reagent formed from 10.1 g. (0.062 mole) of cyclopentylcarbinyl bromide and 1.51 g. (0.062 g. atom) of magnesium turnings there was obtained 5 g. (63%) of cyclopentaneacetic acid, b.p. 224-230, n_D^{25} 1.4512. (Literature value b.p. 224-228, n_D^{25} 1.4520 (36).)

Preparation of the Acid Chlorides

The acid chlorides were prepared from the corresponding acids by either of two procedures, exchange with benzoyl chloride or reaction with thionyl chloride. An example of each procedure is given below.

Cyclopropanecarbonyl Chloride

A 100-ml. round-bottomed flask equipped for distillation was charged with 22 g. (0.256 mole) of cyclopropanecarboxylic acid and 70 g. (0.5 mole) of benzoyl chloride. Cyclopropanecarbonyl chloride was distilled directly from the mixture and upon redistillation there was obtained

19.5 g. (73%), b.p. 113°-115° (literature value b.p. 112-115° (37)).

Cyclopentanecarbonyl Chloride

A 100-ml. round-bottomed flask equipped with a reflux condenser was charged with 10 g. (0.088 mole) of cyclopentanecarboxylic acid and 10.4 g. (0.092 mole) of thionyl chloride. After the initial reaction had subsided, the solution was heated gently on the steam bath for one hour. After two distillations, there was obtained 8.6 g. (73%) of cyclopentanecarbonyl chloride, b.p. 150-160°. (Literature value b.p. 155-159° (38).)

Preparation of Other Acid Chlorides

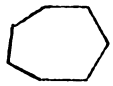
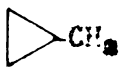
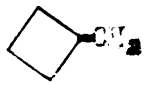
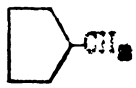
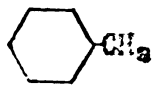
Cyclopropaneacetyl chloride and cyclobutanecarbonyl chloride were prepared by the benzoyl chloride procedure. Cyclohexanecarbonyl chloride, cycloheptanecarbonyl chloride, cyclobutaneacetyl chloride, cyclopentaneacetyl chloride, and cyclohexaneacetyl chloride were prepared by the thionyl chloride method. The yields and boiling points are listed in Table 3.

Preparation of the Diacyl Peroxides

The peroxides were prepared by the action of sodium peroxide in moist ether on the corresponding acid halides. Two specific examples will be given.

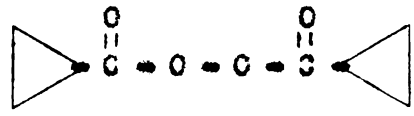
TABLE 3

YIELDS AND BOILING POINTS OF THE ACYCLIC ACID CHLORIDES

Acid Chloride, RCOCl R	Yield (%)	Boiling Point, °C.
	75*	112-115
	77*	142-145
	73	165-170
	82	172-175
	71	220-221 at 760 mm.
	75*	132-133
	81	154-157
	78	90-93 at 15 mm.
	74	110-112 at 15 mm.

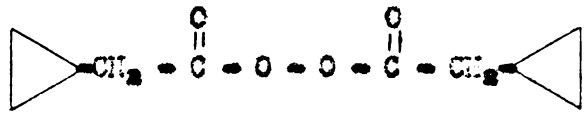
*Benzoyl chloride procedure. All others by the thionyl chloride procedure.

Bis-cyclopropanoformyl Peroxide



A 500-ml. three-necked round-bottomed flask equipped with a Hirshberg stirrer, dropping funnel, reflux condenser, and thermometer was charged with 6.9 g. (0.088 mole) of sodium peroxide and 45 ml. of ethyl ether. The peroxide was stirred to a slurry in the ether and there was then added 18.5 g. (0.177 mole) of cyclopropanocarbonyl chloride over a period of 10 minutes. The reaction was initiated by the addition of 1-2 drops of water. This caused the reaction to proceed at a rate sufficient to reflux the ether. When the reaction subsided and addition of a drop of water no longer caused an increase in the reaction temperature, the stirrer was stopped and the peroxide-salt mixture was extracted with water. The ether solution was then separated and dried over anhydrous calcium chloride. The aqueous solution at this point was basic to litmus. Evaporation of the ether in a stream of dry air left the crystalline bis-cyclopropanoformyl peroxide as a residue. The yield was 12.3 g. (83%). The unique stability of this peroxide permitted it to be recrystallized from pentane (m.p. 79.2-80.0°). Iodometric analysis by the method of Swain et al. (37) indicated the recrystallized material to be over 99% pure.

Biscyclopropanacetyl Peroxide



Biscyclopropanacetyl peroxide was prepared in the same manner as biscyclopropanaformyl peroxide with the following exceptions: the quantities of reactants were much smaller, the reaction temperature was not allowed to exceed 2° C, the end of reaction was assumed to coincide with the disappearance of the yellow color of sodium peroxide, and the reaction mixture was washed with ice water. In a typical preparation, there was obtained from 0.86 g. (0.011 mole) of sodium peroxide and 3.9 g. (0.0213 mole) of cyclopropanacetyl chloride 1.83 g. (3[illegible]%) of biscyclopropanacetyl peroxide. The product was not obtained in crystalline form, but as a clear colorless liquid. Iodometric analysis indicated a purity of 8[illegible]-8[illegible]%. The contaminant, for the most part, was cyclopropylcarbinyl cyclopropanacetate, as judged from its infrared spectrum. (See the appendix of this thesis for the infrared spectra of the peroxides.)

Other Acyl Peroxides

The other acyl peroxides used in this study were prepared in a manner similar to that employed in the preparation of biscyclopropanacetyl peroxide with the exception that the reaction temperature was allowed to extend as high as 8° C.

The yields and purities of all peroxides prepared are listed in Table 4. The purity was determined iodometrically and duplicate numbers are for duplicate preparations. The reason for the purity being less than 100% in many cases may be due to failure to remove all of the solvent.

TABLE 4

YIELDS OF VARIOUS ACYL PEROXIDES PREPARED

Diacyl Peroxide $(RCO_2)_2$ R	Total Yield	Purity (%)
Cyclopropyl	83,84	100
Cyclobutyl	84,84	92,94
Cyclopentyl	80,85	91,94
Cyclohexyl	78,81*	94,95
Cycloheptyl	85,87*	92,93
Cyclopropylcarbinyl	84,85	84,86
Cyclobutylcarbinyl	88,88	88,89
Cyclopentylcarbinyl	87,91*	91,93
Cyclohexylcarbinyl	78,80*	96,97

*Those peroxides were crystalline when stored in the freezer, but liquified at room temperature. All the peroxides (except the first one in the table) were clear, colorless liquids at room temperature.

Preparation of Certain Esters

In order to determine quantitatively the amount of ester produced in the decomposition of certain of the peroxides, it was necessary to prepare pure samples of several esters. These preparations are described below.

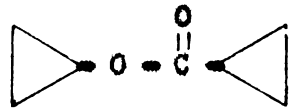
Cyclopropyl Cyclopropanecarboxylate

(a) Trifluoroperoxyacetic Acid

F_3C-CO_3H

Trifluoroperoxyacetic acid was prepared by the method of Emmons and Lucas (30). In a typical preparation, a thoroughly cleaned 500-ml. three-necked round-bottomed flask equipped with a Hirshberg stirrer, reflux condenser, and dropping funnel was cooled in an ice bath and charged with 10.8 ml. (0.4 mole) of 90% hydrogen peroxide and 100 ml. of methylene chloride. To this well-stirred solution was added 67.6 ml. (0.48 mole) of bistrifluoroacetic anhydride dropwise over a period of one hour. The resulting solution of trifluoroperoxyacetic acid was used without delay in the subsequent reaction.

(b) Cyclopropyl Cyclopropanecarboxylate



Cyclopropyl cyclopropanecarboxylate was prepared by the Baeyer-Villiger reaction of dicyclopropyl ketone with trifluoroperoxyacetic acid. In a typical preparation, a 1-l. three-necked round-bottomed flask equipped with a Hirshberg stirrer, dropping funnel, and reflux

condenser was charged with 142 g. (1 mole) of disodium hydrogen phosphate, 22 g. (0.2 mole) of dicyclopropyl ketone, and 200 ml. of methylene chloride. The trifluoroperoxyacetic acid solution previously described was added to the well-stirred slurry over a period of 25 minutes. The methylene chloride refluxed during this addition. After the addition was complete, the reaction mixture was gently refluxed for one hour. The solids were then filtered and washed with 100 ml. of methylene chloride, and the filtrates were collected. The combined filtrates were washed with 100 ml. of 10% sodium carbonate followed by 100 ml. of water, and then dried over anhydrous magnesium sulfate. After removing the methylene chloride by distillation, there remained a residue which, upon distillation *in vacuo*, yielded a mixture of ester and unconverted ketone, b.p. 60° at 15 mm. From the relative intensities of the ester and ketone peaks in the infrared spectrum, it was estimated that the mixture contained 55-60% ester and 40-45% ketone. Since cyclopropyl cyclopropanecarboxylate and dicyclopropyl ketone boil at essentially the same temperature, it was not possible to separate them by distillation. Repeated attempts to separate the mixture by chromatography on activated alumina, using pentane as the eluant were unsuccessful.

Test experiments to determine the reactivity of Girard's reagents T and P (39) towards dicyclopropyl ketone resulted, in each case, in essentially complete recovery of the unchanged starting ketone.

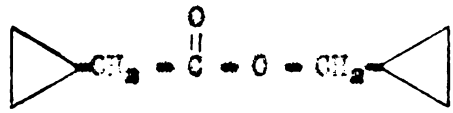
It was subsequently discovered that dicyclopropyl ketone reacted quantitatively with hydroxylamine hydrochloride. In a typical separation,

a 50 ml. round-bottomed flask equipped with a reflux condenser was charged with 9 g. of the ester ketone mixture, 5 g. of hydroxylamine hydrochloride, 10 ml. of pyridine, and 15 ml. of absolute ethyl alcohol. The reaction mixture was refluxed for 1.5 hours, after which the pyridine and alcohol were removed *in vacuo*. Careful distillation of the residue, also *in vacuo*, yielded 5 g. of cyclopropyl cyclopropanecarboxylate, b.p. 163° at atmospheric pressure, 62° at 15 mm., n_D^{25} 1.4528, saponification equivalent (40) 127, calculated 126.

Anal.* Calc'd for $C_7H_{10}O_2$: C, 66.6%; H, 8.0%

Found: C, 66.9%; H, 8.07

Cyclopropylcarbinyl Cyclopropaneacetate

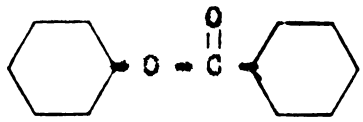


A 50-ml. Erlenmeyer flask was charged with 20 ml. of pyridine, 2.4 g. (0.033 mole) of cyclopropylcarbinol, and 4 g. (0.033 mole) of cyclopropaneacetyl chloride. The mixture was allowed to stand at room temperature for two hours after which it was diluted with 50 ml. of ether. The ethereal solution was washed in turn with two 25-ml. portions of water, a 25-ml. portion of 6*N* hydrochloric acid, a 25-ml. portion of 10% sodium carbonate, and finally with a 50-ml. portion of water. After drying over magnesium sulfate, the ether was removed *in vacuo*; distillation then yielded 4.1 g. (70%) of cyclopropylcarbinyl cyclopropaneacetate, b.p. 63-65° at 2 mm., n_D^{25} 1.4475.

Anal.* Calc'd. for $C_8H_{14}O_2$: C, 70.10; H, 8.75

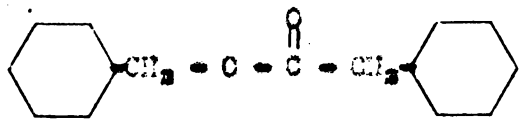
Found: C, 69.93; H, 8.68

Cyclohexyl Cyclohexanecarboxylate



Cyclohexyl cyclohexanecarboxylate was prepared in the same manner as cyclopropylcarbinyl cyclopropaneacetate. From 5 g. (0.034 mole) of cyclohexanecarbonyl chloride and 3.4 g. (0.034 mole) of cyclohexanol there was obtained 5.4 g. (75.5%) of cyclohexyl cyclohexanecarboxylate, b.p. 132-134° at 10 mm., n_D^{25} 1.4644. (Literature values b.p. 132-133° at 10 mm., n_D^{20} 1.4620 (41).)

Cyclohexylcarbinyl Cyclohexaneacetate



Cyclohexylcarbinyl cyclohexaneacetate was prepared in the same manner as cyclopropylcarbinyl cyclopropane acetate. From 5.15 g. (0.035 mole) of cyclohexaneacetyl chloride and 3.53 g. (0.035 mole) of cyclohexylcarbinol there was obtained 5.7 g. (75%) of cyclohexylcarbinyl cyclohexaneacetate, b.p. 132-135° at 10 mm., n_D^{25} 1.4701. (Literature values, b.p. 144-145° at 10 mm., n_D^{25} 1.4699 (42).)

Phenyl Benzoate

Phenyl benzoate was prepared by the Schotten-Baumann procedure described by Hickenbotton (42).

Apparatus for Products and Kinetics of Decomposition of Various Acyl Peroxides

The decomposition vessel consisted of a 250-ml. round-bottomed flask to the top of which was attached a sealed-on Graham condenser. A gas inlet tube, extending to the bottom of the flask, was sealed into the top of one side of the vessel, and a cold-finger ground-glass stopper was affixed in similar position on the other. An eight mm. glass tube holding a three-way stopcock and outlets, was attached to the top of the condenser.

Nitrogen was admitted through the gas inlet tube; it was purified by passing it through a train consisting of two 200-ml. portions of Fieser's solution (43), 100 ml. of lead acetate, 350 ml. of concentrated sulfuric acid, and finally a drying tower filled with anhydrous calcium chloride.

The exit gases from the reaction vessel were allowed to pass through a train assembled in series as follows: a 30% solution of aniline in carbon tetrachloride, two cold traps contained in dry ice-isopropyl alcohol baths, a tared U-tube containing ascarite, another protective ascarite-filled U-tube, a U-tube filled with anhydrone, a cold trap maintained at dry ice-isopropyl alcohol temperatures, and a calcium chloride drying tube. In those cases wherein the apparatus was being used for kinetic studies, the absorption train for exit gases consisted only of an ascarite U-tube and an anhydrone U-tube. In order to remove samples during the kinetics experiments, the nitrogen flow through the gas inlet tube was stopped and caused to flow in the reverse direction through the top of the condenser by means of the three-way

stopcock. Aliquots were thus forced out of the gas inlet tube into a receiver.

The reaction vessel, in all cases, was contained in a mineral oil bath. Heating was accomplished by a knife-blade heater and controlled by a Bethotinsky mercury thermoregulator connected through a Fisher-Serfass electronic relay.

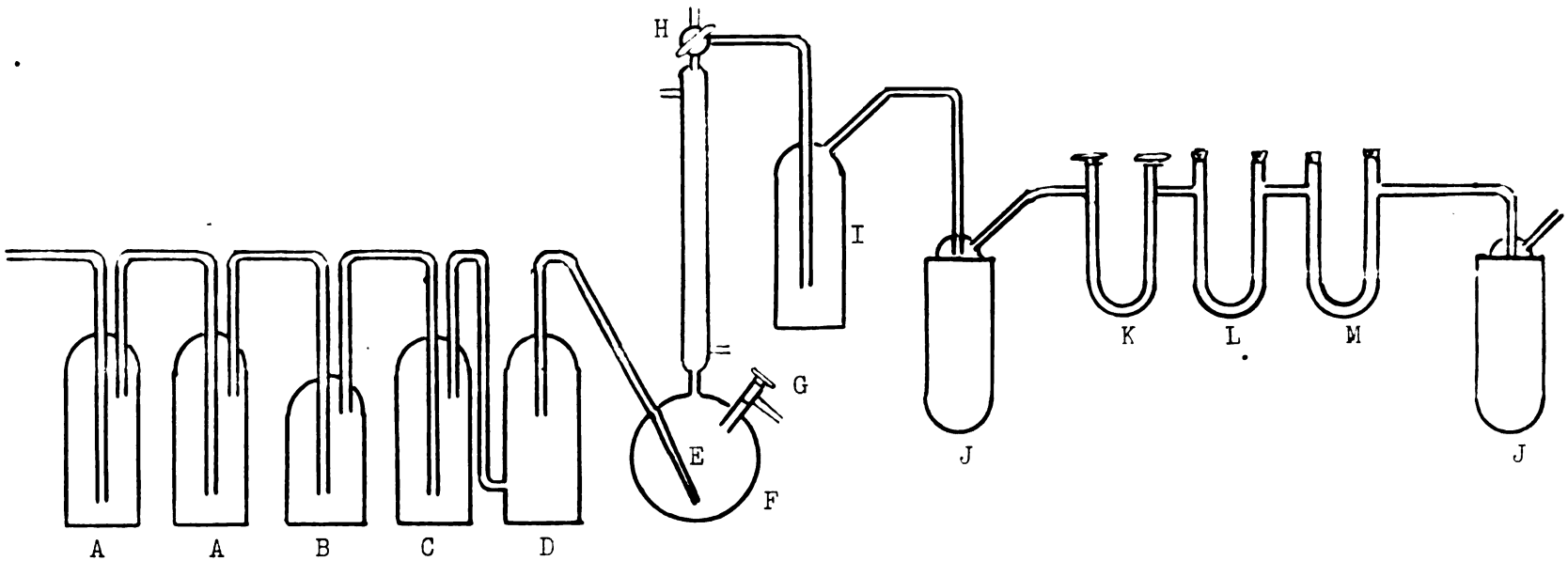
The apparatus is shown schematically in Figure 5.

Quantitative Determination of Products

Phosgene was determined gravimetrically as diphenylurea isolated from the aniline trap. Carbon dioxide was also determined gravimetrically by measuring the increase in weight of the tared ascarite tube. All other determinations were accomplished by the use of quantitative infrared, employing the base line technique (44).

In the infrared measurements it was necessary to determine unique bands for the compounds in question. It was also necessary to determine whether these bands adhered to Beer-Lambert-Bouguer law over the concentration ranges encountered. In those cases where the determination of peroxides were being performed, and the peroxides were not of 100% purity, corrections based on iodometric analysis were employed in the determination of the amount of peroxide in a given sample.

When determining the adherance to Beer's law of the various compounds encountered, measurements were made at three varying concentrations (in the range to be studied) and then the constancy of a in the expression $\log I_o/I = abc$, where a is a constant, b is cell width



(A) Fieser's solution
(B) Lead acetate
(C) Sulfuric acid
(D) Calcium chloride
(E) Nitrogen inlet
(F) Decomposition flask
(G) Cold finger stopper
(H) 3-way stopcock
(I) Aniline trap
(J) Cold trap
(K) Tared ascarite tube
(L) Protective ascarite tube
(M) Anhydrone tube

Figure 5. Apparatus used for the decomposition of various acyl peroxides.

(cm.), and c is concentration in g. per liter was determined. If the band was then unique to the compound in question and obeyed Beer's law in the necessary concentration range, the predetermined value of a was used to determine concentration. For example, measurement at three different concentrations gave values of a for biscyclopropaneformyl peroxide of 0.3475, 0.3467, and 0.3477, an average of 0.3473. This value was then used to determine unknown concentrations of peroxide. In a test experiment, 0.241 g. of peroxide were placed into 100 ml. of carbon tetrachloride and a quantitative spectrum taken. There was found 0.239 g. by this method. A detailed description of the product analyses from the decomposition of biscyclopropaneformyl and -acetyl peroxides is given below. The results are summarized in Tables 5, 6 and 7. The results for biscyclohexaneformyl and -acetyl peroxides, and for benzoyl peroxide are given in Tables 8, 9 and 10.

Products from the Decomposition of Biscyclopropaneformyl Peroxide

In all cases, purified carbon tetrachloride (45) was used as the solvent. Carbon dioxide and phosgene were analyzed gravimetrically as previously described. Cyclopropyl chloride was isolated and determined by infrared spectroscopy using the bands at 3.31 and 6.90 microns. Any remaining peroxide was determined by using the band at 5.65 microns. Cyclopropyl cyclopropanecarboxylate was determined by using the band at 5.75 microns. Cyclopropane-carboxylic acid was determined similarly using the band at 5.90 microns.

In a typical decomposition, 1.898 g. of biscyclopropaneformyl peroxide and 100 ml. of carbon tetrachloride were placed in the decomposition vessel. The solution was cooled in an ice-salt bath and then swept with nitrogen for 30 minutes, after which it was heated in a slow stream of nitrogen for 72 hours at a temperature of 70°. The solution was then transferred to a 100-ml. volumetric flask. Approximately 7 ml. of carbon tetrachloride had been lost during the heating period and this was added to bring the volume up to 100 ml. again. A quantitative infrared spectrum was taken to determine the amount of ester and acid produced, and the amount of undecomposed peroxide, after which the solution was distilled *in vacuo* through a preheated seven-plate helice-packed column. Spectra of the distillate, taken periodically as it was collected, indicated that all of the cyclopropyl chloride was collected in the first 10 ml. of distillate. The residual solution was rediluted to 100 ml. with carbon tetrachloride and another quantitative infrared spectrum obtained. There was no measurable difference between the quantities of peroxide, ester, and acid obtained before and after distillation. A similar distillation was performed on the aniline trap. Infrared spectra of the various cold trap contents indicated only cyclopropyl chloride. The two distillates and the cold trap contents were combined and diluted to 100 ml. with carbon tetrachloride. The quantity of cyclopropyl chloride was then measured by quantitative infrared. All liquids were evaporated from the aniline trap *in vacuo*. The residual solid was washed with several portions of water to remove the aniline

hydrochloride, and the remaining diphenylurea was dried and weighed to determine the amount of phosgene produced. Hexachloroethane was also a product from the decomposition, but attempts to isolate it were not quantitative.

Two separately prepared batches of peroxide were decomposed and analyzed as described in detail immediately above. The results are shown in Table 5.

TABLE 5

PRODUCTS FROM DECOMPOSITION OF BISCYCLOPROPANECARBONYL PEROXIDE AT 70° IN CARBON TETRACHLORIDE AFTER 72 HOURS

(R =)

	Amount of Peroxide Decomposed	RCl	CO_2	RCO_2H	RCO_2R	$COCl_2$
g.	1.329*	0.842	0.603	0.043	0.210	0.0012
moles / mole of peroxide	1	1.41	1.75	0.064	0.162	—
g.	1.303**	0.73	0.501	0.0859	0.211	0.0034
moles / mole of peroxide	1	1.25	1.48	0.129	0.162	—
Average moles / mole of peroxide	1	1.33	1.62	0.096	0.21	—

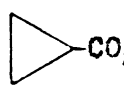
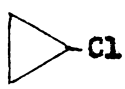
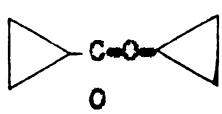
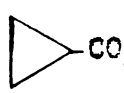
*0.569 g. of peroxide were undecomposed.

**1.760 g. were originally taken, of which 1.303 g. were decomposed.

The values of a (Beer's Law constant) for the various compounds were found to be as shown in Table 6.

TABLE 6

BEER'S LAW CONSTANTS

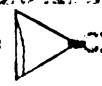
Compound	a $(\frac{l.}{g.\ cm.})$	Wave Length of Analytic Band (Microns)
(	0.3473	5.65
	0.01318, 0.01905	3.31, 6.90
	0.3103	5.75
	0.710	5.90

Products of Decomposition of Biscyclopropanacetyl Peroxide

Biscyclopropanacetyl peroxide was decomposed by a method analogous with that described in the case of biscyclopropanaformyl peroxide (page). The peroxide decomposed very rapidly and completely (heating period of six hours). The amount of peroxide decomposed was corrected for impurities by iodometric analysis. The amount of ester obtained was also corrected for the amount of ester present in the original peroxide. The quantities and kinds of products, are listed in Table 7.

TABLE 7

PRODUCTS FROM DECOMPOSITION OF DICYCLOPROPANEACETYL PEROXIDE AT 70° IN CARBON TETRACHLORIDE FOR SIX HOURS

(R = )

	Amount of Peroxide Decomposed	RCl	CO_2	RCO_2H	RCO_2R	$COCl_2$
g.	0.716	0	0.1285	0.022	0.4461	0.008
$\frac{\text{moles}}{\text{mole of peroxide}}$	1	0	0.88	0.0615	0.85	—

The Beer's Law Constants

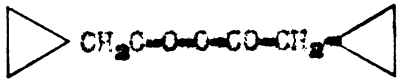
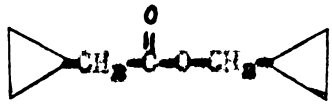
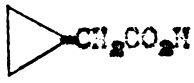
Compound	a ($\frac{l.}{g.\ cm.}$)	Analytical Band (Microns)
	0.1715	5.65
	0.2972	5.75
	0.5502	5.92

TABLE 8

PRODUCTS FROM DECOMPOSITION OF BISCYCLOHEXANECARBONYL PEROXIDE AT 70° IN CARBON TETRACHLORIDE FOR 40 HOURS

	Peroxide Decomposed	RCl	CO_2	RCO_2H	RCO_2R	$COCl_2$
g.	0.861	0.615	0.280	small	0.161	0.001
$\frac{\text{moles}}{\text{mole of peroxide}}$	—	1.51	1.87	—	0.225	—
g.	0.815	0.590	0.280	small	0.0161	0.003
$\frac{\text{moles}}{\text{mole of peroxide}}$	—	1.55	1.87	—	0.238	—
Average $\frac{\text{moles}}{\text{mole of peroxide}}$	—	1.53	1.87	—	0.232	—

The Beer's Law Constants

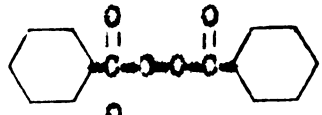
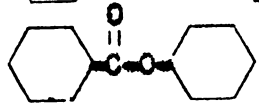
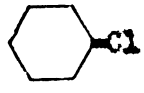
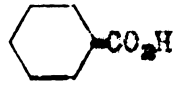
Compound	$k\ (\frac{l}{g.\ cm.})$	Analytical Band (Microns)
	0.2721	5.65
	0.2043	5.75
	0.0998	11.20
	0.4077	5.91

TABLE 9

PRODUCTS FROM DECOMPOSITION OF BIS(PHENYLACETYL) PEROXIDE AT 70° IN CARBON TETRACHLORIDE FOR 72 HOURS

	Peroxide Decomposed	RCl	CO_2	RCO_2H	RCO_2R	$CHCl_3$
g.	1.125	0.698	0.310	0.021	0.286	0.002
$\frac{\text{Moles}}{\text{Mole of peroxide}}$	1	1.32	1.77	0.025	0.30	---

The Beer's Law Constants

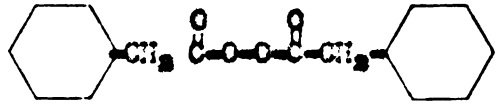
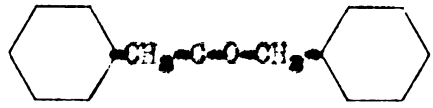
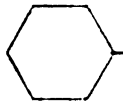
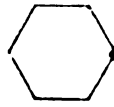
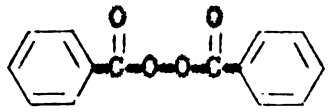
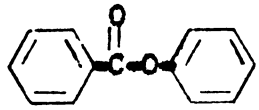
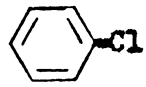
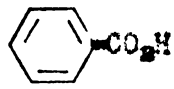
Compound	a ($\frac{\text{l.}}{\text{g. cm.}}$)	Analytical Band (Microns)
	0.1402	5.65
	0.1153	5.75
	0.0875	11.21
	0.3443	5.91

TABLE 10

PRODUCTS FROM DECOMPOSITION OF BENZOYL PEROXIDE AT 70°
IN CARBON TETRACHLORIDE FOR 72 HOURS

	Peroxide Decomposed	RCl	CO_2	RCO_2H	RCO_2R	$COCl_2$
g.	1.554	0.925	0.490	0.0120	0.321	0.008
$\frac{\text{moles}}{\text{mole of peroxide}}$	1	1.271	1.725	0.0155	0.255	—

The Beer's Law Constants

Compound	a $(\frac{l}{g.\ cm.})$	Analytical Band (Microns)
	0.3564	5.65
	0.3211	5.75
	0.1189	8.90
	0.763	5.90

Decomposition of Biscyclopropanoformyl Peroxide in the Presence of Iodine and Water

A carbon tetrachloride solution (about 10 ml.) containing 1.250 g. (0.007 mole) of biscyclopropanoformyl peroxide per liter was placed in a glass vial. Iodine (0.2 g., 0.008 mole) and 2 ml. of water were added and the vial was then sealed. After heating at 75° for 65 hours, the vial was placed in a dry ice-acetone bath and opened. The contents were washed with sodium hydrosulfite to remove the excess iodine, and then dried over anhydrous calcium chloride. A quantitative spectrum was then taken. Cyclopropyl iodide was determined by using the strong peak at 8.03 microns (a = 0.6557). The ester and acid were determined as described previously (page 43). The solution was found to contain 1.121 g./l. of cyclopropyl iodide, or 45% of the theoretical amount, 0.516 g./l. of cyclopropanecarboxylic acid (41% of the theoretical quantity), and about 0.04 g./l. of ester.

Kinetics of Decomposition of Various Acyl Peroxides

The apparatus and method of sampling were previously described (page 40). The reaction was followed by the rate of disappearance of peroxide as determined on aliquots by quantitative infrared. The intregrated form of the first order kinetic equation,

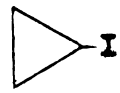
$$\log P = \frac{-kt}{2.303} + \log P_o$$

was used to determine the rate constant k. In practice, k was determined from the least squares slope of a plot of log P versus t. The rate data for various runs are given in the Appendix of this thesis.

C. Miscellaneous Experiments

1. Reactions of Simple Cyclopropane Derivatives

Cyclopropyl Iodide



A 1-l. round-bottomed flask equipped with a reflux condenser was charged with 14 g. (0.0825 mole) of biscyclopropaneformyl peroxide, 22.9 g. (0.09 mole) iodine, and 700 ml. of carbon tetrachloride. The solution was refluxed for 60 hours, after which it was cooled and then washed with sufficient sodium hydrogen sulfite solution to remove any remaining iodine. After drying over anhydrous magnesium sulfate, the solution was fractionally distilled through a 30-inch helice-packed column. After removal of all the carbon tetrachloride, there remained a residue which was fractionated through a small 7-plate column. The yield of cyclopropyl iodide was 13 g. (61%) b.p. 96°, n_D^{27} 1.5320. The dipole moment (1.53 D) was determined by Professor M. T. Rogers.

Anal. Calc'd. for C_3H_5I: I, 75.55%

Found: I, 75.31, 75.12

Reaction of Cyclopropyl Iodide with Magnesium

A 500-ml. three-necked round-bottomed flask equipped with a reflux condenser, Hirshberg stirrer, and dropping funnel was charged with 0.73 g. (0.03 mole) of magnesium turnings. Cyclopropyl iodide (5 g., 0.03 mole) in 30 ml. of ether was then added dropwise over a period of ten

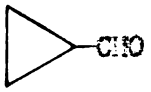
minutes. Gentle heating initiated the reaction. After the initial reaction had subsided, the system was heated under reflux for one hour. At this time it was poured onto approximately 50 g. of crushed dry ice. The reaction mixture was then allowed to stand until all the dry ice had evaporated. Sufficient 10% sulfuric acid was then added to make the solution acid to congo red. The organic and aqueous layers were separated and the aqueous portion was extracted with two 50-ml. portions of ether. The combined organic solutions were dried over anhydrous calcium chloride. Removal of the solvents in vacuo left 1.1 g. of a liquid residue which upon distillation in vacuo through a micro distilling flask yielded 0.77 g. (30%) of cyclopropanecarboxylic acid, identified through its infrared spectrum and physical constants.

Oxidation of β-Cyclopropaneethanol with Potassium Permanganate

A 2-l. two-necked round-bottomed flask equipped with a reflux condenser and Hirshberg stirrer was charged with 25 g. (0.29 mole) of β-cyclopropaneethanol, and 61 g. (0.385 mole) of potassium permanganate in 1200 ml. of water. The solution was cooled in an ice bath and stirred for four hours, after which it was allowed to warm to room temperature and stir for an additional eight hours. The manganese dioxide was filtered and the filtrate was then evaporated on the steam bath until the volume of liquid remaining was approximately 100 ml. The aqueous solution was covered with 300 ml. of ether, acidified with 10% sulfuric acid, then saturated with sodium chloride. The aqueous and organic layers were separated, and the aqueous portion was extracted with 100 ml. of ether.

The combined ether extracts were dried over anhydrous magnesium sulfate, and the ether was then removed *in vacuo*. Distillation of the residue yielded 13 g. (approximately 50%) of an acid presumed to be cyclopropaneacetic acid. However, subsequent reactions, especially the formation of peroxide from this substance, showed it to be an approximately equimolar mixture of cyclopropanecarboxylic and cyclopropaneacetic acids.

Cyclopropanecarboxaldehyde



Cyclopropanecarboxaldehyde was prepared from cyclopropylcarbinol by the same procedure employed in the preparation of cyclopropaneacetaldehyde (page 27).

From 35 g. (0.465 mole) of cyclopropylcarbinol there was obtained 7 g. of unreacted starting material and 21 g. (75% based on reacted carbinol) of cyclopropanecarboxaldehyde, identified by its infrared spectrum and physical constants (46).

2. Attempted Preparation of Dimethylcyclopropylcarbinyl Chloride

Reaction of Phosphorus Trichloride with Dimethylcyclopropylcarbinol

A 100-ml. round-bottomed flask was cooled in an ice bath and charged with 11.3 g. (0.083 mole) of phosphorus trichloride. A solution of 24.3 g. (0.243 mole) of dimethylcyclopropylcarbinol and 5.4 g. of pyridine was added dropwise over a period of one-half hour. The upper liquid layer was separated and distilled. There was obtained 14 g. (70%) of

2-cyclopropylpropene, b.p. 74-77°, n_D^{25} 1.4218. The infrared spectrum of this compound was identical with that reported in the literature (47).

Triphenyl Phosphite (48)

$(C_6H_5O)_3P$

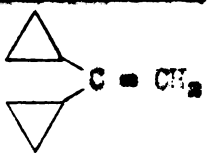
A 2-l. round-bottomed flask equipped with a reflux condenser was charged with 138.5 g. (1 mole) of phosphorus trichloride and 282 g. (3 moles) of phenol. The solution was refluxed for six hours resulting in the formation of a pale yellow liquid. Upon distillation through a 12-inch Vigreux column there was obtained 272 g. (86%) of triphenyl phosphite, b.p. 223-224° at 5 mm., m.p. 23-24°.

Reaction of Triphenyl Phosphite and Benzyl Chloride with Dicyclopropylcarbinol

A 250-ml. round-bottomed flask equipped with a preheated two-foot helices-packed column was charged with 22 g. (0.22 mole) of triphenyl phosphite and 26.5 g. (0.21 mole) of benzyl chloride. The pot temperature was maintained between 130-142° and the column temperature between 105-131°. After 48 hours there was obtained 4.9 g. of 2-cyclopropylpropene, identified by its physical constants and infrared spectrum. No other product could be isolated.

3. Reactions of Dicyclopropyl Ketone

1,1-Dicyclopropylethylene



A 100-ml. round-bottomed flask was equipped with a preheated 15-inch helice-packed column was charged with 30 g. (0.238 mole) of dicyclopropylmethylcarbinol and two drops of concentrated sulfuric acid. The pressure in the system was reduced to 105-110 mm. and a mixture of 1,1-dicyclopropylethylene, and water was distilled into a receiver. The olefin was separated from the water, dried over anhydrous magnesium sulfate and then redistilled. There was obtained 22.6 g. (80%) of 1,1-dicyclopropylethylene, b.p. 65° at 100 mm., n_D^{20} 1.4646.

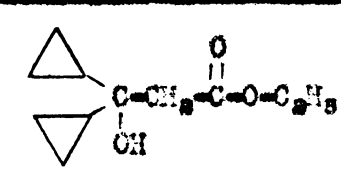
Anal.* Calc'd for C_8H_{12}: C, 88.82; H, 12.52

Found: C, 88.80; H, 12.39

Proof of Structure of 1,1-Dicyclopropylethylene

A 500-ml. Erlenmeyer flask equipped with a Hirshberg stirrer was charged with 10 g. (0.093 mole) of 1,1-dicyclopropylethylene, 19 g. of potassium permanganate, and 200 ml. of water. The mixture was cooled in an ice bath and stirred vigorously for a period of three days. Manganese dioxide was removed by filtration and washed with ether. The aqueous filtrate was saturated with potassium carbonate, and then extracted with five 100-ml. portions of ether. The ethereal solutions were combined and dried over anhydrous potassium carbonate. Removal of the ether *in vacuo* left 6.5 g. (70%) of dicyclopropyl ketone, identified by means of its physical constants and infrared spectrum.

Ethyl Beta,beta-dicyclopropyl-beta-hydroxypropionate



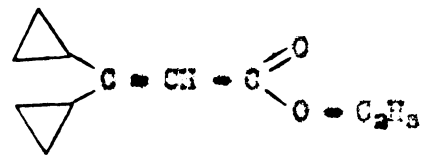
A 3-l. round-bottomed flask equipped with a Hirshberg stirrer, reflux condenser, and dropping funnel was charged with 65.4 g. (1 g. atom) of zinc dust. A 50-ml. portion of a solution of 110 g. (1 mole) of dicyclopropyl ketone, 167 g. (1 mole) of ethyl bromoacetate, 200 ml. of dry toluene, and 200 ml. of dry benzene was added and then heated gently. A vigorous exothermic reaction was initiated after which the rest of the solution was added at a rate sufficient to maintain a very rapid reflux. After the addition was complete, the reaction mixture was allowed to stir for two hours more. Sufficient ice-cold 10% sulfuric acid was then added to cause the formation of two layers and the dissolution of the zinc salts. The organic and aqueous layers were separated and the aqueous layer was then extracted with 100 ml. of benzene. The organic portions were combined, dried over anhydrous calcium chloride, and distilled *in vacuo*. After removal of the toluene and benzene, there remained a residue which upon further distillation yielded 121 g. (58%) of ethyl beta, beta-dicyclopropyl-beta-hydroxypropionate, b.p. 103-105° at 2 mm., n_D^{25} 1.4634.

Saponification equivalent Calc'd: 198
Found: 196, 196.5

Anal.* Calc'd for $C_{11}H_{18}O_3$: C, 72.49; H, 8.95
Found: C, 71.75; H, 10.03

This substance was contaminated with small amounts of the corresponding acrylate.

Ethyl Beta,beta-dicyclopropylacrylate



A 200-ml. round-bottomed flask equipped for distillation was charged with 96 g. (0.46 mole) of ethyl beta, beta-dicyclopropyl-beta-hydroxypropionate and six drops of concentrated sulfuric acid. The pressure in the system was reduced to 85 mm. and a mixture of acrylate and water was distilled and collected in a receiver. The organic product was separated from the water, dried over anhydrous calcium chloride, and redistilled. The yield was 76 g. (87%) of ethyl beta, beta-dicyclopropylacrylate, b.p. 156-158° at 85 mm., 96° at 2 mm., n_D^{25} 1.5050.

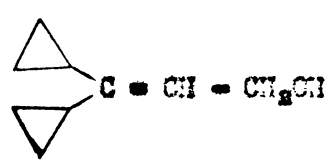
Saponification equivalent: Calc'd: 180

Found: 178.1, 178.7

Anal.* Calc'd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95

Found: C, 72.91; H, 8.95

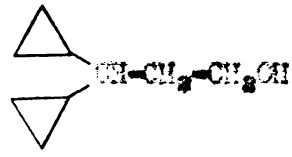
3,3-Dicyclopropyl Allyl Alcohol



A 1-l. three-necked round-bottomed flask equipped with a Hirshberg stirrer, reflux condenser, and dropping funnel was charged with 11.4 g. (0.3 mole) of lithium aluminum hydride and 500 ml. of anhydrous ethyl ether. Ethyl beta, beta-dicyclopropylacrylate (36 g., 0.2 mole) was

added dropwise to the stirred solution over a period of 45 minutes. Hydrolysis was then accomplished by the cautious addition of 100 ml. of water followed by sufficient ice-cold 10% sulfuric acid to make the solution acid to congo red. The organic and aqueous layers were separated, and the aqueous layer was extracted with 100 ml. of ether. The organic portions were combined and dried over anhydrous potassium carbonate. The ether was removed *in vacuo*, leaving a residue of 3,3-dicyclopropylallyl alcohol. Attempts to distill this substance were unsuccessful since it invariably set up to a glass and began to decompose upon heating. Therefore, the crude product was used for subsequent reactions. The yield of crude alcohol was 24 g. (86%).

3,3-Dicyclopropylpropanol

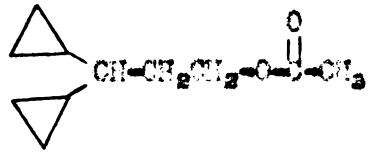


A low pressure hydrogenation bottle was charged with 26 g. (0.188 mole) of beta, beta-dicyclopropylallyl alcohol, 0.1 g. platinum oxide catalyst, and 50 ml. of ethyl alcohol. The initial pressure was 50 pounds per square inch and the reaction was accomplished at room temperature. The theoretical uptake of hydrogen was complete in 15 minutes. The catalyst was removed by filtration and the ethanol by distillation *in vacuo*. Distillation of the residue yielded 25 g. (essentially quantitative) of 3,3-dicyclopropylpropanol, b.p. 90-91° at 3 mm., n_D^{25} 1.4432.

Anal.* Calc'd for $C_9H_{16}O$: C, 77.70; H, 11.50

Found: C, 77.45; H, 11.29

3,3-Dicyclopropylpropyl Acetate



A 250-ml. round-bottomed flask equipped with a reflux condenser was charged with 42 g. (0.3 mole) of 3,3-dicyclopropylpropanol, 46 g. (0.45 mole) of acetic anhydride, and 100 ml. of glacial acetic acid. The solution was refluxed for 2.5 hours after which it was cooled and diluted with one liter of water. The upper layer was separated and dried over anhydrous calcium chloride. Distillation yielded 49.5 g. (91%) of 3,3-dicyclopropylpropyl acetate, b.p. 101-103° at 3 mm., n_D^{25} 1.4500.

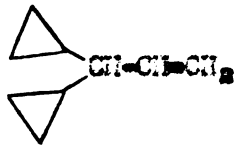
Saponification equivalent: Calc'd: 182.3

Found: 181.8, 183.2

Anal. Calc'd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.93

Found: C, 72.40; H, 10.09

3,3-Dicyclopropyl-1-propene



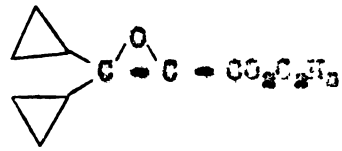
3,3-Dicyclopropyl-1-propene was prepared by pyrolysis of 3,3-dicyclopropylpropyl acetate using the general procedure described by Bailey (49). The apparatus consisted of a 16.5 inch Pyrex column filled with 1/16 inch glass helices and wrapped with number 18 Nichrome wire (6 turns to the inch). The bottom of the column was attached to a

two-necked round-bottomed receiver holding a dry ice condenser. The top of the column held a gas inlet tube, dropping funnel, and thermocouple well which extended halfway into the column. In a typical preparation, the receiver was placed in a dry ice-isopropyl alcohol bath and the column was heated to 520 ± 5°. The temperature was determined by use of a chromel-alumel thermocouple connected to a Leeds-Northrup model 8686 potentiometer. The ester, 3,3-dicyclopropylpropyl acetate, (19 g. 0.095 mole) was dropped onto the top of the column (nitrogen atmosphere) at the rate of 2 ml. per minute. After removal of the acetic acid by washing with 10% sodium carbonate, distillation of the receiver contents yielded 5.1 g. of olefin, b.p. 138°, n_D^{25} 1.3918, and 2 g. of starting material.

Anal. Calc'd for C_9H_{14}: C, 88.39; H, 11.11

Found: C, 88.35; H, 11.27

Attempted Preparation of Dicyclopropyl Glycidic Ester



The reaction was attempted following the general procedure given for acetophenone in Organic Syntheses (30). In a typical preparation, a 1-l. three-necked round-bottomed flask equipped with a Hirshberg stirrer, reflux condenser, thermometer, and solid addition tube was charged with 80 g. (0.73 mole) ethyl bromoacetate, 80 g. (0.73 mole) of dicyclopropyl ketone and 140 ml. of dry freshly distilled benzene.

The solution was cooled to 15° in an ice bath and 35 g. (0.9 mole) of sodium amide were added through the addition tube over a period of two hours. The mixture was subsequently allowed to stir at 20° for six hours, after which it was poured onto 400 g. of ice. After the ice had melted, the organic layer was separated. The aqueous layer was extracted with 100 ml. of benzene and the extract was then combined with the original organic fraction and dried over anhydrous calcium chloride. Removal of the benzene *in vacuo* left a residue which upon fractionation *in vacuo* yielded 40 g. of starting ketone and 7.5 g. of ethyl bromoacetate. A large quantity of resinous tar remained.

Further attempts to prepare the glycidic ester, including the use of other bases, the use of chloroester, the omission of solvent, heating, and inverse addition failed to cause reaction. At no time could more than a small amount of the bromoester be recovered.

Reaction of Perbenzoic Acid with 1,1-dicyclopropylethylene

Perbenzoic acid was prepared by the method of *Organic Syntheses* (31).

A 1-l. Erlenmeyer flask was cooled in an ice bath and charged with 20 g. (0.145 mole) of perbenzoic acid and 500 ml. of ethyl ether. To this was added 17 g. (0.155 mole) of 1,1-dicyclopropylethylene over a period of 30 minutes. After the addition was complete, the Erlenmeyer flask was tightly stoppered and allowed to stand in the dark for three days. The solution was then neutralized (phenolphthalein indicator) with cold 1N sodium hydroxide. The organic layer was separated and dried over anhydrous calcium chloride, after which the ether and excess

1,1-dicyclopropylethylene were removed *in vacuo*. The bulk of the residue boiled about 70° at 7 mm.

The infrared spectrum of the distillate showed no bands which could be attributed to an epoxide. There was a strong carbonyl band at 5.80 microns, and a carbonyl shoulder at 5.90 microns. A strong hydroxyl band at 2.80 microns, and bands attributable to cyclopropane were also present.

Part of the distillate probably contained an aldehyde or ketone carbonyl, since a small amount of it formed an immediate precipitate with 2,4-dinitrophenylhydrazine. No further attempts were made to resolve the distillate into its possible components.

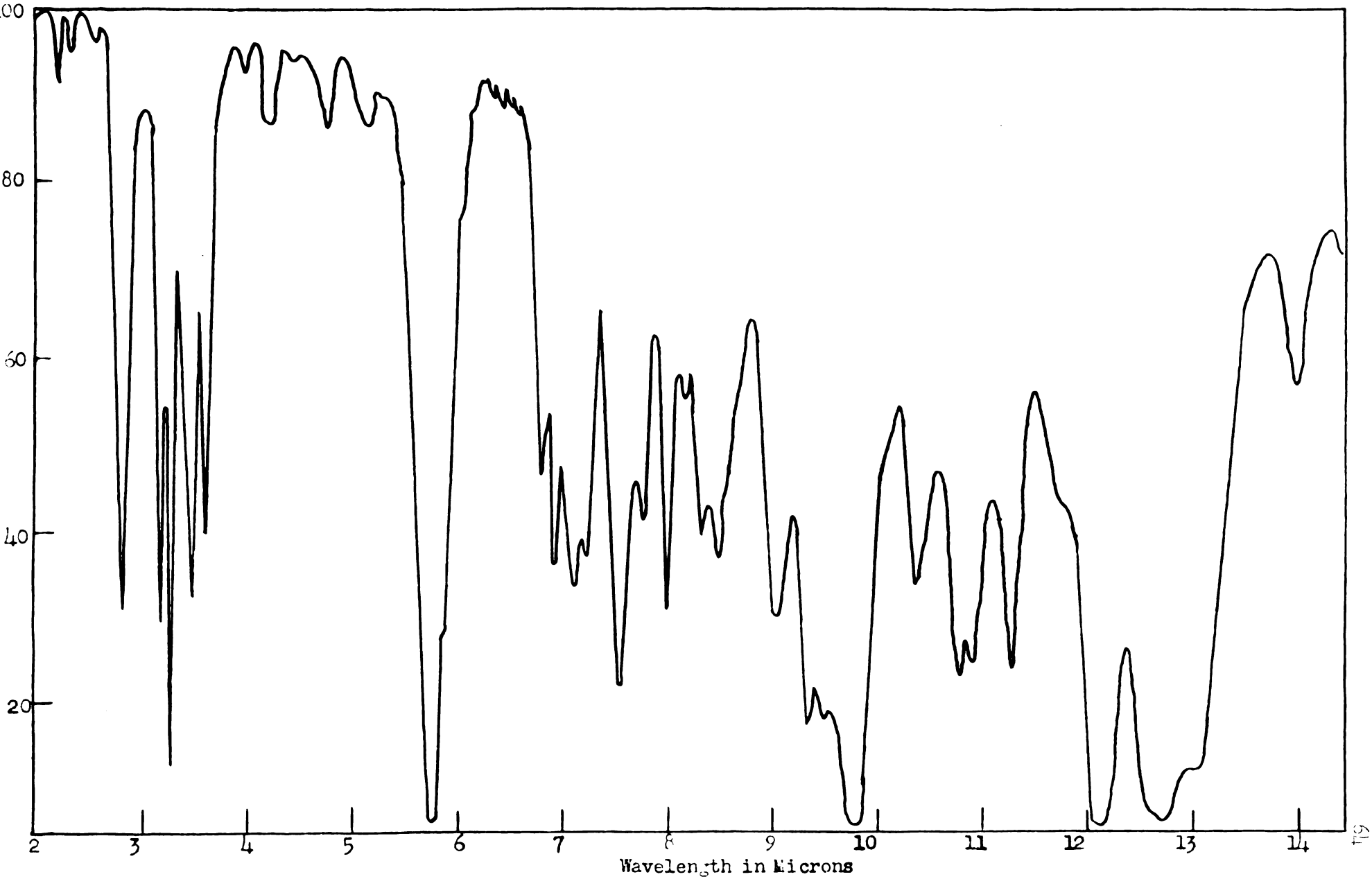


Figure 6. Infrared Spectrum of the Product from the Reaction of 1,1-Dicyclopropylethylene with Perbenzoic Acid.

DISCUSSION

A. Free Radical Chlorinations

The free radical chlorination of hydrocarbons has been the object of many researches. Most of the investigations pertaining to aliphatic systems have indicated that chlorinations are characterized by comparatively long chain reactions. In the case of photochemical chlorinations, these long chains result in high quantum yields. For example, it was reported that the photochlorination of heptane in carbon tetrachloride gave a quantum yield of 7.3×10^3 (52), and that hexadecane under similar conditions gave a quantum yield of 7×10^4 (53). The proposed mechanism is:

$$Cl_2 + H \longrightarrow 2Cl\cdot$$

$$Cl\cdot + RH \longrightarrow R\cdot + HCl$$

$$R\cdot + Cl_2 \longrightarrow RCl + Cl\cdot, \text{ chain continues}$$

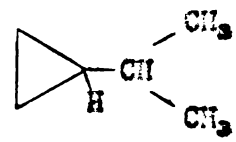
$$\left.\begin{array}{l} R\cdot + R\cdot \\ R\cdot + Cl\cdot \\ Cl\cdot + Cl\cdot \end{array}\right\} \longrightarrow \text{chain termination}$$

In the preceding examples, no effort was made to characterize the position of substitution. However, various investigations have shown that certain generalities concerning the site of substitution of a chlorine atom for a hydrogen atom can be expressed (54,55). These studies have shown that a tertiary hydrogen atom is more easily substituted than a secondary, which in turn is more easily substituted than a primary

hydrogen atom. Brown (56) has rationalized these results from the viewpoint that the reactions are controlled in part by inductive effects. This was considered to be reasonable since the hydrogen atom bound to the carbon atom possessing the greatest electron density tended to be replaced the most readily, i.e., a tertiary hydrogen atom. However, in many cases, this tendency for tertiary substitution is somewhat counteracted by the fact that there are statistically more secondary and primary positions available than tertiary ones.

In this thesis, the free radical chlorination of isooctane and 2,3-dimethylbutane under varying conditions yielded results in accord with the discussion. The monochlorinated products were dimethylneopentylcarbinyl and dimethylisopropylcarbinyl chlorides respectively. Similar results were reported by Russell(57) and by Brown (58).

It seemed of interest to study the chlorination of isopropylcyclopropane, which has two tertiary hydrogen atoms, one acyclic and one



alicyclic in a highly strained ring. Previous work has shown that even a primary acyclic hydrogen is chlorinated in preference to a tertiary hydrogen on a cyclopropane ring. Thus, from methylcyclopropane, the principal product (without rearrangement) was cyclopropylcarbinyl chloride (13,14).

It was originally thought that isopropylcyclopropane upon free radical chlorination would undergo exocyclic tertiary substitution

leading to dimethylcyclopropylcarbinyl chloride. Unfortunately this did not turn out to be the case. The fact that the product readily formed a Grignard reagent, which upon hydrolysis yielded the original isopropylcyclopropane indicated that there was no skeletal rearrangement and that the chlorine atom was probably not on the cyclopropane ring. This premise is based upon the fact that cyclopropyl chloride is reported to form a Grignard reagent only extremely sluggishly and in very poor yield (59). Further, it was considered that the ring probably would not be chlorinated with so many other positions available for substitution, since it has been shown that the abstraction of a hydrogen atom from cyclopropane proceeds with considerable difficulty. For example, Trotman-Dickenson and Steacie (60) studied the ease of abstraction of hydrogen atoms from various alicyclic hydrocarbons by determining the rate of removal by methyl radicals of hydrogen atoms from hydrocarbons, as contrasted with the rate of combination of methyl radicals to form ethane.

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \longrightarrow CH_3\cdot$$

$$CH_3\cdot + RH \xrightarrow{k_1} CH_4 + R\cdot$$

$$CH_3\cdot + CH_3\cdot \xrightarrow{k_2} C_2H_6$$

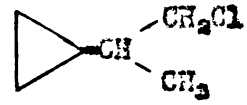
Hydrocarbon	$k_1/\sqrt{k_2} \times 10^{13}$ per Hydrogen Atom	E^* Kcal./mole
n-Pentane	4.0 (for CH_2)	9.3
Cyclohexane	3.8	---
Cyclopentane	4.7	9.3
Cyclobutane	2.8	---
Cyclopropane	0.4	13.1
Benzene	0.3	---

Their results show that the removal of a hydrogen atom from cyclopropane is more difficult than from other alicyclic hydrocarbons and indeed is almost as difficult as the removal of a hydrogen atom from the benzene ring. A more recent investigation has indicated that in the reactions above, the cyclopropyl radical, when formed, rearranges to an allyl radical (61). Since it gains stability (looses energy) in so doing, the value 0.4 for cyclopropane in the preceding table may be high.

The most probable explanation for the reluctance of cyclopropane to form a free radical is based upon I-strain (3). Thus, cyclopropane, a highly strained molecule as such, would undergo an even further increase in internal strain upon becoming a radical due to a change in hybridization of orbitals from sp^3 to sp^2.

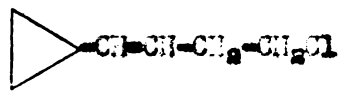
molecule radical

The attempted ethanolysis of the product of chlorination of isopropylcyclopropane indicated that there was little if any reactive tertiary chloride in the molecule. Attempts to measure the rate of the reaction showed it to be extremely slow (almost negligible), and not of the first order kinetically. Had the chlorine been on a tertiary carbon, it would have been expected to undergo S_N1 solvolysis at a fairly rapid rate under the reaction conditions used. For these reasons it was concluded that the structure of the chlorinated compound was probably 1-chloro-2-cyclopropyl-propane.

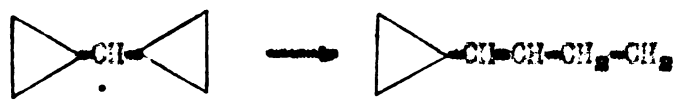


That this, rather than the expected dimethylcyclopropylcarbinyl chloride, was formed, was probably due to the statistical factor of there having been six primary and only one tertiary hydrogens, coupled with the fact that the tertiary position was well shielded from attack by the methyl and cyclopropyl groups.

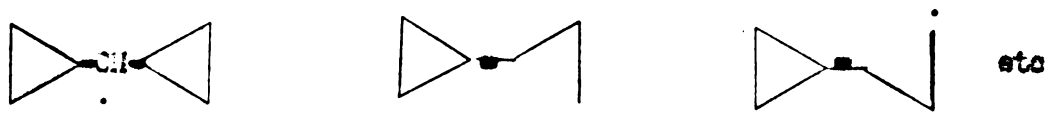
The next compound studied was dicyclopropylmethane which was selected as a compound for chlorination upon the assumption that this would lead to an intermediate dicyclopropylcarbinyl free radical. This apparently turned out to be the case, although the product was shown to have undergone skeletal rearrangement. By oxidation of the olefin obtained in the chlorination, it was established that the product was 1-cyclopropyl-4-chlorobutene-1.



This result was analogous to that obtained by Roberts, who isolated allylcarbinyl chloride from the chlorination of methylcyclopropane (13). In accord with Roberts explanation, it is probable that this product arose from the rearrangement of a dicyclopropylcarbinyl free radical.



It was particularly interesting that the intermediate dicyclopropylcarbinyl radical did not maintain its identity. By analogy with a similar type carbonium ion, it is possible to formulate several resonance structures which could easily apply to this system.

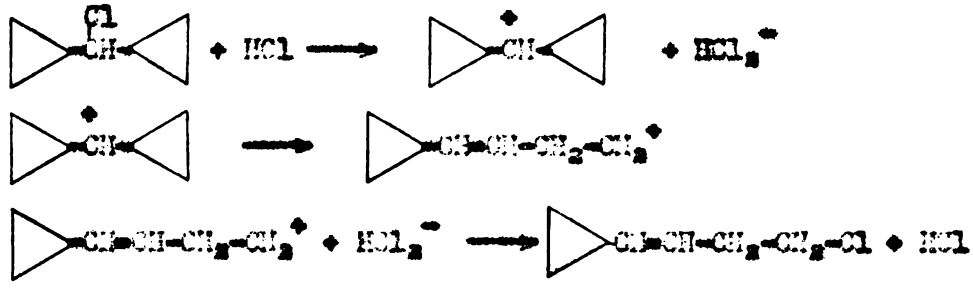


I II III

However, it is apparent from the major product isolated that structures (II) and (III) above were not part of a resonance hybrid but,

rather, must have been discrete intermediates at the time they reacted with the chlorine. However, there remains a possibility which would not necessarily rule out the importance of the resonance depicted above in other reactions. Thus, since the product obtained was undoubtedly the most stable one derivable from dicyclopropylethane, it is possible that the reaction (chlorination) was subject to thermodynamic control. If this was the case, then the product obtained was the one which would be expected. Furthermore, the comparatively high yields of product obtained at very low temperature might be taken as an indication of the relative ease of formation of the cyclopropylcarbinyl radical.

It should be pointed out that the postulated rearrangement is not at all unequivocably established as a free radical reaction, either in the present instance or in the work of Roberts (13). Since hydrogen chloride is produced in quantity during the chlorination, and since it is known that cyclopropylcarbinyl chlorides ionize very readily (14), it is possible that the observed product was produced by a carbonium ion rearrangement. Such rearrangements are well known in this system (13,62).



B. General Considerations Regarding the Decomposition of Acyl Peroxides

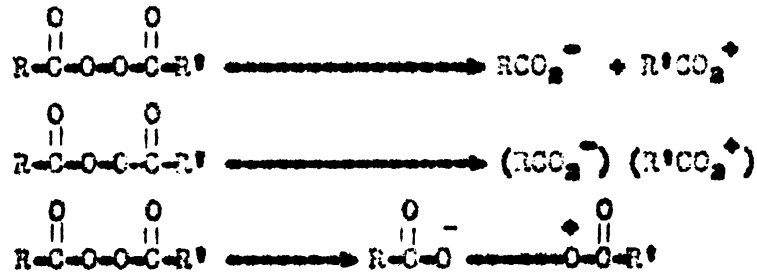
Since a major portion of this thesis deals with the decomposition of alicyclic diacyl peroxides, it will be well to review briefly the extensive literature on the mechanism of such peroxide decompositions.

An acyl peroxide may undergo spontaneous decomposition via a homolytic fission wherein the original molecule yields two free radicals,

or, under certain conditions, it may undergo heterolytic cleavage to yield initially a pair of ions (63).

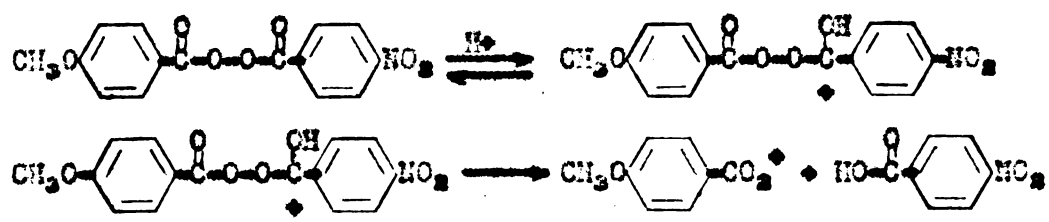
It has usually been observed that the former situation prevails for symmetrical peroxides undergoing decomposition in relatively non-polar solvents such as carbon tetrachloride, benzene, hydrocarbons, etc. This mode of decomposition by homolytic fission of an oxygen-oxygen bond is probably a consequence of the relatively low bond dissociation energy of that particular bond. The values of the bond dissociation energies for acetyl and benzoyl peroxides, for example, have been estimated to be between 27-35 kilocalories per mole (64). On the other hand, the tendency for acyl peroxides to decompose heterolytically is increased by a decrease of symmetry in the original molecule. In principle, this type of decomposition may run the entire gamut from complete dissociation

into free ions, through ion-pair formation, down to a more polarization of the oxygen-oxygen bond.



It is readily concluded from the above that solvents of high dielectric constant would favor heterolytic cleavage of acyl peroxides.

In addition to the spontaneous decompositions discussed above, an acyl peroxide may undergo an induced decomposition caused by ions (65) or by radicals (66). An example of the former reaction is the hydrogen ion catalyzed decomposition of p-methoxyl-p'-nitrobenzoyl peroxide.



An example of the latter process is the cleavage of benzoyl peroxide by the triphenylmethyl radical (66). Hexaphenylethane in benzene solution dissociates to a considerable extent into triphenylmethyl radicals. When these solutions are added to benzoyl peroxide (either dry or in solution) a rapid reaction occurs at room temperature. No carbon dioxide is evolved and the products are benzoic acid, trityl benzoate, and tetraphenylmethane. The proposed mechanism was as follows:

(1) $(C_6H_5)_3C\cdot + (C_6H_5CO_2)_2 \longrightarrow C_6H_5CO_2C(C_6H_5)_3 + C_6H_5CO_2\cdot$

(2) $(C_6H_5)_3C\cdot + C_6H_5CO_2\cdot \longrightarrow C_6H_5CO_2C(C_6H_5)_3$

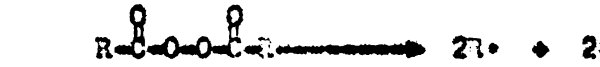
(3) $C_6H_5CO_2\cdot + C_6H_6 \longrightarrow C_6H_5CO_2H + C_6H_5\cdot$

(4) $C_6H_5\cdot + (C_6H_5)_3C\cdot \longrightarrow (C_6H_5)_4C$

Reaction (3) above may not take place as such, since no carbon dioxide was detected. Rather, reactions (3) and (4) may be simultaneous.

$$C_6H_5CO_2\cdot + C_6H_6 + (C_6H_5)_3C\cdot \longrightarrow C_6H_5CO_2H + (C_6H_5)_4C$$

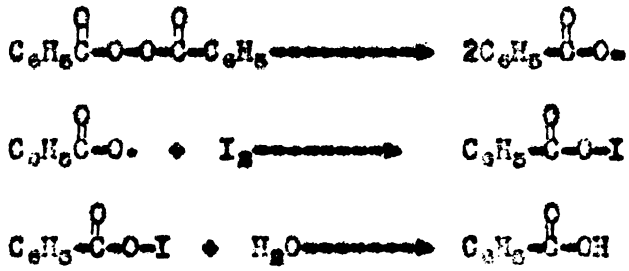
The initial step in the free radical decomposition of acyl peroxides has been a subject of some speculation. After the free radical nature of the process had been accepted, it was postulated that the initial step involved simultaneous rupture of two carbon-carbon bonds and an oxygen-oxygen bond resulting in the formation of two molecules of carbon dioxide and two hydrocarbon radicals (67).



However, the appearance of significant amounts of ester and acid among the decomposition products in those cases where induced decomposition was unimportant, more or less excludes this postulate. It was later suggested (68) that the initial step yielded a molecule of carbon dioxide, an acyloxy radical and a hydrocarbon radical.

There was considerable merit in this explanation in that it accounted for the origin of certain decomposition products as well as some rate data. More recent investigations have indicated that an acyl peroxide upon spontaneous thermal decomposition yields initially two acyloxy radicals.

For example, Hammond (59) decomposed benzoyl peroxide in carbon tetrachloride containing an equimolar quantity of iodine and water. There was obtained from this reaction a quantitative yield of benzoic acid, which was postulated to have been formed by means of the following steps.



In other words, since the yield of benzoic acid was quantitative, it was concluded that the initial decomposition step yielded two benzoate radicals which immediately combined with the very active scavenger iodine to yield an acyl hypoiodite. This in turn was hydrolyzed by the water to yield benzoic acid. In a control experiment in the absence of iodine, no significant amount of benzoic acid was produced, the principal products being chlorobenzene and hexachloroethane.

In a study of the decomposition of acetyl peroxide (70), it was stated that the products could be explained only on the assumption that

one dealt wholly, or at least to a great extent with acetate radicals which decarboxylate as they react. A more detailed mechanism which explains the origin of all the decomposition products obtained will be given later in the discussion.

Several detailed kinetic investigations of the free radical decompositions of acyl peroxides have been carried out. In essentially all cases, the kinetics could be expressed by the following equation:

$$\frac{-d(p)}{dt} = k_d (p) + k_i (p)^x \quad (71)$$

(p) = concentration of peroxide

k_d = rate constant for spontaneous decomposition

k_i = rate constant for induced decomposition

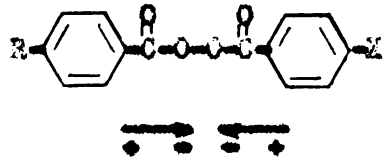
x = order of the induced decomposition reaction

The number, x, has usually been found to vary between 0.5 and 2. It is of particular interest to note that according to the preceding equation, acyl peroxide decompositions are of the first order kinetically if induced decompositions are eliminated.

Acyl peroxides related to benzoyl peroxide have been the most widely studied systems in respect to both products and kinetics. It is felt that it would be advantageous to summarize the results of several of these investigations previous to discussing the results obtained in the present thesis. Included in this discussion will be the results obtained in the case of a non-benzoyl type peroxide in order to point out differences and similarities which exist between the two types. Finally, it is further felt that an indication of the various detailed mechanisms

formulated to explain the origin of the various decomposition products obtained should be of value, and, therefore, these will also be included.

Swain, in a study of the decomposition of substituted benzoyl peroxides, found evidence that they decompose because of electrostatic repulsion between the two benzoate groups (38).



In other words, it was considered that the molecule consisted of two dipoles oriented with their negative ends nearest each other. Such a situation should create a large electrostatic repulsion which would tend to force the molecule apart. This concept predicted that electron-releasing substituents (especially those which were situated in the para position) should increase the rate of decomposition whereas similarly placed electron-withdrawing groups should decrease it. The examples given in Table 11 illustrate this point. The electron-withdrawing cyano and chloro groups decrease the rate (with respect to the unsubstituted peroxide), whereas the electron-releasing methyl and methoxyl groups increase the rate. The effect, however, is not a very large one.

The rate of decomposition of benzoyl peroxide varies somewhat with the solvent used in the decomposition. This may, however, be due in part to inaccuracies in correcting for induced decomposition which is highly solvent dependent. Some representative rate data of this type is listed in Table 12.

TABLE 11

DECOMPOSITION OF SUBSTITUTED BENZOYL PEROXIDES IN DIOXANE AT 80° C. (38)

Substituents	$k_1 \times 10^5$ (min.$^{-1}$)
p,p^1 dimethoxy	7.06
p-methoxy	4.54
p,p^1 dimethyl	3.68
m,m^1 dimethyl	2.64
benzoyl peroxide	2.52
p,p^1 dichloro	2.17
m-cyano	1.64
p,p^1 dicyano	1.22
m,m^1-dicyano	1.02

TABLE 12

THE DECOMPOSITION OF BENZOYL PEROXIDE IN VARIOUS SOLVENTS (73)

Solvent	Temperature °C.	k_d,(sec.$^{-1}$)
benzene	60	1.95×10^{-5}
benzene	80	3.28×10^{-5}
acetic anhydride	60	5.55×10^{-5}
acetic anhydride	80	7.5×10^{-5}
carbon tetrachloride	80	2.08×10^{-5}
toluene	80	3.28×10^{-5}
nitrobenzene	80	3.28×10^{-5}
t-butylbenzene	80	3.28×10^{-5}
cyclohexene	80	1.93×10^{-5}
cyclohexane	80	6.36×10^{-5}
styrene	60	2.25×10^{-6}

This effect has been discussed in detail by Leffler (72).

As might be expected, there is a large diversity in the products obtained from the free radical decomposition of benzoyl peroxide in different solvents (73). There are several factors which contribute to this situation. An important part of the products finally isolated is produced by reaction of the free radicals from the peroxide with the solvent. Also, most of the decompositions have been performed in solutions of sufficient concentration as to allow induced decomposition reactions to become particularly important. Therefore, products resulting from the induced decomposition of the peroxide by solvent radicals will of course be different for different solvents. Some illustrative examples of this are given in Table 13.

TABLE 13

PRODUCTS FROM THE DECOMPOSITION OF BENZOYL PEROXIDE IN VARIOUS SOLVENTS (73)

Solvent	Products
Cyclohexane	CO_2, $C_6H_5CO_2H$, o,p-C_6H_{11}-$C_6H_4CO_2H$, C_6H_{12}, $C_6H_5C_6H_{11}$, $C_6H_5CO_2$ C_6H_5
Carbon tetrachloride	CO_2, $COCl_2$, Cl_2 CC_6H_4COCl, C_2Cl_6, C_6H_5Cl
Benzene	CO_2, $C_6H_5CO_2H$, $C_6H_5C_6H_5$, main products, also, resin, $C_6H_5CO_2$ C_6H_5, triphenyl

A particularly careful study of an aliphatic peroxide decomposition was made by Bolar and Weis (74), who studied the decomposition of bis-delta-phenylvaleryl peroxide in dilute carbon tetrachloride solution. It was considered that a dilute solution of peroxide in a comparatively reactive solvent such as carbon tetrachloride caused the amount of induced decomposition to be negligible. Their product analysis is listed in Table 14. They were able to account for 97% of the carbon dioxide and 89.5% of the phenylbutyl groups. It should be noticed that carbon dioxide and 1-chloro-4-phenylbutane were the major products.

TABLE 14

PRODUCTS FROM THE DECOMPOSITION OF 14.9 MILLIMOLES OF BIS-DELTA-PHENYLVALERYL PEROXIDE IN CARBON TETRACHLORIDE (74)

Product	Millimoles
CO_2	25
$C_6H_5CH_2-CH_2-CH_2-CH_2Cl$	12.2
$CCCl_3$	1.1
HCl	3.6
C_2Cl_6	2.7
$C_6H_5(CH_2)_4CO_2H$	1.1
$C_6H_5(CH_2)_4CO_2(CH_2)_4C_6H_5$	2.6
$C_6H_5(CH_2)_5\ C_6H_5$	3.2
$C_6H_5(CH_2)_3CHCl\ CH_2\ CCl_3$	1.6

In order to rationalise the products obtained, DeTar and Weis proposed the following mechanism:

$$[C_6H_5(CH_2)_4COO]_2 \longrightarrow 2[C_6H_5(CH_2)_4COO\cdot]$$

$$[C_6H_5(CH_2)_4COO\cdot]_{cage} \longrightarrow [C_6H_5(CH_2)_4\cdot] + CO_2$$

$$C_6H_5(CH_2)_4\cdot + CCl_4 \longrightarrow C_6H_5(CH_2)_4Cl + \cdot CCl_3$$

$$2\cdot CCl_3 \longrightarrow C_2Cl_6$$

$$2[C_6H_5(CH_2)_4\cdot]_{cage} \longrightarrow C_6H_5(CH_2)_8C_6H_5$$

$$2[C_6H_5(CH_2)_4\cdot]_{cage} \longrightarrow C_6H_5(CH_2)_3CH_3 + C_6H_5(CH_2)_2CH{=}CH_2$$

$$\left.\begin{matrix} C_6H_5(CH_2)_4\cdot \\ C_6H_5(CH_2)_4COO\cdot \end{matrix}\right\}_{cage} \longrightarrow C_6H_5(CH_2)_4COO(CH_2)_4C_6H_5$$

$$\left.\begin{matrix} C_6H_5(CH_2)_4\cdot \\ C_6H_5(CH_2)_4COO\cdot \end{matrix}\right\} \longrightarrow C_6H_5(CH_2)_4COOH + C_6H_5CH_2CH_2CH{=}CH_2$$

$$\cdot CCl_3 + C_6H_5(CH_2)_2CH{=}CH_2 \longrightarrow C_6H_5(CH_2)_2\dot{C}HCH_2CCl_3$$

$$C_6H_5(CH_2)_2CHCH_2CCl_3 + CCl_4 \longrightarrow C_6H_5(CH_2)_2CHClCH_2CCl_3 + \cdot CCl_3$$

$$2CCl_3\cdot + O_2 \longrightarrow CCl_3OOCCl_3 \text{ or } 2COCl_2 + Cl_2 \text{ or } ClCOOCCl_3 + Cl_2$$

$$C_6H_5(CH_2)_4COOCCl_3 + H_2O \longrightarrow C_6H_5(CH_2)_4COOH + COCl_2 + HCl$$

It should be specifically pointed out that in no case did DeTar and Weis allow for induced decomposition in the mechanistic scheme depicted above. As was previously mentioned, it was felt that this did not occur since the concentration of peroxide was small, and carbon tetrachloride is a comparatively reactive solvent for free radicals (notice, for example, the large quantity of chlorine containing compounds obtained in the decomposition).

In light of the many investigations pertaining to the products obtained from the decomposition of benzoyl peroxide, Tobolsky and

Mesrobian (75) have formulated a rather useful general mechanism to explain the products observed. In the following scheme, P refers to the original peroxide, R is the benzoate radical, and SH and SX are hydrocarbon and halogenated solvents, respectively.

(1) spontaneous cleavage $P \xrightarrow{k_d} 2R\cdot$

(2) transfer of radical activity to solvent $R\cdot + S \xrightarrow{k_s} S\cdot$ (for unsaturated or aromatic solvents)

$R\cdot + SH \longrightarrow S\cdot + RH$

$R\cdot + SH \longrightarrow S\cdot + C_6H_5 + CO_2$

$R\cdot + SX \longrightarrow S\cdot + RX$

$R\cdot + SX \longrightarrow S\cdot + C_3H_5Cl + CO_2$

(3) induced decomposition by R· $R\cdot + P \xrightarrow{k_3} R\cdot + RC_6H_5 + CO_2$

$R\cdot + P \longrightarrow R\cdot + C_6H_5C_6H_5 + CO_2$

(4) induced decomposition by S· $S\cdot + P \xrightarrow{k_4} R\cdot + RS$

$S\cdot + P \longrightarrow R\cdot + C_6H_5S + CO_2$

(5) termination $R\cdot + R\cdot \xrightarrow{k_6}$ products of combination and disproportionation

$R\cdot + S\cdot \xrightarrow{k_8}$ products of combination and disproportionation

$S\cdot + S\cdot \xrightarrow{k_7}$ products of combination and disproportionation

Although Tobolsky and Mesrobian formulated this scheme for benzoyl peroxide, comparison of its various steps (with or without those which are based upon induced decompositions) with those proposed by DeTar and

Weiss, indicates enough similarity between the two that it might be considered to be a general scheme applicable to all acyl peroxides.

C. Preparation and Properties of Various Acyl Peroxides

All of the peroxides used in this thesis, with the exception of benzoyl peroxide which was commercially available, were prepared by the reaction of the appropriate acid chloride with sodium peroxide in ethyl ether containing a few drops of water.

$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl + Na_2O_2 \xrightarrow[H_2O]{\text{ether}} R\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}R + NaCl$$

In those cases where R in the above equation was cyclohexyl, cycloheptyl, cyclopentylcarbinyl, and cyclohexylacetyl, the peroxides were solids when stored in the freezer, but liquified at room temperature. All of the others, except biscyclopropanoformyl peroxide, were clear colorless oils even at the temperature of the freezer. Biscyclopropanoformyl peroxide was a white crystalline material which melted at 79.8-80.5°. Its crystalline character and unusual thermal stability allowed it to be purified by recrystallization from pentane before use.

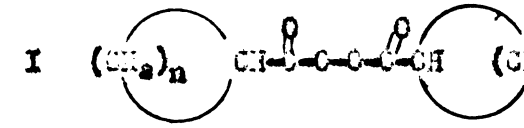
In the cases of biscyclohexanoformyl, biscycloheptanoformyl, and biscyclopropaneacetyl peroxides, the original preparations were found to contain small portions of the corresponding ester. This was corrected for in the subsequent kinetic determinations and product analyses. In those cases where no ester could be detected in the peroxide, and where the peroxide still was not of 100% purity, as determined by iodometric

titration, it was probable that small amounts of solvent (ether) remained. The reaction mixtures, in which the appropriate peroxides were formed, were invariably basic to litmus at the conclusion of the reaction; organic acids were therefore not contaminants.

For both quantitative product analyses and kinetic determinations, the original peroxide concentrations were corrected for impurities by iodimetric analyses. Often, product analyses and kinetic determinations were performed on separately prepared batches of the various peroxides; the results were generally in very good agreement.

D. Products of the Decomposition of Some Diacyl Peroxides

Two classes of diacyl peroxides were studied. These may be represented by the following general formulas.



I $\quad n = 2\text{-}6$

II $\quad n = 2\text{-}5$

In all cases, the decompositions were performed in dilute carbon tetrachloride solution. In the light of the work of Bartlett and Weiss (page 80), it was felt that this eliminated induced decomposition. A check experiment on the kinetics in the presence of iodine confirmed this, and will be discussed in the section on kinetics.

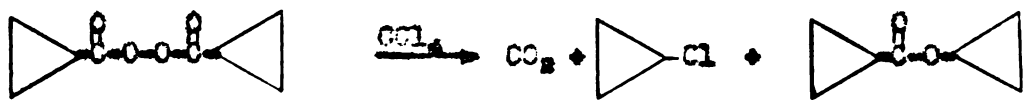
For each of the above structures, the products were examined in detail (qualitatively and quantitatively) when n was 2 and 5. For other

values of n, the identity of the products was established, and the approximate ratios of the principal products was noted.

In reference to the general formula (I), when n = 2 the products were cyclopropyl chloride, carbon dioxide, cyclopropyl cyclopropanecarboxylate, cyclopropanecarboxylic acid, and phosgene. Based upon the decomposition of one mole of bicyclopropanaformyl peroxide, the number of moles, on an average, of each of those products was as follows:

Product	Moles
carbon dioxide	1.62
cyclopropyl chloride	1.33
cyclopropyl cyclopropanecarboxylate	0.21
cyclopropanecarboxylic acid	0.096
phosgene	trace

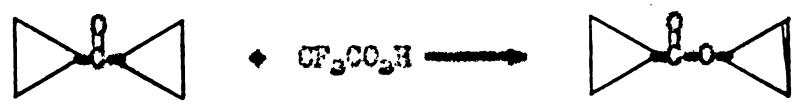
It should be pointed out that in two separate experiments 91-91% of the peroxide decomposed was accounted for by the products shown. Further, it will be noted that there was obtained 67% of the theoretical amount of cyclopropyl chloride, and 21% of the theoretical quantity of cyclopropyl cyclopropanecarboxylate.



Small but measurable amounts of cyclopropanecarboxylic acid were also present (about 5% of the products). It will be noted that the total number of moles of carbon dioxide should be equal to the sum of the number of moles of chloride and ester produced. This was essentially the case. Phosgene was also a product; however, it was obtained in very small yield (less than 0.01 g.) and was definitely a minor constituent.

Hexachloroethane was also a major reaction product, but the amount was not quantitatively established, although attempts were made to do so. No olefin was detected in the infrared spectrum of the reaction mixture, nor in the spectra of the various trap contents. This is particularly noteworthy because it demonstrates that the cyclopropyl free radical retained its identity and did not rearrange to an allyl radical.

The identity of the products obtained in this case, and in those which will be discussed below, was established by an unambiguous synthesis of each, and then comparison of their infrared spectra. Thus, cyclopropyl chloride was produced by photochemical chlorination of cyclopropane, and its infrared spectrum was found to be identical with that of the chlorinated product from the peroxide decomposition. Cyclopropyl cyclopropanecarboxylate, a new compound, was prepared by the Baeyer-Villiger reaction of dicyclopropyl ketone with trifluoroperoxyacetic acid.



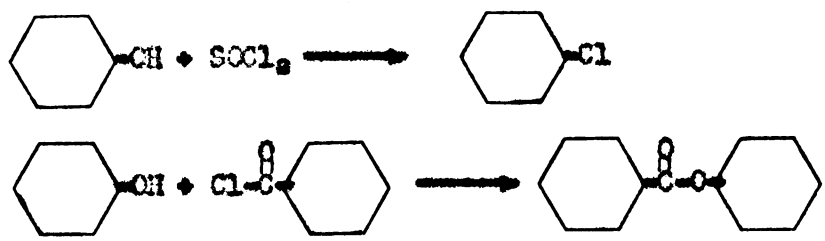
That this was the compound obtained is based upon its elemental analysis, saponification equivalent, and infrared spectrum. This material had an infrared spectrum which was identical with that of the ester obtained in the decomposition of the peroxide.

In the case of formula I where n = 5 (biscyclohexaneformyl peroxide), it was found that the products were very similar in type and quantity to those obtained in the decomposition of biscyclopropaneformyl peroxide. Cyclohexyl chloride and carbon dioxide were the major compounds identified.

The materials determined and their quantities were as follows (based upon the decomposition of one mole of peroxide):

Products	Moles
carbon dioxide	1.87
cyclohexyl chloride	1.53
cyclohexyl cyclohexanecarboxylate	0.232
cyclohexanecarboxylic acid	trace
phosgene	trace

In this case also, phosgene was a minor product. There was obtained 93.5% of the theoretical amount of carbon dioxide, and 76.5% of the theoretical amount of cyclohexyl chloride. The total quantities of ester and chloride are about equal to the amount of carbon dioxide detected. A small amount of cyclohexanecarboxylic acid was present, but not in sufficient quantity to measure reliably via infrared. Hexachloroethane was also a product, but its quantity was not established. The products obtained were once again established by unambiguous synthesis followed by comparison of the infrared spectra of the known materials with those obtained from the peroxide decomposition.



In this particular instance, the products isolated accounted for 95% of the peroxide decomposed.

In reference to general formula (II), the bisalicyclicacetyl peroxides, the products when n = 2 were cyclopropylcarbinyl cyclopropaneacetate, carbon dioxide, cyclopropaneacetic acid, and phosgene. The amounts of these materials obtained from the decomposition of one mole of peroxide were as follows:

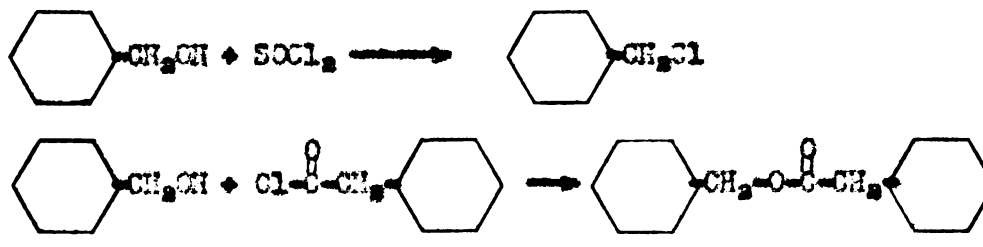
Compound	Moles
carbon dioxide	0.88
cyclopropylcarbinyl cyclopropaneacetate	0.85
cyclopropaneacetic acid	0.065
phosgene	0.001

It will be noted that only 44% of the theoretical amount of carbon dioxide was obtained. However, 85% of the theoretical ester was found, and the quantity of carbon dioxide evolved and the amount of ester found corresponded very well. About 5% of the products obtained was cyclopropaneacetic acid. No olefin could be detected, either in the reaction mixture, or in the various traps situated in the absorption train. Thus, if a cyclopropylcarbinyl radical was formed, it did not rearrange to a butenyl radical. The material isolated accounted for 85% of the peroxide decomposed. It should further be emphasized that this particular case was unique in that no chlorinated product was detected. Careful fractionation of the reaction mixture (approximately 80% was distilled) failed to yield any product which showed a carbon-hydrogen band in the infrared. Similarly, none was found in the various traps. Thus, it was decided that cyclopropylcarbinyl chloride (b.p. 87°) was not a product. The compounds that were obtained were again established by synthesis and direct comparison of infrared spectra.

In the case of formula II where n = 5, (biscyclohexaneacetyl peroxide) the products obtained were similar in type and quantity to those obtained from the decomposition of biscyclohexaneformyl peroxide. Thus, the following materials and their quantities were found from the decomposition of one mole of peroxide:

Compound	Moles
carbon dioxide	1.77
cyclohexylcarbinyl chloride	1.32
cyclohexylcarbinyl cyclohexanecarboxylate	0.30
cyclohexaneacetic acid	0.0125

These products accounted for 91% of the peroxide. It will be noted that 89% of the theoretical carbon dioxide and 66% of the theoretical cyclohexylcarbinyl chloride was obtained. The ester accounted for 30% of the products. Phosgene was again obtained in very small quantity. These products were established in a manner similar to those described previously for the other peroxides. The difference in the nature of the products produced when n = 5 and when n = 2 is striking.



The decomposition of benzoyl peroxide in dilute carbon tetrachloride solution was also studied. Surprising as it may seem, despite the large

volume of literature on the decomposition of benzoyl peroxide, no quantitative study of the products from non-induced decomposition in carbon tetrachloride has been reported. The products and their quantities were found to be as follows (based on the decomposition of one mole of peroxide):

Compound	Moles
carbon dioxide	1.725
chlorobenzene	1.271
phenyl benzoate	0.295
benzoic acid	0.015

These substances account for 92% of the peroxide. The amounts of chlorobenzene and carbon dioxide were 64% and 86.5% respectively. The ester accounted for 25.5% of the products. Phosgene was also present, but again in trace quantities. It will also be noted that the amount of benzoic acid obtained was small. The quantity of chloride and ester agrees reasonably well with the amount of carbon dioxide. The products were established as before (i.e., synthesis and comparison of the infrared spectra).

Chlorobenzene was commercially available. Phenyl benzoate was prepared by esterification of phenol and benzoyl chloride in a basic medium.

When biscyclopropaneformyl peroxide was decomposed in carbon tetrachloride containing an excess of iodine, the principal product was cyclopropyl iodide (isolated in 66% yield, but undoubtedly produced in higher yield). Other organic products present in minor quantity were cyclopropyl chloride, cyclopropyl cyclopropanecarboxylate and cyclopropanecarboxylic acid. The structure of the iodide was established by infrared (no double bond), elemental analysis, and preparation of the Grignard

reagent which was carbonated to cyclopropanecarboxylic acid.

Unlike benzoyl peroxide, which Kharasch (6) found to give a quantitative yield of benzoic acid when decomposed in carbon tetrachloride containing iodine and water, bicyclopropaneformyl peroxide did not give a quantitative yield of cyclopropanecarboxylic acid. The quantity of acid was, however, considerably increased at the expense of cyclopropyl iodide. The results were as follows (based upon the decomposition of one mole of peroxide):

Compound	Moles
cyclopropyl iodide	0.71
cyclopropanecarboxylic acid	0.62
cyclopropyl cyclopropanecarboxylate	0.04

Therefore, 45% of the theoretical amount of iodide, and 41% of the theoretical amount of acid was obtained. Approximately 4% of the product was attributable to ester. Since these reactions were carried out in sealed tubes, analysis for carbon dioxide was not attempted. Phosgene was also present; however, its amount was again small.

In the cases of the other bisalicyclicformyl and acetyl peroxides, quantitative product analyses were not performed. However, it was qualitatively established that the major product was the chloride corresponding to the alkyl radical formed by decomposition of the appropriate peroxide. This premise is based upon the fact that a considerable amount of carbon dioxide was evolved when these materials decomposed. Furthermore, at the conclusion of each kinetic experiment (discussed in the following section) an infrared spectrum was run on the reaction mixture. The ester

and acid carbonyl bands were present but small in comparison with the O-H stretching bands. This implies that the principal organic product was neither the ester nor the acid, but the alkyl halide.

Thus, it was found that in every case studied, except one, the major products from the spontaneous decomposition of the various acyl peroxides were carbon dioxide and alkyl chloride. The one exception, that of biscyclopropaneacetyl peroxide, in which the corresponding ester was predominately formed, was somewhat analogous to the case of biphenylacetyl peroxide reported by Bartlett and Leffler (71). They found the following products from the decomposition of one mole of peroxide:

Compound	Moles
benzyl chloride	0
benzyl phenylacetate	0.18

E. Kinetics of the Decomposition of Various Acyl Peroxides

All kinetic determinations were performed in dilute carbon tetrachloride solutions, the molarity of peroxide ranging from 0.01-0.1. The decompositions followed the first order kinetic equation:

$$\frac{-dP}{dt} = k_d (P),$$

which upon integration gives

$$\log (P) = -\frac{k_d}{2.3} t + \log (P_o)$$

(P) = concentration of peroxide at time t,

(P_o) = initial concentration of peroxide

k_d = first order rate constant.

In practice, the rate of disappearance of peroxide was followed by quantitative infrared, using the band at 5.65 microns. An example of the procedure is given in Figure 7. In every case, the base lines were freshly established before each series of determinations. The rate constant, k_d, was then calculated from the least squares slope of a plot of log [P] versus t (see Figures 8 and 9 for typical plots).

$$k_d = -2.3 \text{ slope}$$

Activation energies were calculated via the integrated Arrhenius equation:

$$\log k_d = -\frac{E_a}{2.3R} \frac{1}{T} + Z$$

The plots of log k_d vs 1/T for the various peroxides appear in Figures 11 to 19 in the Appendix. In each case, the activation energy was calculated from the least squares slope of the plot.

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

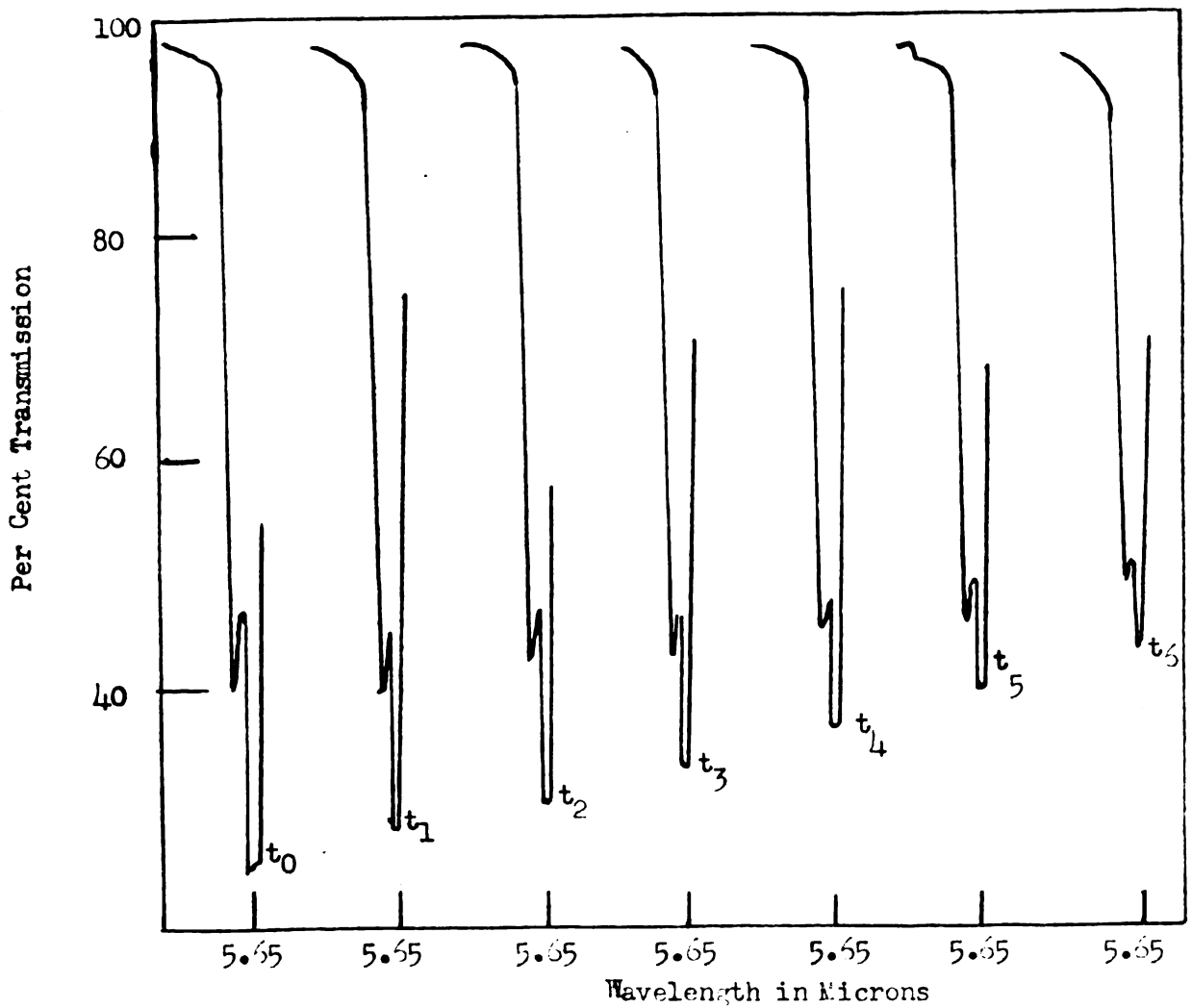
$$R = 1.987 \text{ calories degree}^{-1} \text{ mole}^{-1}$$

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

$$\triangle H^* = E_a - RT$$

The entropy of activation, $\triangle S^*$, was calculated from the Eyring equation (32).

Figure 7. Quantitative Infrared Spectra used in Determining the Kinetics of Decomposition of Biscyclohexaneacetyl Peroxide at 75° C.



t_0 = 0 min.
t_1 = 15 min.
t_2 = 30 min.
t_3 = 45 min.
t_4 = 60 min.
t_5 = 75 min.
t_6 = 90 min.

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

or $$\Delta S^* = 2.3R \log \frac{k_d h}{k_B T} + \frac{\Delta H^*}{T}$$

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

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

The various rate constants are listed in Tables 15, 16, and 17. The activation energies, enthalpies, and entropies for the various peroxides are listed in Table 18.

The rate constants show that in the case of the bis(alicyclicformyl) peroxides there was a steady increase in the rate of decomposition as the number of ring carbons increased. However, it is evident that the rates began to level off in the range C_8-C_9 (see Figure 10). On the other hand, the series of bisalicyclicacetyl peroxides showed an amazingly fast rate of decomposition for biscyclopropaneacetyl peroxide, and a very slow, nearly constant rate for the C_4-C_8 substituted peroxides. It is evident from Tables 17 and 18 that the rates seem to be somewhat dependent upon the activation energies. Especially striking is the fact that there are about seven kilocalories per mole difference between biscyclopropaneformyl peroxide and biscyclopropaneacetyl peroxide, the slowest and fastest decomposing materials, respectively. Although not as striking as the above comparison, careful examination of the results in Table 18 shows that there is a general, if slow, decline in activation energies as the rate of decomposition increased. The activation energy for the decomposition of biscyclopropaneformyl peroxide (29 kilocalories

TABLE 15

KINETIC RATE CONSTANTS FOR THE DECOMPOSITION OF SOME CYCLOALKANEFORMYL PEROXIDES

$(RCO_2)_2$ R	Temperature °C.	k_1 sec.$^{-1}$ x 10^5
cyclopropyl	63	0.255
cyclopropyl	70	0.481**
cyclopropyl	70	0.506***
cyclopropyl	75	1.19
cyclobutyl	65	5.81
cyclobutyl	70	8.33**
cyclobutyl	75	15.2
cyclopentyl	40	1.25
cyclopentyl	45	2.69
cyclopentyl	50	4.91
cyclopentyl	55	7.47**
cyclohexyl	35	2.57
cyclohexyl	40	4.97**
cyclohexyl	45	10.32
cycloheptyl	35	8.05
cycloheptyl	40	15.2**
cycloheptyl	45	18.4
phenyl*	70	1.12*

*Although not a cycloalkaneformyl peroxide, benzoyl peroxide was studied and is listed for comparison purposes.

**The average of two runs performed upon different preparations of peroxide. For a complete compilation of all the kinetic data, reference should be made to the Appendix of this thesis.

***This rate constant was determined with excess iodine present.

TABLE 16

KINETIC RATE CONSTANTS FOR THE DECOMPOSITION OF SOME CYCLOALKANEACETYL PEROXIDES

$(RCH_2CO_2)_2$	Temperature °C.	k_1 sec.$^{-1}$ x 10^5
cyclopropyl	14	23.6
cyclopropyl	25	102.1*
cyclobutyl	65	1.56
cyclobutyl	70	2.0*
cyclobutyl	75	3.96
cyclopentyl	65	1.57
cyclopentyl	70	3.12*
cyclopentyl	75	4.91
cyclohexyl	60	1.43
cyclohexyl	70	2.87*
cyclohexyl	75	3.78

*The average of two runs performed upon different preparations of peroxide. For a complete compilation of all the kinetic data reference should be made to the Appendix of this thesis.

Figure 8. Plot of log (P) versus t for the Decomposition of Bis-cyclopentaneformyl Peroxide at 45°, 50°, and 55° C.

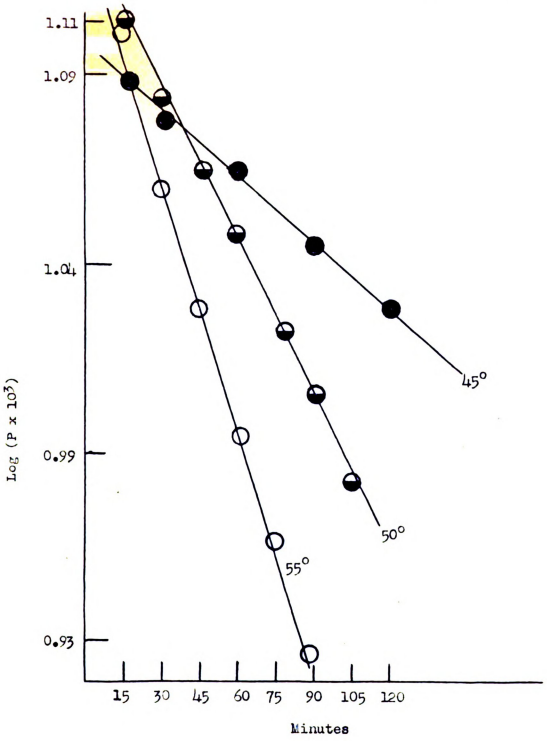


Figure 9. Plot of log (P) versus t for the Decomposition of Biscyclobutaneacetyl Peroxide at 65°, 70°, and 75° C.

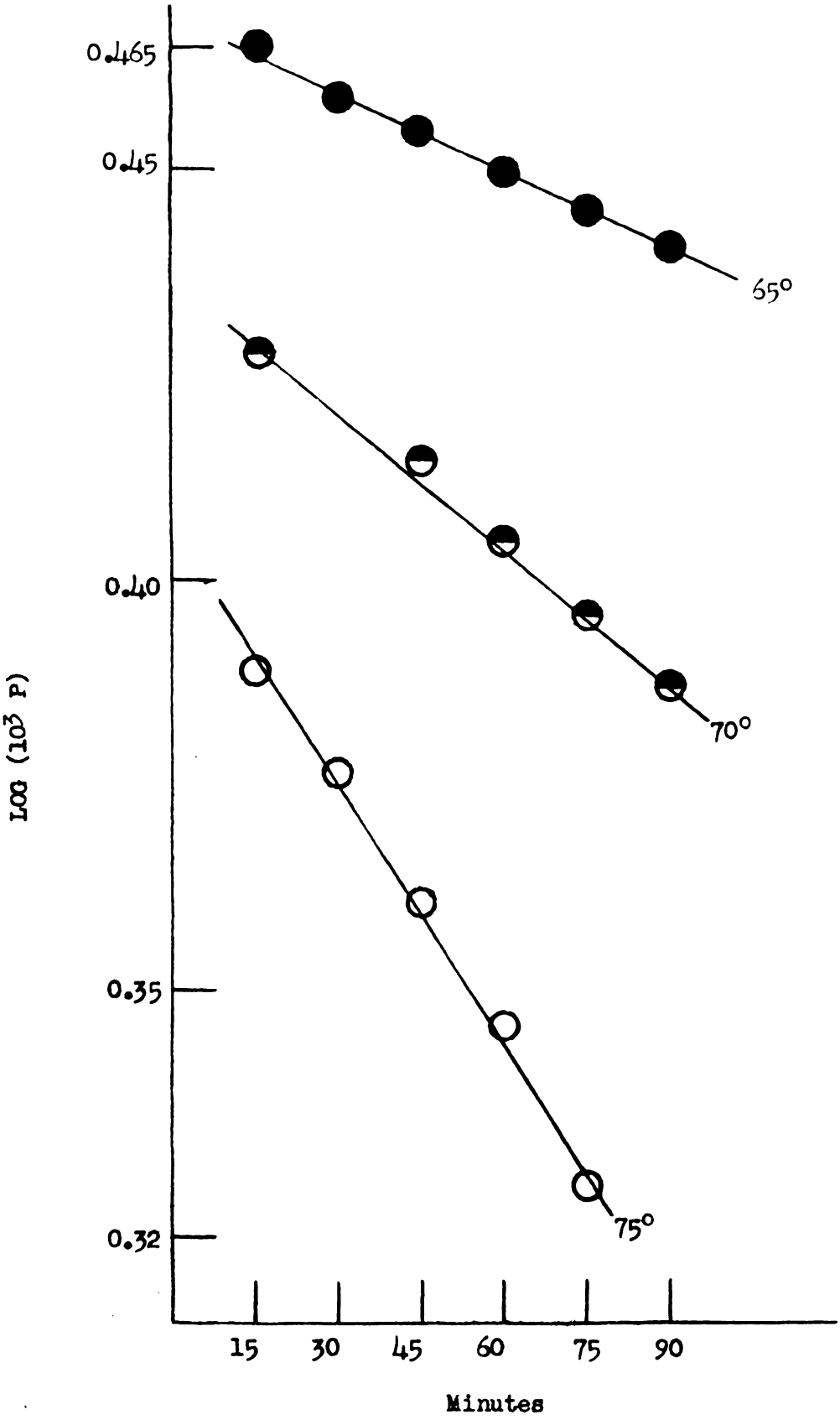


TABLE 17

KINETIC RATE CONSTANTS FOR THE DECOMPOSITION OF VARIOUS ACYL PEROXIDES AT 70° C.

$(RCO_2)_2$ R	$k_1 \times 10^{-5}$ sec.$^{-1}$
cyclopropane	0.49
benzene	1.12
cyclobutane	8.3
cyclopentane	35.5*
cyclohexane	67.5**
cycloheptane	79.5**
cyclopropylcarbinyl	1200.0***
cyclopentylcarbinyl	3.12
cyclobutylcarbinyl	2.0
cyclohexylcarbinyl	2.87

*Extrapolated value from the Arrhenius equation; actual rates were measured at 40-55°.

**Extrapolated value from the Arrhenius equation; actual rates were measured at 35-40°.

***Extrapolated value from the Arrhenius equation; actual rates were measured at 14-25°.

TABLE 18

ACTIVATION ENERGIES, ENTHALPIES, AND ENTROPIES FOR VARIOUS ACYL PEROXIDES

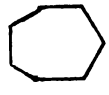
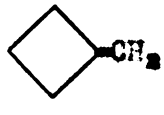
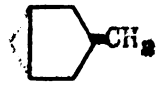
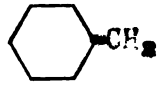
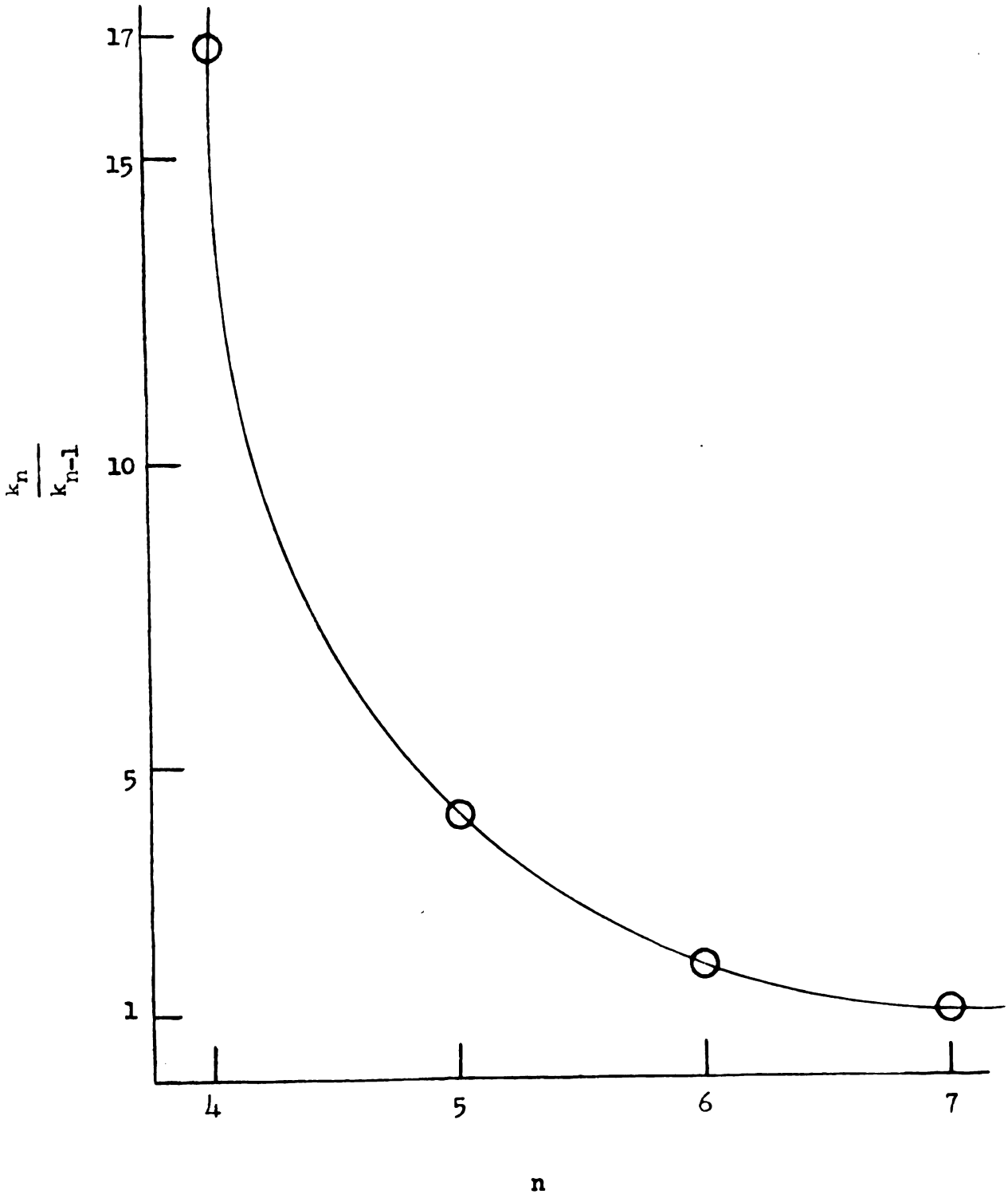
Peroxide $(RCO_2)_2$ R	Ea	H^*	S^*
	29.0 ± 0.9	28.3	-5.7 ± 2
	27.3 ± 0.4	26.6	-4.2 ± 1
	25.6 ± 1.0	25.0	-5.4 ± 2
	26.7 ± 1.1	26.1	-3.1 ± 0.8
	25.4 ± 0.4	24.8	-0.4 ± 1
	22.0 ± 1.5	21.4	-4.6 ± 1
	26.4 ± 1.0	25.7	-9.9 ± 0.8
	27.0 ± 1.1	26.3	-8.8 ± 2
	26.4 ± 0.8	25.7	-10.3 ± 2

Figure 10. Plot of $\frac{k_n}{k_{n-1}}$ versus n (n = number of Carbon Atoms in the Ring) for Several Biscycloalkaneformyl Peroxides.



per mole), is about the same as that for the decomposition of benzoyl peroxide (71). Also, the activation energy for the decomposition of cyclopropaneacetyl peroxide compares well in magnitude with that of bisphenylacetyl peroxide reported by Bartlett (71), the values being 22 and 23 kilocalories per mole respectively. Bartlett also found that bisphenylacetyl peroxide decomposed as fast at zero as benzoyl peroxide did at 70°. The situation is apparently the same when biscyclopropaneformyl and biscyclopropaneacetyl peroxides are compared. In the same study, Bartlett found that bisphenylacetyl peroxide underwent a hydrogen ion induced decomposition along with the free radical reaction. In that particular system, phenylacetic acid was a decomposition product which furnished the hydrogen ion; i.e., it was an autocatalyzed system. However, analysis of the rate data showed that the magnitude of the ionic reaction was very small compared to the free radical reaction. Since cyclopropaneacetic acid was one of the decomposition products formed in this study, it is possible that a similar type of ionic reaction may have occurred. No attempt was made to analyze the data for this; however, it is felt that the magnitude of this reaction was not important when compared with that of the free radical reaction.

It was interesting to find that the entropy of activation values were negative, and not particularly large. Only in the cases of biscyclobutaneacetyl, biscyclopentaneacetyl, and biscyclohexaneacetyl peroxides did the values approach -10 entropy units. As will be discussed more fully in the section on mechanism, the larger negative values

obtained in those cases may be associated with the relative size of certain solvent cages which may be important.

As can be seen in Table 17, biscyclopropaneformyl peroxide decomposed only one-half as fast as benzoyl peroxide. The fact that its rate of decomposition in the presence of iodine was essentially the same as it was in its absence, showed that induced decomposition was not taking place. If it had occurred, the very efficient radical scavenger, iodine, would have caused the rate to be slower.

There is a striking similarity between the rates of decomposition of the bisalicyclicformyl peroxides and the rates of abstraction of hydrogen atoms from alicyclic hydrocarbons reported by Trotman-Dickenson and Steacie (page 68). Further, the similarity between the rates of decomposition of the bisalicyclicacetyl peroxides and the decomposition of various alicyclic substituted bisazonitriles reported by Overberger (page 6) is evident. These points will be discussed more fully in the section on mechanism.

F. Proposed Mechanisms for the Decomposition of the Various Acyl Peroxides

In the study of the decomposition of variously substituted benzoyl peroxides it was suggested that electrostatic repulsion between the benzoate groups caused the peroxides to decompose, and that the stability of the subsequently formed radicals had no influence on the rate (38). However, this suggestion predicts that other alicyclic acyl peroxides

should decompose at very nearly the same rate. The kinetic results listed in this thesis show that this is not the case.

It was apparent from the decomposition rates of the bisalicyclicformyl peroxides that they generally tended to follow the order of hydrogen atom abstraction found by Trotman-Dickenson and Steacie (page 68). The only exception was that of biscyclopentaneformyl peroxide, which decomposed more slowly than biscyclohexaneformyl peroxide. Also, there was a definite parallel trend among the bisalicyclicacetyl peroxides when compared to the rates of decomposition of various bis-azonitriles investigated by Overberger (page 6).

The activation energies showed sufficient divergence to be important. This would not have been expected if the rates were controlled solely by fission of the oxygen-oxygen bond.

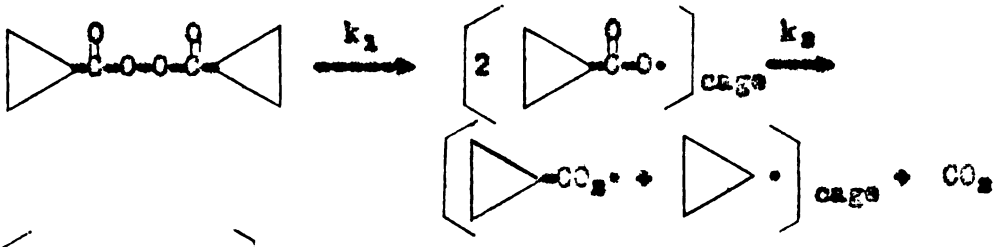
It is true that inductive effects of groups attached to the -C-O- bond would influence the energy required for its fission. The cyclopropyl group is electron-withdrawing with respect to other alkyl groups (76), and would be expected to slow down the rate of decomposition. The effect, however, should be a small one (even para-nitro groups in benzoyl peroxide only decreased its rate of decomposition by about one-half), whereas, in fact, the difference between a cyclopropyl and a cyclohexyl group was some two powers of ten.

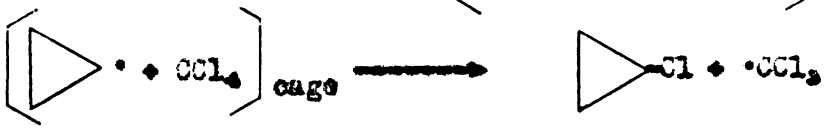
It would appear, therefore, that the rate of decomposition is controlled, in part at least, by another process as well; an attractive possibility is the step in which the alkyl radical is formed.

$$R\text{-}C(=O)\text{-}O\text{-}O\text{-}C(=O)\text{-}R \xrightarrow{k_1} 2RCO_2\cdot \xrightarrow{k_2} RCO_2\cdot + R\cdot + CO_2$$

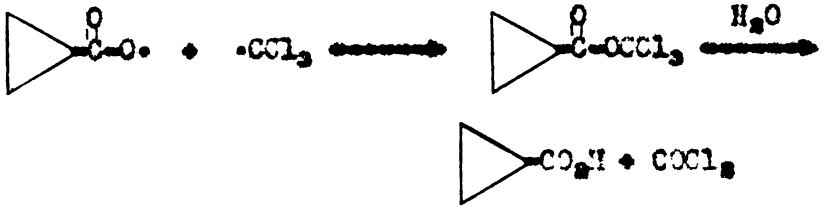
In other words, neither k_1 nor k_2 above would be small enough to exclude the other from helping to determine the rate. The experimentally measured rate constant k_d would be the sum of k_1 and k_2.

The following series of equations was formulated for biscyclopropaneformyl peroxide to explain the rate data and the products.

(1) 

(2) 

(3) 

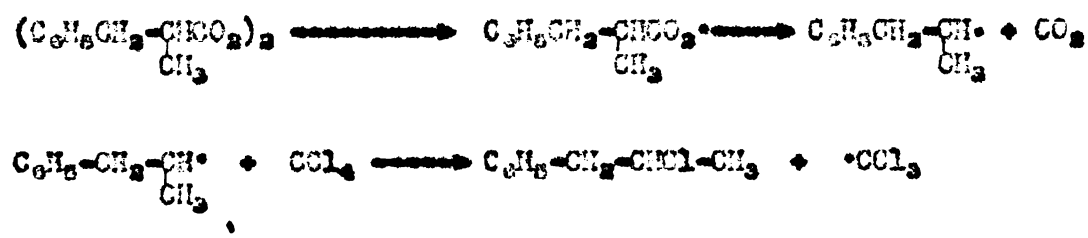
(4) 

(5) $\cdot CCl_2 + \cdot CCl_3 \longrightarrow C_2Cl_5$

No induced decomposition steps are included in the above schema. Bafar and Wais (77), in a recent paper, found no evidence for induced decomposition in the fission of bis-delta-phenylvaleryl peroxide in concentrations as high as 0.5 molar in carbon tetrachloride solutions since the peroxide

concentrations in this thesis were usually on the order of 0.01-0.02 molar, it is considered improbable that induced decomposition occurred. Both steps depicted in equation (1) are thought to determine the rate of decomposition. Equation (2) has two implications; first, that a cyclopropyl radical was produced (which led to cyclopropyl chloride) and second that this radical did not rearrange to an allyl radical. The former postulate is based upon two arguments. First, it is felt that the formation of a cyclopropyl radical, a difficult process because of I-strain, contributed to the slow rate of decomposition. Cyclopropyl chloride might arise from a reaction such as

which does not require the discrete formation of a cyclopropyl radical. Bellar and Weis (78) recently demonstrated the unlikelihood of such a process in acyl peroxide decompositions. They decomposed optically active bis-beta-phenylisobutyryl peroxide in carbon tetrachloride and found that the products were very similar in kind and quantity to those obtained from the decomposition of bis-delta-phenylvaleryl peroxide. Furthermore, since the 2-chloro-1-phenylpropane obtained was optically inactive, whereas the ester showed 75% retention of activity, the chloride presumably had been formed by reaction of hydrocarbon radical with carbon tetrachloride rather than by the reaction of an acyloxy radical with carbon tetrachloride.



It is considered that such evidence would also apply to the present system, and that cyclopropyl chloride, therefore, arose from a reaction such as depicted in equation (2). The fact that the solution was very dilute makes the idea of a radical in a solvent cage plausible.

Reaction (3) which leads to ester, may or may not occur in a solvent cage. The fact that optically active peroxides give ester in which the alkyl portion has retained considerable activity (79,80) suggests that this step occurs predominantly within a solvent cage, possibly by a concerted mechanism.

The small amounts of acid detected probably arose from a reaction such as (4). Although efforts were made to keep the system anhydrous, traces of moisture were probably present, and it would take only a very small amount of water to yield the quantity of acid produced. This does not completely rule out the possibility that acid arose by means of the acyloxy radical extracting a hydrogen atom from a cyclopropane ring. But this process is particularly difficult, and probably did not occur.

It follows that a mechanism similar to that postulated for bis-cyclopropaneformyl peroxide would fit the data for all of the peroxides (except biscyclopropaneacetyl peroxide, which will be discussed separately below).

Although considerably faster than biscyclopropaneformyl peroxide, the cyclobutane analog is nevertheless much slower than the higher members of the series. This can be ascribed to I-strain in the four-membered ring radical which, although not as great as in a three-membered ring radical, may still be significant. On the basis of non-bonded interactions between hydrogen atoms, one probably would have expected the biscyclopentaneformyl peroxide (and the corresponding cycloheptyl compound) to decompose more rapidly than the cyclohexyl analog (31). The reason for the slower rate of the cyclopentyl compound is not apparent, but it should be noted that all three of these peroxides decompose at comparable rates, all of which are appreciably faster than the smaller ring members of the series.

Biscyclobutaneacetyl peroxide, and higher members of this series all decompose at about the same rate which, however, was appreciably slower than the corresponding biscycloalkaneformyl peroxides. This may be due simply to the fact that primary alkyl, rather than secondary alkyl radicals are being produced. Secondary alkyl radicals are more stable than primary alkyl radicals, and are therefore formed more easily. This provides another argument for including the formation of the alkyl radical as one of two rate-determining steps.

In the cases of biscyclobutaneacetyl, biscyclopentaneacetyl, and biscyclohexaneacetyl peroxides it was found that the entropy was somewhat more negative, than for the other peroxides. It may well be that this is due, in part at least, to the fact that these comparatively bulky

substances would have a larger solvent cage, hence a greater ordering of the system associated with them.

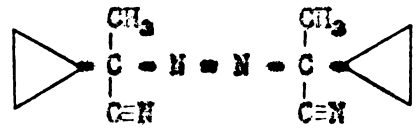
The behavior of biscyclopropaneacetyl peroxide was truly remarkable. One has to account for the extremely rapid decomposition rate, and also for the fact that the product was principally the ester and that no compound corresponding to removal of a chlorine atom from the solvent was encountered. The activation energy for this decomposition was some four kilocalories per mole less than the other peroxides (and seven kilocalories per mole less than biscyclopropaneformyl peroxide). A satisfactory mechanism must account for all these facts.

The scheme written above for the other peroxides can readily explain these results provided one allows that the cyclopropylcarbinyl free radical can be stabilized by resonance, perhaps in a fashion similar to that already demonstrated for the cyclopropylcarbinyl carbonium ion (see page 4). The first steps are identical with those shown in the previous scheme.

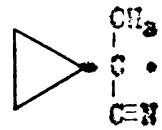
$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}R \xrightarrow{k_1} [2RC\text{-}O\cdot]_{cage} \xrightarrow{k_2} [RCO_2\cdot + R\cdot + CO_2]_{cage}$$

The second of these steps is particularly favorable because of stabilization of R· by resonance. This accounts for the low activation energy. It is suggested that R· (that is, the cyclopropylcarbinyl radical) is sufficiently stabilized so that it does not abstract a chlorine atom from the surrounding carbon tetrachloride molecules. Its only recourse, then, is to combine with acyloxy radicals (an energetically favorable

process) in the cage to produce ester. This mechanism accounts for all the observed facts. It should be noted that Overberger (14) has explained the rapid decomposition of



by a similar stabilization of the

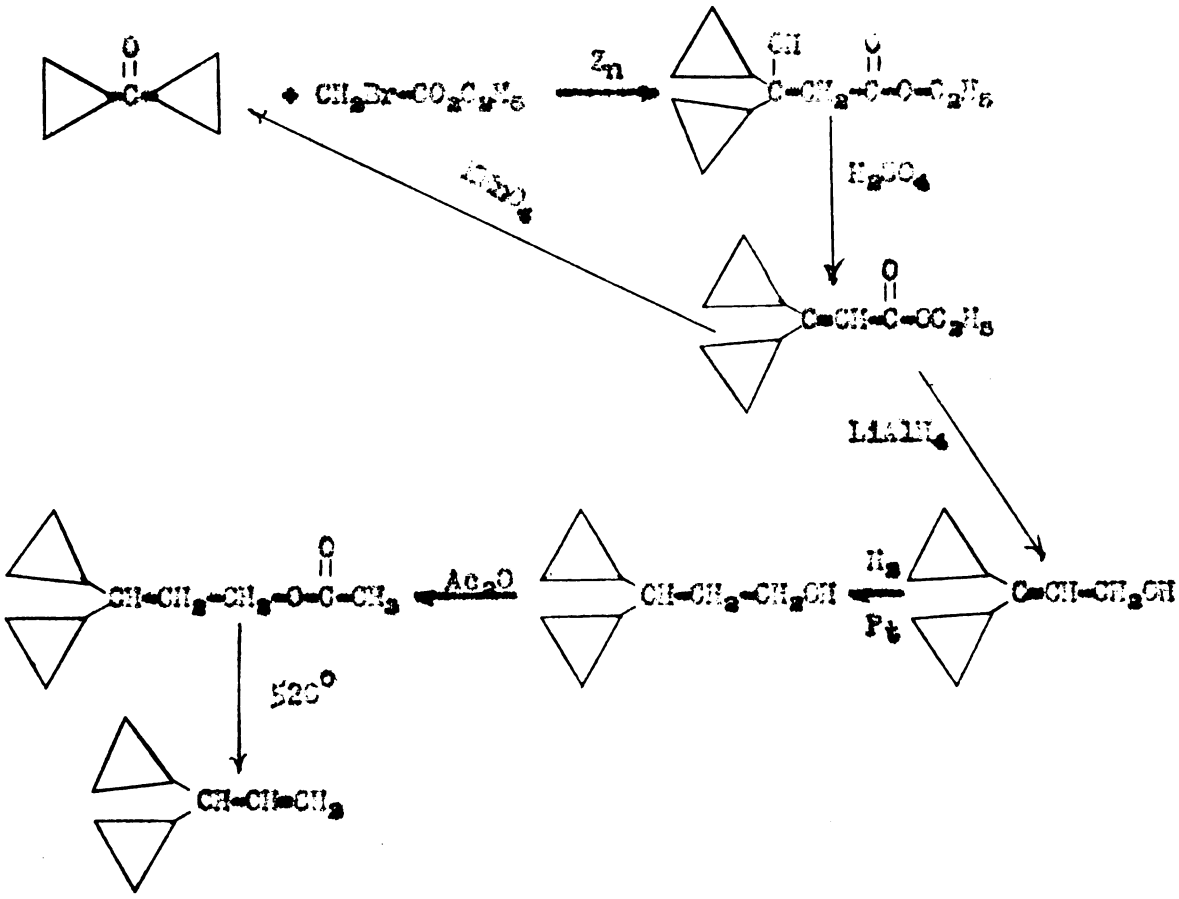


radical.

C. Miscellaneous Experiments

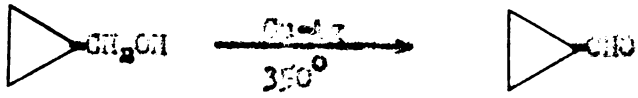
Certain of these experiments were directed toward the synthesis of dicyclopropylacetic acid, the intent being to study the decomposition of its peroxide. The radical thus produced (dicyclopropylcarbinyl radical) would be the same as that initially formed in the chlorination of dicyclopropylmethane. The synthesis was side-tracked shortly before its conclusion because simpler systems (already discussed) seemed worthy of prior investigation. The synthesis, as far as it was carried, will be discussed here.

Dicyclopropyl ketone condensed with ethyl bromoacetate in a Reformatsky reaction to produce ethyl β,β-dicyclopropyl-β-hydroxypropionate in 58.7% yield. Dehydration (90%), reduction with lithium aluminum hydride (84%) and hydrogenation over platinum led to



3,3-dicyclopropyl-1-propanol. This was converted to the acetate (91%) which, when pyrolyzed at 520° gave a 75% yield of what was presumed to be 3,3-dicyclopropyl-1-propene, as shown in the scheme. This olefin, on oxidation should furnish the desired dicyclopropylacetic acid.

A new synthesis of cyclopropanecarboxaldehyde was devised; catalytic oxidation of cyclopropylcarbinol over silver-copper on pumice with air gave good yields of the aldehyde.



This method is more conducive to large scale preparations of the aldehyde than those given in the literature (46).

An interesting oxidation of a side-chain on the cyclopropane ring was observed when it was found that β-cyclopropylethanol (from cyclopropyl lithium and ethylene oxide) was oxidized by neutral permanganate to a mixture of cyclopropaneacetic and cyclopropanecarboxylic acids.

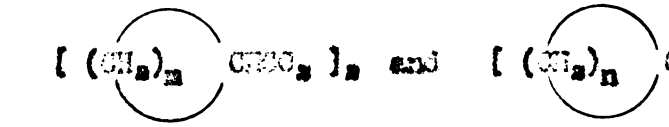
Finally, dicyclopropylmethylcarbinol was shown to dehydrate readily to 1,1-dicyclopropylethylene with sulfuric acid.

Attempts to make the epoxide with perbenzoic acid gave inconclusive results. It is interesting that the dicyclopropylcarbonium ion, which presumably is an intermediate in the dehydration, did not give rearranged product.

SUMMARY

1. The products from the monochlorination of isopropylcyclopropane and dicyclopropylmethane were found to be 2-cyclopropyl-1-chloropropane and 1-cyclopropyl-4-chlorobutene-1, respectively. Explanations for these somewhat unexpected products were offered.

2. Two new series of acyl peroxides were prepared which may be represented by the formulas:



where n = 2-7 and n = 2-6.

3. The products and rates of decomposition for the described acyl peroxides were determined. All of the decompositions were performed in dilute solutions in carbon tetrachloride and followed strict first order kinetics. The principal products from $(RCO_2)_2$ in all cases but one were carbon dioxide, alkyl chloride (RCl), and lesser amounts of ester (RCO_2R) and acid (RCO_2H). Traces of phosgene were produced, and hexachloroethane was formed in large but undetermined quantities. When R was $-CH_2$, the ester was the major product (85%), and no RCl was detected. In all cases $\geq$ 90% of the peroxide was accounted for and R maintained its structural integrity. Authentic samples of the products were synthesized for comparison.

The relative rates of decomposition of the various peroxides at 70° in carbon tetrachloride were:

m =	2	3	4	5	6
k =	0.35	7.4	31.6	60.5	70.8
n =	2	3	4	5	
k =	1100	1.79	2.78	2.56	

where benzoyl peroxide has a value of 1.0. Rates were determined at at least three temperatures, and on duplicate samples. The activation energies for m = 3-6 and n = 3-5 were about 26 ± 1 kilocalories per mole. When m = 2, E^* was 29 kilocalories per mole, whereas when n = 2, it was only 22 kilocalories per mole.

4. The rates, products, and entropies and enthalpies of activation were all consistent with a mechanism which included the formation of an alkyl radical as one of two rate determining steps. The resonance energy of a cyclopropylcarbinyl radical appears to be significant.

5. Several new compounds were prepared in connection with the peroxide work. These were cyclopropyl iodide, cyclopropyl cyclopropanecarboxylate, cyclopropylcarbinyl cyclopropaneacetate, 2-cyclopropaneethanol, and cyclopropaneacetaldehyde.

6. Some miscellaneous reactions involving cyclopropyl substituted compounds were described. These included an improved synthesis of cyclopropanecarboxaldehyde, the preparation of 1,1-dicyclopropylethylene, ethyl 3,3-dicyclopropyl-3-hydroxypropionate, ethyl 3,3-dicyclopropylacrylate,

3,3-dicyclopropylallyl alcohol, 3,3-dicyclopropylpropanol-1, 3,3-dicyclopropylpropyl acetate, and 3,3-dicyclopropylpropane-1, all new compounds.

LITERATURE CITED

LITERATURE CITED

1. C. G. Bergstrom and S. Siegel, J. Am. Chem. Soc., 74, 145 (1952).
2. J. D. Roberts and V. C. Chambers, J. Am. Chem. Soc., 73, 5034 (1951).
3. H. C. Brown, R. S. Fletcher, and R. B. Johannesen, J. Am. Chem. Soc., 73, 212, (1951).
4. J. D. Roberts and P. H. Firestine, J. Am. Chem. Soc., 67, 1281 (1945).
5. H. B. Hass and H. Schecter, J. Am. Chem. Soc., 75, 1382 (1953).
6. J. D. Roberts and V. C. Chambers, J. Am. Chem. Soc., 73, 3176 (1951).
7. Fr. Fichter and H. Reeb, Helv. Chim. Acta, 6, 450 (1923).
8. J. N. Pitts and I. Norman, J. Am. Chem. Soc., 76, 4815 (1954).
9. J. D. Roberts and R. H. Mazur, J. Am. Chem. Soc., 73, 2509 (1951).
10. E. M. Kosower and S. Winstein, J. Am. Chem. Soc., 78, 4354 (1956).
11. A. Streitwieser, Jr., Chem. Revs., 56, 571 (1956).
12. J. M. Sandri, Ph. D. Thesis, Michigan State University, (1956).
13. J. D. Roberts and R. H. Mazur, J. Am. Chem. Soc., 73, 2509 (1951).
14. H. D. Brown and M. Borkowski, J. Am. Chem. Soc., 74, 1894 (1952).
15. C. G. Overberger et al., J. Am. Chem. Soc., 75, 2078 (1953).
16. K. N. Gaind and P. C. Guha, J. Ind. Chem. Soc., 11, 421 (1934).
17. A. C. Cope and E. M. Hancock, J. Am. Chem. Soc., 60, 2644 (1938).
18. H. Pines, W. Huntsman, and V. N. Ipatieff, J. Am. Chem. Soc., 62, 1197 (1947).
19. R. R. Umhoefer, Anal. Ed., Ind. and Eng. Chem., 15, 383 (1943).
20. E. H. Huntress, "Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, 1948, p. 1110.

21. H. C. Brown and R. S. Fletcher, J. Am. Chem. Soc., 71, 1845 (1949).

22. Huang Minlon, J. Am. Chem. Soc., 68, 2487 (1946).

23. "Organic Syntheses," Collective Volume III, John Wiley and Sons, Inc., New York, 1955, p. 221.

24. Ibid., p. 213.

25. Ibid., p. 119.

26. C. D. Nenitzescu and I. P. Cantuniari, Ber., 65, 811 (1932).

27. E. P. Kohler, J. Am. Chem. Soc., 61, 1057 (1939).

28. L. Ruzicka, Helv. Chim. Acta, 23, 395 (1945).

29. E. Haworth and W. H. Perkin, J. Chem. Soc., 65, 591 (1894).

30. H. Hart and J. M. Sandri, Chemistry and Industry, 1014 (1956).

31. R. R. Davies and Hurbert H. Hodgson, J. Chem. Soc., 282 (1943).

32. J. H. Turnbull and E. S. Wallis, J. Org. Chem., 21, 666 (1956).

33. A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., New York, 1948, p. 253.

34. N. V. Zelinsky, Ber., 41, 2629 (1908).

35. G. Crane, C. E. Boord, and A. L. Henne, J. Am. Chem. Soc., 67 1237 (1948).

36. O. Wallach, Ann., 353, 304 (1907).

37. C. G. Swain, W. H. Stockmayer, and J. T. Clarke, J. Am. Chem. Soc., 72, 5426 (1950).

38. W. D. Emmons and G. B. Lucas, J. Am. Chem. Soc., 77, 2287 (1955).

39. E. E. Royals, "Advanced Organic Chemistry," Prentice-Hall, Inc., New York, 1954, p. 666.

40. R. L. Shriner and R. C. Fuson, "Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, 1948, p. 133.

41. G. S. Hiers and R. Adams, J. Am. Chem. Soc., 48, 2392 (1926).

42. W. J. Hickinbotton, "Reactions of Organic Compounds," Longmans, Green and Company, 1950, p. 98.

43. L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Company, Boston, 1955, p. 299.

44. W. R. Brode, "Chemical Spectroscopy," John Wiley and Sons Inc., New York, 1943, p. 245.

45. L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Company, Boston, 1955, p. 293.

46. J. D. Roberts, J. Am. Chem. Soc., 73, 2959, (1951).

47. V. A. Slabey and P. H. Wise, Nat'l. Advisory Comm. Aeronautics, Tech. Note 2293 (1951).

48. H. B. Gottlieb, J. Am. Chem. Soc., 54, 748 (1932).

49. W. J. Dailey and R. Barclay, J. Org. Chem., 21, 328 (1956).

50. "Organic Syntheses," 24, 82 (1944).

51. "Organic Syntheses," Collective Volume I, John Wiley and Sons, Inc., New York, 1956, p. 431.

52. J. Stauff and H. J. Schumacher, Z. Elektrochem., 48, 271 (1942).

53. J. Stauff, Z. Elektrochem., 46, 570 (1942).

54. H. B. Hass and J. R. Marshall, Ind. Eng. Chem., 23, 352 (1931).

55. F. F. Rust and W. E. Vaughn, J. Org. Chem., 6, 479 (1941).

56. H. C. Brown and A. B. Ash, J. Am. Chem. Soc., 77, 4019 (1955).

57. G. A. Russell, J. Am. Chem. Soc., 72, 2977 (1957).

58. M. S. Kharasch and H. C. Brown, J. Am. Chem. Soc., 61, 3432 (1939).

59. J. D. Roberts and V. C. Chambers, J. Am. Chem. Soc., 73, 3176 (1951).

60. A. F. Trotman-Dickenson and E. W. R. Steacie, J. Chem. Phys., 19, 329 (1951).

61. J. R. McNesby and A. S. Gordon, J. Am. Chem. Soc., 72, 825 (1957).

62. H. Meerwein and K. van Emster, Ber., 53, 1815 (1920).

63. A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, 1954, p. 107.

64. M. Swarc, Chem. Revs., 47, 75 (1950).

65. J. E. Leffler, J. Am. Chem. Soc., 73, 3929 (1951).

66. G. Hammond, J. T. Rudesill, and F. J. Modic, J. Am. Chem. Soc., 73, 3929 (1951).

67. C. H. Hey and W. A. Waters, Chem. Revs., 21, 169 (1937).

68. K. Nozaki, and P. D. Bartlett, J. Am. Chem. Soc., 68, 1686 (1946).

69. G. Hammond and L. M. Soffer, J. Am. Chem. Soc., 72, 4711 (1950).

70. F. G. Edwards and F. R. Mayo, J. Am. Chem. Soc., 72, 1265 (1950).

71. P. D. Bartlett and J. E. Leffler, J. Am. Chem. Soc., 72, 3032 (1950).

72. J. E. Leffler, "The Reactive Intermediates of Organic Chemistry," Interscience Publishers, Inc., New York, 1956, p. 34.

73. A. V. Tobolsky and R. B. Mesrobian, loc. cit., p. 85.

74. D. DeTar and C. Weis, J. Am. Chem. Soc., 78, 4296 (1956).

75. A. V. Tobolsky and R. B. Mesrobian, loc. cit., p. 83.

76. T. L. Brown, H. Hart, and J. M. Sanderi, J. Phys. Chem., 61, 698 (1957).

77. D. DeTar and C. Weis, J. Am. Chem. Soc., 79, 3041 (1957).

78. D. DeTar and C. Weis, ibid., 3045 (1957).

79. M. S. Kharasch, J. Kuderna, and W. Nudenberg, J. Org. Chem., 19, 1283 (1954).

80. F. D. Greene, J. Am. Chem. Soc., 77, 4869 (1955).

81. P. B. D. de la Mare and P. W. Robertson, J. Chem. Soc., 279 (1943).

82. A. R. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, 1953, p. 95.

APPENDIX

TABLE 19

DECOMPOSITION OF BICYCLO[2.2.1]HEPTANE-2-CARBONYL PEROXIDE IN CARBON TETRACHLORIDE AT 63 ± 0.2°

I_0 = 18.85 cm. P = concentration (g./l)
a = 0.3473 P_m = concentration (molarity)
P_0 = 1.234 g./l = 7.26 x 10^{-3} molar t = time (hours)

Sample	I cm.	log I_0/I	P	$P_m \times 10^3$	log $P_m \times 10^3$	t
1	11.70	0.20712	1.193	7.02	0.846	5
2	11.90	0.19976	1.150	6.76	0.830	8.5
3	12.13	0.19145	1.101	6.48	0.812	17
4	12.31	0.18505	1.066	6.27	0.797	21
5	12.55	0.17667	1.017	5.98	0.777	27

k = 9.2 ± 0.5 x 10^{-3} hrs.$^{-1}$ = 2.56 ± 0.21 x 10^{-6} sec.$^{-1}$

TABLE 20

DECOMPOSITION OF BIS(TRICHLOROMETHANESULFENYL) PEROXIDE IN CARBON TETRACHLORIDE AT 70 ± 0.2° (I)

I_0 = 18.48 cm.
a = 0.3473
P_0 = 2.43 g./l = 1.43 x 10^{-2} molar

P = concentration (g./l)
P_n = concentration (molarity)
t = time (hours)

Sample	I cm.	log I_0/I	P	$P_n \times 10^2$	log $P_n \times 10^2$	t
1	7.31	0.40278	2.32	13.6	1.134	4
2	7.80	0.37461	2.16	12.7	1.104	7.5
3	8.18	0.35395	2.04	12.0	1.079	12.
4	8.52	0.33626	1.94	11.4	1.057	14
5	9.25	0.30056	1.73	10.2	1.0086	21
6	10.53	0.24221	1.41	8.3	0.919	28
7	10.90	0.22927	1.32	7.8	0.892	33.25

k = 1.77 ± 0.11 x 10^{-2} hrs.$^{-1}$ = 4.92 ± 0.30 x 10^{-6} sec.$^{-1}$

TABLE 21

DECOMPOSITION OF BISCYCLOPROPANECARBONYL PEROXIDE IN CARBON TETRACHLORIDE AT 70 ± 0.2° (II)

I_0 = 18.79 cm.
a = 0.3473
P_0 = 2.95 g./l = 1.735 x 10^{-2} molar

P = concentration (g./l)
P_n = concentration (molarity)
t = time (hours)

Sample	I cm.	log I_0/I	P	$P_n x 10^2$	log $P_n x 10^2$	t
1	6.34	0.47184	2.72	16.00 15.90	1.204	4
2	6.80	0.44142	2.54	14.94	1.174	8
3	8.14	0.36331	2.09	12.29	1.0896	18.5
4	8.90	0.32454	1.87	11.00	1.0414	24
5	9.29	0.30591	1.76	10.35	1.0149	29
6	9.65	0.29040	1.67	9.82	0.992	34

k = 1.68 ± 0.1 x 10^{-2} hrs.$^{-1}$ = 4.69 ± 0.20 x 10^{-6} sec.$^{-1}$

TABLE 22

DECOMPOSITION OF BISCYCLOPROPANECARBONYL PEROXIDE IN CARBON TETRACHLORIDE CONTAINING AN EQUIMOLAR QUANTITY OF IODINE AT 70 ± 0.2°

I_o = 19.16 cm.
a = 0.3873
P_o = 2.45 g./l = 1.45 x 10^{-2} molar

P = concentration (g./l)
P_n = concentration (molarity)
t = time (hours)

Sample	I cm.	log I_o/I	P	$P_n x 10^2$	log $P_n x 10^2$	t
1	7.60	0.40159	2.31	13.58	1.13290	4
2	8.17	0.37018	2.13	12.53	1.09795	7
3	9.00	0.32816	1.89	11.12	1.04610	13
4	10.40	0.26537	1.53	9.00	0.95424	22
5	10.91	0.24468	1.41	8.29	0.91855	27

k = 1.82 ± 0.1 x 10^{-2} hrs^{-1} = 5.06 ± 0.25 x 10^{-6} $sec.^{-1}$

TABLE 23

DECOMPOSITION OF DIBUTYLCHROMATOXYL PEROXIDE
IN CARBON TETRACHLORIDE AT 75 ± 0.2°

I_o = 17.92 cm. P = concentration (g./l)
a = 0.3473 P_n = concentration (molarity)
P_o = 3.45 g./l = 2.03 x 10^{-3} molar t = time (hours)

Sample	I cm.	log I_o/I	P	$P_n \times 10^3$	log $P_n \times 10^3$	t	k
1	5.35	0.52109	3.02	17.76	1.24944	4	
2	6.29	0.45469	2.62	15.41	1.18780	9.25	
3	7.18	0.39722	2.29	13.47	1.12937	12.5	
4	10.51	0.23180	1.34	7.91	0.89812	23.5	
5	11.20	0.20412	1.18	6.94	0.84136	27.25	

k = 4.23 ± 0.5 x 10^{-2} hrs^{-1} = 1.19 ± 0.20 x 10^{-5} $sec.^{-1}$

TABLE 24

DECOMPOSITION OF BENZOYL PEROXIDE IN CARBON TETRACHLORIDE
70 ± 0.2°

I_o = 18.00 cm.
a = 0.3564
P_o = 2.52 g./l = 1.04 x 10^{-2} molar

P = concentration g./l
P_n = concentration (molarity)
t = time (hours)

Sample	I cm.	log I_o/I	P	$P_n \times 10^3$	log $P_n \times 10^3$	t
1	6.93	0.41454	2.33	9.62	0.98318	4
2	7.63	0.37275	2.09	8.63	0.93601	8
3	8.84	0.30882	1.73	7.20	0.85733	12
4	10.93	0.21655	1.22	5.04	0.70243	23
5	12.22	0.16020	0.944	3.90	0.59106	28

k = 4.03 ± 0.55 x 10^{-2} hrs^{-1} = 1.12 ± 0.15 $sec.^{-1}$ ± 10^{-5}

TABLE 25

DECOMPOSITION OF BENZOYL PEROXIDE
IN CARBON TETRACHLORIDE AT 65 ± 0.2°

I_o = 18.38 cm.
a = 0.2084
P_o = 9.731 g./l = 4.915 x 10^{-2} molar

P = concentration (g./l)
P_n = concentration (molarity)
t = time (minutes)

Sample	I cm.	log I_o/I	C	$C_n \times 10^2$	log $C_n \times 10^2$	t
1	1.95	0.97432	9.35	4.722	0.67413	15
2	2.11	0.94007	9.022	4.557	0.65869	30
3	2.34	0.89513	8.591	4.339	0.63739	45
4	2.61	0.84771	8.135	4.109	0.61374	60
5	2.91	0.80046	7.682	3.880	0.58883	75
6	3.50	0.72028	6.912	3.491	0.54295	105
7	3.91	0.67217	6.451	3.258	0.51295	120
8	4.12	0.64945	6.233	3.148	0.49803	135
9	4.40	0.62090	5.959	3.009	0.47812	150

k = 3.48 ± 0.15 x 10^{-3} mins.$^{-1}$ = 5.81 ± 0.25 sec.$^{-1}$

TABLE 25

DECOMPOSITION OF BICYCLOBUTANECARBONYL PEROXIDE IN CARBON TETRACHLORIDE AT 70 ± 0.2° (I)

I_o = 17.76 cm.
a = 0.2084
P_o = 7.343 g./l = 3.709 x 10^{-2} molar

P = concentration (g./l)
P_n = concentration (molarity)
t = time (minutes)

Sample	I cm.	log I_o/I	P	$P_n \times 10^2$	log $P_n \times 10^2$	t
1	3.40	0.71796	6.890	3.480	0.54158	15
2	4.61	0.58574	5.621	2.839	0.45317	45
3	4.95	0.55483	5.325	2.689	0.42959	60
4	5.49	0.50987	4.893	2.471	0.39287	75
5	5.91	0.47785	4.586	2.316	0.36474	90
6	6.48	0.43786	4.202	2.122	0.32675	105
7	6.71	0.42272	4.057	2.049	0.31154	120

k = 5.20 ± 0.18 x 10^{-3} mins.$^{-1}$ = 8.55 ± 0.30 sec.$^{-1}$

TABLE 27

DECOMPOSITION OF BICYCLOHEXANECARBONYL PEROXIDE IN CARBON TETRACHLORIDE AT 70 ± 0.2° (II)

I_0 = 17.80
a = 0.2004
P_0 = 6.028 g./l = 3.044 x 10^{-2} molar

P = concentration (g./l)
P_n = concentration (molarity)
t = time (minutes)

Sample	I cm.	log I_0/I	P	$P_n x 10^2$	log $P_n x 10^2$	t
1	4.65	0.58394	5.604	2.830	0.45179	15
2	4.98	0.55416	5.318	2.686	0.42911	30
3	5.22	0.53372	5.122	2.587	0.41280	45
4	5.72	0.49399	4.741	2.394	0.37912	60
5	6.12	0.46464	4.459	2.252	0.35257	75
6	6.55	0.43515	4.176	2.109	0.32408	9

k = 4.85 ± 0.17 x 10^{-3} mins.$^{-1}$ = 8.10 ± 0.30 x 10^{-5} secs.$^{-1}$

TABLE 28

DECOMPOSITION OF BISCYCLOBUTANEFORMYL PEROXIDE
IN CARBON TETRACHLORIDE AT 75 ± 0.2°

I_o = 18.50
a = 0.2084
P_o = 5.80 g./l = 2.929 x 10^{-3} molar

P = concentration (g./l)
P_n = concentration (molarity)
t = time (minutes)

Sample	I cm.	log I_o/I	P	$P_n x 10^2$	log $P_n x 10^2$	t
1	5.20	0.55117	5.290	2.672	0.42684	15
2	6.21	0.47408	4.550	2.298	0.36135	30
3	7.13	0.41408	3.974	2.007	0.30255	45
4	8.04	0.36191	3.473	1.754	0.24403	60
5	8.89	0.31827	3.054	1.542	0.18808	75
6	9.80	0.27594	2.648	1.337	0.12613	90

k = 9.14 ± 0.55 x 10^{-3} mins.$^{-1}$ = 1.52 ± 0.11 x 10^{-4} secs.$^{-1}$

TABLE 29

DECOMPOSITION OF BISCYCLOPENTANEFORMYL PEROXIDE IN CARBON TETRACHLORIDE AT 40 ± 0.1°

I_o = 18.89 cm.
a = 0.2752
P_o = 2.612 g./l = 1.156 x 10^{-2} molar

P = concentration (g./l)
P_n = concentration (molarity)
t = time (minutes)

Sample	I cm.	log I_o/I	P	$P_n \times 10^2$	log $P_n \times 10^2$	t
0	3.61	0.71872	2.612	1.156	0.06296	0
1	3.73	0.70452	2.540	1.124	0.05077	15
2	4.00	0.67417	2.450	1.084	0.03503	75
3	4.20	0.65298	2.373	1.050	0.02119	105
4	4.26	0.64682	2.350	1.040	0.01703	120

k = 7.52 ± 0.45 x 10^{-4} mins.$^{-1}$ = 1.25 ± 0.08 x 10^{-5} sec.$^{-1}$

TABLE 30

DECOMPOSITION OF BIS(2,6-DIMETHOXYBENZOYL) PEROXIDE IN CARBON TETRACHLORIDE AT 45 ± 0.1°

I_0 = 19.17 cm.
a = 0.2752
P_0 = 2.927 g./l = 1.295 x 10^{-2} molar

P = concentration (g./l)
P_n = concentration (molarity)
t = time (minutes)

Sample	I cm.	log I_0/I	P	$P_n \times 10^2$	log $P_n \times 10^2$	t
1	3.19	0.77883	2.830	1.252	0.09760	15
2	3.31	0.76279	2.772	1.226	0.08849	30
3	3.48	0.74104	2.693	1.191	0.07591	60
4	3.78	0.70513	2.562	1.134	0.05461	90
5	4.01	0.67918	2.469	1.092	0.03822	120

k = 1.61 ± 0.15 x 10^{-3} mins.$^{-1}$ = 2.69 ± 0.24 x 10^{-5} sec.$^{-1}$

TABLE 31

DECOMPOSITION OF BENZENEAZOTRIPHENYLMETHANE
IN CARBON TETRACHLORIDE AT 50 ± 0.1°

I_o = 19.17
a = 0.2752
P_o = 2.303 g./l = 1.355×10^{-2} molar

P = concentration (g./l)
P_n = concentration (molarity)
t = time (minutes)

Sample	I cm.	log I_o/I	P	$P_n \times 10^3$	log $P_n \times 10^3$	t
1	3.01	0.80405	2.923	12.93	1.11160	15
2	3.31	0.76279	2.772	12.26	1.08849	30
3	3.49	0.73979	2.688	11.89	1.07518	45
4	3.68	0.71677	2.605	11.52	1.06145	60
5	4.10	0.66984	2.434	10.77	1.03222	75
6	4.30	0.64915	2.359	10.44	1.01870	90
7	4.69	0.61145	2.222	9.831	0.99260	105

$k = 2.94 \pm 0.12 \times 10^{-2}$ mins.$^{-1}$ = $4.91 \pm 0.2 \times 10^{-4}$ sec.$^{-1}$

TABLE 32

DECOMPOSITION OF BIS(CHLOROMETHANESULFONYL) PEROXIDE IN CARBON TETRACHLORIDE AT 55 ± 0.1° (I)

I_0 = 19.17 cm.
a = 0.2752
P_0 = 3.081 g./l = 1.365 x 10^{-2} molar

P = concentration (g./l)
P_n = concentration (molarity)
t = time (minutes)

Sample	I cm.	log I_0/I	P	$P_n \times 10^2$	log $P_n \times 10^2$	t
1	3.00	0.80350	2.927	12.95	1.11227	15
2	3.56	0.73117	2.657	11.76	1.07041	30
3	4.00	0.68056	2.473	10.94	1.03902	45
4	4.49	0.63037	2.291	10.14	1.00604	60
5	4.93	0.59977	2.183	9.683	0.97695	75
6	5.40	0.55023	1.999	8.847	0.94680	90

k = 4.55 ± 0.16 x 10^{-2} mins.$^{-1}$ = 7.61 ± 0.27 x 10^{-4} sec.$^{-1}$

TABLE 33

DECOMPOSITION OF DICHLOROMETHANESULFENYL PYRIDINE IN CARBON TETRACHLORIDE AT 55 ± 0.1° (II)

I_o = 19.17 cm.
a = 0.2752
P_o = 4.850 g./l = 2.137 x 10^{-2} molar

P = concentration (g./l)
P_n = concentration (molarity)
t = time (minutes)

Sample	I cm.	log I_o/I	P	$P_n \times 10^2$	log $P_n \times 10^2$	t
1	4.68	0.61237	4.450	1.969	0.29425	15
2	5.14	0.57166	4.155	1.838	0.26435	30
3	5.56	0.53755	3.907	1.729	0.23779	45
4	6.01	0.50375	3.661	1.620	0.20952	60
5	6.43	0.47104	3.423	1.515	0.18041	75
6	6.97	0.43939	3.193	1.413	0.15014	90

k = 4.38 ± 0.13 x 10^{-3} mins.$^{-1}$ = 7.32 ± 0.21 x 10^{-5} sec.$^{-1}$

TABLE 34

DECOMPOSITION OF BIS(CYCLOPENTADIENYL) PEROXIDE IN CARBON TETRACHLORIDE AT 35 ± 0.1°

I_0 = 19.00 cm.
a = 0.2721
P_0 = 7.00 g./l = 2.718 x 10^{-2} molar

P = concentration (g./l)
P_n = concentration (molarity)
t = time (minutes)

Sample	I cm.	log I_0/I	P	$P_n \times 10^2$	log $P_n \times 10^2$	t
1	2.31	0.91514	6.724	2.647	0.42275	15
2	2.51	0.87908	6.459	2.543	0.40535	45
3	2.78	0.83471	6.133	2.415	0.38272	75
4	3.01	0.80018	5.879	2.315	0.36455	105
5	3.30	0.76024	5.586	2.199	0.34223	135

k = 1.54 ± 0.18 x 10^{-3} mins.$^{-1}$ = 2.57 ± 0.30 x 10^{-5} sec.$^{-1}$

TABLE 35

DECOMPOSITION OF DICYCLOHEXANESULFONYL PEROXIDE IN CARBON TETRACHLORIDE AT 40 ± 0.1° (I)

I_o = 18.94 cm.
a = 0.2721
P_o = 3.384 g./l = 1.21 x 10^{-2} molar

P = concentration (g./l)
P_M = concentration (molarity)
t = time (minutes)

Sample	I cm.	log I_o/I	C	$C_M \times 10^3$	log $C_M \times 10^3$	t
1	7.08	0.42735	3.140	11.25	1.05115	30
2	7.49	0.39990	2.938	10.57	1.02407	45
3	8.00	0.36927	2.720	9.800	0.99123	60
4	8.50	0.33796	2.557	9.198	0.96369	90
5	8.72	0.33686	2.473	8.896	0.94919	105

k = 3.06 ± 0.18 x 10^{-3} mins.$^{-1}$ = 5.12 ± 0.30 x 10^{-5} sec.$^{-1}$

TABLE 36

DECOMPOSITION OF DICYCLOHEXANEFORMYL PEROXIDE
IN CARBON TETRACHLORIDE AT 40 ± 0.1° (II)

I_o = 19.00 cm. P = concentration (g./l)
a = 0.2721 P_n = concentration (molarity)
P_o = 7.66 g./l = 3.017 x 10^{-2} molar t = time (minutes)

Sample	I cm.	log I_o/I	P	$P_n x 10^2$	log $P_n x 10^2$	t
1	1.92	0.99545	7.314	2.879	0.45924	15
2	2.13	0.95037	6.983	2.749	0.43913	30
3	2.33	0.91139	6.696	2.602	0.41531	45
4	2.64	0.85715	6.298	2.480	0.39445	60
5	2.84	0.82543	6.065	2.388	0.37803	75
6	3.14	0.78182	5.744	2.261	0.35430	90

k = 2.88 ± 0.21 x 10^{-3} mins.$^{-1}$ = 4.82 ± 0.35 x 10^{-5} sec.$^{-1}$

TABLE 37

DECOMPOSITION OF BISCYCLOHEXANEPONYL PEROXIDE IN CARBON TETRACHLORIDE AT 45 ± 0.1°

I_0 = 18.42 cm. P = concentration (g./l)
a = 0.2721 P_n = concentration (molarity)
P_0 = 5.550 g./l = 2.27 x 10^{-2} molar t = time (minutes)

Sample	I cm.	log I_0/I	P	$P_n x10^3$	log $P_n x10^3$	t
1	3.35	0.74025	5.439	21.41	1.33062	15
2	4.20	0.64204	4.717	18.57	1.26881	30
3	4.70	0.59319	4.358	17.16	1.23452	45
4	5.43	0.53049	3.898	15.35	1.18611	60
5	6.14	0.47712	3.506	13.80	1.13988	75
6	6.55	0.44905	3.299	12.99	1.11361	90
7	7.34	0.39959	2.936	11.56	1.06296	105
8	7.95	0.36492	2.681	10.56	1.02366	120

k = 6.20 ± 0.4 x 10^{-3} mins.$^{-1}$ = 1.032 ± 0.05 x 10^{-4} sec.$^{-1}$

TABLE 38

DECOMPOSITION OF BISCYCLOHEPTANEFORMYL PEROXIDE IN CARBON TETRACHLORIDE AT 35 ± 0.1°

I_o = 17.03 cm.
a = 0.2738
P_o = 4.620 g./l = 1.638 x 10^{-2} molar

P = concentration (g./l)
P_n = concentration (molarity)
t = time (minutes)

Sample	I cm.	log I_o/I	P	$P_n x10^2$	log $P_n x10^2$	t
1	4.30	0.59774	4.366	1.548	0.18977	15
2	4.81	0.54906	4.011	1.422	0.15290	30
3	5.28	0.50853	3.715	1.317	0.11959	45
4	5.64	0.47993	3.506	1.243	0.09447	60
5	6.10	0.44588	3.257	1.155	0.06253	75

k = 4.82 ± 0.15 x 10^{-3} mins.$^{-1}$ = 8.05 ± 0.25 x 10^{-5} sec.$^{-1}$

TABLE 39

DECOMPOSITION OF BIS(TRICHLOROHEPTAFLUOROPROPYL) PEROXIDE IN CARBON TETRACHLORIDE AT 40 ± 0.1° (I)

I_0 = 17.03 cm.
a = 0.2733
P_0 = 7.463 g./l = 2.646 x 10^{-2} molar

P = concentration (g./l)
P_n = concentration (molarity)
t = time (minutes)

Sample	I cm.	log I_0/I	P	$P_n \times 10^2$	log $P_n \times 10^2$	t
1	2.23	0.88291	6.449	2.287	0.35927	15
2	3.00	0.75409	5.508	1.953	0.29070	30
3	3.81	0.65029	4.750	1.684	0.22634	45
4	4.52	0.57607	4.208	1.492	0.17377	60
5	5.10	0.52334	3.823	1.355	0.11561	75

k = 9.45 ± 0.55 x 10^{-3} mins.$^{-1}$ = 1.57 ± 0.10 x 10^{-4} sec.$^{-1}$

TABLE 40

DECOMPOSITION OF DISCYCLOPENTANONYL PEROXIDE
IN CARBON TETRACHLORIDE AT 40 ± 0.1° (II)

I_o =
a = 0.2738
P_o = 4.361 g./l = 15.46 x 10^{-3} molar

P = concentration (g./l)
P_n = concentration (molarity)
t = time (minutes)

Sample	I cm.	log I_o/I	C	$C_n x10^3$	log $C_n x10^3$	t
1	5.04	0.52802	3.857	13.68	1.13609	15
2	5.82	0.46553	3.401	12.06	1.08135	30
3	6.57	0.41283	3.016	10.70	1.02938	45
4	7.19	0.37372	2.730	9.680	0.98583	60
5	7.91	0.33227	2.427	8.606	0.93480	75
6	8.67	0.29243	2.136	7.574	0.87933	90

k = 8.74 ± 0.47 x 10^{-3} mins.$^{-1}$ = 1.46 ± 0.08 x 10^{-4} sec.$^{-1}$

TABLE 41

DECOMPOSITION OF BICYCLOHEPTANEFORMYL PEROXIDE IN CARBON TETRACHLORIDE AT 45 ± 0.1°

I_o = 17.03 cm.
a = 0.2738
P_o = 6.840 g./l = 2.390 x 10^{-2} molar

P = concentration (g./l)
P_n = concentration (molarity)
t = time (minutes)

Sample	I cm.	log I_o/I	C	C_n	log C_n	t
1	2.88	0.77182	5.638	1.999	0.29885	15
2	3.92	0.63792	4.660	1.652	0.21801	30
3	4.82	0.54816	4.004	1.420	0.15229	45
4	5.65	0.47916	3.500	1.241	0.09377	60
5	6.85	0.39552	2.889	1.024	0.1030	75

k = 1.1 ± 0.09 x 10^{-1} mins.$^{-1}$ = 1.84 ± 0.15 x 10^{-4} sec.$^{-1}$

TABLE 42

DECOMPOSITION OF BISCYCLOPROPANEACETYL PEROXIDE
IN CARBON TETRACHLORIDE AT 14 ± 0.2°

I_o = 18.85
a = 0.1715
P_o = 6.09 g./l = 30.55 x 10^{-2} molar

P = concentration (g./l)
P_n = concentration (molarity)
t = time (minutes)

Sample	I cm.	log I_o/I	P	$P_n x10^2$	log $P_n x10^2$	t
1	6.28	0.47735	5.57	28.19	1.46598	15
2	6.74	0.44650	5.21	25.67	1.40943	30
3	7.50	0.40022	4.67	23.56	1.37218	45
4	8.09	0.36765	4.29	21.78	1.33806	60
5	8.48	0.34709	4.05	20.42	1.31952	75

k = 14.1 ± 0.18 x 10^{-2} mins.$^{-1}$ = 23.6 ± 0.30 x 10^{-4} sec.$^{-1}$

TABLE 43

DECOMPOSITION OF DISUCCINOPEROXIDE IN CARBON TETRACHLORIDE AT 25 ± 0.1° (I)

I_o = 18.85
a = 0.1715
P_o = 27.8 g./l = 141.3 x 10^{-3} molar

P = concentration (g./l)
P_n = concentration (molarity)
t = time (minutes)

Sample	I cm.	log I_o/I	P	$P_n \times 10^3$	log $P_n \times 10^3$	t
1	2.83	1.11657	12.871	65.01	1.81298	15
2	9.24	0.30973	3.612	18.24	1.26102	30
3	14.79	0.10539	1.229	6.207	0.79288	45
4	17.12	0.04186	0.4876	2.463	0.39146	60
5	17.75	0.02617	0.3051	1.541	0.18700	75

k = 6.32 ± 0.5 x 10^{-3} mins.$^{-1}$ = 1.05 ± 0.08 x 10^{-3} sec.$^{-1}$

TABLE 44

DECOMPOSITION OF DICHLOROACETYL PEROXIDE IN CARBON TETRACHLORIDE AT 25 ± 0.1° (II)

I_o = 13.85 cm.
a = 0.1715
P_o = 24.39 g./l = 123.3 x 10^{-3} molar

P = concentration (g./l)
P_n = concentration (molarity)
t = time (minutes)

Sample	I cm.	log I_o/I	P	$P_n \times 10^3$	log $P_n \times 10^3$	t
1	2.24	0.92147	19.781	54.449	1.73600	15
2	8.55	0.34326	4.003	20.217	1.30578	30
3	14.15	0.15533	1.811	9.145	0.96123	45
4	16.91	0.06725	0.351	2.703	0.43451	60
5	17.63	0.02378	0.138	1.707	0.23223	75

k = 5.95 ± 0.11 x 10^{-2} mins.$^{-1}$ = 9.92 ± 0.18 x 10^{-4} sec.$^{-1}$

TABLE 45

DECOMPOSITION OF BENZOYLPEROXIDE
IN CARBON TETRACHLORIDE AT 65 ± 0.1

I_o = 17.10 cm.
a = 0.1002
P_o = 5.755 g./l = 2.525 x 10^{-2} molar

P = concentration (g./l)
P_n = concentration (molarity)
t = time (minutes)

Sample	I cm.	log I_o/I	P	$P_n \times 10^2$	log $P_n \times 10^2$	t
1	5.30	0.50872	5.646	2.478	0.39459	15
2	5.38	0.50282	5.574	2.446	0.38829	30
3	5.43	0.49922	5.535	2.429	0.38507	45
4	5.54	0.49149	5.453	2.394	0.37863	60
5	5.61	0.48684	5.372	2.377	0.37533	75
6	5.74	0.47809	5.262	2.328	0.36698	90

k = 9.33 ± 0.52 x 10^{-4} mins.$^{-1}$ = 1.56 ± 0.09 x 10^{-5} sec.$^{-1}$

TABLE 46

DECOMPOSITION OF BISCYCLOPENTADIENYL PYRIDINE IN CARBON TETRACHLORIDE AT 70 ± 0.1° (I)

I_o = 17.10 cm.
a = 0.1302
P_o = 6.621 g./l = 2.736 x 10^{-2} molar

P = concentration (g./l)
P_n = concentration (molarity)
t = time (seconds)

Sample	I cm.	log I_o/I	P	$P_n x 10^2$	log P_n	t
1	4.46	0.58367	6.478	2.677	0.42765	15
2	4.64	0.56148	6.287	2.598	0.41464	45
3	4.75	0.55361	6.144	2.539	0.40466	60
4	4.91	0.54102	6.015	2.486	0.39550	75
5	5.02	0.53230	5.903	2.441	0.38757	90

k = 1.25 ± 0.12 x 10^{-3} mins.$^{-1}$ = 2.10 ± 0.20 x 10^{-5} sec.$^{-1}$

TABLE 47

DECOMPOSITION OF BICYCLOHEPTENYLACETYL PEROXIDE IN CARBON TETRACHLORIDE AT 70 ± 0.1° (II)

I_0 = 17.10 cm.
a = 0.1302
P_0 = 6.695 g./l = 2.905 x 10^{-3} molar

P = concentration (g./l)
P_n = concentration (molarity)
t = time (minutes)

Sample	I cm.	log I_0/I	P	$P_n \times 10^3$	log $P_n \times 10^3$	t
1	4.50	0.57979	6.435	2.847	0.45439	15
2	4.68	0.54275	6.246	2.764	0.44154	30
3	4.80	0.52176	6.124	2.710	0.43297	45
4	4.95	0.50039	5.975	2.644	0.42226	60
5	5.07	0.48299	5.860	2.593	0.41380	75
6	5.21	0.46516	5.729	2.534	0.40381	90

k = 1.14 ± 0.15 x 10^{-3} mins.$^{-1}$ = 1.91 ± 0.25 x 10^{-5} sec.$^{-1}$

TABLE 48

DECOMPOSITION OF BISCYCLOHEXANECARBONYL PEROXIDE IN CARBON TETRACHLORIDE AT 75 ± 0.1°

I_0 = 17.10 cm. — P = concentration (g./l)
a = 0.1802 — P_n = concentration (molarity)
P_0 = 6.144 g./l = 2.53 x 10^{-2} molar — t = time (minutes)

Sample	I cm.	log I_0/I	P	$P_n \times 10^2$	log $P_n \times 10^2$	t
1	5.00	0.53403	5.927	2.449	0.38899	15
2	5.13	0.51367	5.757	2.379	0.37639	30
3	5.40	0.50061	5.556	2.296	0.36097	45
4	5.62	0.48326	5.364	2.217	0.34577	60
5	5.80	0.46215	5.129	2.119	0.32613	75

k = 2.36 ± 0.14 x 10^{-2} $mins.^{-1}$ = 3.96 ± 0.23 x 10^{-4} $sec.^{-1}$

TABLE 49

DECOMPOSITION OF DISOBUTYLPHENOXYETHYL PEROXIDE IN CARBON TETRACHLORIDE AT 65 ± 0.1°

I_o = 17.10 cm.
a = 0.1912
P_o = 6.455 g./l = 2.543 x 10^{-2} molar

P = concentration (g./l)
P_n = concentration (molarity)
t = time (minutes)

Sample	I cm.	log I_o/I	P	$P_n \times 10^2$	log $P_n \times 10^2$	t
1	4.20	0.60975	6.378	2.511	0.39985	15
2	4.28	0.60156	6.292	2.477	0.39393	30
3	4.36	0.59351	6.210	2.445	0.38823	45
4	4.45	0.58464	6.115	2.407	0.38148	60
5	4.52	0.57786	6.045	2.380	0.37658	75
6	4.60	0.57024	5.965	2.348	0.37070	90

k = 9.43 ± 0.18 x 10^{-4} mins.$^{-1}$ = 1.57 ± 0.03 x 10^{-5} secs.$^{-1}$

TABLE 50

DECOMPOSITION OF BISCYCLOPENTANEACETYL PEROXIDE IN CARBON TETRACHLORIDE AT 70 ± 0.1° (I)

I_o = 17.10 cm.
a = 0.1912
P_o = 6.115 g./l = 2.408 x 10^{-2} molar

P = concentration (g./l)
P_n = concentration (molarity)
t = time (minutes)

Sample	I cm.	log I_o/I	P	$P_n x 10^2$	log $P_n x 10^2$	t
1	4.64	0.56648	5.926	2.333	0.36791	15
2	4.80	0.55176	5.772	2.272	0.35641	30
3	4.98	0.53577	5.604	2.206	0.34361	45
4	5.12	0.52373	5.478	2.157	0.33385	60
5	5.30	0.50872	5.321	2.095	0.32113	75
6	5.48	0.49422	5.170	2.035	0.30856	90

k = 1.83 ± 0.09 x 10^{-3} $mins.^{-1}$ = 3.06 ± 0.15 x 10^{-5} $sec.^{-1}$

TABLE 51

DECOMPOSITION OF BICYCLO[2.2.1]HEPTANEACETYL PEROXIDE IN CARBON TETRACHLORIDE AT 10 ± 0.1° (II)

I_o = 17.10 cm.
a = 0.1912
P_o = 5.548 g./l. = 2.179 x 10^{-2} molar

P = concentration (g./l)
P_n = concentration (molarity)
t = time (minutes)

Sample	I cm.	log I_o/I	P	$P_n \times 10^2$	log $P_n \times 10^2$	t
1	5.20	0.51700	5.408	2.129	0.33818	15
2	5.42	0.49900	5.220	2.055	0.31281	30
3	5.60	0.48181	5.071	1.996	0.30016	45
4	5.76	0.47258	4.943	1.946	0.28914	60
5	5.94	0.45921	4.803	1.891	0.27669	75
6	6.12	0.44625	4.668	1.838	0.26435	90

$k = 1.90 \pm 0.09 \times 10^{-3}$ mins.$^{-1}$ = $3.17 \pm 0.12 \times 10^{-5}$ sec.$^{-1}$

TABLE 52

DECOMPOSITION OF BISCYCLOPENTANEACETYL PEROXIDE
IN CARBON TETRACHLORIDE AT 75 ± 0.1°

I_0 = 17.10 cm.
a = 0.1912
P_0 = 5.496 g./l = 2.154 x 10^{-2} molar

P = concentration (g./l)
P_n = concentration (molarity)
t = time (minutes)

Sample	I cm.	log I_0/I	P	$P_n x 10^2$	log $P_n x 10^2$	t
1	5.40	0.50061	5.237	2.062	0.31429	15
2	5.64	0.48172	5.039	1.984	0.29754	30
3	5.92	0.46068	4.819	1.897	0.27807	45
4	6.20	0.44061	4.609	1.815	0.25888	60
5	6.50	0.42009	4.394	1.730	0.23805	75
6	6.76	0.40305	4.216	1.660	0.22011	90

k = 2.94 ± 0.14 x 10^{-4} mins.$^{-1}$ = 4.91 ± 0.31 x 10^{-6} sec.$^{-1}$

TABLE 53

DECOMPOSITION OF BISCYCLOHEXANEACETYL PEROXIDE
IN CARBON TETRACHLORIDE AT 60 ± 0.1°

I_o = 14.84 cm.
a = 0.1402
P_o = 3.839 g./l = 1.36 x 10^{-2} molar

P = concentration (g./l)
P_n = concentration (molarity)
t = time (minutes)

Sample	I cm.	log I_o/I	P	$P_n x10^2$	log $P_n x10^2$	t
1	4.35	0.52294	3.730	1.323	0.12156	60
2	4.70	0.48933	3.490	1.238	0.09272	120
3	4.83	0.47748	3.406	1.208	0.08207	180
4	5.20	0.44543	3.177	1.127	0.0[illegible]192	240
5	5.47	0.42344	3.020	1.071	0.02979	300

k = 5.16 ± 0.43 x 10^{-3} hrs.$^{-1}$ = 1.43 ± 0.12 x 10^{-6} sec.$^{-1}$

TABLE 54

DECOMPOSITION OF BISCYCLOHEXANEACETYL PEROXIDE IN CARBON TETRACHLORIDE AT 70 ± 0.1° (I)

I_o = 14.84
a = 0.1402
P_o = 4.060 g./l = 1.440 x 10^{-2} molar

P = concentration (g./l)
P_n = concentration (molarity)
t = time (minutes)

Sample	I cm.	log I_o/I	P	$P_n \times 10^2$	log $P_n \times 10^2$	t
1	4.03	0.55612	3.967	1.407	0.14829	15
2	4.13	0.54548	3.891	1.380	0.13988	30
3	4.30	0.52796	3.766	1.335	0.12548	45
4	4.48	0.51015	3.639	1.290	0.11059	60
5	4.60	0.49867	3.557	1.261	0.10072	75
6	4.70	0.48933	3.490	1.238	0.09272	90

k = 1.76 ± 0.18 x 10^{-3} mins.$^{-1}$ = 2.93 ± 0.3 x 10^{-5} sec.$^{-1}$

TABLE 55

DECOMPOSITION OF BISCYCLOHEXANEACETYL PEROXIDE IN CARBON TETRACHLORIDE AT 70 ± 0.1° (II)

I_o = 14.84 cm.
a = 0.1402
P_o = 6.63 g./l = 2.361×10^{-2} molar

P = concentration (g./l)
P_n = concentration (molarity)
t = time (minutes)

Sample	I cm.	log I_o/I	P	$P_n \times 10^2$	log $P_n \times 10^2$	t
1	5.18	0.45710	6.521	2.312	0.36399	15
2	5.30	0.44715	6.379	2.262	0.35449	30
3	5.46	0.43424	6.195	2.197	0.34183	45
4	5.64	0.42015	5.994	2.126	0.32756	60
5	5.75	0.41176	5.874	2.083	0.31869	75
6	5.86	0.40353	5.756	2.041	0.30984	90

$k = 1.68 \pm 0.09 \times 10^{-3}$ mins.$^{-1}$ = $2.81 \pm 0.15 \times 10^{-5}$ sec.$^{-1}$

TABLE 56

DECOMPOSITION OF BISCYCLOHEXANEACETYL PEROXIDE IN CARBON TETRACHLORIDE AT 75 ± 0.1°

I_o = 14.84 cm. P = concentration (g./l)
a = 0.1402 P_n = concentration (molarity)
P_o = 4.190 g./l = 1.486 x 10^{-2} molar t = time (minutes)

Sample	I cm.	log I_o/I	P	$P_n \times 10^2$	log $P_n \times 10^2$	t
1	3.89	0.57148	4.076	1.445	0.15987	15
2	4.12	0.54653	3.898	1.382	0.14051	30
3	4.21	0.53715	3.831	1.359	0.13322	45
4	4.45	0.51307	3.660	1.298	0.11327	60
5	4.60	0.49867	3.557	1.261	0.10072	75
6	4.83	0.47748	3.406	1.208	0.08207	90

k = 2.27 ± 0.11 x 10^{-3} mins.$^{-1}$ = 3.78 ± 0.18 x 10^{-5} sec.$^{-1}$

Figure 11. Plot of log k versus 1/T for the Decomposition of Biscyclopropaneformyl Peroxide.

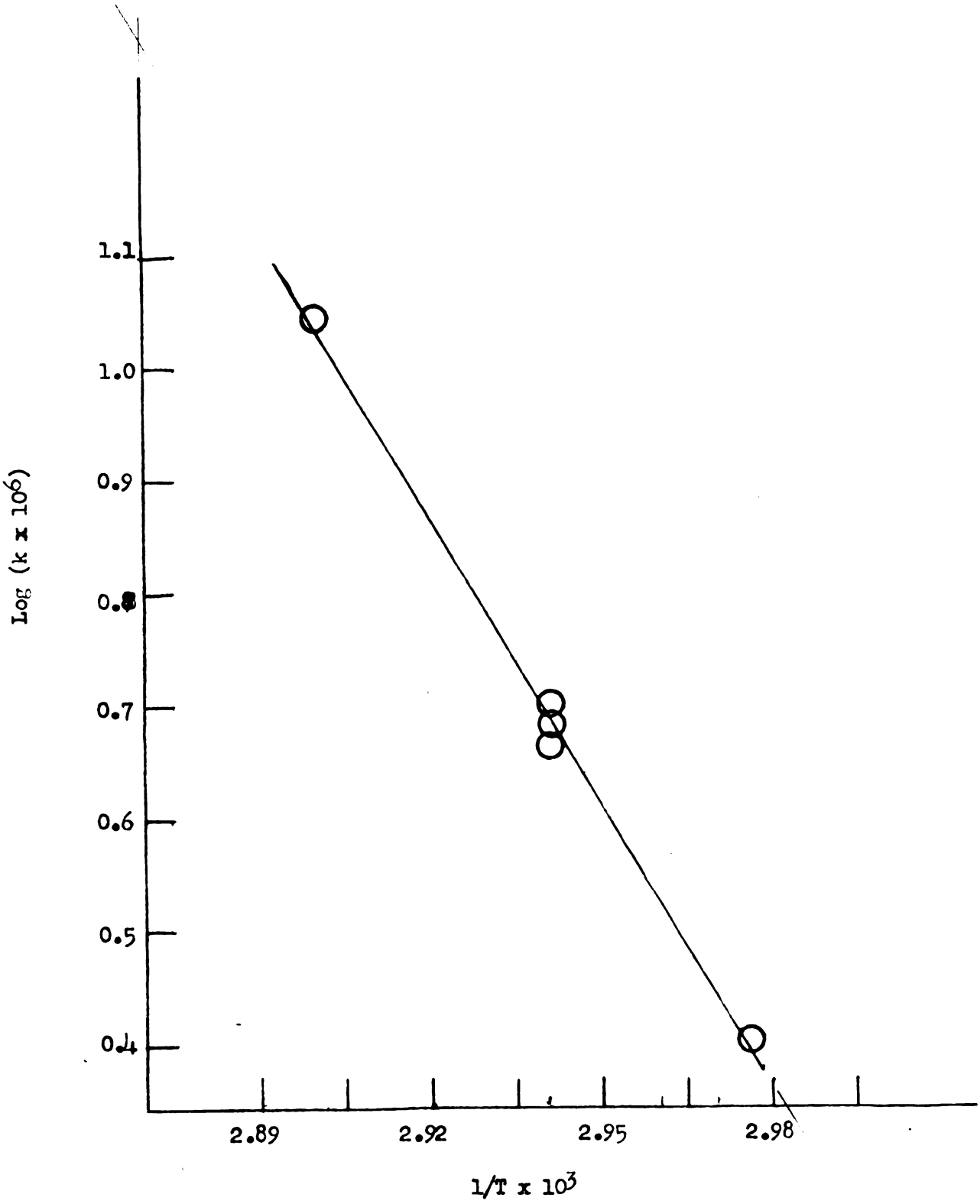


Figure 12. Plot of log k versus 1/T for the Decomposition of Biscyclobutaneformyl Peroxide.

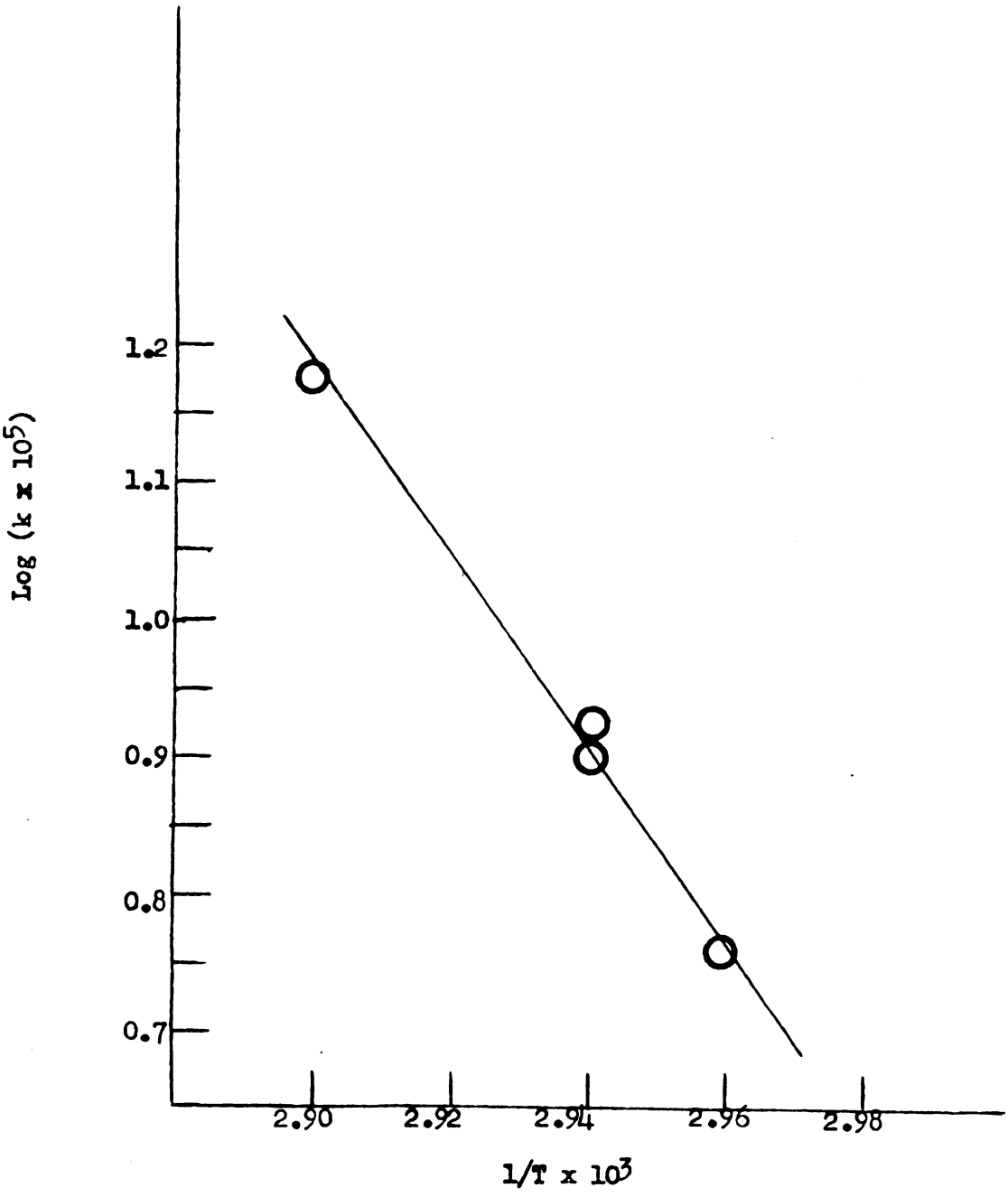


Figure 13. Plot of log k versus 1/T for the Decomposition of Biscyclopentaneformyl Peroxide.

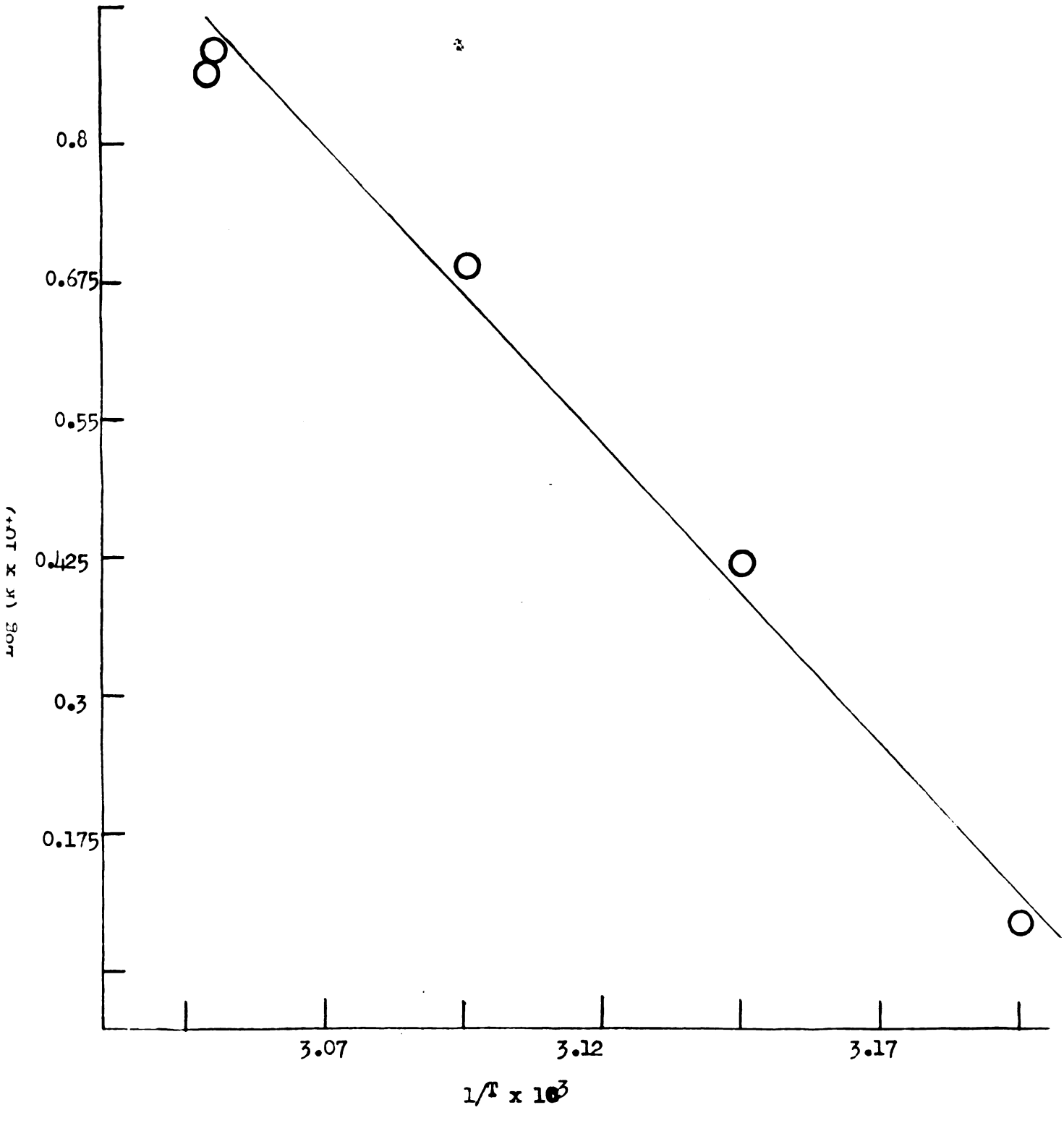


Figure 14. Plot of log k versus $1/T$ for the Decomposition of Biscyclohexaneformyl Peroxide.

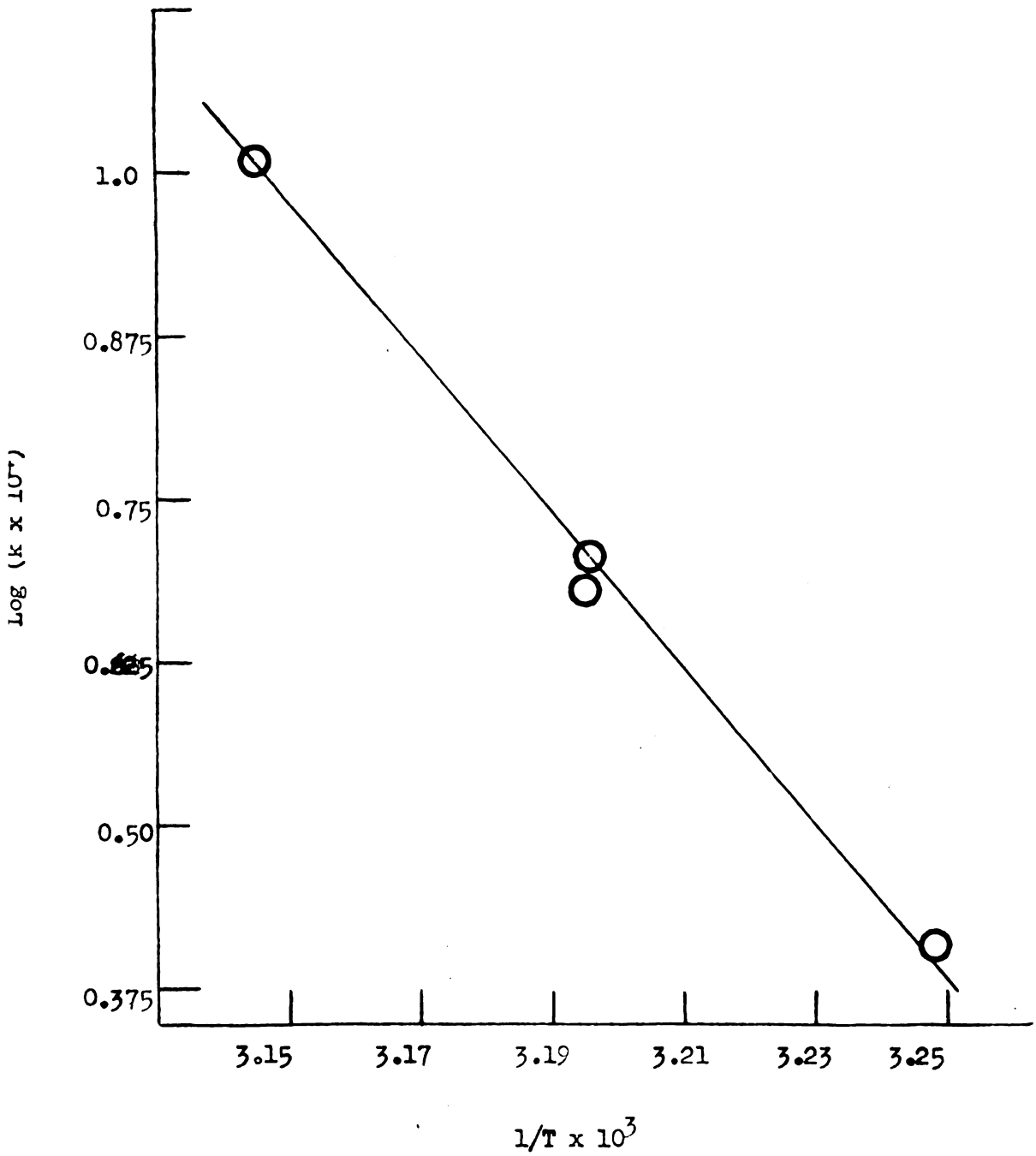


Figure 15. Plot of log k versus 1/T for the Decomposition of Bis(cloheptanoformyl Peroxide.

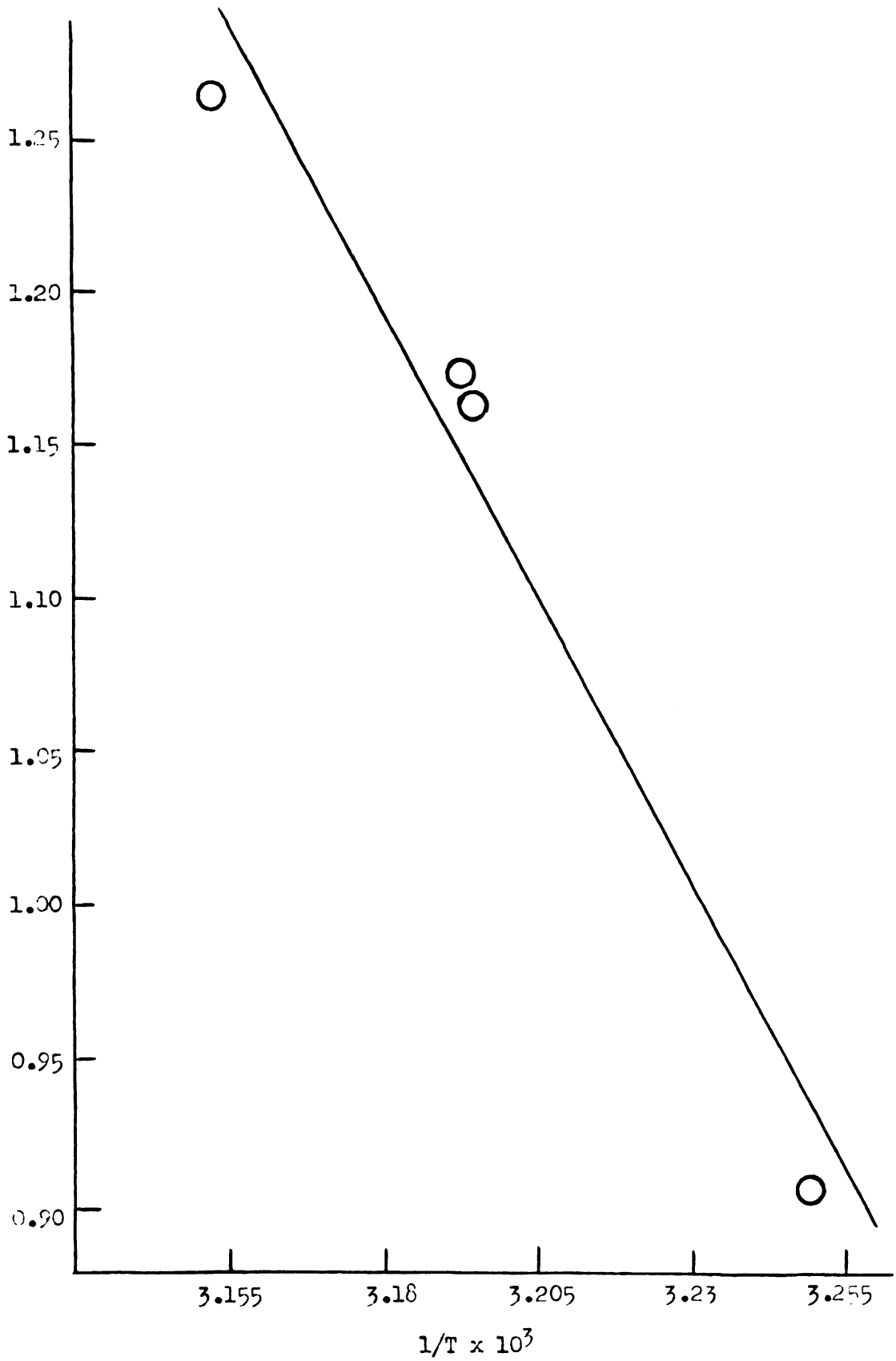


Figure 15. Plot of log k versus 1/T for the Decomposition of Biscyclopropaneacetyl Peroxide.

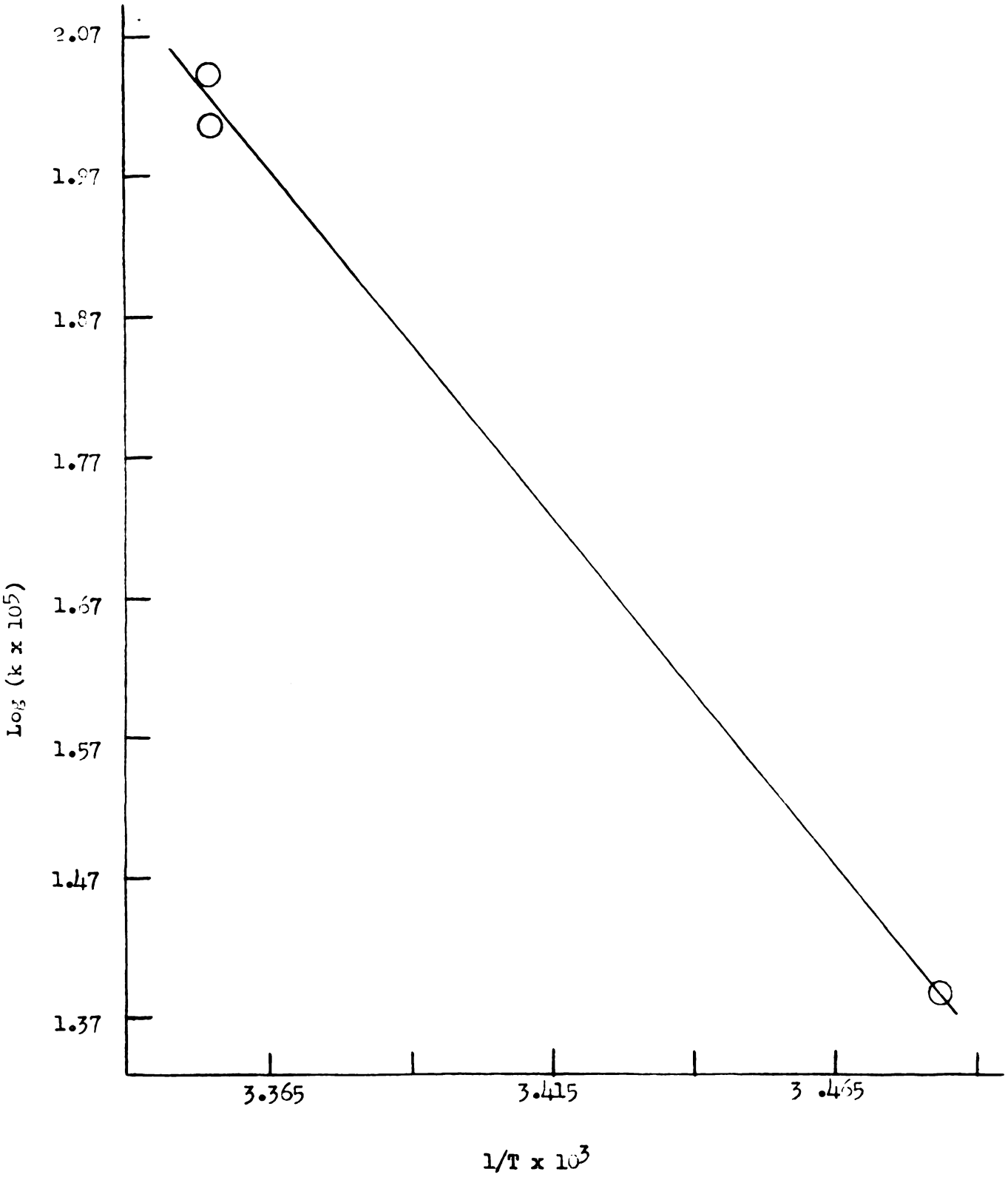


Figure 17. Plot of log k versus 1/T for the Decomposition of Biscyclobutaneacetyl Peroxide.

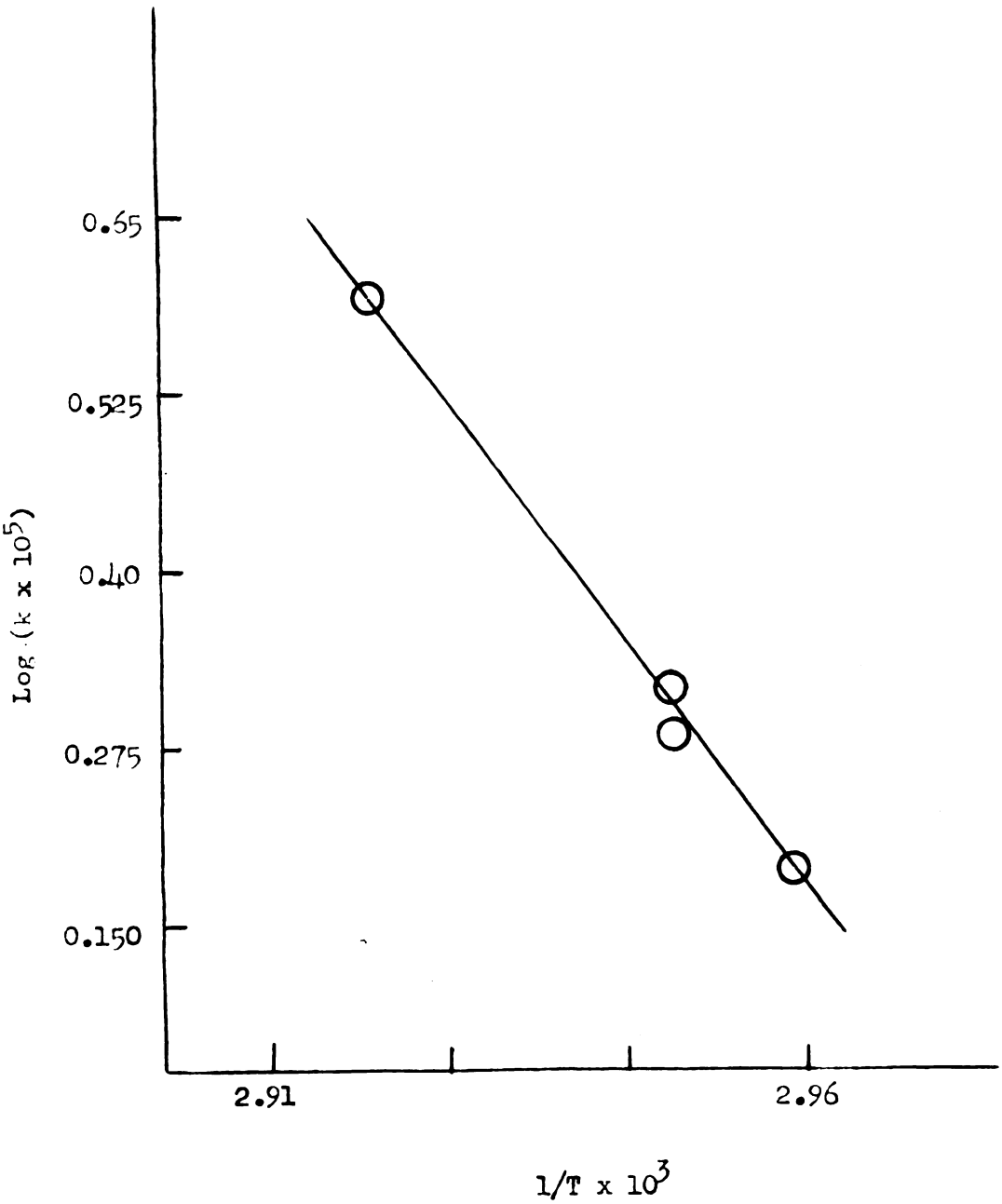


Figure 18. Plot of log k versus 1/T for the Decomposition of Biscyclopentaneacetyl Peroxide.

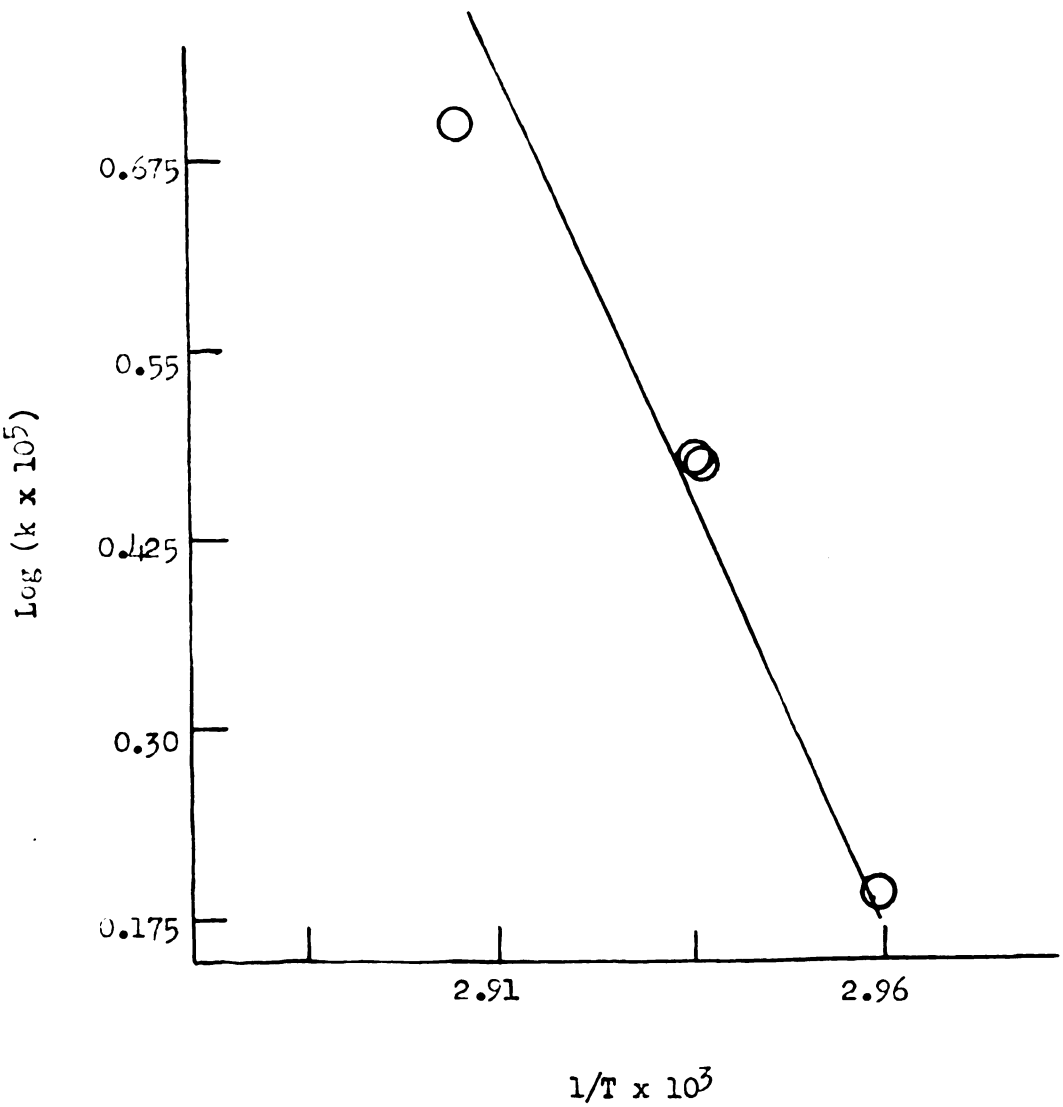
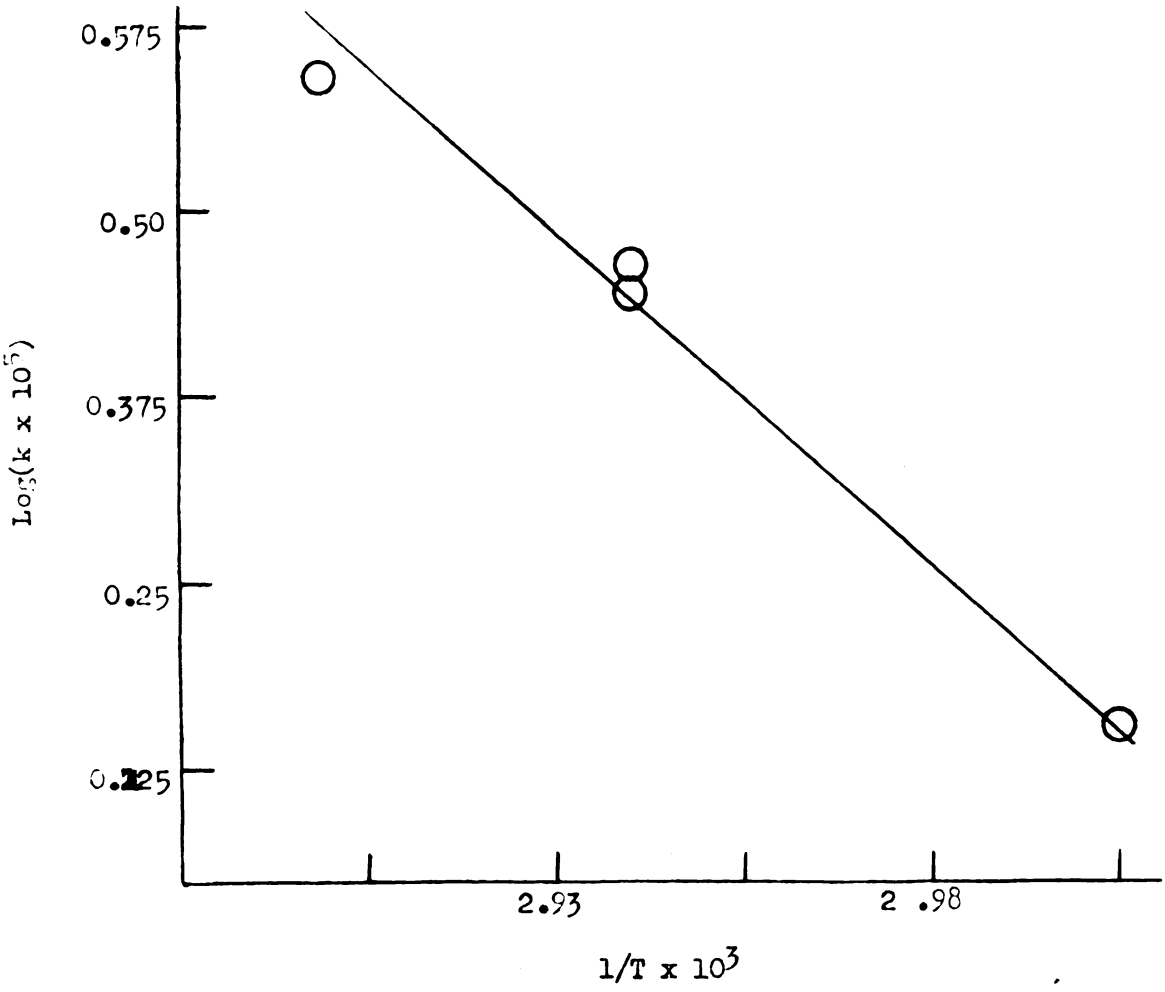


Figure 19. Plot of log k versus 1/T for the Decomposition of Biscyclohexaneacetyl Peroxide.



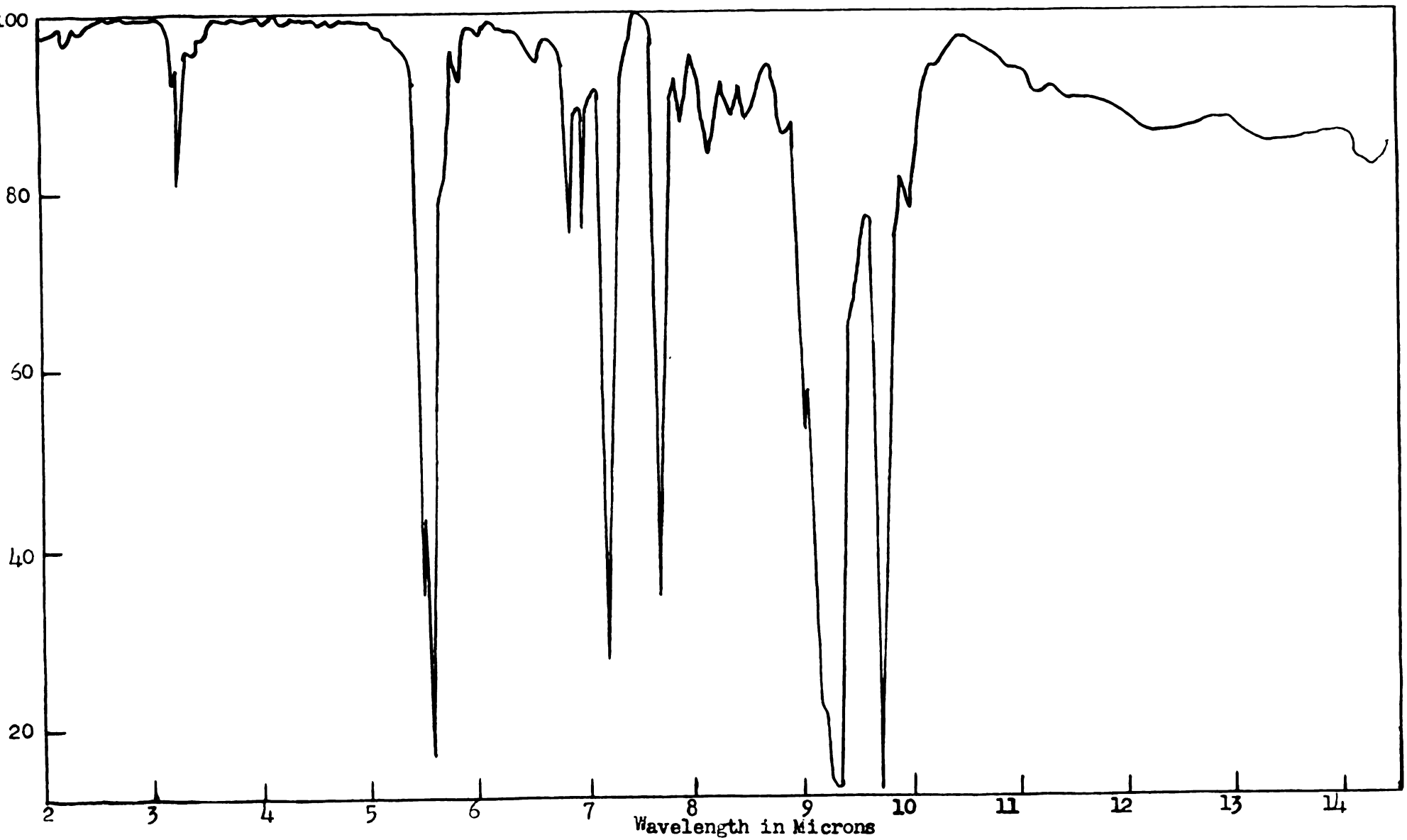


Figure 20. Infrared Spectrum of Biscyclopropaneformyl Peroxide

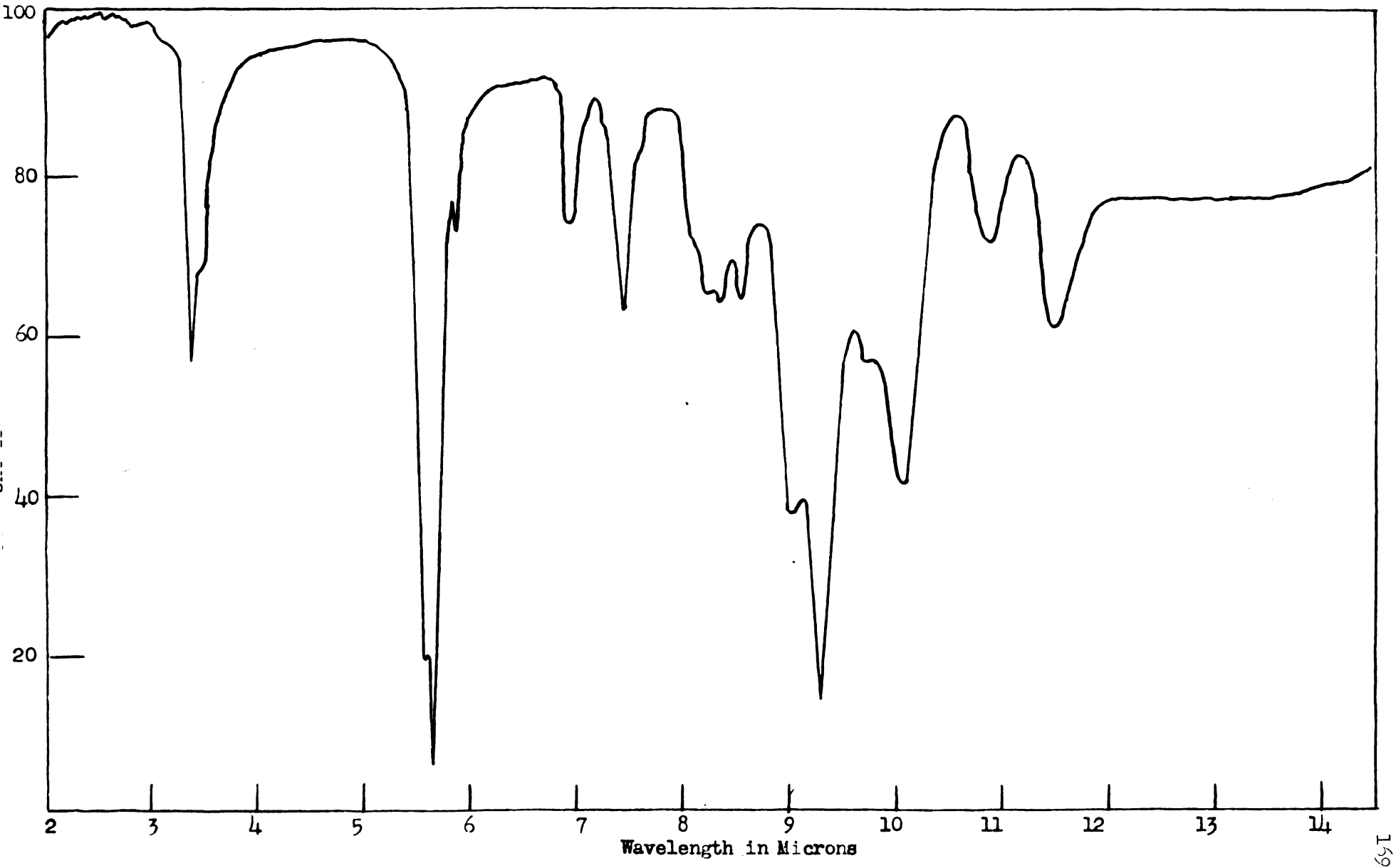


Figure 21. Infrared Spectrum of Biscyclobutaneformyl Peroxide.

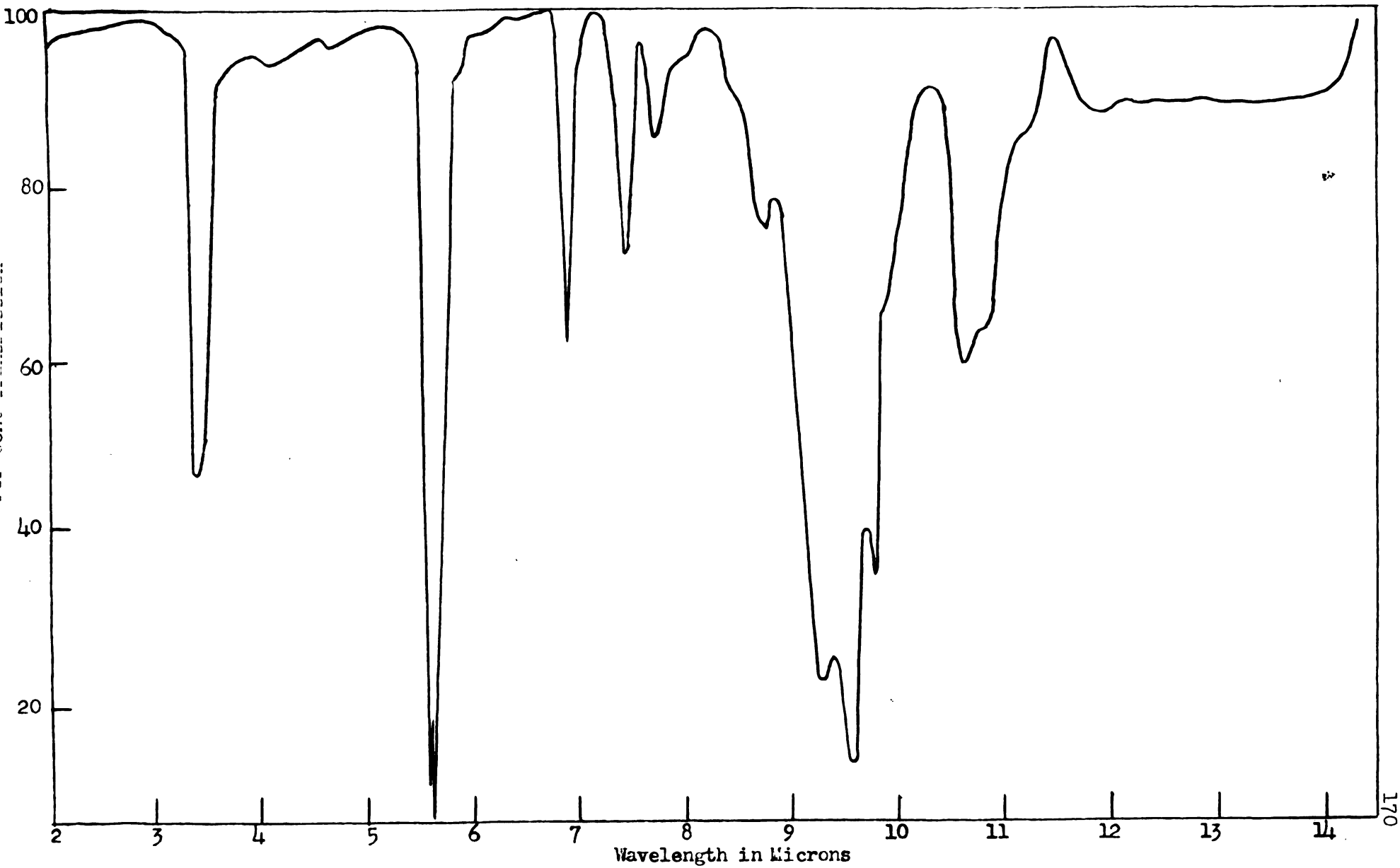


Figure 22. Infrared Spectrum of Biscyclopentaneformyl Peroxide.

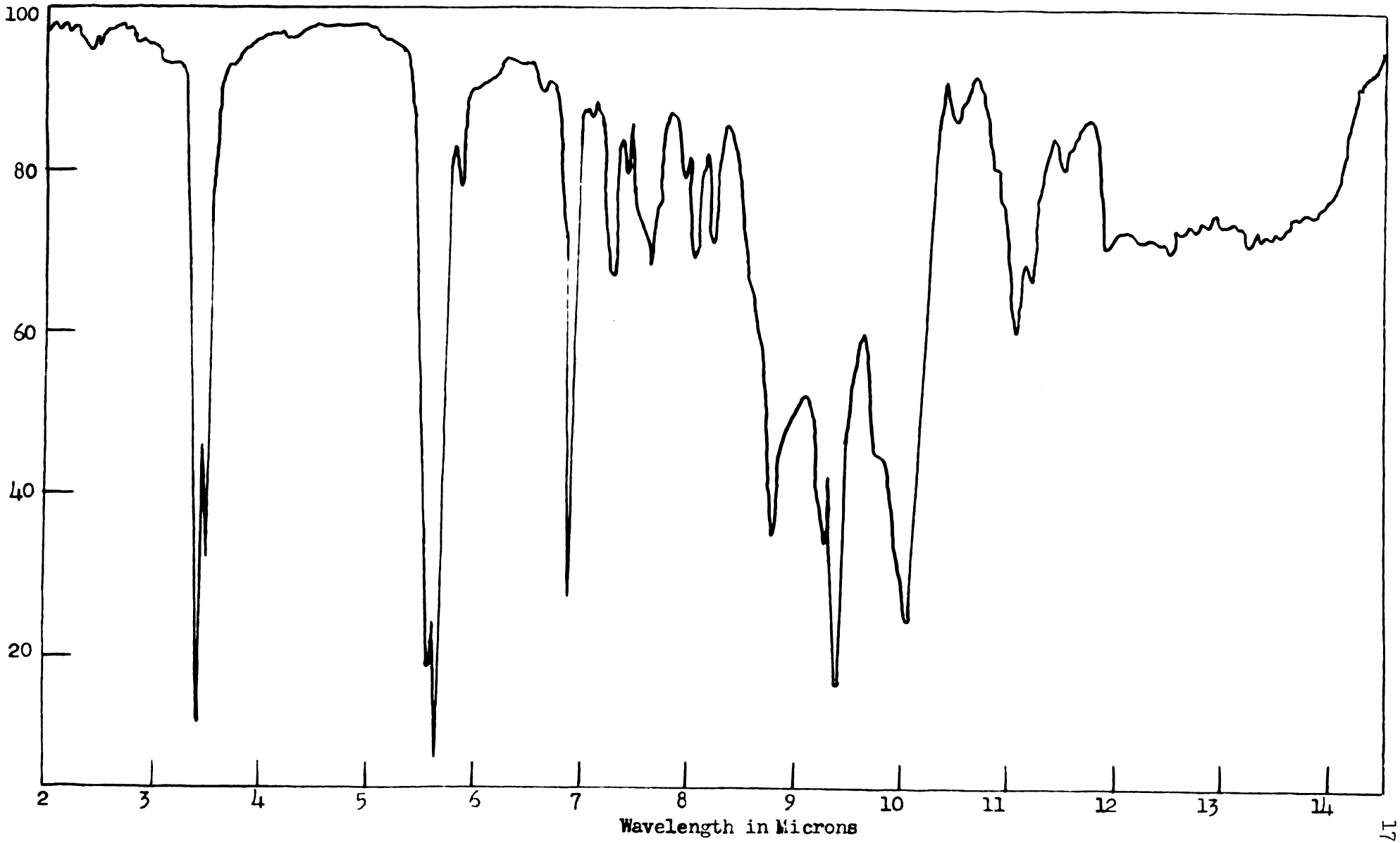


Figure 23. Infrared Spectrum of Biscyclohexaneformyl Peroxide.

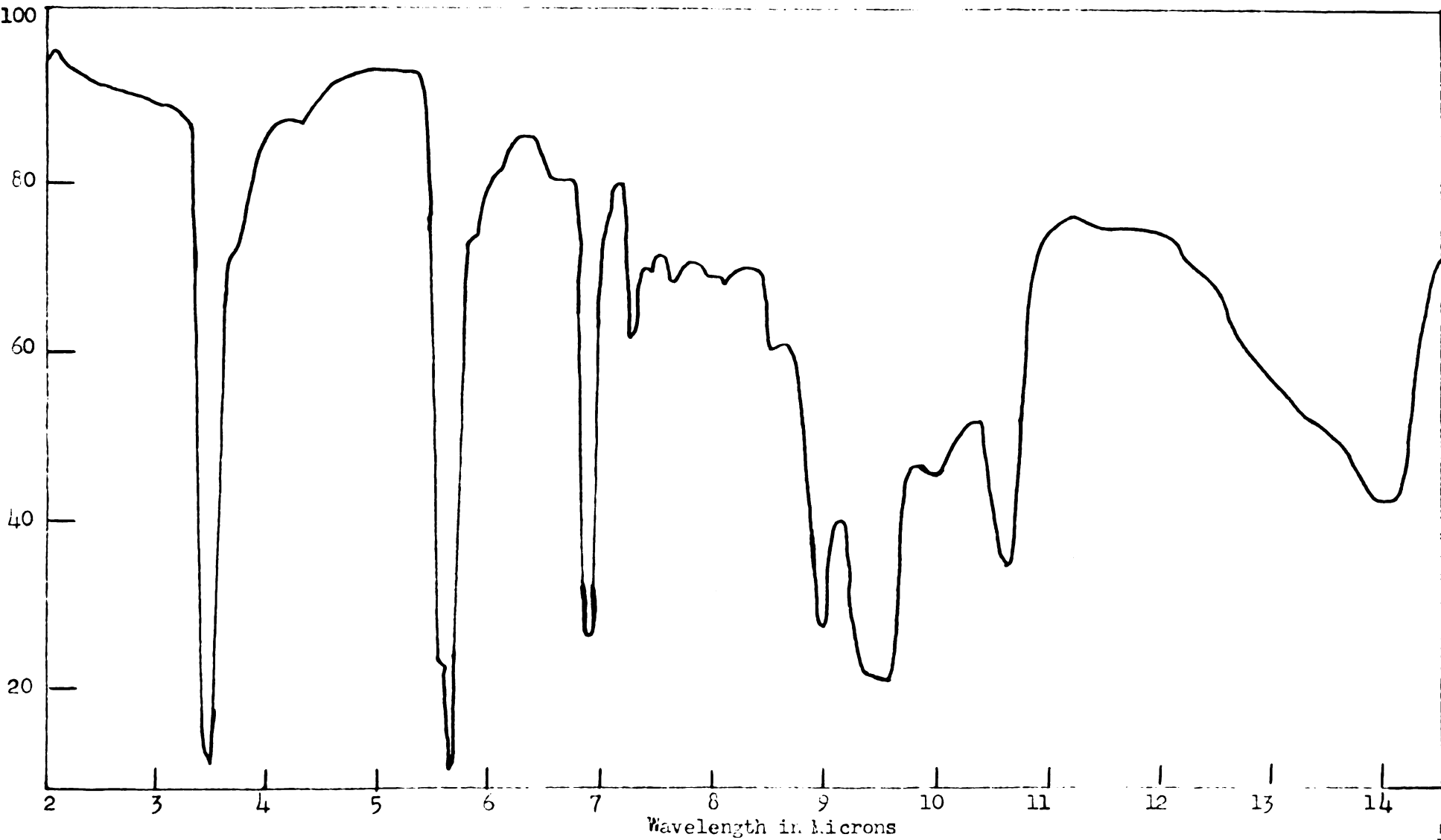


Figure 24. Infrared Spectrum of Bisc cloheptaneform l Peroxide.

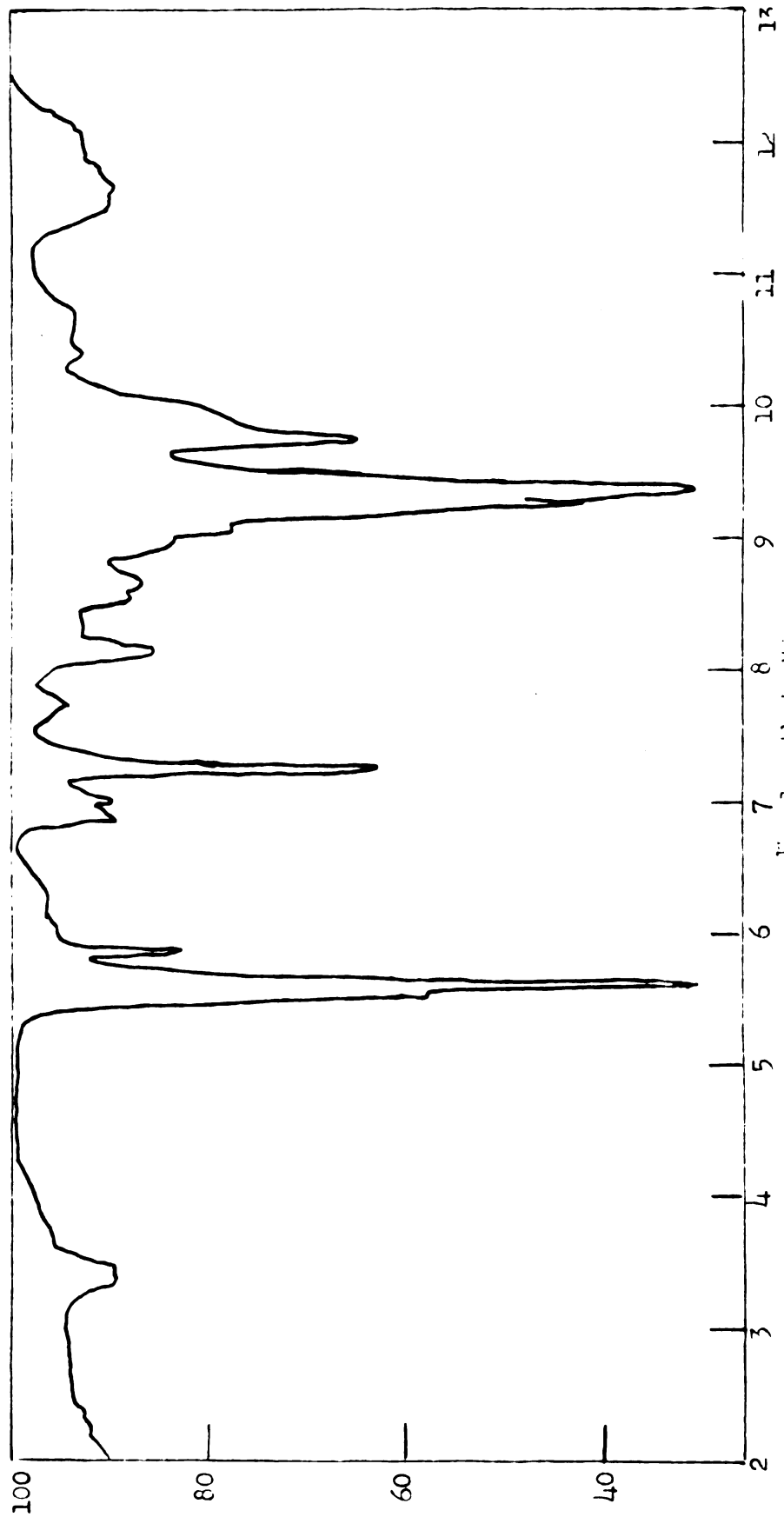


Figure 25. Infrared Spectrum of Biscyclopropaneacetyl Peroxide.

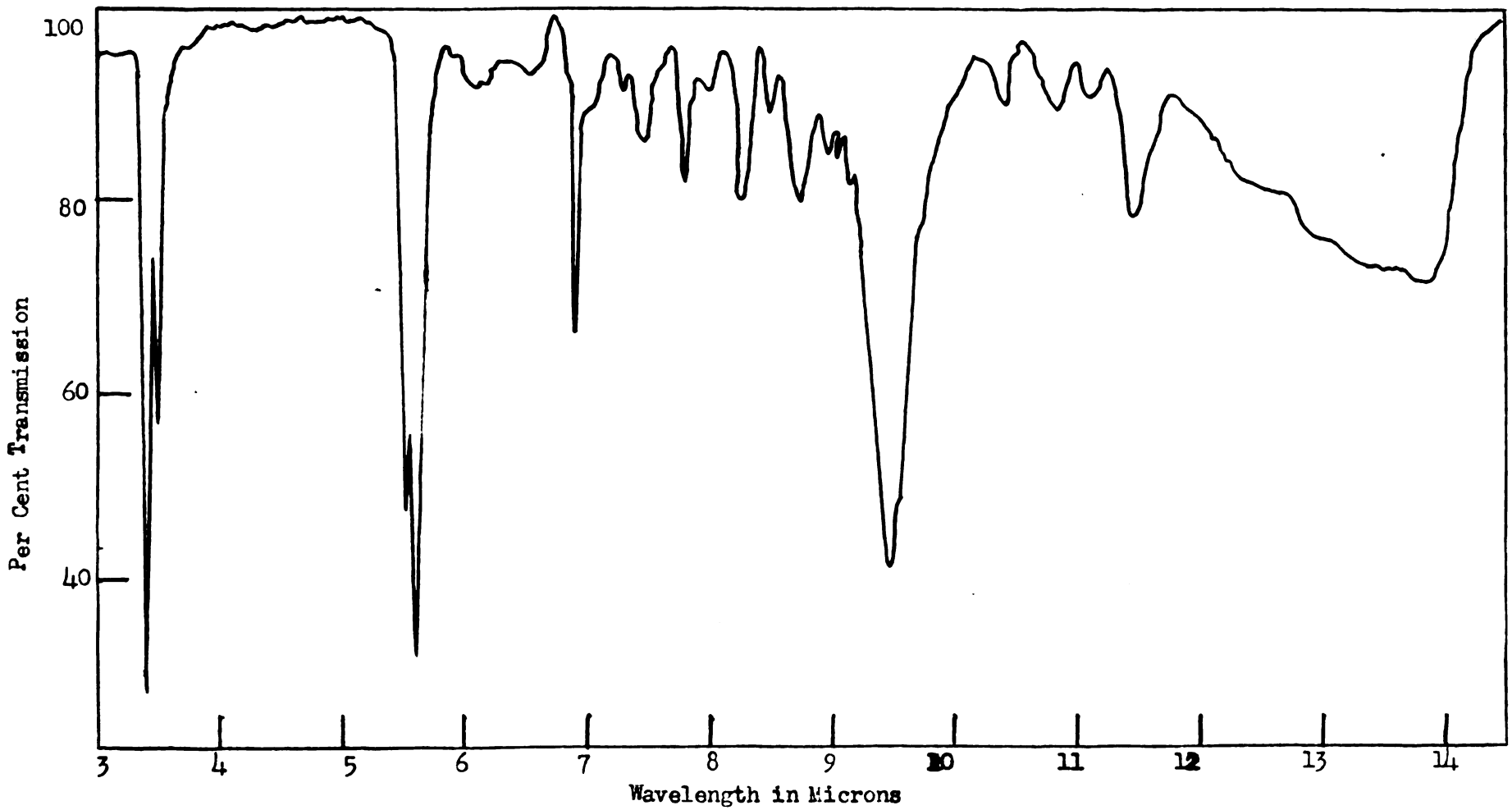


Figure 26. Infrared Spectrum of Biscyclobutaneacetyl Peroxide.

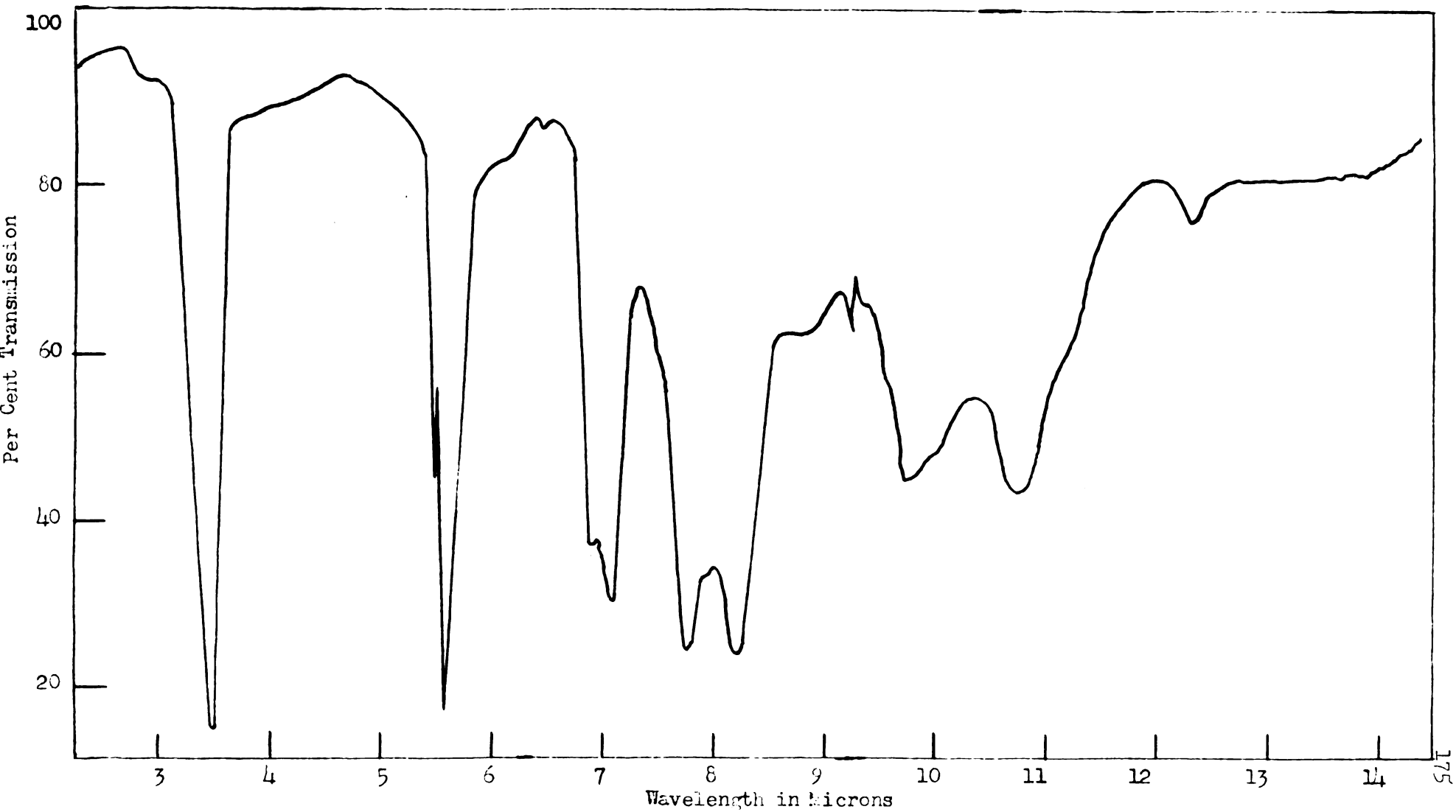


Figure 27. Infrared Spectrum of Biscyclopentaneacetyl Peroxide.

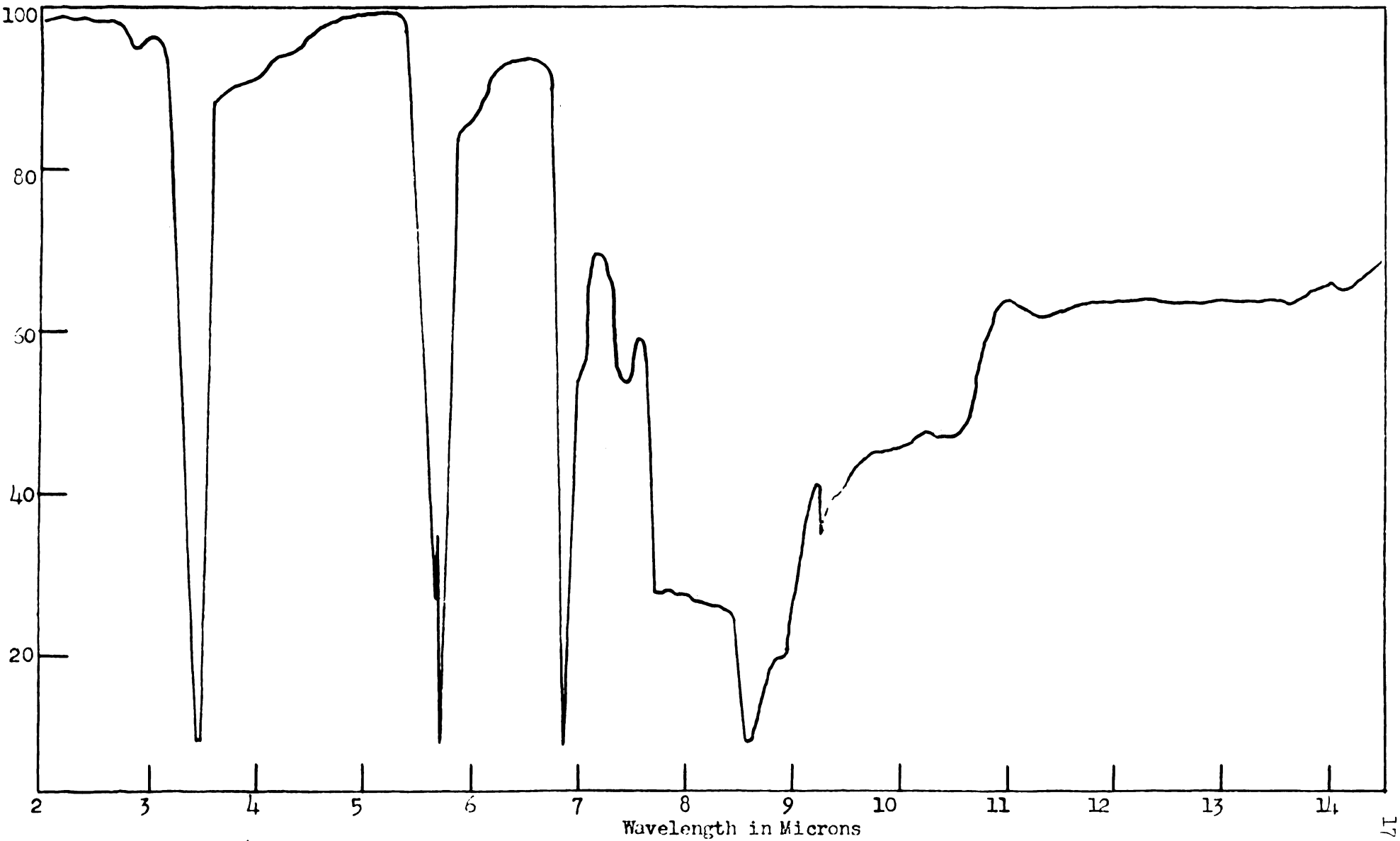


Figure 28. Infrared Spectrum of Biscyclohexaneacetyl Peroxide.

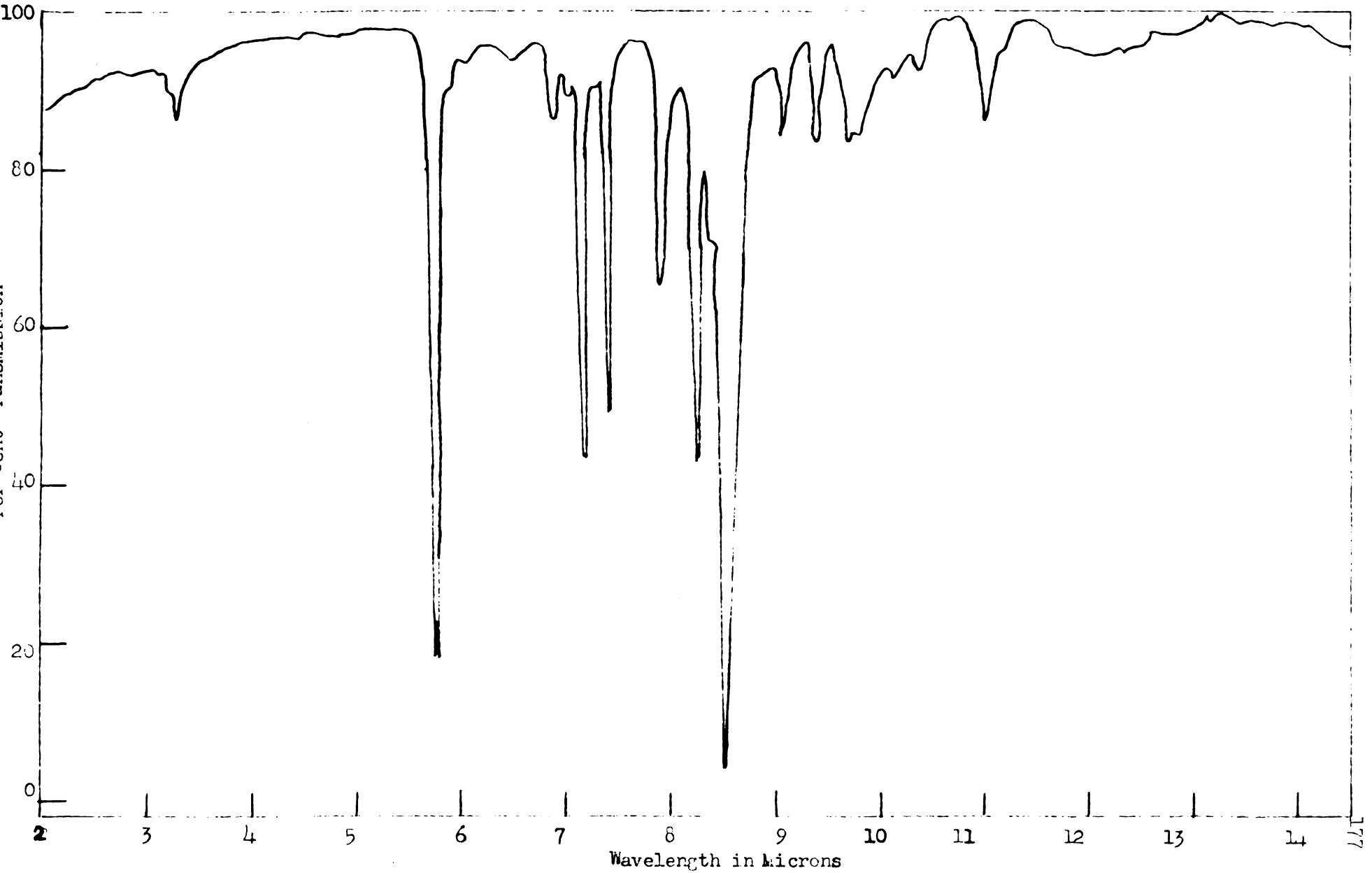


Figure 29. Infrared Spectrum of Cyclopropyl Cyclopropanecarboxylate.

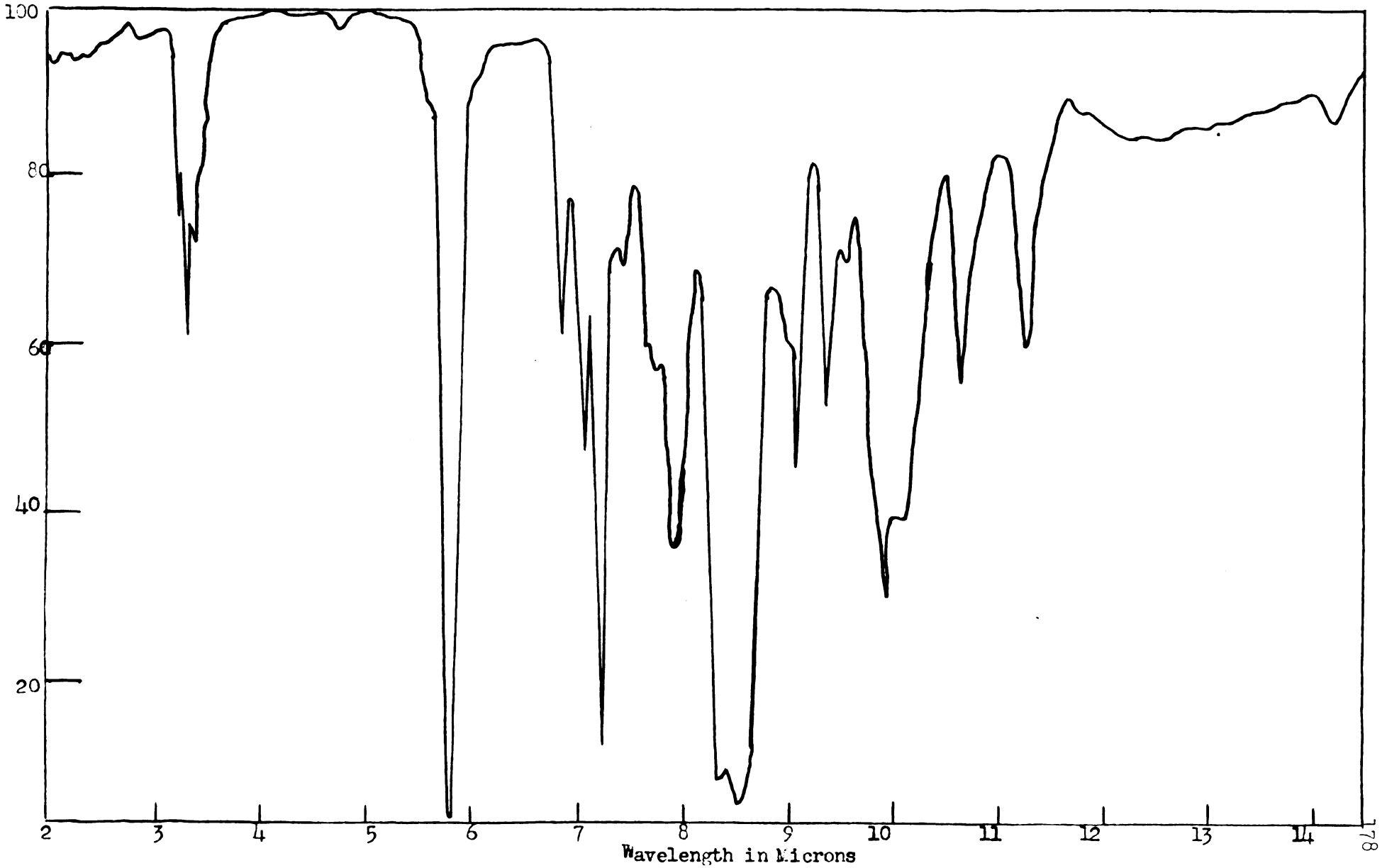


Figure 30. Infrared Spectrum of Cyclopropylcarbinyl Cyclopropaneacetate.

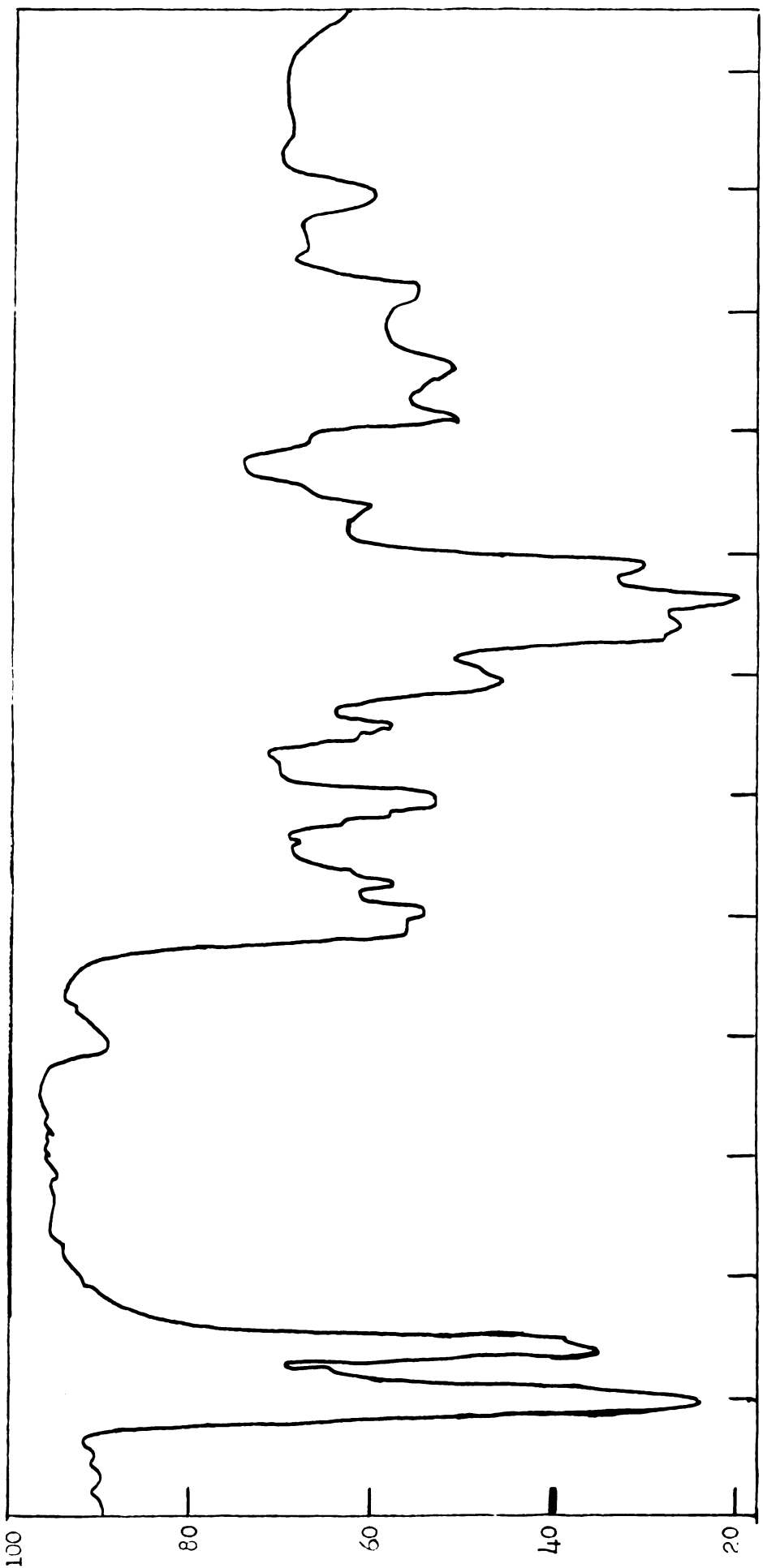


Figure 31. Infrared Spectrum of Cyclopropaneethanol.

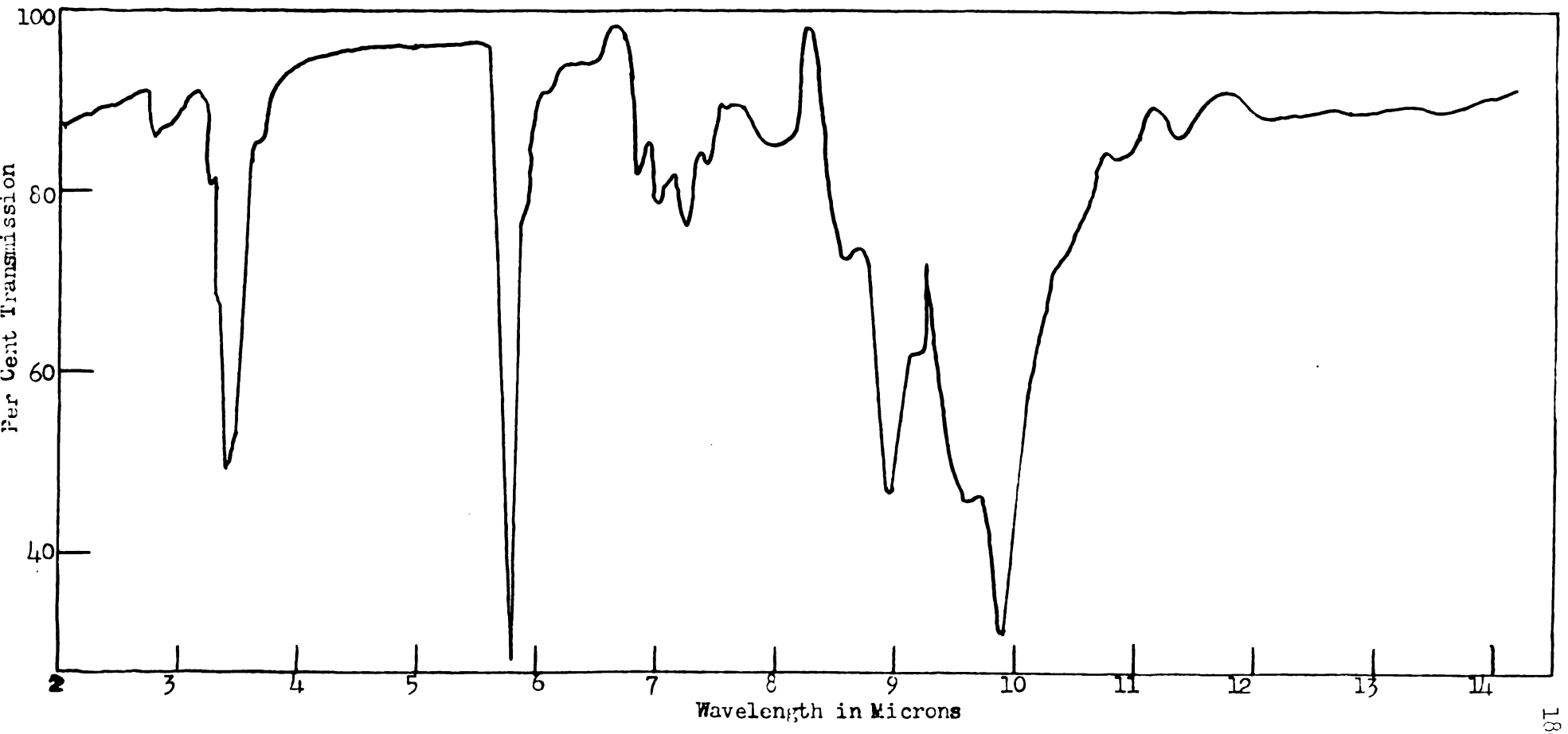


Figure 32. Infrared Spectrum of Cyclopropaneacetaldehyde.

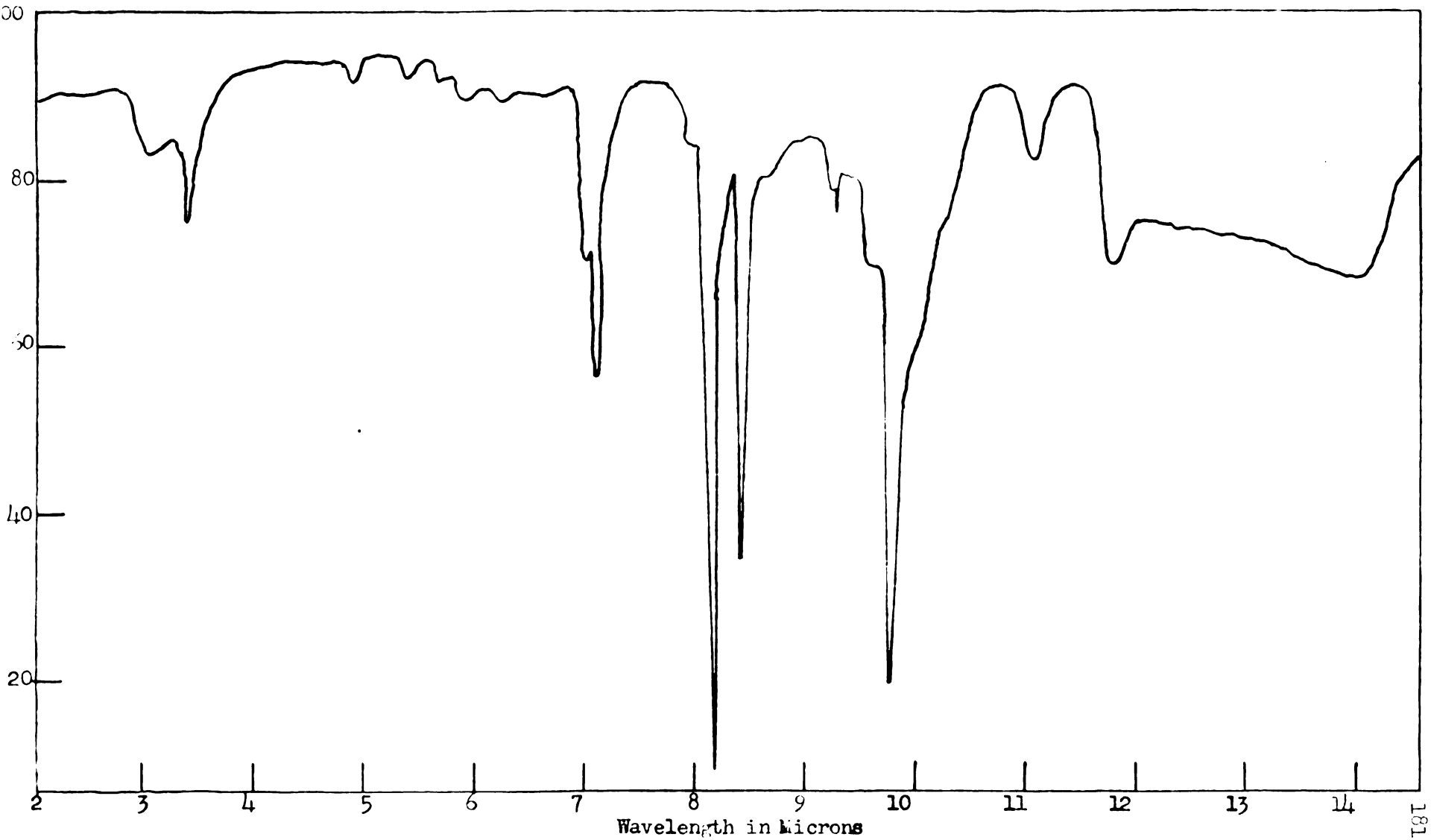


Figure 33. Infrared Spectrum of Cyclopropyl Iodide.

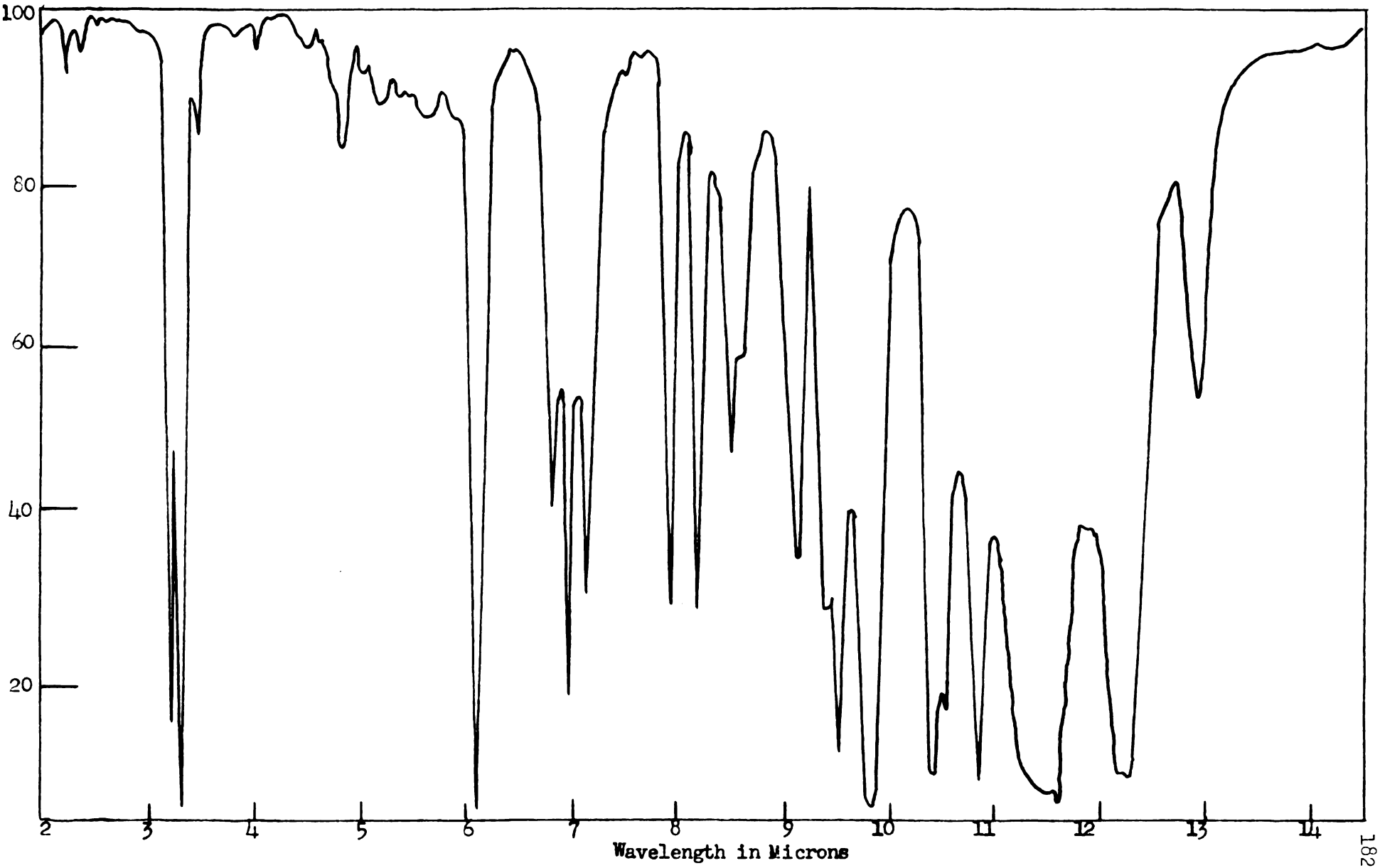


Figure 34. Infrared Spectrum of 1,1-Dicyclopropylethylene.

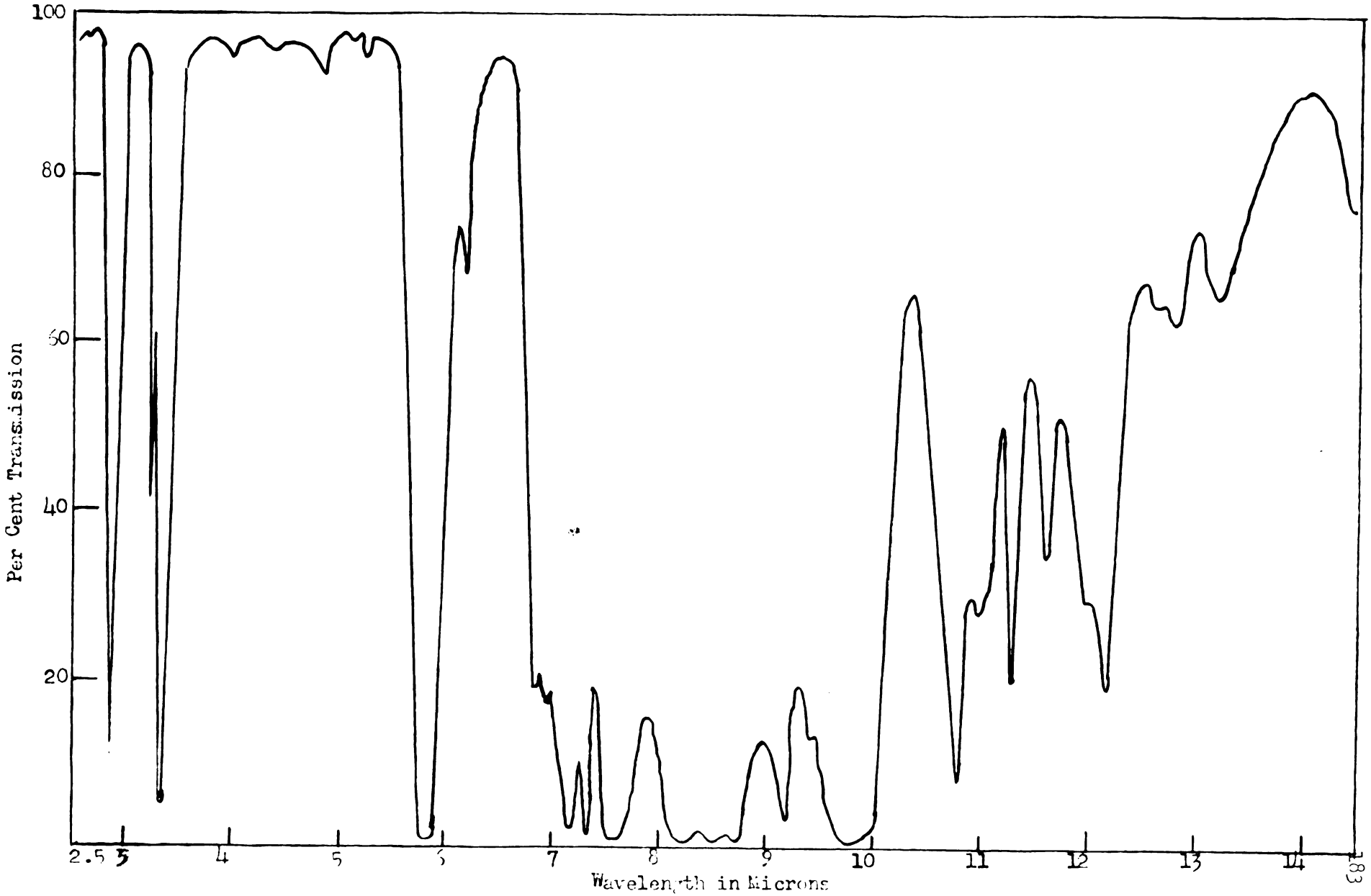


Figure 35. Infrared Spectrum of Ethyl 3,3-Dicyclopropyl-3-hydroxypropionate

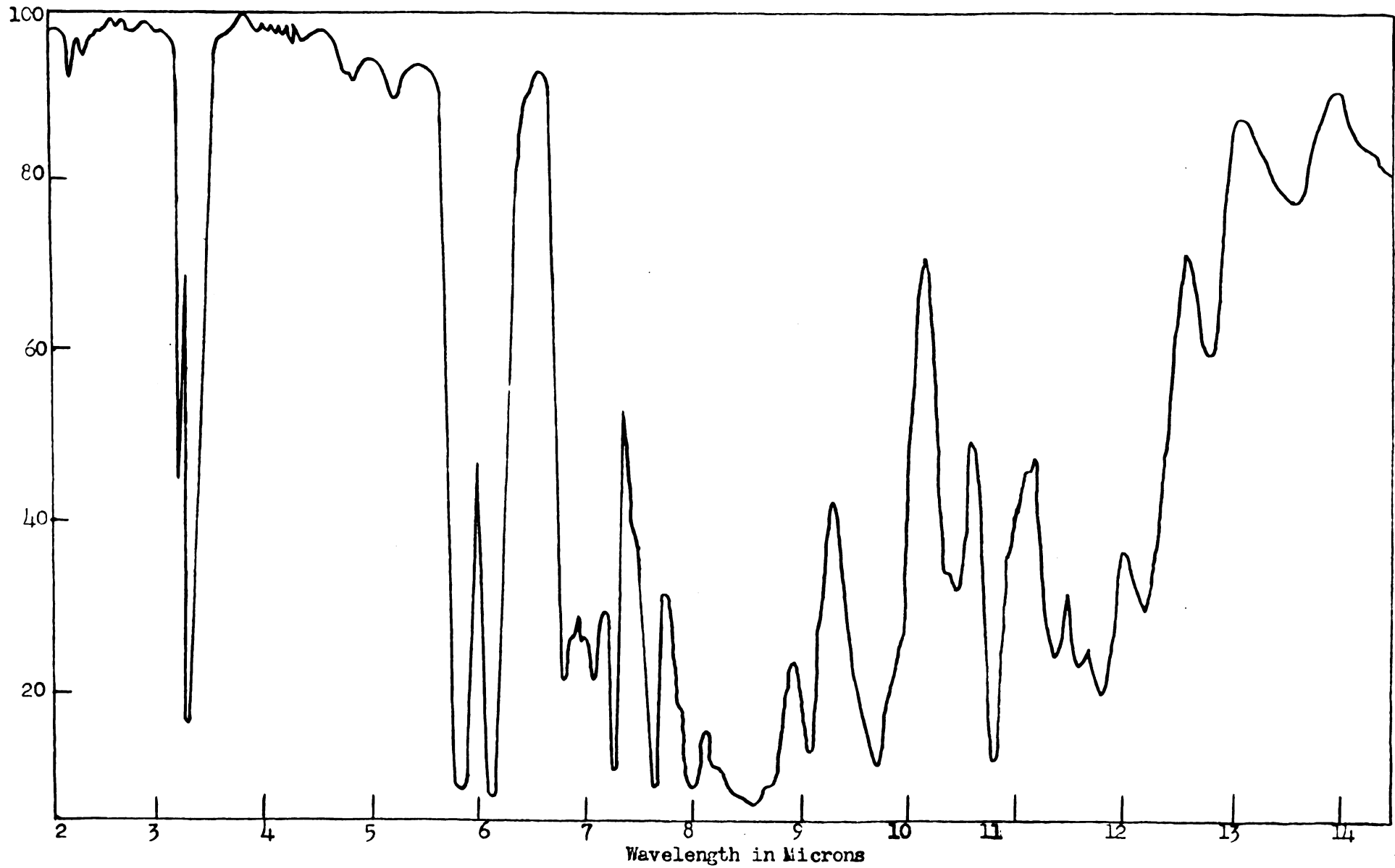


Figure 36. Infrared Spectrum of Ethyl 3,3-Dicyclopropylacrylate.

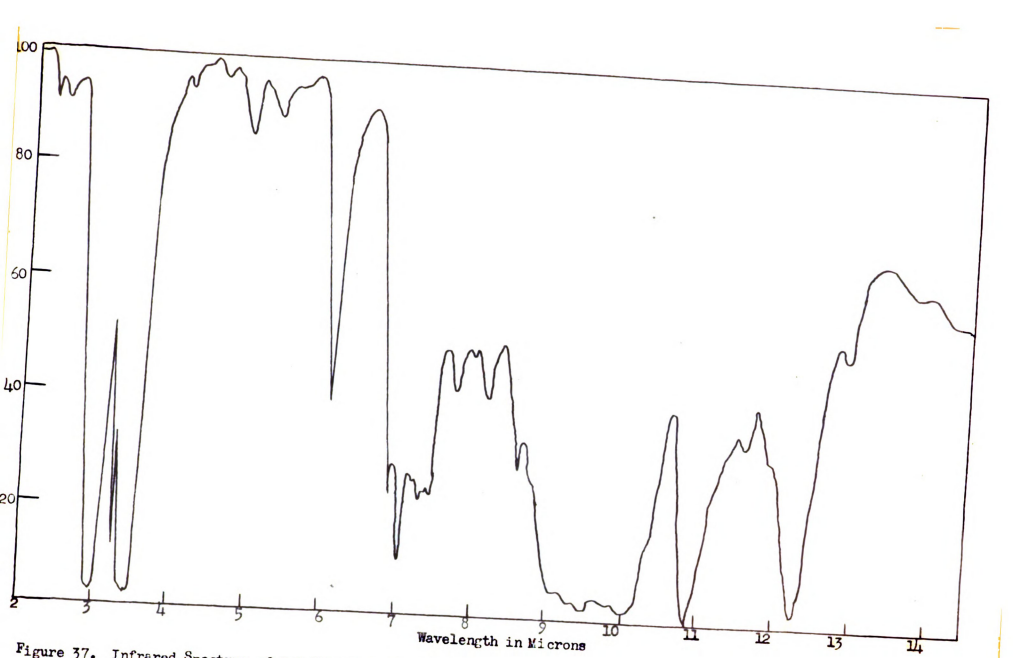


Figure 37. Infrared Spectrum of 3,3-Dicyclopropylallyl Alcohol.

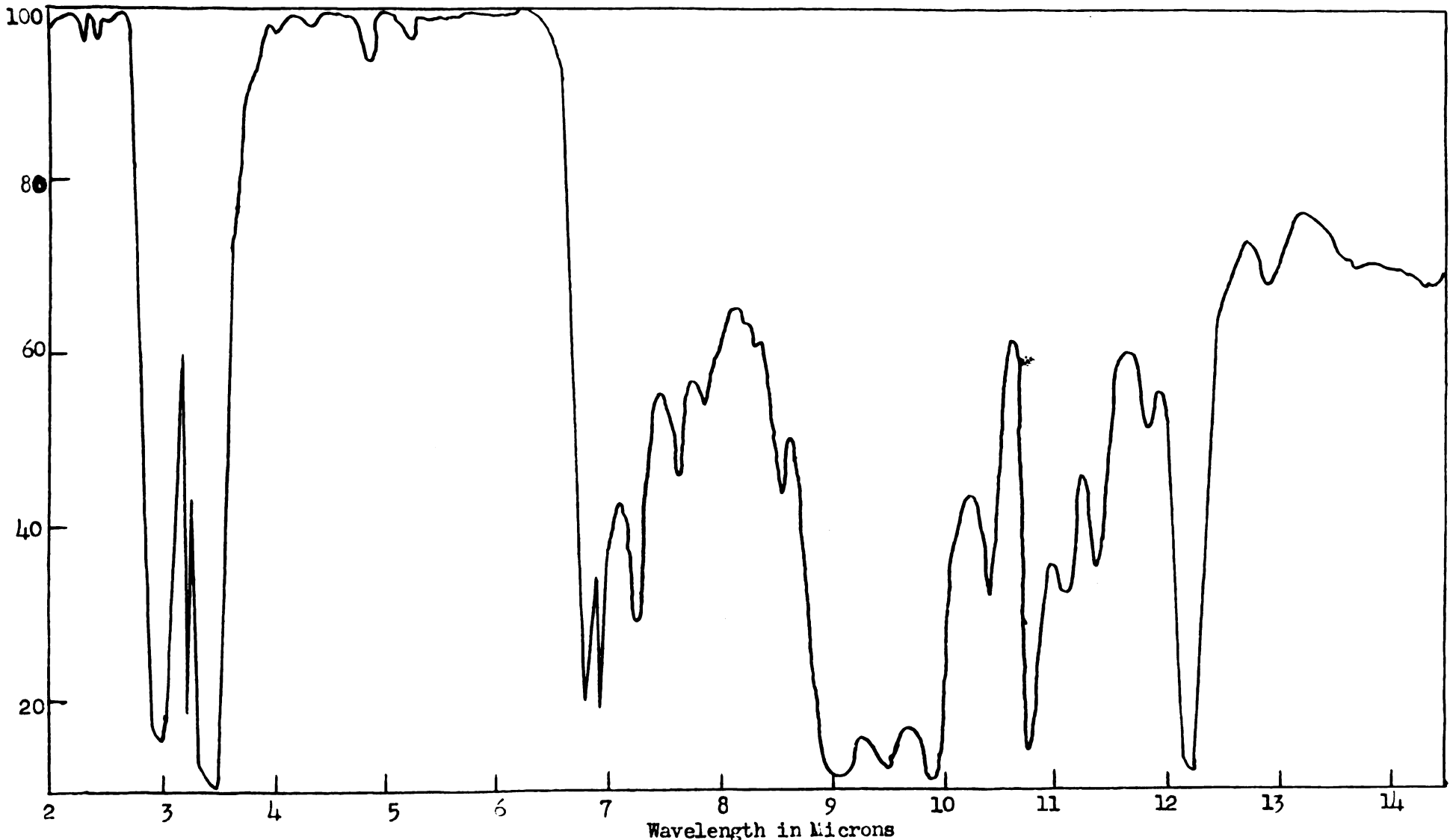


Figure 38. Infrared Spectrum of 3,3-Dicyclopropylpropanol-1.

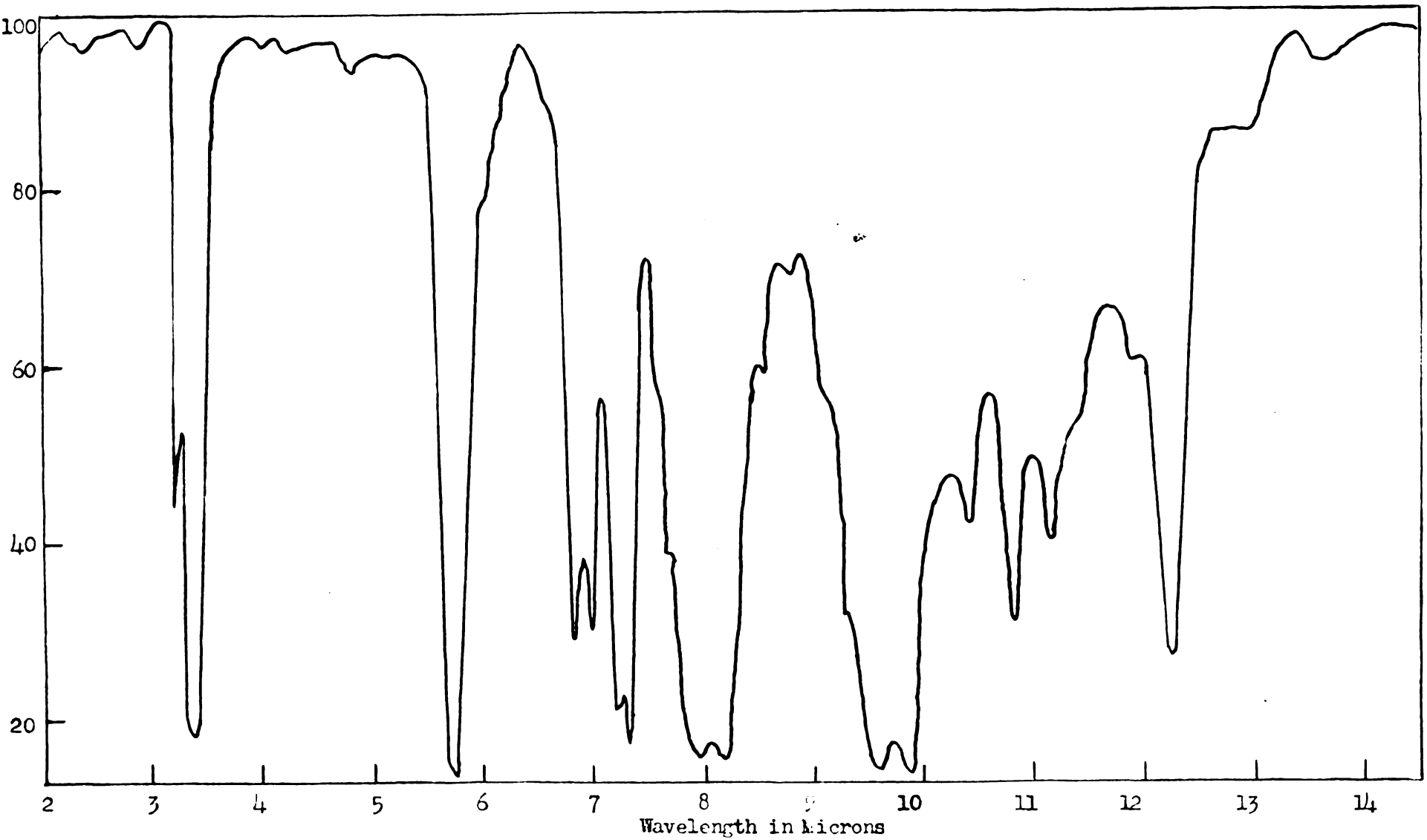


Figure 39. Infrared Spectrum of Ethyl 3,3-Dicyclopropylpropionate.

DEC 13 '57
MAY 30 '56
AUG 5 '61

CHEMISTRY LIBRARY

APR 25 '62