PRODUCTS AND RATES OF DECOMPOSITION OF SOME BICYCLIC DIACYL PEROXIDES

Thesis for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY
Frank J. Chloupek
1961

ABSTRACT

PRODUCTS AND RATES OF DECOMPOSITION OF SOME BICYCLIC DIACYL PEROXIDES

by Frank J. Chloupek

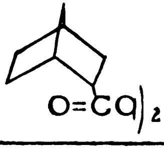
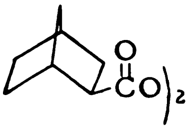
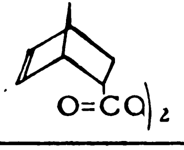
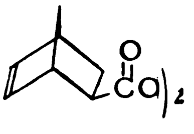
The purpose of this investigation was to obtain information concerning the behavior of free radicals in the bicyclo [2, 2, 1] heptane ring system. In particular, the question of whether or not participation would be significant in radical reactions was examined. Four diacyl peroxides derived from 2-exo- and 2-endonorbornanecarboxylic acids, and 5-exo- and 5-endonorbornenecarboxylic acids were prepared, and their rates and products of decomposition in carbon tetrachloride studied.

The principal products from 2-endonorbornanecarbonyl peroxide were carbon dioxide (79.3%), 2-endonorbornyl 2-endonorbornanecarboxylate (10.2%), 2-endonorbornanecarboxylic acid (11.2%) and 2-exochloronorbornane (not determined quantitatively). 2-Exonorbornanecarbonyl peroxide produced carbon dioxide (73.7%), 2-exonorbornyl 2-exonorbornanecarboxylate (14.8%), 2-exonorbornanecarboxylic acid (6.2%) and 2-exochloronorbornane (not determined quantitatively). 5-Endonorbornenecarbonyl peroxide yielded carbon dioxide (48.5%), 5-endonorbornenyl 5-endonorbornenecarboxylate (9.7%), the gamma-3 lactone of 2-exotrichloromethyl-3-endohydroxy-5-endonorbornanecarboxylic acid (39%), 5-exochloronorbornane (not determined quantitatively), and polychloroalkanes (not determined quantitatively). 5-Exonorbornenecarbonyl peroxide produced carbon dioxide (56.4%), 5-exonorbornenyl 5-exonorbornenecarboxylate (14.6%), a lactone

(15.3%), an acid (not determined quantitatively), 5-exochloronorbornene (not determined quantitatively), and polychloroalkanes (not determined quantitatively).

The production of the gamma-3-lactone of 2-exotrichloromethyl-3-endohydroxy-5-endonorbornanecarboxylic acid from 5-endonorbornenecarbonyl peroxide represents a novel induced decomposition involving an intramolecular attack of a radical on a carboxyl group. The production of a lactone from 5-exonorbornenecarbonyl peroxide is evidence for the occurrence of a free radical Wagner-Meerwein rearrangement.

The rates and products from decomposition produced little or no evidence for participation in free radical reactions. Steric crowding in 2-endonorbornanecarbonyl peroxide appears to be significant. The relative rates of decomposition of the various peroxides at 44.5° in carbon tetrachloride, and their energies of activation are given below.

Compound				
Relative rate	1	8	10.8	11.2
Ea (kcal. /mole)	32.8	27.1	24.0	24.7

Several new compounds in the bicyclo [2, 2, 1] heptane series were prepared. Some miscellaneous experiments involving the attempted preparations of 7-norbornenecarboxylic acids and the identification of the ester produced from the decomposition of cyclopropylacetyl peroxide are described.

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By

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A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1961

ACKNOWLEDGMENTS

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

Grateful acknowledgment is extended to Dr. William H. Reusch and Dr. Morley Russell for helpful suggestions and discussions.

Appreciation is also extended to the National Science Foundation whose fellowship program provided personal financial assistance from September, 1959 through June, 1961.

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To Trilby, My Wife, for Her Patience,
and to My Late Father for His Faith.

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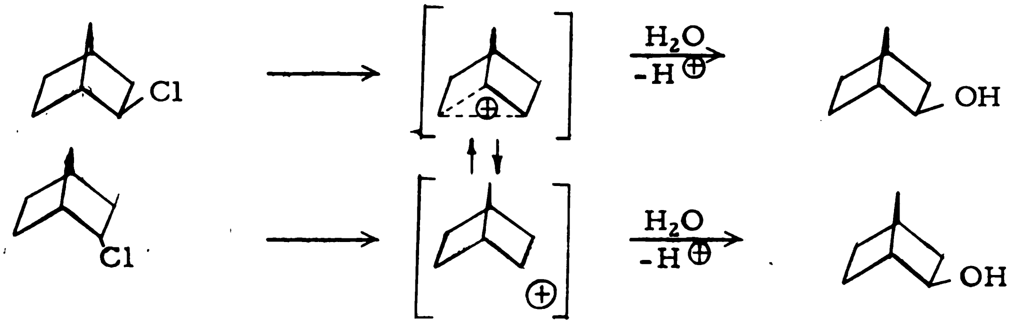
INTRODUCTION AND HISTORICAL

The bicyclo [2, 2, 1] heptane ring system has been a model structure in the study of reaction mechanisms, particularly because of its well-defined geometry and its propensity for molecular rearrangement. The classical Wagner-Meerwein rearrangement and a major part of nonclassical carbonium ion theory have been developed using this ring system (1, 2, 3).

Although this thesis is concerned with free radical reactions in the bicycloheptane series, a brief review of pertinent ionic reactions will be helpful.

Roberts (4) found that the solvolysis of 2-exochloronorbornane in 80% aqueous ethanol was 70 times faster than the corresponding endo isomer. In the exo case, the ethylene bridge can assist the ionization since it is trans to the departing chlorine (equation 1). In 2-endochloronorbornane, the ethylene bridge lies cis to the departing chlorine and the ionization must proceed without assistance (equation 2).



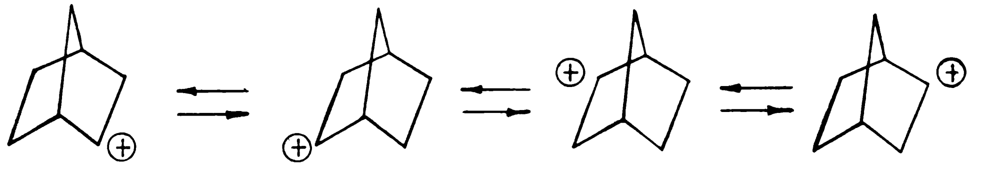
(1)

(2)

In the endo case, once the chlorine is ionized, the delocalization of appropriate bonds may occur to give the same intermediate as in the exo case. This would account for the production of only exo alcohol from either isomer.

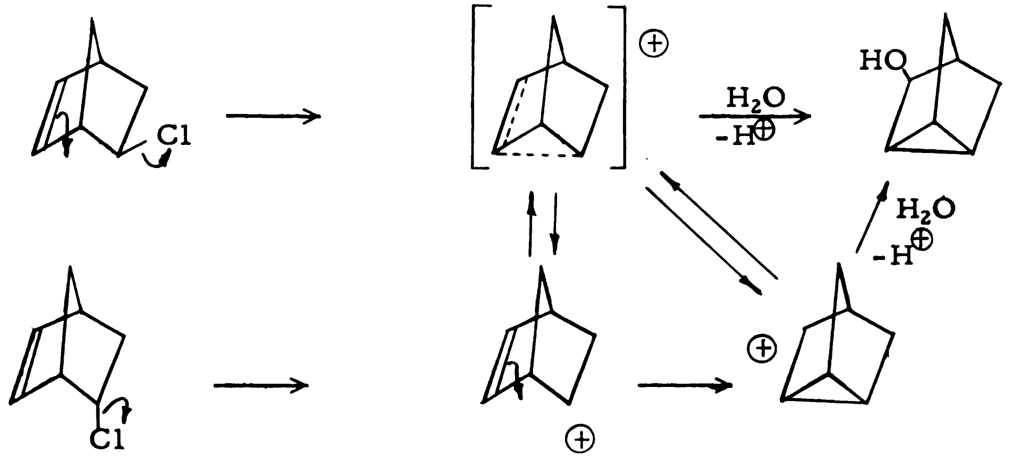
An alternate but perhaps less satisfactory explanation for the difference in rates may be steric hindrance to ionization. In the endo chloride, the change in bond hybridization from sp^3 to the sp^2 hybridization of the carbonium ion would force the departing chlorine further under the ring in close proximity to the endo hydrogens.

By using C^{14} labeling, Roberts (5) found considerable scrambling in the product, indicating hydride shifts as well as skeletal rearrangements.



(3)

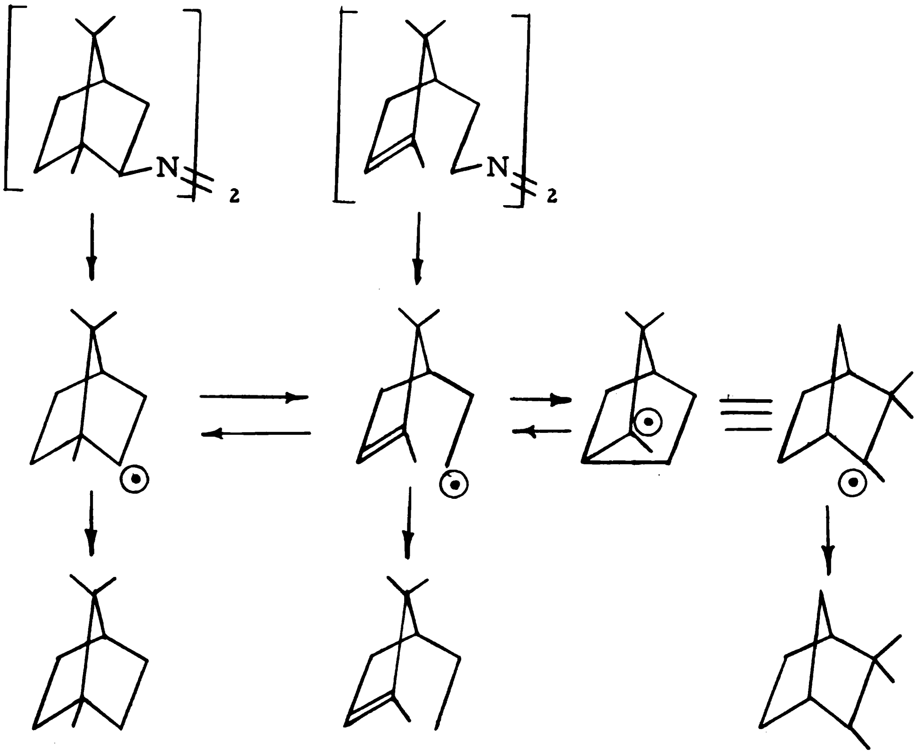
Roberts (4) also found that the solvolysis of 5-exochloronorbornene in 80% aqueous ethanol was 150 times faster than the corresponding endo isomer. This he attributed to the ability of the double bond to participate in the ionization of the chloride. Again the exo isomer has the necessary trans configuration.



(4)

Alkyl rearrangements of free radicals are not as well known. Berson (6) has presented evidence for a free radical Wagner-Meerwein rearrangement in the decomposition of 2, 2'-bisazocamphane. Along with camphane and the disproportionation products, Berson obtained

2,3,3-trimethyl-4-ethylcyclopentene and isocamphane. The same products were formed in the decomposition of the azo compound prepared from campholenaldehyde. Berson postulates the following mechanism:



(5)

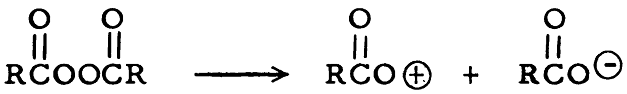
The work described in this thesis was undertaken to examine the behavior of free radicals in the bicyclo[2, 2, 1]heptane ring system. In particular, the question of whether or not participation would be significant in radical reactions, as it is known to be in ionic reactions, was examined. Four diacyl peroxides, derived from 2-exo-and 2-endonorbornanecarboxylic acids, and 5-exo- and 5-endonorbornenecarboxylic acids were prepared, and their rates and products of decomposition in carbon tetrachloride studied.

Diacyl peroxides are of considerable interest in that they provide a convenient route to free radicals, are generally easy to prepare, and are sufficiently unstable to allow investigation not too far above room temperature. A number of textbooks (9, 10, 11, 12) contain excellent reviews of diacyl peroxide decomposition.

There are essentially two modes of diacyl peroxide decomposition, the <u>spontaneous</u> fission of the oxygen-oxygen bond homolytically to form radicals,

$$R\overset{O}{\overset{\|}{C}}OO\overset{O}{\overset{\|}{C}}R \longrightarrow 2R\overset{O}{\overset{\|}{C}}O\cdot \qquad (6)$$

or heterolytically to form ions,

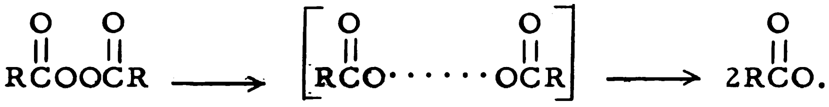


$$R\overset{O}{\overset{\|}{C}}OO\overset{O}{\overset{\|}{C}}R \longrightarrow R\overset{O}{\overset{\|}{C}}O\oplus + R\overset{O}{\overset{\|}{C}}O^{\ominus} \qquad (7)$$

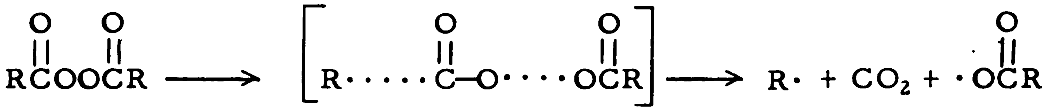
and the corresponding <u>induced</u> decomposition by radicals (13, 14) or by ions (15).

The decomposition of a dilute solution of a symmetrical diacyl peroxide in a non-polar solvent provides the most favorable conditions for homolytic fission. This appears to be a direct result of the small bond dissociation energy of the oxygen-oxygen linkage. This energy has been estimated at 27-35 kcal./mole (16).

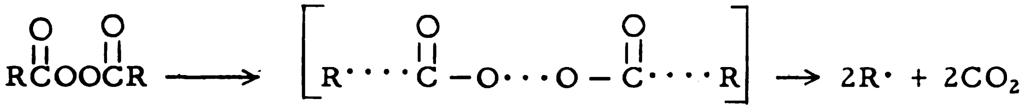
A major problem in the homolytic mode of decomposition is the extent of carbon-carbon breakage in the rate-determining step. The decomposition can proceed in any or all of the three paths shown in equations 8, 9, and 10.



$$R\overset{O}{\overset{\|}{C}}OO\overset{O}{\overset{\|}{C}}R \longrightarrow \left[R\overset{O}{\overset{\|}{C}}O\cdot\cdots\cdots O\overset{O}{\overset{\|}{C}}R\right] \longrightarrow 2R\overset{O}{\overset{\|}{C}}O. \qquad (8)$$

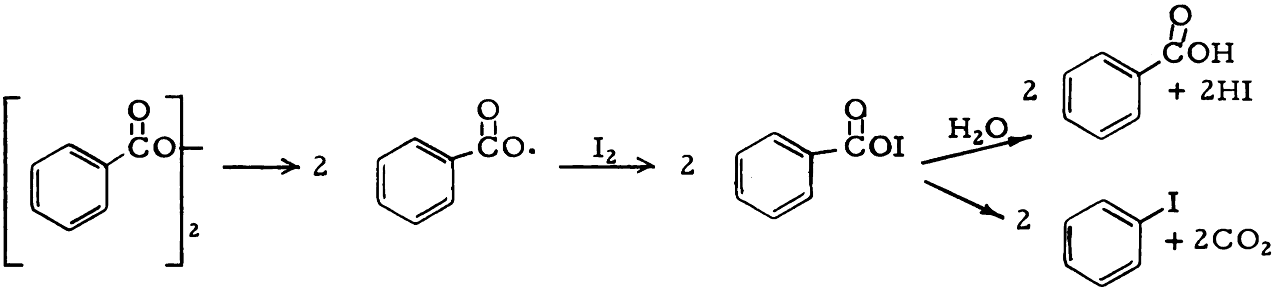


$$R\overset{O}{\overset{\|}{C}}OO\overset{O}{\overset{\|}{C}}R \longrightarrow \left[R\cdot\cdots\cdot\overset{O}{\overset{\|}{C}}\text{—}O\cdot\cdots O\overset{O}{\overset{\|}{C}}R\right] \longrightarrow R\cdot + CO_2 + \cdot O\overset{O}{\overset{\|}{C}}R \qquad (9)$$



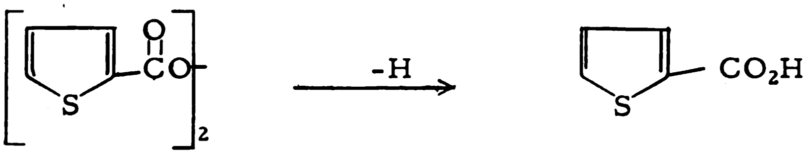
$$R\overset{O}{\overset{\|}{C}}OO\overset{O}{\overset{\|}{C}}R \longrightarrow \left[R\cdot\cdots\overset{O}{\overset{\|}{C}}-O\cdots O-\overset{O}{\overset{\|}{C}}\cdots R\right] \longrightarrow 2R\cdot + 2CO_2 \qquad (10)$$

When R is aryl, there is good evidence for equation 8 as a model for spontaneous decomposition. Hammond and Soffer (17) obtained benzoic acid quantitatively by decomposing benzoyl peroxide in the presence of iodine and water. In the absence of water, iodobenzene was obtained in better than 90% yield.



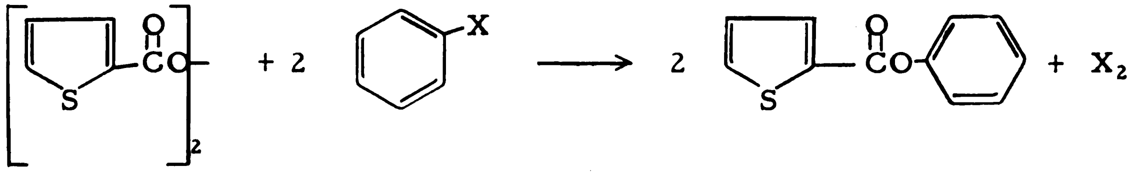
(11)

Ford and Mackay (18, 19) and also Teller (20) in their work with heterocyclic diacyl peroxides have shown that even in the absence of inhibitors, only small amounts of carbon dioxide are liberated and the major product is the corresponding acid.



(12)

In the presence of halogenated benzenes, the phenyl ester and halogen are major products.



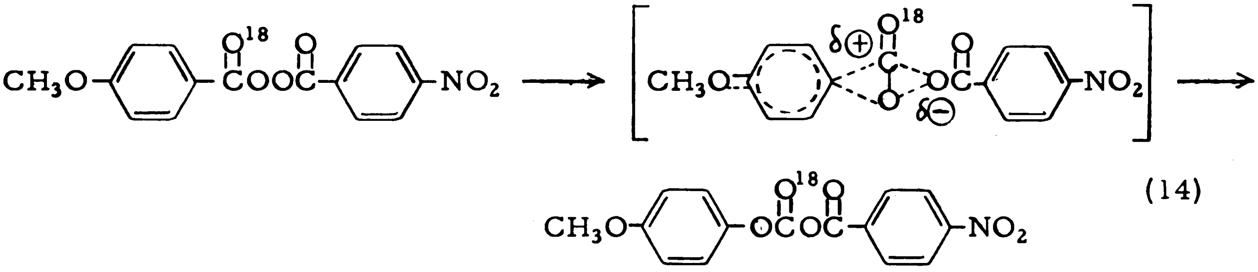
(13)

Walling and Hodgdon (7) reported that in the decomposition of acetyl peroxide in the presence of iodine and water, no acetic acid is produced, the main product being methyl iodide. This supports equation 10 but Szwarc (21) and also DeTar and Weis (22) have substantial evidence to indicate the absence of acid is due to the very rapid loss of carbon dioxide from the acyloxy radical. More recently, Shine and Hoffman (8) have provided evidence for the existence of the acetoxy free radical.

There is some evidence for multiple bond scission. This can be important when a radical of high stability such as t-butyl or trichloromethyl is produced. A notable example stems from the work of Bartlett and Leffler (23) with phenylacetyl peroxide. They found that phenylacetyl peroxide decomposes faster at 0^{o} than benzoyl peroxide at 80^{o}, and attributed the rate increase to multiple scission as shown in equation 9.

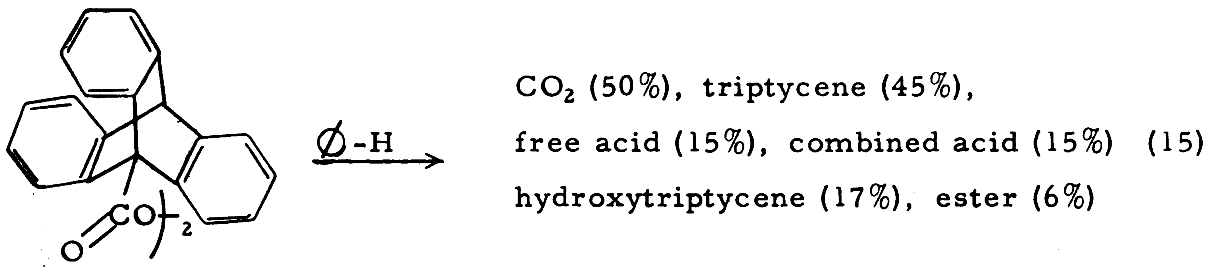
Homolytic fission is often accompanied by induced decomposition due to the presence of radicals in solution. Since this complicates the kinetics by giving rise to higher reaction order, it must be corrected for or eliminated. Kinetic analysis (14) or the use of a radical trap (17) has been effective. Concentration is a very important factor in controlling induced decomposition (24). The nature of the solvent (14) and temperature (24) are also factors. The position of attack of the inducing agent varies, and may be determined by isolation of the products (25, 26).

Heterolytic fission of diacyl peroxides is favored by a decrease in symmetry of the molecule and the use of solvents of high polarity. The transition state can vary from a slight polarization of the oxygen-oxygen bond to complete dissociation into ions. Leffler (15) in his study of 4-methoxy-4'-nitrobenzoyl peroxide found that in non-polar solvents, this peroxide decomposes at the same rate as benzoyl peroxide. But in polar solvents, the rate is increased markedly. Leffler attributed this to an ionic mechanism (equation 7) supplanting the homolytic fission. This is supported by the ability to induce decomposition by acids at a rate proportional to the acidity constant of the acid. In later work, Leffler and Petropoulos (27) found that 3, 5-dinitro-4'-methoxybenzoyl peroxide was even more susceptible to acid than the 4-methoxy-4'-nitrobenzoyl peroxide. Making use of oxygen^{18}, Denny has shown (28) that the 4-methoxy-4'-nitrobenzoyl peroxide decomposition mechanism is not adequately represented by equation 7 since no equilibration of oxygens was found. If the ions were free, the oxygens should equilibrate. Denny's postulated mechanism is shown in equation 14.



(14)

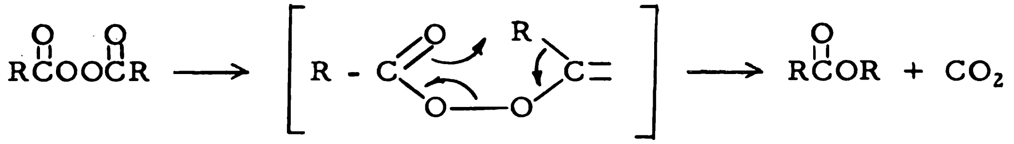
Bartlett and Greene (29) in their investigation of ditriptoyl peroxide, have made a detailed product study which indicates the operation of three separate mechanisms in the decomposition.



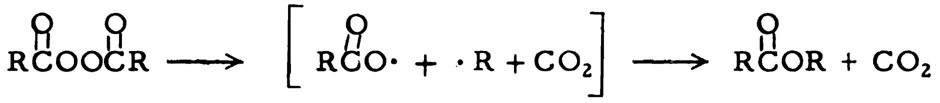
(15)

In the presence of iodine, 45% of iodotriptycene was obtained, but the amount of alcohol remained 17%. Equation 9 accounts for the major products while equations 8 and 14 account for the lesser products. The formation of ester will be discussed in the following paragraph.

The formation of ester in diacyl peroxide decompositions can run from 0-100% of theoretical. The mechanism of ester formation is thought to be of a cyclic intramolecular nature (22) or a geminate recombination process (30, 31).

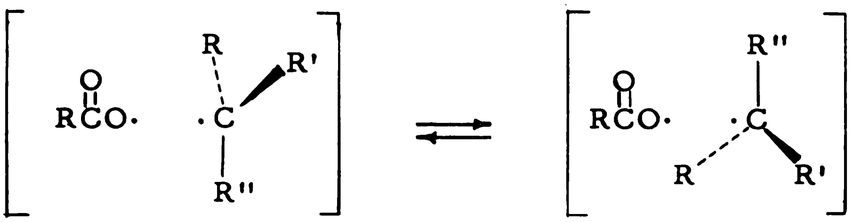


(16)



$$R\overset{O}{\overset{\|}{C}}OO\overset{O}{\overset{\|}{C}}R \longrightarrow \left[R\overset{O}{\overset{\|}{C}}O\cdot + \cdot R + CO_2\right] \longrightarrow R\overset{O}{\overset{\|}{C}}OR + CO_2 \qquad (17)$$

Either reaction would occur in a solvent "cage." The formation of nearly quantitative amounts of ester as found by Hart and Lau (32) in the decomposition of trans-4-t-butylcyclohexanecarbonyl peroxide tends to refute the geminate recombination mechanism since one might expect some diffusion into the solvent. There are also numerous examples of optically active diacyl peroxides that give rise to optically active esters (33, 34, 35). Although there is some racemization, this is also evidence against equation 17 since if one estimates the energy of activation for racemization at 2 kcal./mole, one would expect random rotation of the planar free radical to occur before recombination. One must, however, take into account the fact that the reaction takes place in a solvent "cage," and even if one considers the alkyl radical in equation 17 to be planar, a fully racemic product would necessitate a 180° rotation before recombination.



(18)

Thus the formation of ester may very well be a highly stereospecific recombination of radicals.

RESULTS AND DISCUSSION

I. Decomposition Products from Diacyl Peroxides

A. Products from Saturated Peroxides

1. Products from 2-Endonorbornanecarbonyl Peroxide

The products from the decomposition of 2-endonorbornanecarbonyl peroxide are consistent with other aliphatic diacyl peroxides. The major products (see Table 1) were alkyl halide, carbon dioxide, acid, and ester. The large yields of carbon dioxide (73.7%) and small yields of acid (11.2%) and ester (14.8%) parallel the products of decomposition of delta-phenylvaleryl peroxide. DeTar and Weis (22) found that in carbon tetrachloride, this peroxide produced 84% carbon dioxide, 4% delta-phenylvaleric acid, and 17.5% gamma-phenylbutyryl delta-phenylvalerate. They concluded that two acyloxy radicals were formed initially, and that subsequent loss of carbon dioxide occurred rapidly.

The ester formed from 2-endonorbornanecarbonyl peroxide was 2-endonorbornyl 2-endonorbornanecarboxylate. Starting with 6.25 mmoles of peroxide, 0.512 mmoles of pure ester was isolated. Using infrared analysis, the total ester produced was 0.204 mmoles/mmoles of peroxide. The similarity of infrared spectra of endo and exo isomers, and the complexity of the product spectrum did not allow setting a limit of detection on any one isomer. On the basis of isolation, 46% of the ester formed retains the endo configuration. It must be emphasized, however, that recovery involves a sublimation and a crystallization to yield analytically pure material and handling losses are considerable.

Alkyl halide was distilled along with the last traces of carbon tetrachloride. The alkyl halide was identified as 2-exochloronorbornane by infrared but was not determined quantitatively.

Table 1. Products of Decomposition of 2-Endonorbornanecarbonyl Peroxide in Carbon Tetrachloride After 72 Hours at 78° (1.17 mmoles of peroxide in 50 ml. of carbon tetrachloride).

Product	Mmoles	Mmoles/mmoles peroxide	Av. mmoles/ mmoles peroxide	$\%CO_2$	%R
Carbon dioxide	1.73 1.72	1.475 1.470	1.473	73.7[a]	0
	1.77* 1.76*	1.509 1.503	1.506	75.3[b]	0
Ester (ϵ=489 l./g.-cm)	0.35 0.34	0.299 0.291	0.295	14.8[a]	29.5[a]
	0.27* 0.28*	0.231 0.239	0.235	11.8[b]	23.5[b]
Acid (ϵ=505 l./g.-cm)	0.14 0.15	0.120 0.128	0.124	11.2[a]	11.2[a]
	0.19* 0.19*	0.162 0.162	0.162	14.8[b]	14.8[b]

* 0.2 M Styrene present

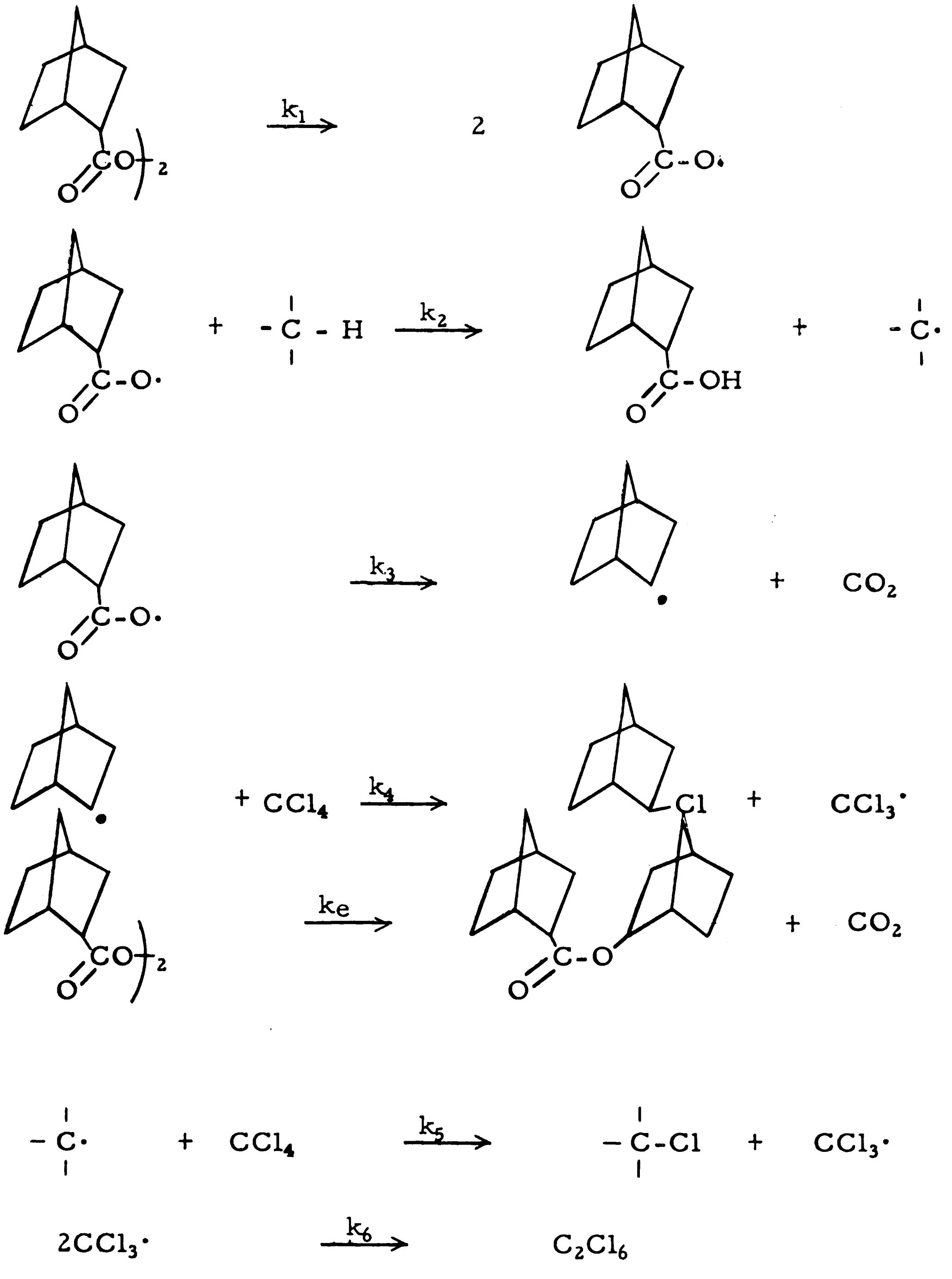
[a] Accounts for 100.7% of carbonyl, 40.7% of alkyl.

[b] Accounts for 101.9% of carbonyl, 38.3% of alkyl.

2-Exochloronorbornane was identified but not determined quantitatively.

Extraction of the decomposition products with 5% sodium carbonate produced 2-endonorbornanecarboxylic acid. Identification of the acid and the ester was based on melting points, mixed melting points, and infrared spectra.

On the basis of products formed, a mechanism can be written:



(17)

Applying steady state approximations, there is obtained the same form of rate expression as calculated by Bartlett and Nozaki for the decomposition of benzoyl peroxide (14).

$$-\frac{dp}{dt} = k_1 p + k_e p + k_i p^{\frac{3}{2}} \qquad (18)$$

For the mechanism written, the k_i term is zero since no induced decomposition is illustrated.

2. Products from 2-Exonorbornanecarbonyl Peroxide.

The products from the decomposition of 2-exonorbornanecarbonyl peroxide parallel those obtained from the endo isomer. The products are summarized in Table 2. The methods of detection and identification were identical to those employed in the endo case.

The major products included carbon dioxide (79.3%), 2-exonorbornanecarboxylic acid (6.2%), and 2-exonorbornyl 2-exonorbornanecarboxylate (10.2%). The alkyl halide was identified as 2-exochloronorbornene by infrared but was not determined quantitatively.

The mechanism for this decomposition would be identical to sequence 17, and the kinetic expression identical to equation 18.

B. Products from Unsaturated Peroxides

1. Products from 5-Endonorbornenecarbonyl Peroxide

5-Endonorbornenecarbonyl peroxide produced 48.5% of the theoretical carbon dioxide. This is less than one would expect from an alkyl diacyl peroxide. For example, Wyman (47) found 93.5% carbon dioxide evolution from cyclohexanecarbonyl peroxide. Table 3 summarizes the products from the decomposition of 5-endonorbornenecarbonyl peroxide.

Table 2. Products of Decomposition of 2-Exonorbornanecarbonyl Peroxide in Carbon Tetrachloride After 72 Hours at 78° (1.11 mmoles of peroxide in 50 ml. of carbon tetrachloride).

Product	Mmoles	Mmoles/mmoles peroxide	Av. mmoles/ mmoles peroxide	%CO_2	%R
Carbon dioxide	1.75	1.590	1.586	79.3[a]	0
	1.74	1.582			
	1.65*	1.499	1.500	75.0[b]	0
	1.66*	1.509			
Ester (ϵ=470 l./g.-cm.)	0.22	0.200	0.204	10.2[a]	20.4[a]
	0.23	0.208			
	0.28*	0.254	0.254	12.7[b]	25.4[b]
	0.28*	0.254			
Acid (ϵ=499 l./g.-cm.)	0.24	0.218	0.223	6.2[a]	6.2[a]
	0.25	0.227			
	0.33*	0.300	0.296	8.1[b]	8.1[b]
	0.32*	0.292			

* 0.2 M Styrene present

[a] Accounts for 95.7% of carbonyl, 26.6% of alkyl.

[b] Accounts for 95.8% of carbonyl, 33.5% of alkyl.

2-Exochloronorbornane was identified but not determined quantitatively.

Table 3. Products of Decomposition of 5-Endonorbornenecarbonyl Peroxide in Carbon Tetrachloride After 72 Hours at 78° (1.25 mmoles of peroxide in 50 ml. of carbon tetrachloride).

Product	Mmoles	Mmoles/mmoles peroxide	Av. mmoles/ mmoles peroxide	%CO_2	%R
Carbon dioxide	1.23	0.985	0.969	48.5[a]	0
	1.19	0.953			
	1.35*	1.082	1.072	53.6[b]	0
	1.33*	1.062			
Ester (ϵ=409 l./g.-cm.)	0.23	0.184	0.194	9.7[a]	19.4[a]
	0.19	0.152			
	0.31	0.247			
	0.34*	0.272	0.275	13.8[b]	27.6[b]
	0.33*	0.264			
	0.36*	0.288			
Lactone (ϵ =726 l./g.-cm.)	1.00	0.800	0.779	39.0[a]	39.0[a]
	0.94	0.753			
	0.98	0.784			
	0.71*	0.568	0.522	26.1[b]	26.1[b]
	0.62*	0.503			
	0.63*	0.496			

* 0.2 M Styrene present

[a] Accounts for 97.2% of carbonyl, 58.4% of alkyl.

[b] Accounts for 93.5% of carbonyl, 53.7% of alkyl.

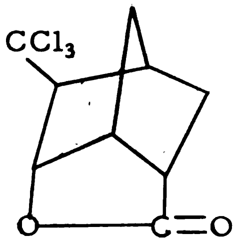
5-Exochloronorbornene was identified but not determined quantitatively.

5-Endonorbornenyl 5-endonorbornenecarboxylate was produced to the extent of 19.4%. The ester was identified by extracting the crude products with base, treating the basic and/or neutral fraction with lithium aluminum hydride, and derivatizing the resulting alcohols. The only crystalline material isolated retained the endo configuration. The complexity of the infrared spectrum of the products, and the great similarity of the infrared spectra of compounds having either exo or endo configurations made it impossible to set a minimal limit of detection on the amount of endo-endo isomer.

Alkyl halide codistilled when the last traces of carbon tetrachloride were removed from the reaction mixture. Separation using a Beckman Megachrom vapor phase chromatograph at 150° produced only trace amounts of 5-exochloronorbornene. This alkyl halide was identified by its infrared spectrum.

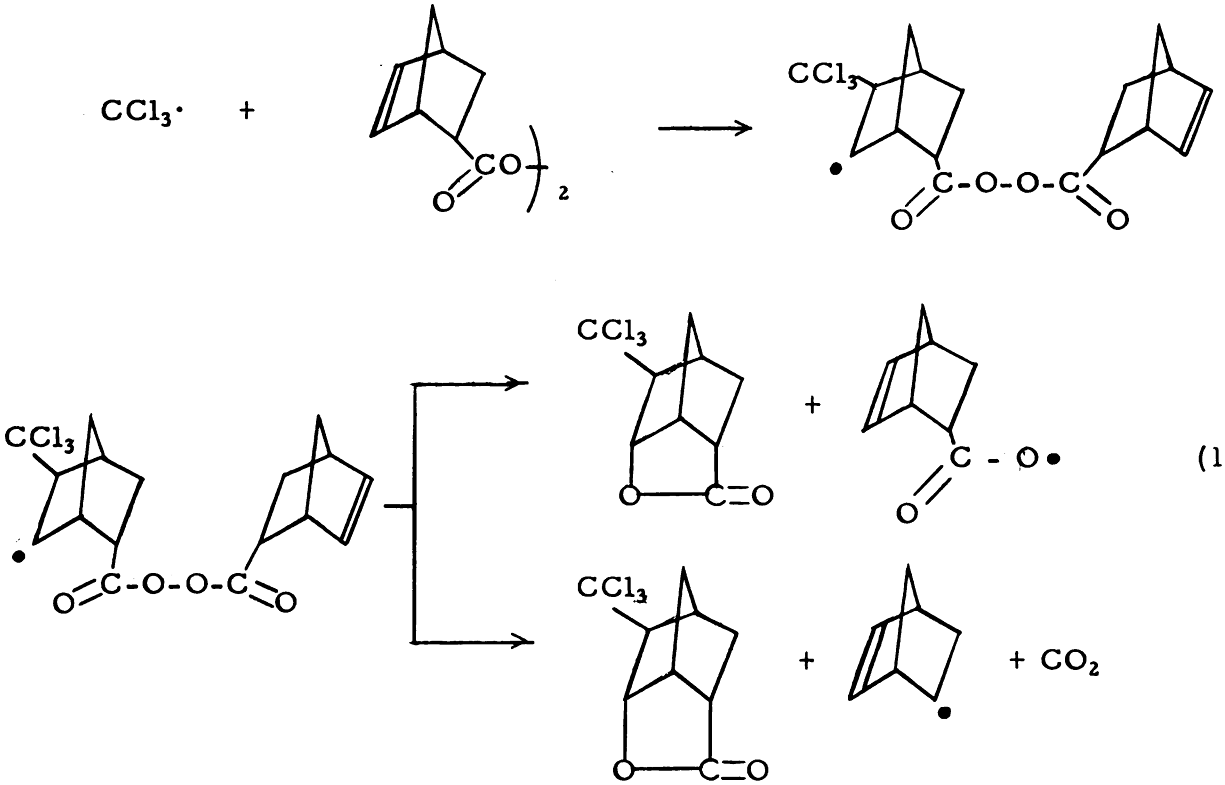
When the distillation of the reaction mixture was continued, material containing a carbonyl absorbtion at 5.58 μ in the infrared sublimed. The material was crystallized from ether and melted at 100-101°. Elemental analysis indicated an empirical formula $C_8H_9O_2Cl_3$. The chlorines were extremely resistant to hydrolysis which indicates a trichloromethyl group (54). The infrared carbonyl absorbtion indicated a lactonic material and comparison with known lactones in the norbornane ring system bears out this hypothesis. Comparison of the n.m.r. spectrum of this compound with those of known lactones also indicates a lactonic structure.

This compound is most likely the gamma-3-lactone of 2-exotrichloromethyl-3-endohydroxy-5-endonorbornanecarboxylic acid.



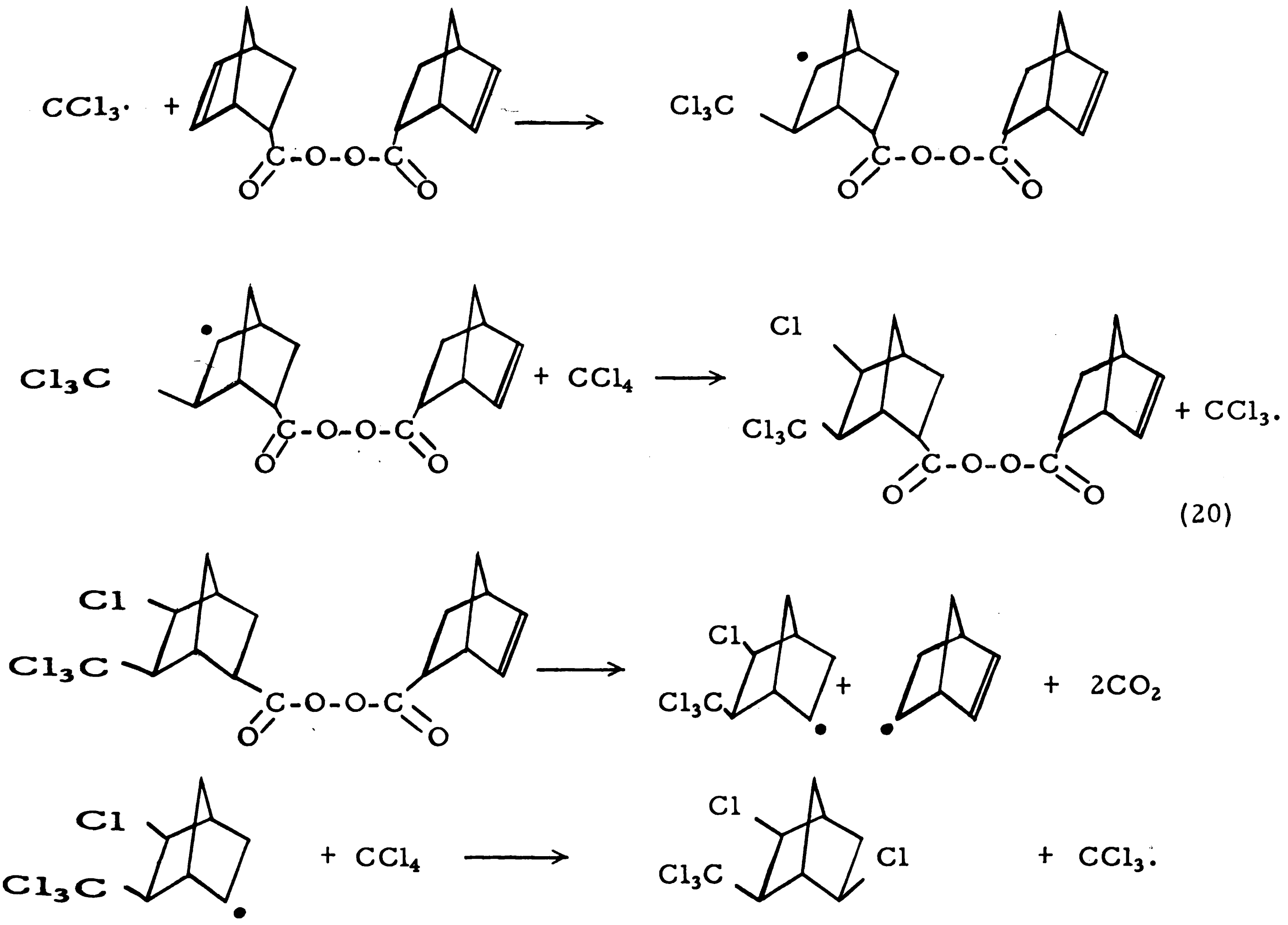
(A)

It can arise by attack of a trichloromethyl radical on one of the double bonds of the peroxide molecule with the resultant radical attacking either the carbonyl oxygen or the peroxidic oxygen with the displacement of an acyloxy radical. Perhaps a more likely second step would be the displacement of carbon dioxide and an alkyl radical.



(19)

One cannot disregard the fact that one end of the double bond is as susceptible to attack as the other. This would lead to the addition of the elements of carbon tetrachloride across the double bond with subsequent loss of carbon dioxide and abstraction of another chlorine atom. Lactone formation is not as likely in this case. The distance of the carboxyl group from the radical site is much greater.

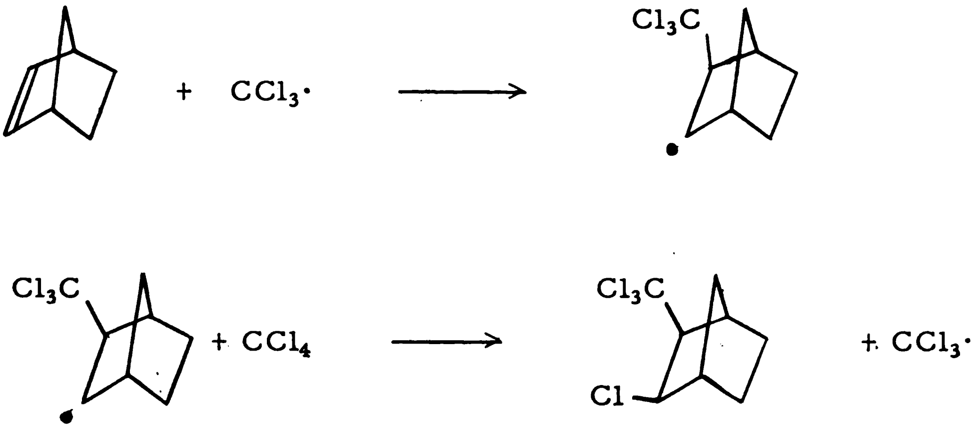


(20)

Polychlorinated alkanes were isolated from the reaction mixture but they could not be purified sufficiently for positive identification. A typical sample analyzed for 60% chlorine. This would also account for the production of only trace amounts of alkyl halide since the latter could be attacked in a similar manner. Some of the ester probably had the elements of carbon tetrachloride added also.

Benzotrichloride, tetrabromoethane, bromotrichloromethane, and iodine in carbon tetrachloride were used as solvents to test the effect of solvent on lactone formation. The amount of lactone remained virtually constant (39% in the case of carbon tetrachloride). In the use of iodine, the lactone may have been iodolactone (identification only by infrared).

Since this mode of decomposition is of an induced nature, inhibitors should reduce the amount of lactone formed as well as retard the rate of decomposition. A four-fold excess of styrene produced only a 25% decrease in the amount of lactone formed and galvinoxyl produced no noticeable effect. This would indicate that the norbornene double bond is about twelve times more reactive toward a CCl$_3$ radical than the styrene double bond. It is conceivable, however, to have attack on the double bond by other radicals (e.g. styryl radical) giving rise to complex lactones. The presence of a four-fold excess of norbornene produced no noticeable change in the rate or in the amount of lactone formed. Presumably the norbornene simply acts as a chain transfer agent.

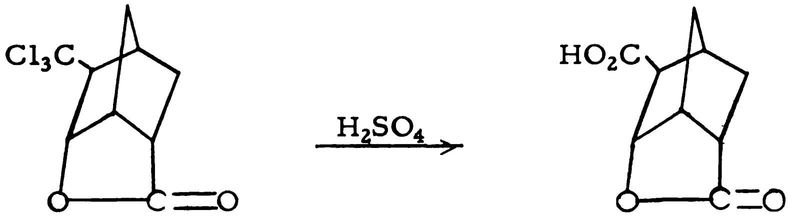


(21)

Kharasch (66) found that the elements of bromotrichloromethane could be added to a double bond using light or organic peroxide to initiate the reaction. Independent synthesis of the postulated trichloromethyl lactone was attempted using 5-endonorbornenecarboxylic acid or its methyl ester and either U.V. light or a trace of benzoyl peroxide. Bromotrichloromethane was used as the solvent. These methods proved unsuccessful.

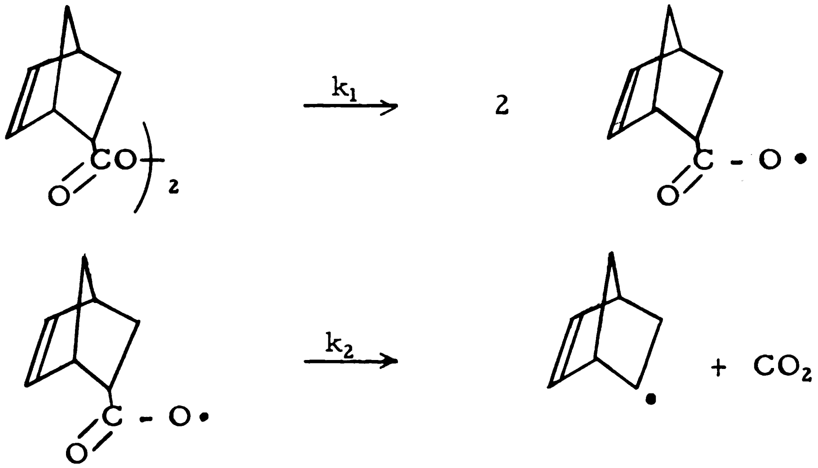
The chlorines of the trichloromethyl group could not be solvolyzed using silver nitrate in aqueous acetone. Fuming nitric acid produced no reaction but concentrated sulfuric acid (54) did give some hydrolysis product.

The acid obtained analyzed for $C_9H_{10}O_4$ and had carbonyl absorbtions in the infrared at 5.58 μ and 5.87 μ (figure 33).

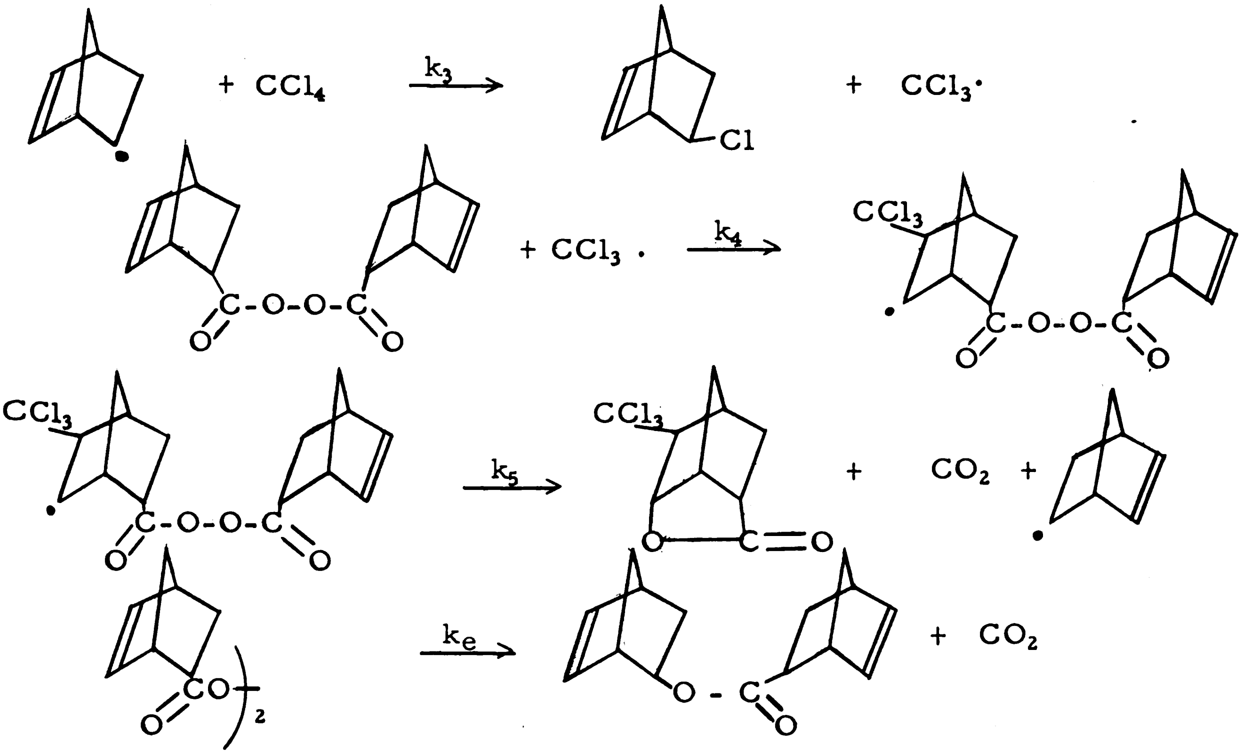


(22)

The following mechanism is postulated.



(23)



$$2CCl_3\cdot \xrightarrow{k_6} C_2Cl_6$$

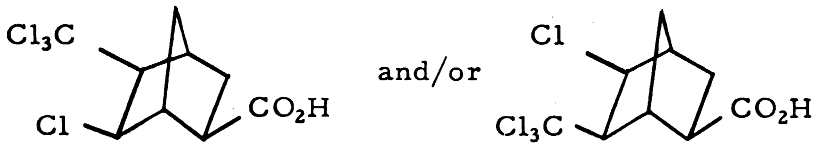
Reactions involving the addition of carbon tetrachloride to the double bond of the alkyl halide, ester, and equations such as 20 have been omitted since they are chain transfer processes and will not appear in the rate expression when steady state approximations are applied. A steady state treatment of the above equations leads to equation 18 where $k_i = k_4 \sqrt{k_1/k_6}$.

2. Products from 5-Exonorbornenecarbonyl Peroxide

As in the case of the endo isomer, the production of carbon dioxide was low (56.4%). The yield of 5-exonorbornenyl 5-exonorbornenecarboxylate amounted to 29.1%. The ester was identified by a degradative procedure identical to the one described for 5-endonorbornenyl 5-endonorbornenecarboxylate. The complexity of the infrared spectrum of the products and similarity of spectra of compounds having either exo or endo configurations prevented the establishment of minimal limits on the amount of exo-exo ester produced. The only crystalline derivatives isolated retained the exo configuration.

Only trace amounts of alkyl halide could be obtained. The alkyl halide was distilled along with the last traces of carbon tetrachloride. Separation on a Beckmann Megachrom vapor phase chromatograph at 150° produced the alkyl halide. Its retention time and infrared spectrum were identical to those of the alkyl halide obtained from the endo peroxide and it was identified as 5-exochloronorbornene by its infrared spectrum. The data are summarized in Table 4.

When the decomposition products were extracted with base, an acid was isolated from the basic extracts. Elemental analysis indicated an empirical formula $C_9H_{10}O_2Cl_4$ and structures B have been assigned to this acid.



(B)

Table 4. Products of Decomposition of 5-Exonorbornenecarbonyl Peroxide in Carbon Tetrachloride After 72 Hours at 78° (1.25 mmoles of peroxide in 50 ml. of carbon tetrachloride).

Product	Mmoles	Mmoles/mmoles peroxide	Av. mmoles/ mmoles peroxide	%CO_2	%R
Carbon dioxide	1.39	1.110	1.128	56.4[b]	0
	1.43	1.145			
	1.52*	1.215	1.215	60.8[c]	0
	1.52*	1.215			
Ester (ε = 473 l./g.-cm.)	0.37	0.296	0.291	14.6[b]	29.1[b]
	0.36	0.288			
	0.37	0.296			
	0.53*	0.424	0.403	20.1[c]	40.3[c]
	0.51*	0.408			
	0.47*	0.376			
Lactone[a] (ε = 726 l./g.-cm.)	0.38	0.303	0.306	15.3[b]	15.3[b]
	0.38	0.303			
	0.39	0.312			
	0.41*	0.328	0.333	16.7[c]	16.7[c]
	0.42*	0.336			
	0.42*	0.336			

* 0.2 M Styrene present

[a] ε is estimated to be the same as in 5-endonorbornenecarbonyl peroxide.

[b] Accounts for 86.3% of carbonyl, 44.4% of alkyl.

[c] Accounts for 97.6% of carbonyl, 57.0% of alkyl.

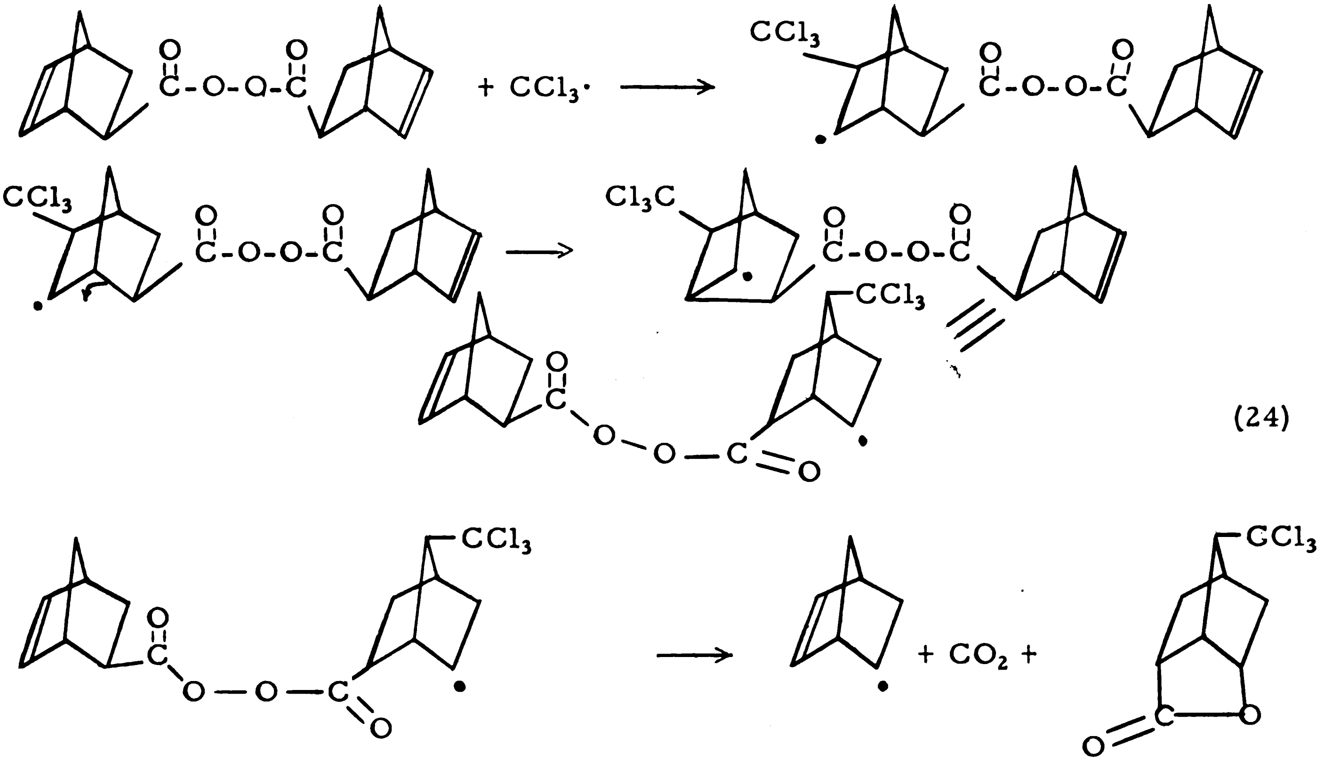
5-Exochloronorbornene was identified but not determined quantitatively.

As in the endo case, a great amount of polychlorinated alkanes were obtained. This material was identical to the material isolated in the endo case in analysis and infrared spectrum. It would arise by a scheme similar to equation 20.

Examination of the infrared spectrum of the crude products indicated a peak at 5.58 μ. It is unusual to have this peak since the stereochemistry is not correct for lactone formation. There is a possibility that the material giving rise to this peak is 5-exonorbornenecarbonyl chloride (from which the peroxide was prepared). There are a number of reasons for discounting this possibility: 1) the peroxide solution was washed with 5% sodium carbonate and the peroxide recrystallized prior to decomposition; 2) the intensity of the 5.58 μ band increased as the decomposition proceeded; 3) the amount of material possessing the 5.58 μ peak is the same using different batches of peroxide.

A second alternative is that the lactone is the same as that formed from the endo peroxide, and is due to contamination of the exo peroxide by the endo isomer. Using the extinction coefficient of the lactone obtained from 5-endonorbornenecarbonyl peroxide, the yield of lactone produced by the exo isomer was 15%. This would necessitate a minimum of 37% of the endo peroxide as a contaminant. A 10% impurity of 5-endonorbornenecarboxylic acid in 5-exonorbornenecarboxylic acid causes the mixture to liquify at room temperature and the exo acid used to prepare the peroxide melted sharply at 43-44°. Also, analysis of methyl 5-exonorbornenecarboxylate (prepared by treating the acid with diazomethane) on a Beckman GC-2 vapor phase chromatograph indicated less than 1% of the endo isomer.

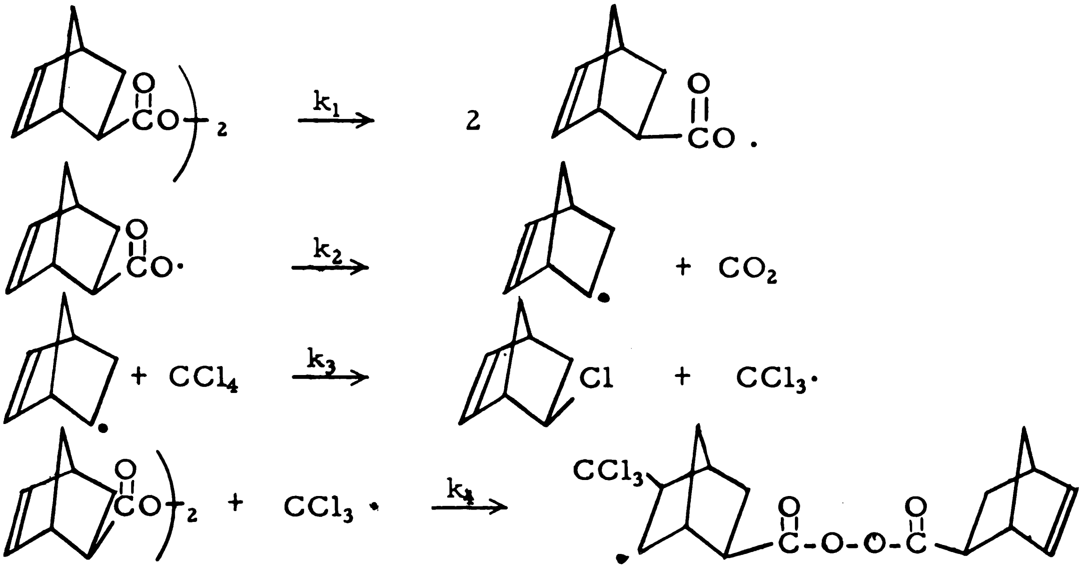
A third alternative is rearrangement of the radical produced after the initial attack of trichloromethyl radical. The stereochemistry would then be correct for lactone formation.



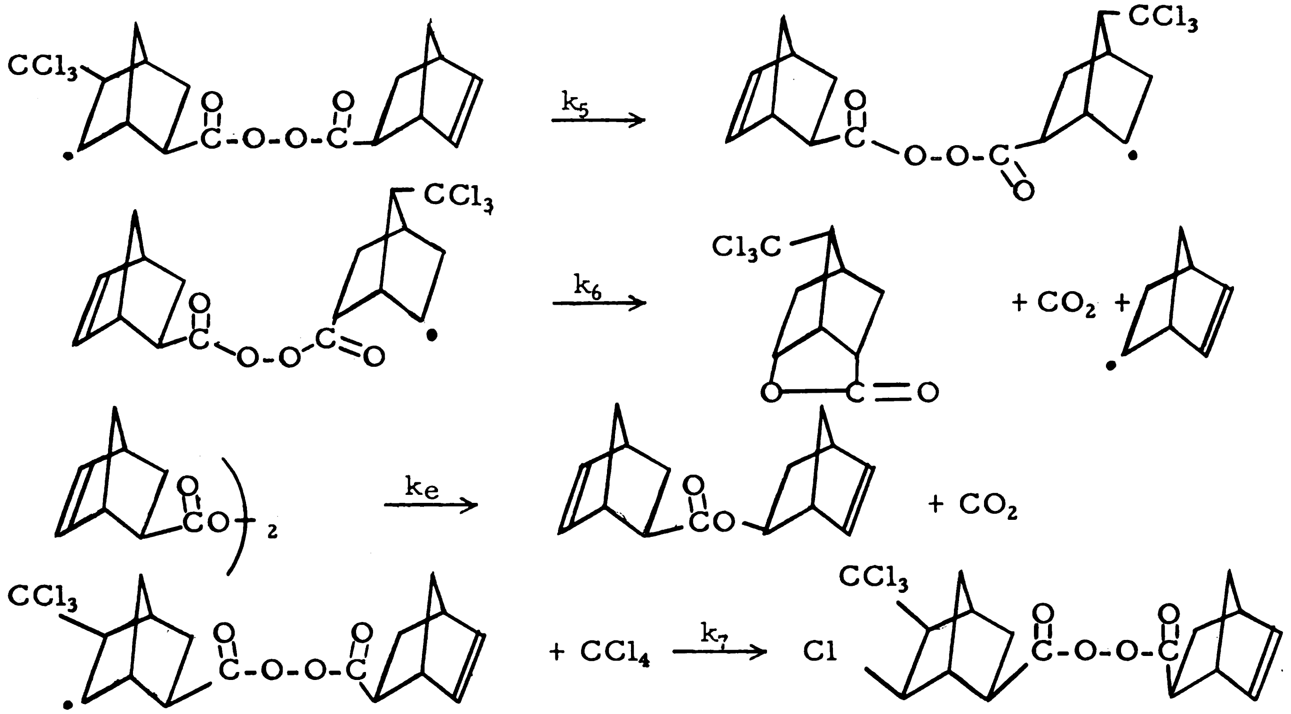
(24)

A rearrangement of this type is not without precedence. Berson (6) has shown good evidence of a free radical Wagner-Meerwein rearrangement in his work on 2,2'-bis-azocamphane.

Using the above products, a mechanism can be written:



(25)



$$2\ CCl_3\cdot \xrightarrow{k_8} C_2Cl_6\ .$$

The acid structure B could arise by a variety of methods. Homolytic fission of the product of k_8 (or of the product with the chlorine and trichloromethyl groups reversed) followed by hydrogen abstraction, or hydrogen abstraction of the acyloxy radical from k_1 followed by addition of the elements of carbon tetrachloride across the double bond.

Using steady state approximations, the rate expression is as equation 18 with $k_i = k_4 \sqrt{k_1/k_8}$.

II. Rates of Decomposition of Diacyl Peroxides

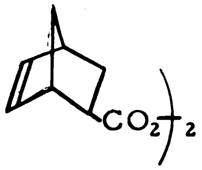
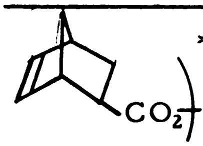
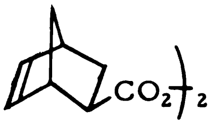
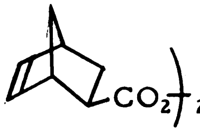
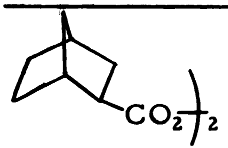
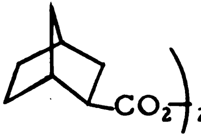
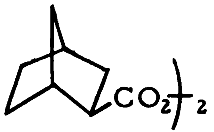
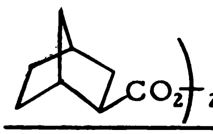
The rates of decomposition of the diacyl peroxides were followed by titrating the peroxide present at various time intervals (iodometrically), and by measuring the rate of disappearance of the 5.63 μ peroxide peak in the infrared. The disappearance of the 5.63 μ peroxide peak of 5-endonorbornenecarbonyl peroxide could not be followed due to interference by the appearance of the 5.58 μ lactone peak.

In the decomposition of the unsaturated peroxides, the appearance of ester was followed by measuring the rate of change of the 5.77 μ ester peak in the infrared. The appearance of acid was followed in the decomposition of the saturated peroxides by measuring the rate of change of the 5.87 μ acid peak. The rate data and the activation parameters for the various decompositions are summarized in Tables 5, 6, 7, and 8. The errors denote mean deviations and not probable error.

The measurements were carried out in the following manner. Nitrogen was passed successively through Fieser's solution, saturated lead acetate solution, concentrated sulfuric acid, and finally potassium hydroxide pellets. A 0.05 N solution of the peroxide in carbon tetrachloride was purged of oxygen by passing the purified nitrogen stream through it for 10 minutes. The solution was placed in ampoules (c.a. 5 ml.) and the ampoules sealed at -70°. The ampoules were placed in an oil bath controlled to ± 0.2° C. Ten minutes were allowed to equilibrate the ampoules to bath temperature. The ampoules were removed at various time intervals, quenched in ice water, and stored at -70° until completion of the run. The tips of the ampoules were broken, the ampoules drained, and the appropriate measurements made.

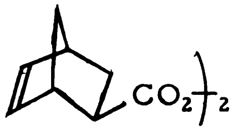
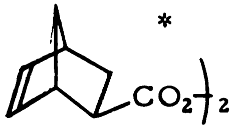
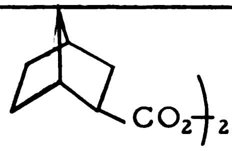
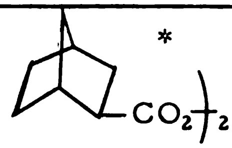
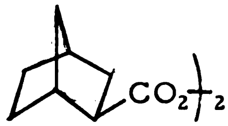
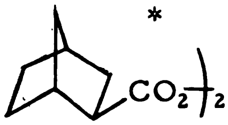
2-Endonorbornanecarbonyl peroxide decomposed seven times slower than the corresponding exo isomer although their respective energies and entropies of activation are within experimental error. The endo isomer is also a factor two slower than cyclohexylcarbonyl peroxide and a factor four slower than cyclopentylcarbonyl peroxide (47). This seems to indicate that carbon-carbon bond stretching is important in the decomposition and steric crowding inhibits carbon-carbon stretching in 2-endonorbornanecarbonyl peroxide. This is further supported by the production of 73.7% carbon dioxide and 11.2% acid from the endo isomer while the exo isomer produced 79.3% carbon dioxide and 6.2% acid.

Table 5. Rate Constants and Activation Parameters for the Decomposition of Various Peroxides in Carbon Tetrachloride Determined by Titrimetric Techniques.

Compound	T/°C	k x 10^3 minutes^{-1}	Ea/kcal./mole	ΔS^*/e.u.
	44.5	3.78 ± 0.16	24.0 ± 1.9	3.50 ± 0.55
	53.9	7.24 ± 0.42		
	62.7	23.5 ± 0.7		
	65.9	43.1 ± 3.3		
 *	44.5	1.33 ± 0.06	24.1 ± 1.7	1.65 ± 0.14
	53.9	2.71 ± 0.17		
	65.9	14.2 ± 0.1		
	44.5	3.95 ± 0.31	20.9 ± 2.0	-6.28 ± 1.20
	53.9	7.28 ± 0.71		
	65.9	30.5 ± 1.0		
 *	44.5	1.55 ± 0.09	33.5 ± 2.2	31.8 ± 4.0
	53.9	7.22 ± 0.35		
	65.9	42.6 ± 1.9		
	44.5	0.367 ± 0.013	30.5 ± 1.8	15.0 ± 1.7
	53.9	1.70 ± 0.10		
	65.9	7.50 ± 0.40		
 *	44.5	0.544 ± 0.077	25.5 ± 3.6	0.32 ± 0.09
	53.9	2.60 ± 0.08		
	65.9	7.70 ± 1.11		
	44.5	2.81 ± 0.60	28.5 ± 6.0	17.5 ± 7.4
	53.9	12.3 ± 0.8		
	65.9	49.1 ± 4.6		
 *	44.5	4.32 ± 0.35	24.8 ± 4.4	6.42 ± 2.26
	53.9	10.2 ± 1.8		
	65.9	50.9 ± 1.0		

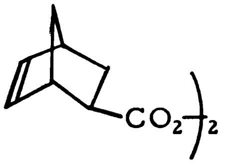
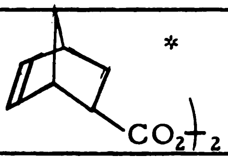
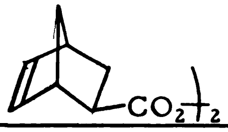
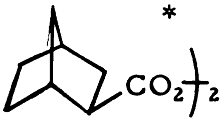
*0.2 M Styrene present.

Table 6. Rate Constants and Activation Parameters for the Decomposition of Various Peroxides in Carbon Tetrachloride Determined by Infrared Techniques.

Compound	T/°C.	k x 10^3/minutes^{-1}	Ea/kcal./mole	ΔS^*/e.u.
	44.5 53.9 65.9	4.45 ± 0.04 10.0 ± 1.2 50.5 ± 1.6	24.7 ± 3.0	6.14 ± 1.48
 *	44.5 53.9 65.9	2.35 ± 0.04 7.95 ± 0.70 37.2 ± 0.8	27.9 ± 2.5	15.16 ± 2.66
	44.5 53.9 65.9	0.297 ± 0.027 1.80 ± 0.05 8.10 ± 0.43	32.8 ± 3.0	22.0 ± 4.0
 *	44.5 53.9 65.9	0.386 ± 0.056 2.10 ± 0.08 8.00 ± 0.82	30.2 ± 4.4	14.3 ± 4.1
	44.5 53.9 65.9	3.38 ± 0.30 10.4 ± 0.5 50.4 ± 0.9	27.1 ± 2.4	13.2 ± 2.4
 *	44.5 53.9 65.9	2.62 ± 0.11 11.7 ± 0.8 60.2 ± 3.8	31.3 ± 2.1	26.1 ± 3.6

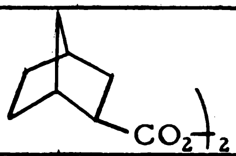
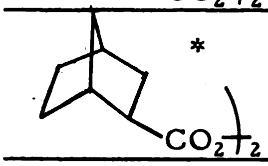
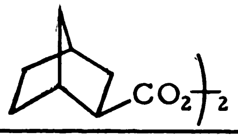
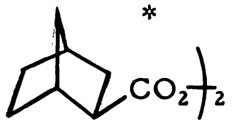
*0.2 M Styrene present.

Table 7. Rate Constants and Activation Parameters for the Appearance of Ester from the Decomposition of Various Peroxides in Carbon Tetrachloride Determined by Infrared Techniques.

Compound	T/°C.	k x 10^3/minutes^{-1}	Ea/kcal./mole	ΔS^*/e.u.
	44.5	5.01 ± 0.61	22.3 ± 2.7	-1.30 ± 0.32
	53.9	8.29 ± 0.05		
	62.7	28.2 ± 1.7		
	65.9	45.9 ± 1.6		
 *	44.5	1.36 ± 0.03	25.2 ± 1.3	5.30 ± 0.54
	53.9	3.78 ± 0.19		
	65.9	16.3 ± 0.8		
	44.5	5.38 ± 0.51	22.4 ± 2.1	-0.74 ± 0.14
	53.9	15.3 ± 0.5		
	65.9	49.2 ± 0.1		
 *	44.5	2.30 ± 0.08	29.2 ± 4.7	19.10 ± 6.2
	53.9	10.5 ± 1.7		
	65.9	41.1 ± 0.8		

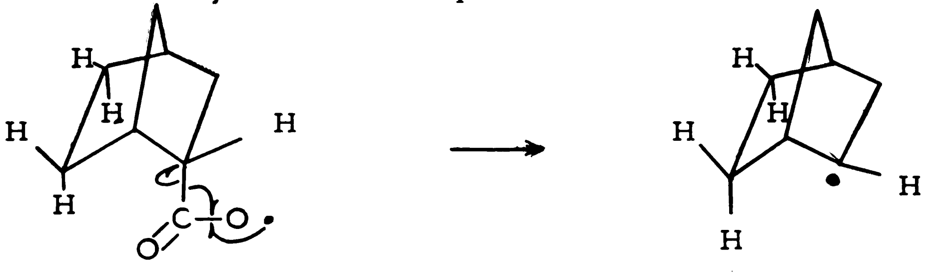
*0.2 M Styrene present.

Table 8. Rate Constants and Activation Parameters for the Appearance of Acid from the Decomposition of Various Peroxides in Carbon Tetrachloride Determined by Infrared Techniques.

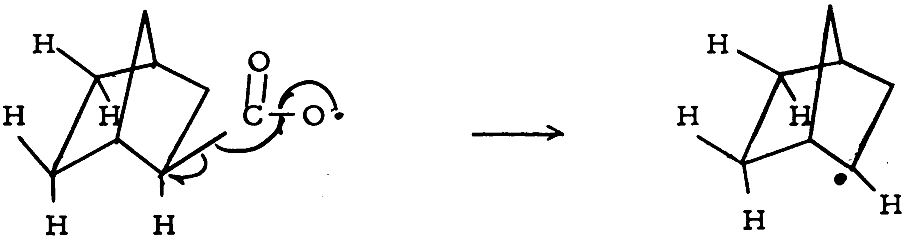
Compound	T/°C	kx10^3/minutes^{-1}	Ea/kcal./mole	ΔS*/e.u.
	44.5	0.353 ± 0.020	30.6 ± 3.6	15.5 ± 3.6
	53.9	1.80 ± 0.21		
	65.9	7.60 ± 0.08		
 *	44.5	0.520 ± 0.028	29.6 ± 3.8	12.5 ± 3.2
	53.9	1.40 ± 0.18		
	65.9	9.80 ± 0.07		
	44.5	3.65 ± 0.53	27.5 ± 4.0	15.2 ± 4.4
	53.9	10.8 ± 0.2		
	65.9	65.9 ± 9.1		
 *	44.5	5.11 ± 0.31	29.6 ± 4.9	21.2 ± 7.2
	53.9	16.2 ± 2.8		
	65.9	79.3 ± 7.2		

*0.2 M Styrene present.

These facts indicate that the reaction represented in equation 26 proceeds with more difficulty than that in equation 27.



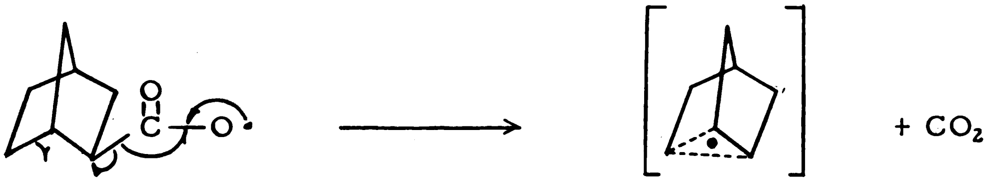
(26)



(27)

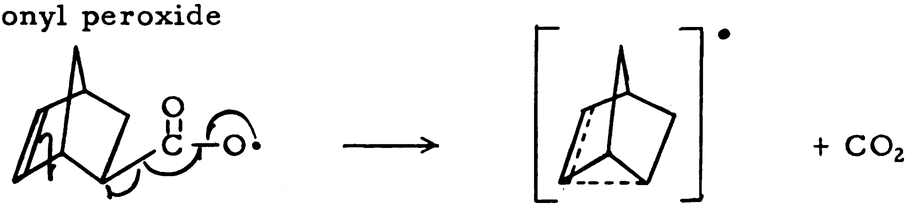
In equation 26, the departing carbonyl function must move under the ring to create a trigonal carbon at position 2. This would cause severe crowding. In equation 27, the departing carbonyl function moves toward the 7 position which is sterically more favorable.

Pincock (63) in his study of the t-butylperoxyesters of 2-exo-and endonorbornanecarboxylic acids found that the endo isomer was a factor four slower than the exo isomer. This rate difference and also the factor 7 found in the diacyl peroxides is too small to consider the formation of a bridged free radical.



(28)

The unsaturated peroxides decomposed at approximately the same rate as 2-exonorbornanecarbonyl peroxide. This also supports the concept of steric crowding in 2-endonorbornanecarbonyl peroxide. Cooper (65) found that dibut-3-enoyl peroxide$[(CH_2{=}CH{-}CH_2{-}CO_2 + _2)]$decomposed fifty times faster than dibut-2-enoyl peroxide$[(CH_3{-}CH{=}CH{-}CO_2 + _2)]$. Cooper attributed the rate difference to the production of an allylic radical in the former case. Double bonds further down the chain as in dioleoyl peroxide $[(CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2\!\!+_2]$ had very little effect on the rate of decomposition. Since the unsaturated peroxides decompose at very nearly the same rate, and 3-chloronortricyclene was not detected in the products, the double bond must not participate in the decomposition of 5-exonorbornene-carbonyl peroxide


(29)

Styrene had very little effect on the rates of decomposition of the saturated peroxides indicating that the k_i term in equation 18 for these peroxides is very small and the observed rate constants are very close to the rate of spontaneous decomposition. Styrene was found to inhibit the rates of decomposition of the unsaturated peroxides but was not effective enough to completely halt the induced decomposition.

EXPERIMENTAL

I. Apparatus and Reagents

A. Apparatus

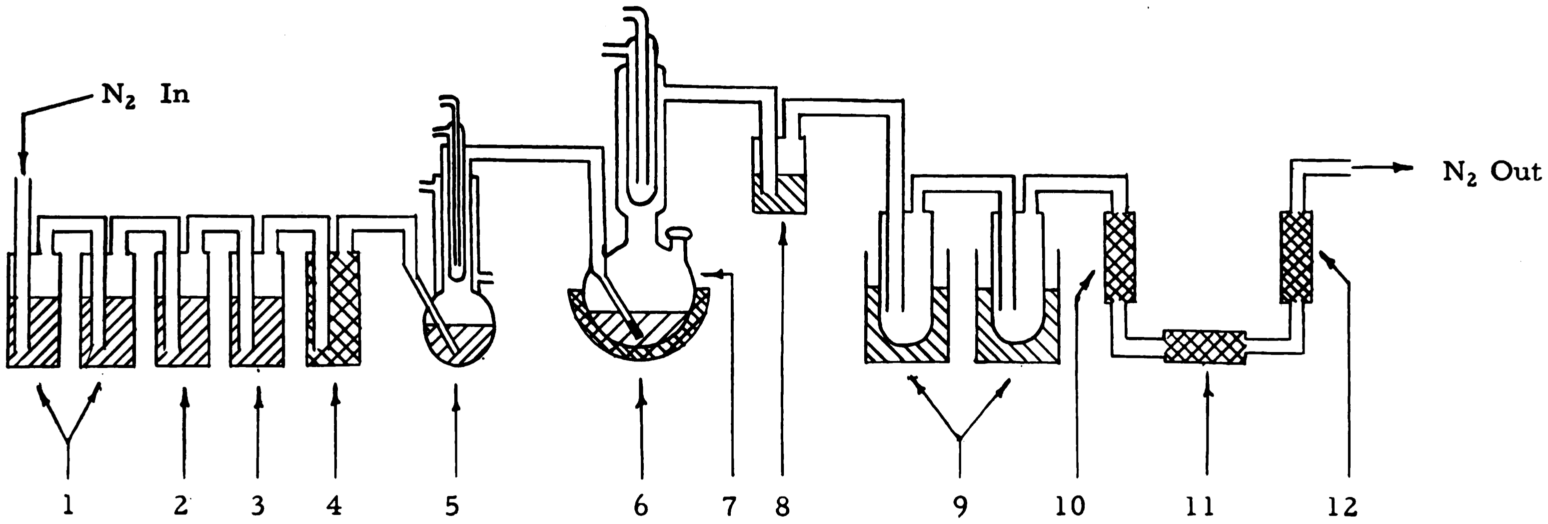
The apparatus used to determine the amount of carbon dioxide produced in the decompositions of the peroxides is illustrated in Figure 1.

All infrared spectra were taken on a Perkin-Elmer model 21 recording infrared spectrophotometer. Unless specified otherwise, all infrared spectra were taken in carbon disulfide solution except for the region of 6.2-7.2 μ which was taken in carbon tetrachloride solution.

Solvent evaporations were performed using a Rinco type rotary evaporator.

B. Purification of Carbon Tetrachloride

Reagent grade carbon tetrachloride was purified using the method of Teller (20). A mixture of 30 g. of potassium hydroxide, 180 ml. of 95% ethanol, and 180 ml. of water was added to 2.5 l. of carbon tetrachloride. The mixture was heated at 60° for 30 minutes, the layers separated, and the process repeated. The carbon tetrachloride was washed twice with water to remove the ethanol, then washed with small portions of concentrated sulfuric acid until the sulfuric acid layer was clear. After washing twice more with water, the carbon tetrachloride was dried over calcium chloride and distilled from phosphorus pentoxide through a 30 x 1 cm. glass helix packed column. The distillate boiling at 76° was collected.



1. Fieser's solution to remove oxygen.
2. Saturated lead acetate in water, to remove sulfur compounds.
3. Concentrated sulfuric acid, to dry nitrogen.
4. Potassium hydroxide, to remove sulfuric acid.
5. Flask equipped with condenser and containing carbon tetrachloride to saturate nitrogen.
6. Heating mantle maintained at desired temperature.
7. Reaction vessel.
8. Aniline, to remove phosgene.
9. Dry-ice traps.
10. Tared ascarite-anhydrone tube.
11. Protective ascarite-anhydrone tube.
12. Protective drierite tube.

Figure 1. Diagram of the Apparatus Used for Carbon Dioxide Determinations.

C. Standardization of Sodium Thiosulfate

The method of Silbert and Swern (36, 37) was used to determine the purity of the diacyl peroxides. To test the method for applicability to diacyl peroxides, the sodium thiosulfate solution was standardized using potassium iodate and highly purified benzoyl peroxide as primary standards.

Appropriate amounts of the above reagents were placed in 125-ml. iodine flasks and a small piece of dry ice added to purge out the oxygen present. Acetic acid (5 ml.) containing 0.0005% ferric chloride hexahydrate, and 0.5 ml. of saturated sodium iodide solution was added. The mixture was allowed to stand in the dark for 25 minutes. Water (20 ml.) was added, and the magnetically stirred mixture was titrated with ca. 0.01 N sodium thiosulfate. Starch solution (5 ml.) was added near the end point and the end point was taken at the disappearance of the purple starch-iodine color. The results obtained from each of the primary standards agreed within experimental error (see Tables 9 and 10).

II. Preparation of Diacyl Peroxides

A. Preparation of Acids

1. Preparation of 5-Endonorbornenecarboxylic Acid

The method of Alder (38) was employed in this preparation. Freshly distilled cyclopentadiene (34 g., 0.51 mole) was added to ice cold acrylic acid (40 g., 0.55 mole) contained in a 125-ml. Erlenmeyer flask. The reaction mixture was cooled intermittently in an ice bath to ensure a temperature maximum of 40°. On occasion the reaction will proceed with enough vigor to cause the reaction mixture to boil, but usually the reaction proceeds smoothly to completion in about 25 minutes. The mixture was dissolved in 5% sodium carbonate solution and washed with ether to remove neutral residues. The aqueous solution was acidified with 6 M sulfuric acid and extracted

Table 9. Standardization of Sodium Thiosulfate Using Potassium Iodate as a Primary Standard.

Sample	1	2	3	4	5	Blank
Titer in Milliliters	16.42	16.40	16.42	16.42	16.40	0.00
Normality in Equivalents/ Liter	0.01309	0.01311	0.01309	0.01309	0.01311	

Average normality 0.01310 ± 0.00004.

Table 10. Standardization of Sodium Thiosulfate Using Benzoyl Peroxide as a Primary Standard.

Sample	1	2	3	4	5	Blank
Titer in Milliliters	16.70	16.68	16.65	16.65	16.67	0.00
Normality in Equivalents/ Liter	0.01315	0.01317	0.01318	0.01318	0.01318	

Average normality 0.01317 ± 0.00004.

with ether. After drying over magnesium sulfate and evaporating the ether, the residue was distilled in vacuo through an 8" Vigreux column to yield colorless acid, b.p. 100-102°/2 mm (lit. value (39), b.p. 118.5-120.5°/5.7 mm.). The acid was then crystallized from pentane by cooling in dry ice to yield 50 g. (0.362 mole, 71%) of white 5-endonorbornenecarboxylic acid, m.p. 43-44° (lit. value (40), m.p. 45-46°).

2. Preparation of Methyl 5-Endonorbornenecarboxylate

The method of Roberts (41) was employed to prepare this compound. A 300-ml. three-necked flask fitted with a mechanical stirrer, reflux condenser, and a dropping funnel was charged with 65 g. (0.75 mole) of methyl acrylate (b.p. 79-80°/1 Atm.), 0.5 g. of hydroquinone, and 50 ml. of anhydrous ether. The reaction mixture was cooled in an ice bath and 45 g. (0.68 mole) of freshly distilled cyclopentadiene was added dropwise with stirring over a 2 hr. period. The mixture was stirred at ice bath temperature for an hour and then an additional hour at room temperature. The ether was evaporated and the residue fractionated in vacuo through a 30 x 1 cm. glass helix packed column to yield 95 g. (92%) of colorless ester, b.p. 58°/4.2 mm., n_D^{25} 1.4726 (lit. values (41), b.p. 63.5°/5.2 mm., n_D^{25} 1.4718).

3. Preparation of 5-Exonorbornenecarboxylic Acid

The method of Roberts (41) was employed in this preparation. A mixture of 65 g. (0.45 mole) of methyl 5-endonorbornenecarboxylate, 39 g. (0.72 mole) of sodium methoxide, and 91 g. of absolute methanol contained in a 500-ml. flask was refluxed on a steam bath for 48 hours. Most of the methanol was then stripped off at aspirator pressure using an ebullator to reduce bumping. Water (50 ml.) was added and the mixture refluxed for 24 hours. The methanol formed was removed by fractionation through an 8" Vigreux column at atmospheric pressure and the residual solution washed with ether. The aqueous layer was acidified with 6 M sulfuric acid to Congo Red and extracted with ether. After drying over magnesium sulfate and evaporating the ether, the residue was distilled in vacuo through an 8" Vigreux column to yield 41 g. (70%) of colorless acid, b.p. 100-102°/1.5 mm. (lit. value (41), 103.5-104°/2.2 mm.).

The crude acid was purified according to the method of Ver Nooy and Rondestvedt (42, 43). The crude acid (41 g., 0.297 mole) was neutralized with 10% sodium hydroxide in a 1-l. separatory funnel. Sodium bicarbonate (7 g.) and excess iodine solution (about 900 ml. of a solution 0.67 M in iodine and 2.0 M in potassium iodide) was then added. The dark oil which formed was extracted with ether. The ether extracts were combined, washed with 10% sodium thiosulfate, and dried over calcium chloride. Evaporation yielded 36 g. (40%) of crude gamma-3 lactone of 2-exoiodo-3-endohydroxy 5-endonorbornanecarboxylic acid. The aqueous layer was treated with 10% sodium thiosulfate, acidified with 6 M sulfuric acid, and extracted with ether. The ether extracts were combined, washed with 1% sodium thiosulfate, and dried over magnesium sulfate. After evaporating the ether, the residue was distilled in vacuo through an 8" Vigreux column to yield 24 g. (58.5%) of white acid, b.p. 100-101°/1.5 mm. The 5-exonorbornenecarboxylic acid was recrystallized from pentane by cooling in dry ice, m.p. 43-44° (lit. (42), b.p. 100-101°/1.25 mm., m.p. 44-45°).

4. Preparation of 2-Endonorbornanecarboxylic Acid

5-Endonorbornenecarboxylic acid (85 g., 0.616 mole) was dissolved in 250 ml. of ethyl acetate and hydrogenated over 0.5 g. of 5% palladium on charcoal at room temperature. Initial hydrogen pressure was 50 pounds per square inch and theoretical hydrogen uptake was complete after 1 hour. The palladium on charcoal was filtered and the ethyl acetate evaporated. The residue was distilled in vacuo and the distillate crystallized from pentane to yield 82 g. (94.5%) of white 2-endonorbornanecarboxylic acid, b.p. 88°/0.7 mm., m.p. 64-66° (lit. values (38, 44), 64-66°, 65°). Its infrared spectrum is shown in Figure 2.

5. Preparation of 2-Exonorbornanecarboxylic Acid

5-Exonorbornenecarboxylic acid (40 g., 0.29 mole) was dissolved in 250 ml. of methanol and hydrogenated over platinum oxide at room temperature. Initial hydrogen pressure was 50 pounds per square inch and theoretical hydrogen uptake was complete after 1 hour. The platinum oxide was filtered and the methanol evaporated. The resultant oil was crystallized from pentane-ether by cooling in dry ice to yield 32 g. (79%) of white 2-exonorbornanecarboxylic acid, m.p. 56-57° (lit. values (44, 45), 58-58.5°, 56-57°). Its infrared spectrum is shown in Figure 3.

B. Preparation of Acid Chlorides

All acid chlorides were prepared by the method of Boehme (40). In a typical preparation, 5-endonorbornenecarboxylic acid (10 g., 0.0725 mole) was added to 11.9 g. (0.10 mole) of thionyl chloride and 25 g. of chloroform contained in a 100-ml. round-bottomed flask. The flask was fitted with a reflux condenser, and after the initial reaction had subsided, the reaction mixture was refluxed for 3.5 hours on a steam bath. The chloroform was fractionated through an 8" Vigreux column. The pressure was lowered and 10.3 g. (90%) of colorless 5-endonorbornenecarbonyl chloride was collected, b.p. 47°/1.5 mm. (lit. value (40), b.p. 84-85/ 14 mm.).

The acid chloride (c.a. 1 g.) was then treated with 5% sodium hydroxide solution. The solution was acidified to Congo Red with 6 M sulfuric acid and extracted with ether. After drying over magnesium sulfate and evaporating the ether, the residue was crystallized from

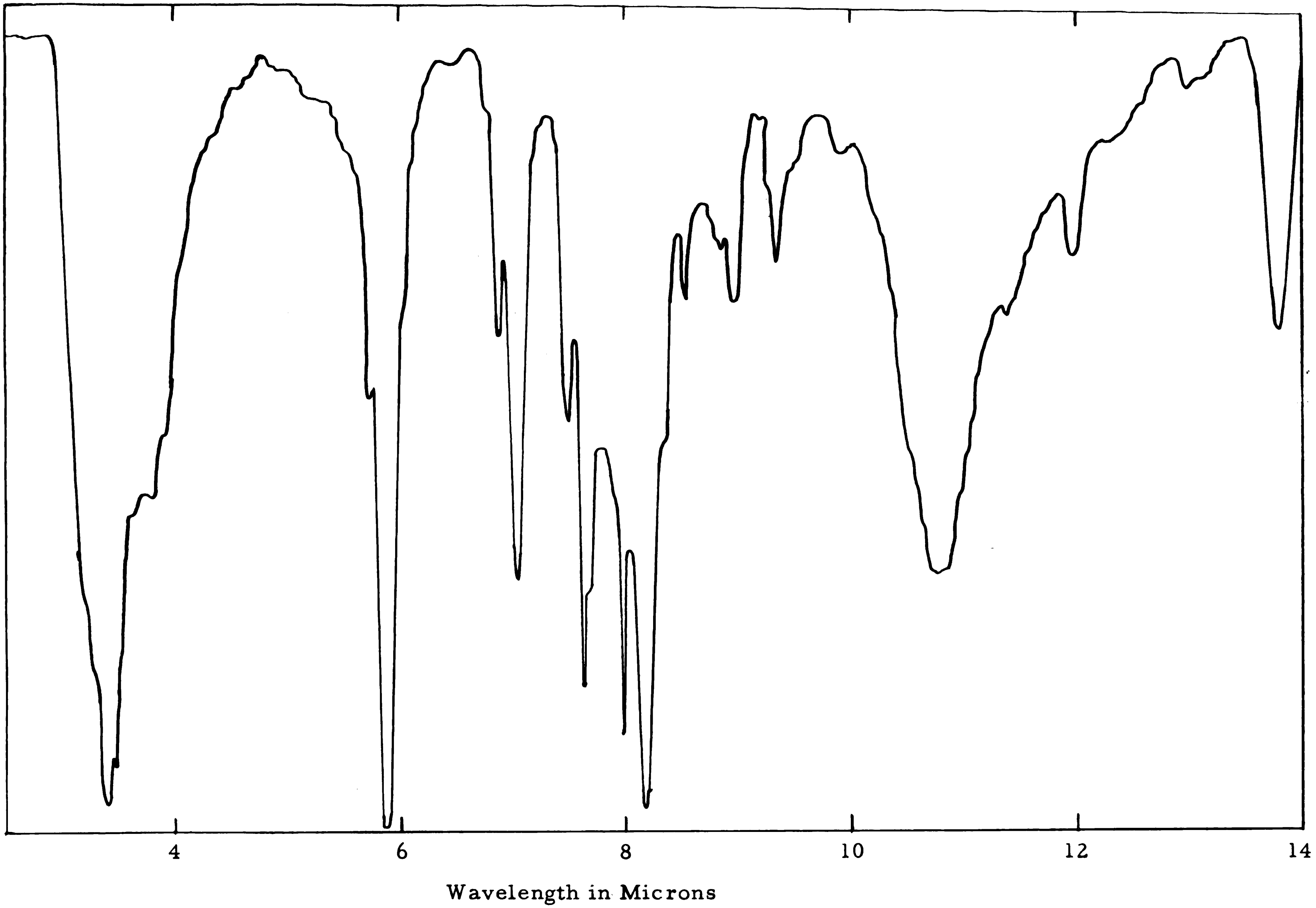


Figure 2. Infrared Spectrum of 2-Endonorbornanecarboxylic Acid.

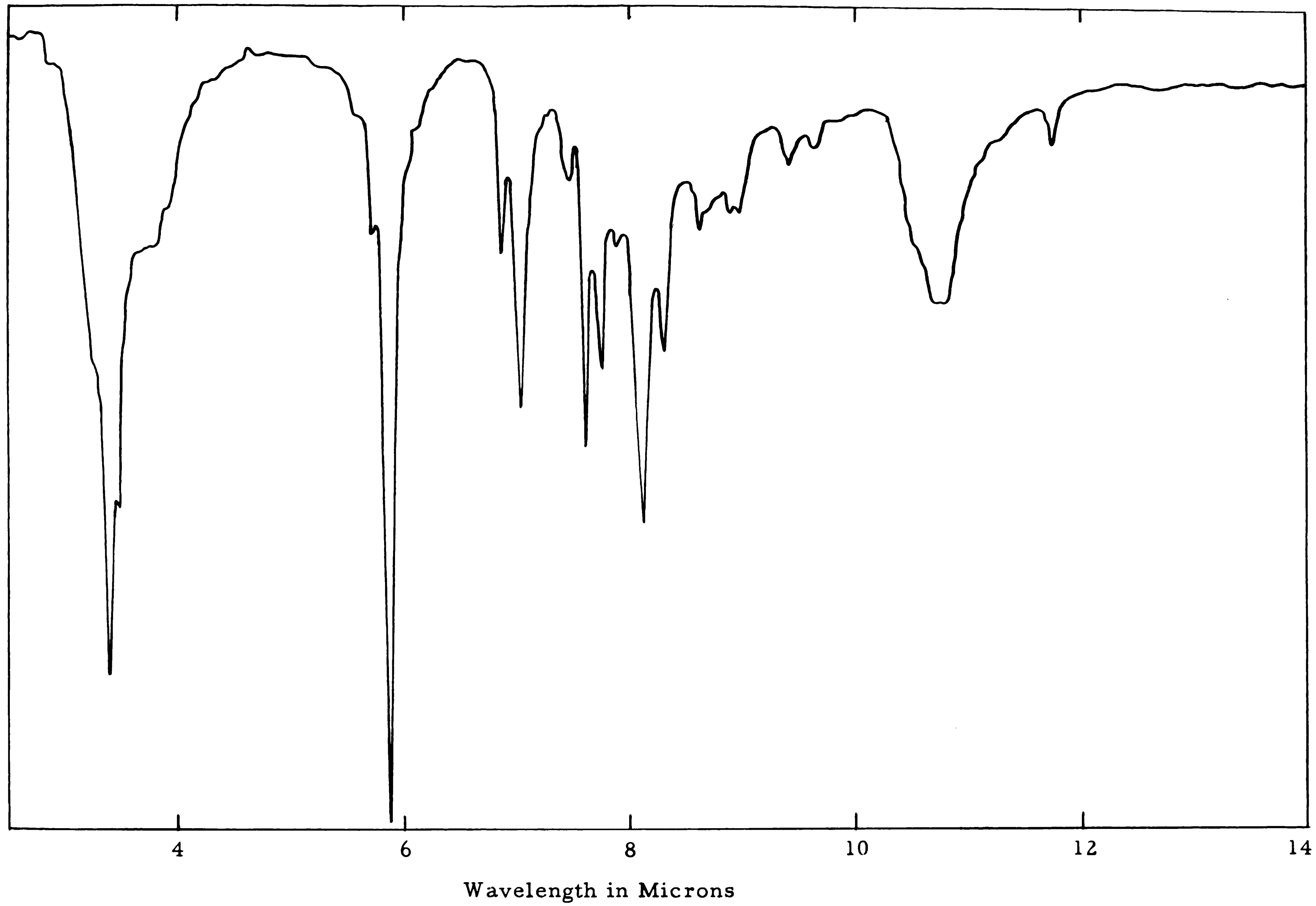


Figure 3. Infrared Spectrum of 2-Exonorbornanecarboxylic Acid.

pentane by cooling in dry ice to yield a colorless acid melting at 43-45°. This acid was found to be identical to the starting acid and illustrates the absence of isomerization in the formation of the corresponding acid chloride.

The properties of the acid chlorides are summarized in Table 11.

C. Preparation of Diacyl Peroxides

All diacyl peroxides were prepared by the method of Wyman (47). In a typical preparation, 5-endonorbornenecarbonyl chloride (0.624 g., 0.004 mole) was added to an ice-cold slurry of 0.156 g. (0.002 mole) of sodium peroxide and 40 ml. of anhydrous ether contained in a 300-ml. 2-necked round-bottomed flask. The flask was fitted with a reflux condenser and a thermometer. The mixture was cooled in an ice bath and stirred magnetically throughout the reaction time. Water (2-4 drops) was added to initiate the reaction. A rise in temperature of 1-2° is noticed upon addition of the water. A few drops of water were added intermittantly through the course of the reaction. The reaction was taken as complete when the yellow sodium peroxide color was replaced by white sodium chloride (about 5 hours). Ice water (15 ml.) was then added and the layers separated. The ether layer was washed successively with ice water, 5% sodium carbonate, and finally ice water again. After drying over magnesium sulfate and evaporating the ether, the residue was taken up in pentane. After drying over drierite and evaporating the pentane, the peroxide solidified. The solid was taken up in pentane and the solution cooled in dry ice. Filtration yielded 0.48 g. (87%) of white 5-endonorbornenecarbonyl peroxide powder, m.p. 45-47° with evolution of gas. Titration indicated 99+% purity.

The properties of the peroxides are summarized in Table 12, their infrared spectra are shown in Figures 4, 5, 6, and 7.

Table 11. Yields and Physical Properties of Various Acid Chlorides.

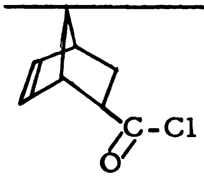
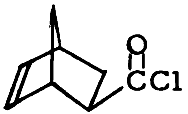
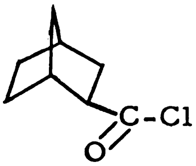
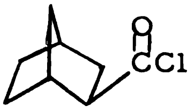
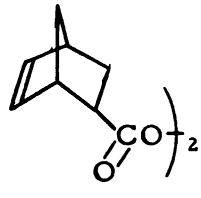
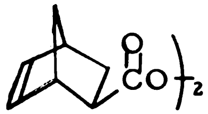
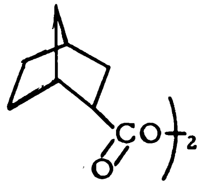
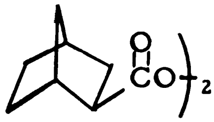
Compound	Reaction Time	Yield	b.p.	Literature Value
	3.5 hours	90%	47°/1.5 mm.	84-85°/14 mm. (40)
	3.5 hours	66%	44-46°/3 mm.	70-72°/8 mm. (40)
	4 hours	79%	82°/10 mm.	84°/12 mm. (38)
	4 hours	75%	83°/10 mm.	83-84°/12 mm. (46)

Table 12. Yields and Physical Properties of Various Diacyl Peroxides.

Compound	Reaction Time	Yield	m.p.	Purity	Figure
	5 hours	87%	45-47°	99+%	4
	4.5 hours	53%	49.5-50.5°	97%	5
	7 hours	60%	87°	99+%	6
	5 hours	72%	55-56°	94%	7

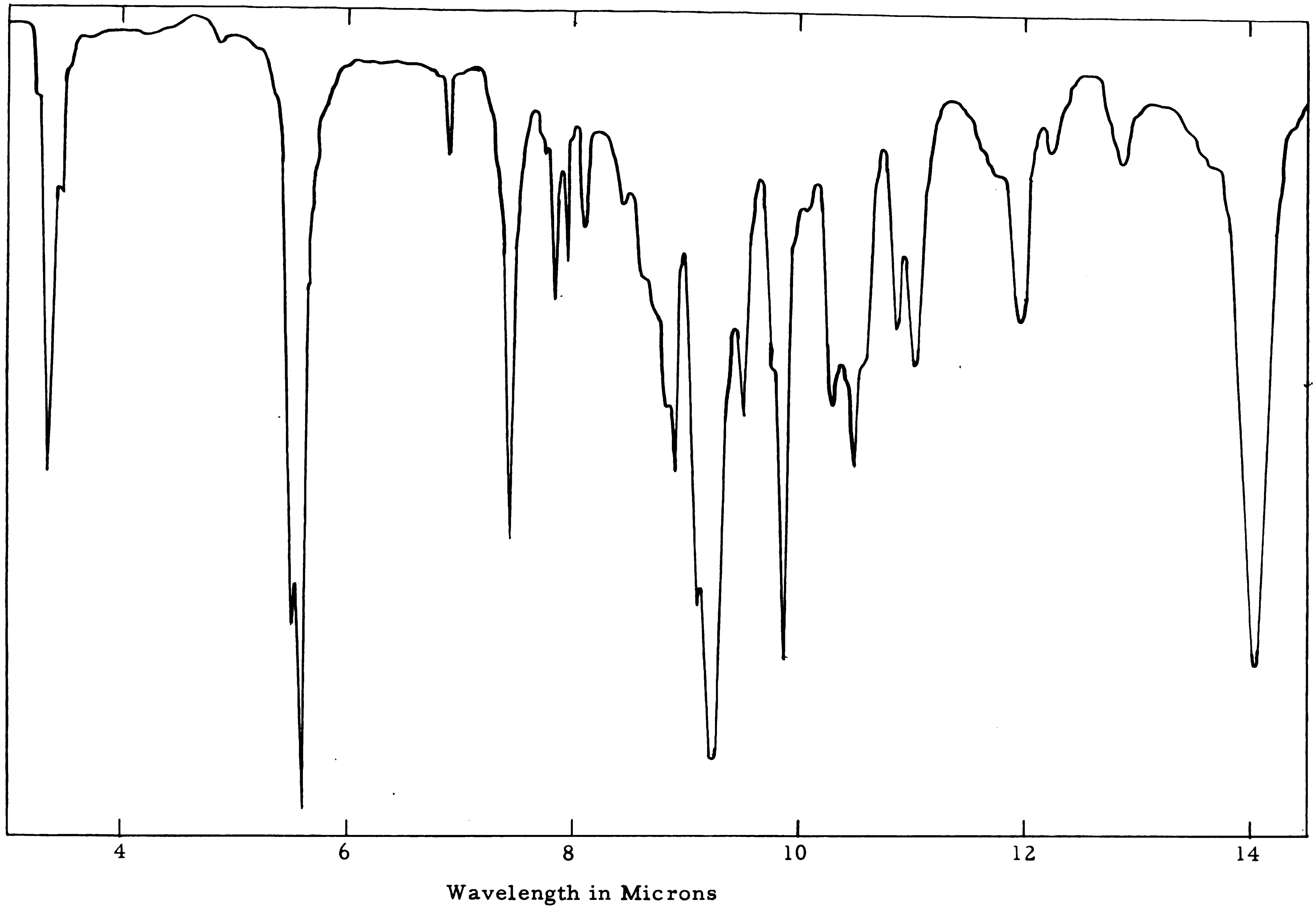


Figure 4. Infrared Spectrum of 5-Endonorbornenecarbonyl Peroxide:

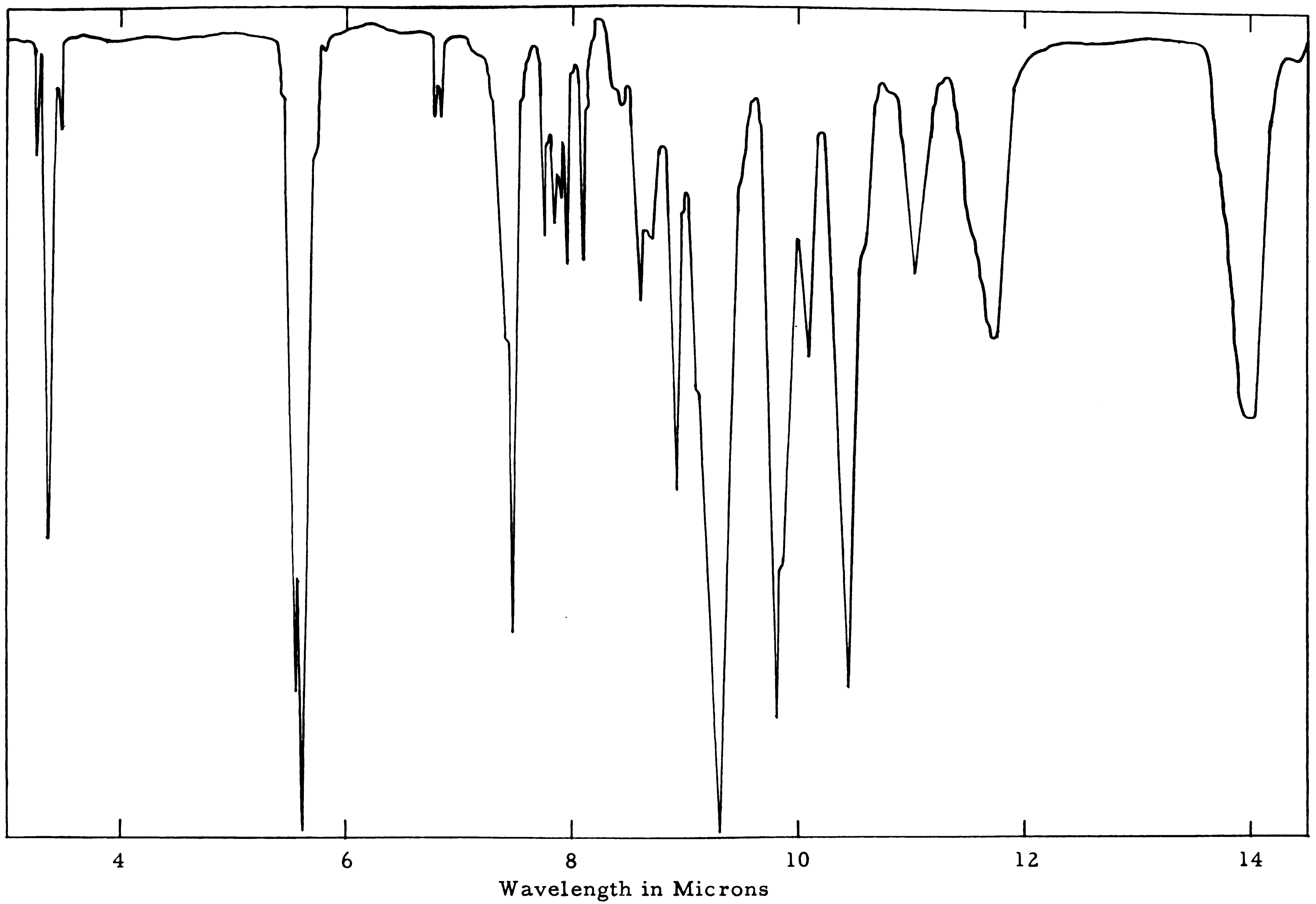


Figure 5. Infrared Spectrum of 5-Exonorbornenecarbonyl Peroxide.

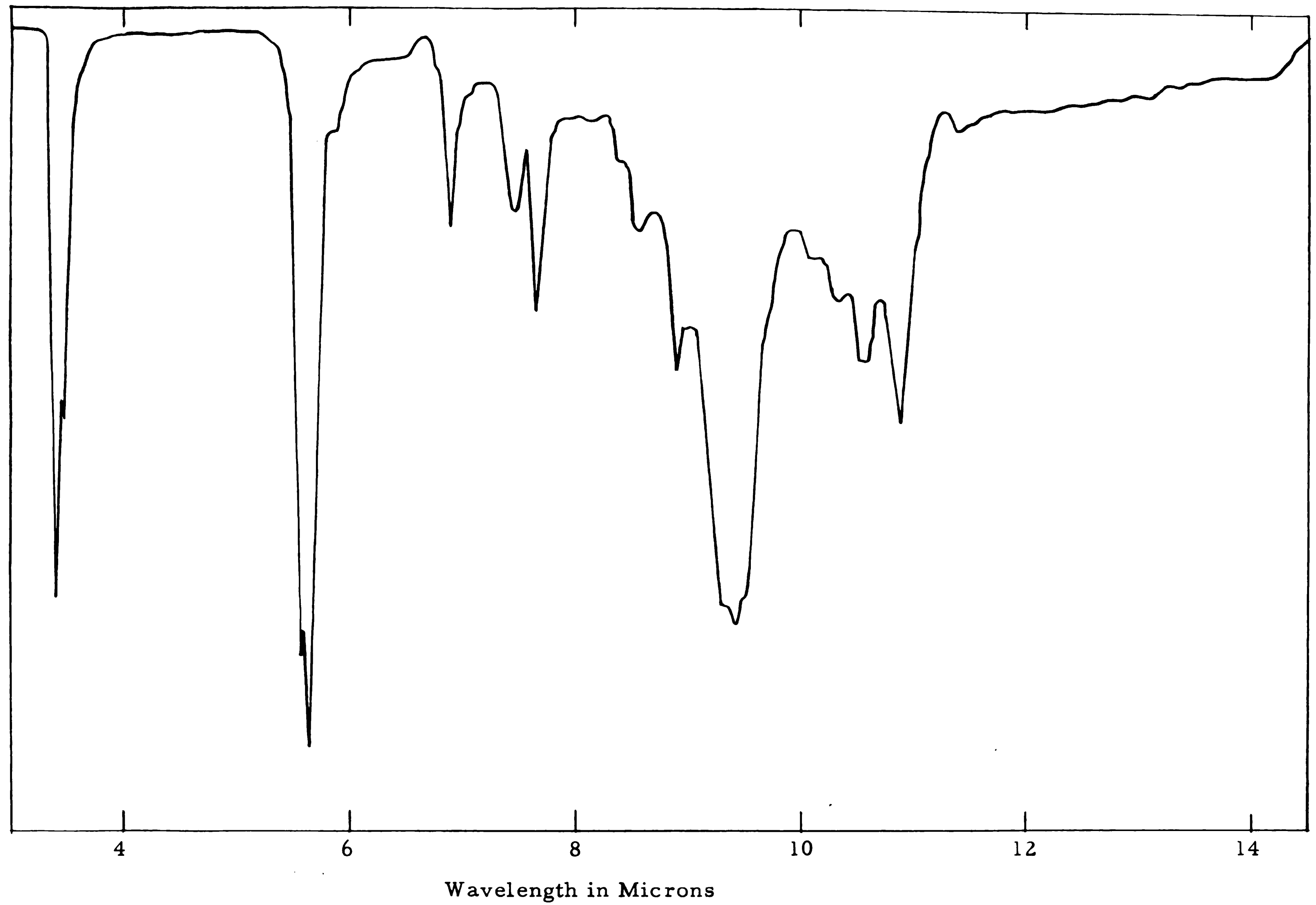


Figure 6. Infrared Spectrum of 2-Endonorbornanecarbonyl Peroxide.

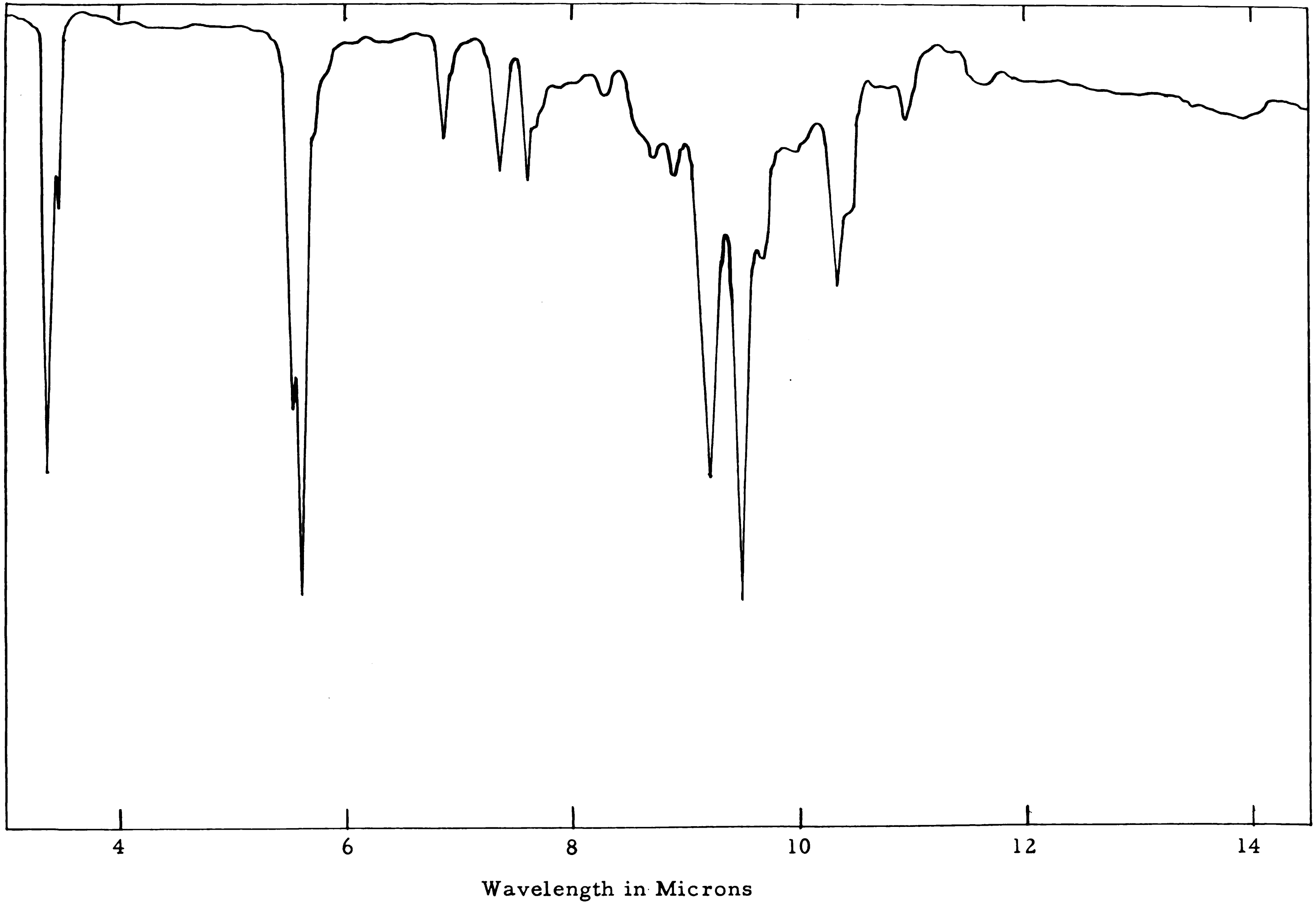


Figure 7. Infrared Spectrum of 2-Exonorbornanecarbonyl Peroxide.

III. Preparation of Lactones

A. Preparation of the Gamma-3 Lactone of 2-Exobromo-2-endohydroxy-5-endonorbornanecarboxylic Acid

The procedure of Roberts (41) was employed in the preparation of this compound. 5-Endonorbornenecarboxylic acid (10 g., 0.0725 mole) was dissolved in a solution of 30 g. of sodium bicarbonate in 450 ml. of water contained in a 500-ml. Erlenmeyer flask. The mixture was cooled in an ice bath and stirred magnetically. Bromine (3.8 ml., 0.0736 mole) was added dropwise to the stirred solution. A light yellow oil separated and the mixture was extracted with ether. The ether solution was washed with 10% sodium thiosulfate and finally with water. After drying over calcium chloride, the ether was evaporated and the residual oil crystallized from ethyl acetate-pentane by prolonged cooling in dry ice. The solid was filtered and recrystallized to yield 4 g. (25%) of the gamma-3 lactone of 2-exobromo-3-endohydroxy-5-endonorbornanecarboxylic acid, colorless needles, m.p. 66-67° (lit. value (41), m.p. 67-68°). Its infrared and n.m.r. spectra are shown in Figures 8 and 32.

B. Preparation of the Gamma-3 Lactone of 2-Exochloro-3-endohydroxy-5-endonorbornanecarboxylic Acid

5-Endonorbornenecarboxylic acid (5 g., 0.0363 mole) was dissolved in a solution of 15 g. of sodium bicarbonate in 225 ml. of water. The magnetically stirred solution was cooled in an ice bath and chlorine gas was passed in until the solution took on a green-yellow color. The mixture was extracted with ether, and the ether solution washed successively with water, 10% sodium thiosulfate, and finally water again. After drying over calcium chloride and evaporating the ether, the residual oil was crystallized from pentane-ethyl acetate by cooling in dry ice. The solid was filtered and recrystallized to yield 3 g. (37%) of lactone, m.p. 75-76°.

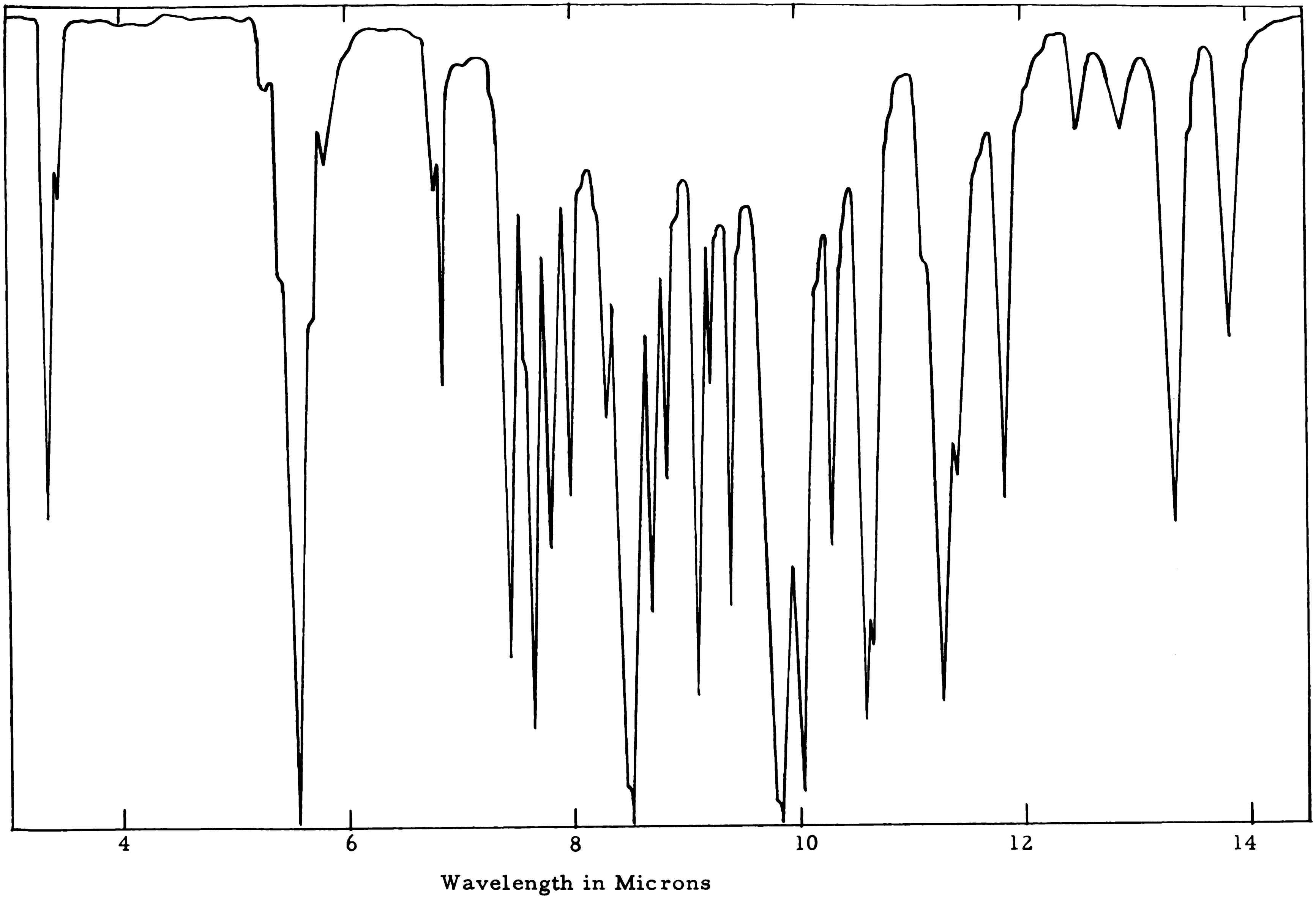


Figure 8. Infrared Spectrum of the Gamma-3 Lactone of 2-Exobromo-3-endohydroxy-5-endonorbornanecarboxylic Acid.

Its infrared and n.m.r. spectra are shown in Figures 9 and 32.

Anal. Calc'd for $C_8H_9O_2Cl$: C, 55.65; H, 5.26; Cl, 20.56.
Found: C, 55.01; H, 5.14; Cl, 21.92.

C. Preparation of the Gamma-3 Lactone of 2-Exoiodo-3-endohydroxy-5-endonorbornanecarboxylic Acid

This compound was obtained in the crude form in the preparation of 5-exonorbornenecarboxylic acid. The crude material was recrystallized twice from ethyl acetate-pentane by cooling in dry ice to yield the lactone, m.p. 58-59° (lit. value (77), 58-59°). Its infrared and n.m.r. spectra are shown in Figures 10 and 32.

IV. Preparation of Esters

A. Preparation of Alcohols

1. Preparation of 5-Endohydroxynorbornene

5-Endoacetoxynorbornene was prepared by the method of Alder (48). Freshly distilled cyclopentadiene (25 g., 0.378 mole) was added to 37.5 g. (0.436 mole) of vinyl acetate in a combustion tube and sealed. The tube was placed in an autoclave and heated at 190° for 12 hours. The contents were distilled *in vacuo* to yield 18 g. (30%) of colorless 5-endoacetoxynorbornene, b.p. 80°/15 mm., n_D^{25} 1.4685 (lit. values (41), b.p. 72°/10 mm., n_D^{25} 1.4668).

The 5-endoacetoxynorbornene (8 g., 0.0526 mole) was added to 125 ml. of 10% sodium hydroxide contained in a 250-ml. round-bottomed flask fitted with a condenser, and the mixture refluxed for 12 hours. The reaction mixture was extracted with ether. After drying over magnesium sulfate and evaporating the ether the residue was sublimed *in vacuo*, 100°/10 mm. The sublimed solid was crystallized from pentane by cooling

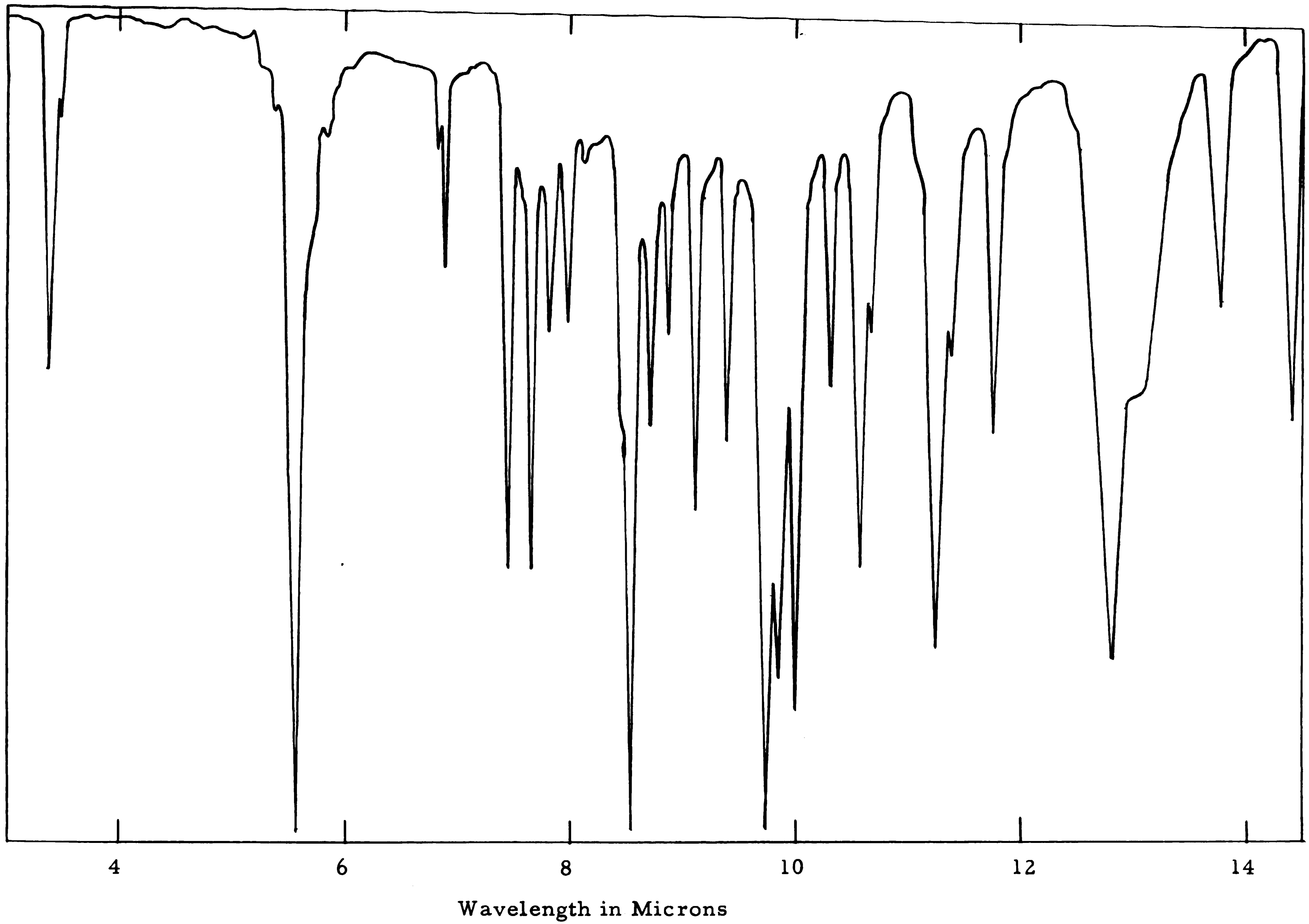


Figure 9. Infrared Spectrum of the Gamma-3 Lactone of 2-Exochloro-3-endohydroxy-5-endonorbornanecarboxylic Acid.

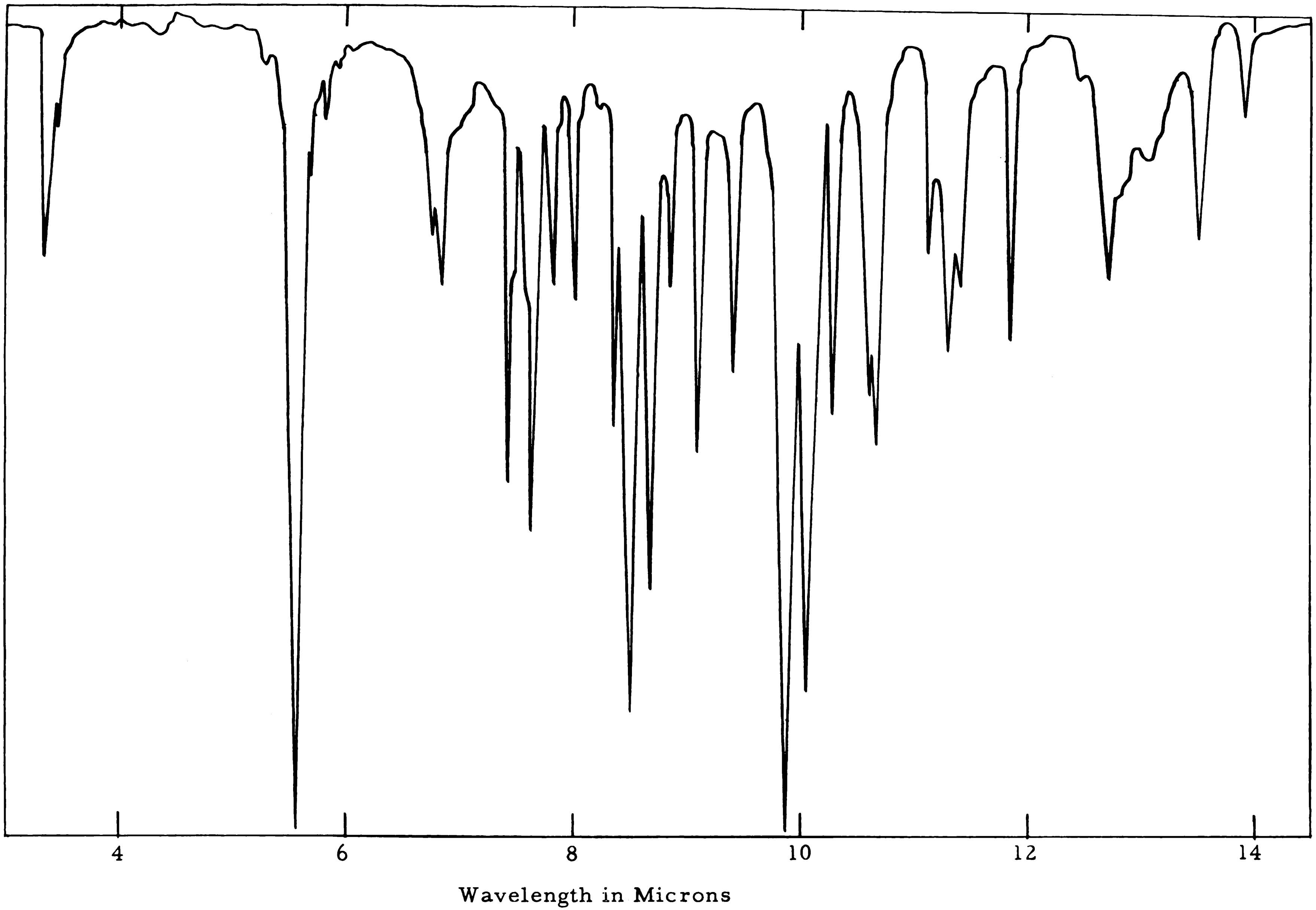


Figure 10. Infrared Spectrum of the Gamma-3 Lactone of 2-Exoiodo-3-endohydroxy-5-endonorbornanecarboxylic Acid.

in dry ice to yield 2.7 g. (46.7%) of white 5-endohydroxynorbornene, m.p. 109-110° (lit. value (41), m.p. 109.4-110.8°).

The 3,5-dinitrobenzoate was prepared by the procedure of Applequist (49). Colorless needles from pentane-ethyl acetate, m.p. 105-106°. Its infrared spectrum is shown in Figure 11.

Anal. Calc'd for $C_{14}H_{12}N_2O_6$: C, 55.26; H, 3.94.
Found: C, 55.16; H, 4.09.

2. Preparation of 5-Exohydroxynorbornene

5-Exohydroxynorbornene was prepared as described by Roberts (41) using the method of Doering and Aschner (50). 5-Endohydroxynorbornene (2 g., 0.0185 mole) was added to a solution of 0.05 g. of fluorenone in 5 ml. of toluene contained in a 10-ml. round-bottomed flask fitted with a reflux condenser. A small piece of sodium was added and the mixture refluxed for 17 hours. The mixture was poured on 25 ml. of water and extracted with ether. After drying over magnesium sulfate and evaporating the ether, the residue was sublimed *in vacuo*, 90°/10 mm. The sublimed solid was crystallized from pentane by cooling in dry ice to yield 1 g. (50%) of white spongy 5-exohydroxynorbornene, m.p. 101.5-103.5° (lit. value (41), 97.5-99.2°).

The 3,5-dinitrobenzoate (49) gave colorless needles from pentane-ethyl acetate, m.p. 104-105°. Its infrared spectrum is shown in Figure 12.

Anal. Calc'd for $C_{14}H_{12}N_2O_6$: C, 55.26; H, 3.94.
Found: C, 55.25; H, 3.98.

3. Preparation of 2-Endoacetoxynorbornane

Into a 250-ml. hydrogenation bottle was placed 12.5 g. (0.08 mole) of 5-endoacetoxynorbornene, 75 ml. of glacial acetic acid, and 0.5 g. of platinum oxide. The mixture was hydrogenated at room temperature with

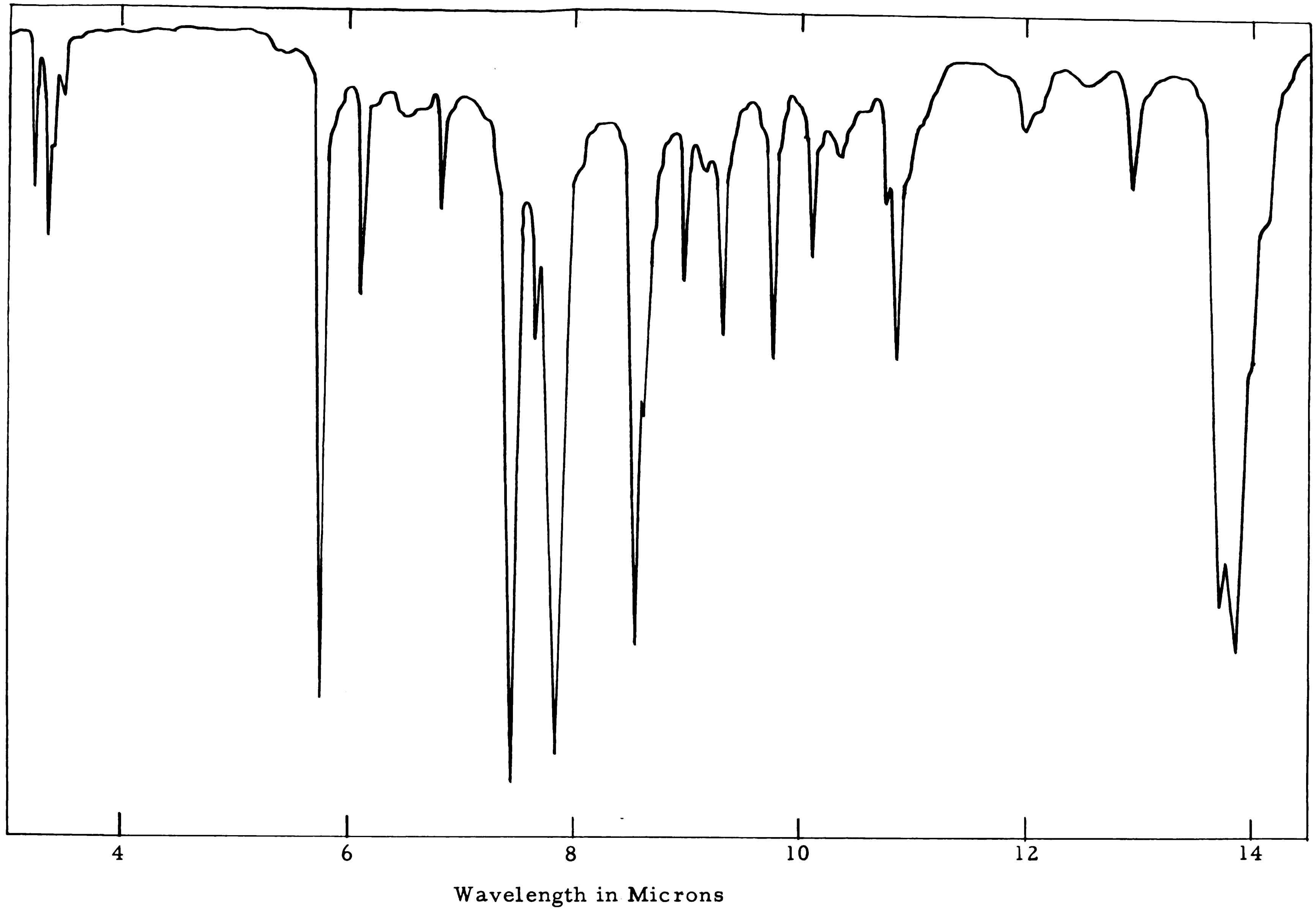


Figure 11. Infrared Spectrum of 5-Endonorbornenyl 3, 5-Dinitrobenzoate.

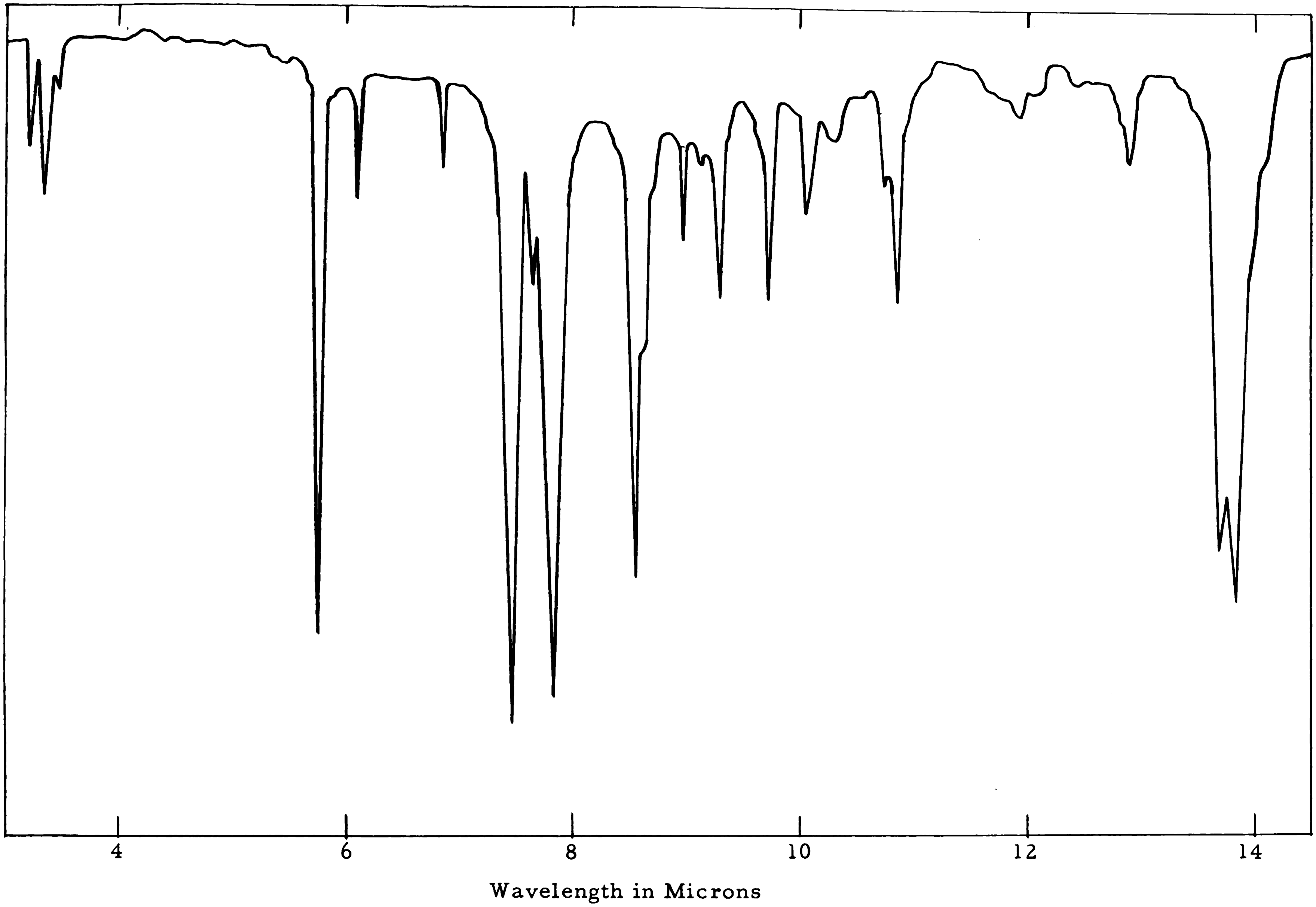


Figure 12. Infrared Spectrum of 5-Exonorbornenyl 3, 5-Dinitrobenzoate.

50 lbs. hydrogen pressure. Hydrogen uptake was complete in 15 minutes. The mixture was filtered and the filtrate poured on 250 ml. of water. The aqueous solution was extracted with ether. The ether extracts were washed with water, 10% sodium carbonate, and finally, water once more. After drying over magnesium sulfate and evaporating the ether, the residue was distilled *in vacuo* to yield 12 g. (96%) of acetate, b.p. 75-77°/ 13 mm., n_D^{25} 1.4577 (reported (48), 81-83°/12 mm., n_D^{25} 1.4578).

4. Preparation of 2-Endohydroxynorbornane

2-Endoacetoxynorbornane (6.5 g., 0.042 mole) was dissolved in 25 ml. of anhydrous ether. The solution was added dropwise to a stirred slurry of 1 g. (0.026 mole) of lithium aluminum hydride in 75 ml. of anhydrous ether contained in a 300-ml. 3-necked round-bottomed flask fitted with a reflux condenser, mechanical stirrer, and a dropping funnel. After the addition was complete (about $\frac{1}{2}$ hour), the mixture was refluxed for $\frac{1}{2}$ hour and stirred for an additional hour. The excess lithium aluminum hydride was destroyed by adding small portions of ice. The mixture was poured on water, acidified with 10% sulfuric acid, and extracted with ether. The ether extracts were washed with 5% sodium carbonate, and finally water. After drying over magnesium sulfate and evaporating the ether, the residue was crystallized from pentane by cooling in dry ice to yield 3 g. (63%) of alcohol, m.p. 144-145° (reported (48), m.p. 149-150°).

5. Preparation of 2-Exohydroxynorbornane

The method of Bruson (51) was employed in the preparation of this compound. Norbornene (35 g., 0.372 mole) was added to 148 g. of 25% sulfuric acid contained in a 300-ml. 3-necked round-bottomed flask fitted with a mechanical stirrer and a reflux condenser. The mixture was stirred and refluxed for 5 hours. The reaction mixture was cooled and extracted with ether. The ether solution was washed with 5% sodium carbonate and finally water. After drying over magnesium sulfate and evaporating the ether, the residue was distilled to yield 9 g. (22%) of alcohol, b.p. 185-190°/1 atm. The alcohol was crystallized from nitromethane, m.p. 123-123.5° (reported (51), m.p. 126°).

6. Preparation of 5-Endohydroxymethylnorbornene

Methyl 5-endonorbornenecarboxylate (5 g., 0.0329 mole) was dissolved in 25 ml. of anhydrous ether and added dropwise to a suspension of 1.89 g. (0.050 mole) of lithium aluminum hydride in 50 ml. of anhydrous ether contained in a 300-ml. 3-necked round-bottomed flask fitted with a dropping funnel and a reflux condenser. The mixture was refluxed for 1 hour on a steam bath, cooled, and the excess lithium aluminum hydride destroyed by adding small portions of ice. Hydrochloric acid (6 N) was added to dissolve the insoluble hydroxides and the mixture filtered. The filtrate was extracted with ether and the ether solution washed with 5% sodium carbonate and finally water. After drying over magnesium sulfate and evaporating the ether, the residue was distilled *in vacuo* to yield 3.0 g. (73.4%) of colorless 5-endohydroxymethylnorbornene, b.p. 98-100°/11 mm., n_D^{25} 1.4949.

The 3, 5-dinitrobenzoate (49) gave a yellow spongy solid from pentane-ethyl acetate, m.p. 80-81°. Its infrared spectrum is shown in Figure 13.

Anal. Calc'd for $C_{15}H_{14}N_2O_6$: C, 56.60; H, 4.40.

Found: C, 56.56; H, 4.41.

7. Preparation of 5-Exohydroxymethylnorbornene

5-Exonorbornenecarboxylic acid (2 g., 0.0135 mole) was dissolved in 25 ml. of anhydrous ether and added dropwise to a suspension of 1 g. (0.025 mole) of lithium aluminum hydride in 50 ml. of anhydrous ether contained in a 300-ml. 3-necked round-bottomed flask fitted with a dropping funnel and a reflux condenser. The mixture was refluxed for

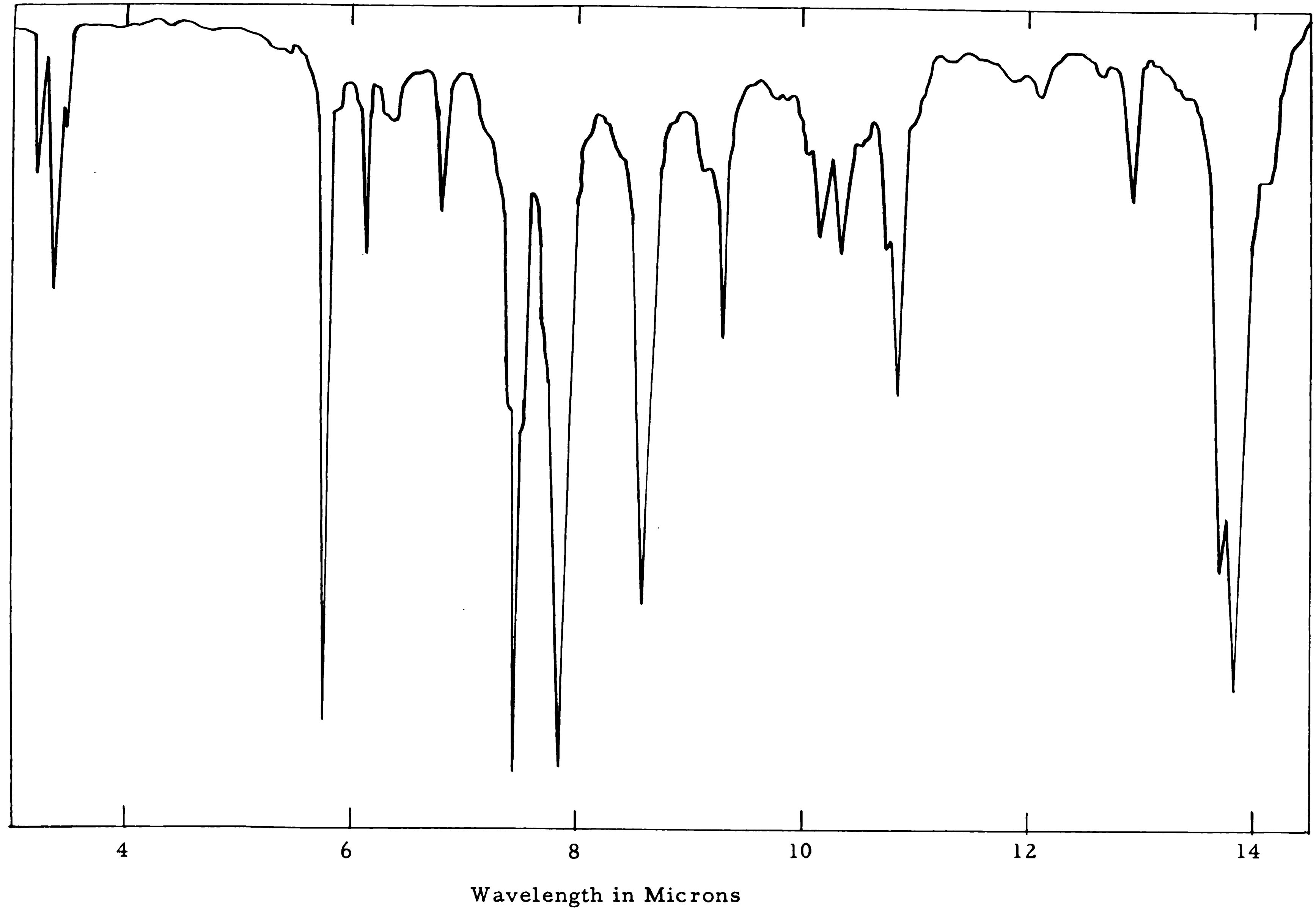


Figure 13. Infrared Spectrum of the 3, 5-Dinitrobenzoate of 5-Endohydroxymethylnorbornene.

1 hour on a steam bath, cooled, and the excess lithium aluminum hydride destroyed by adding small portions of ice. Hydrochloric acid (6 N) was added to dissolve the insoluble hydroxides and the mixture filtered. The filtrate was extracted with ether and the ether solution washed with 5% sodium carbonate and finally with water. After drying over magnesium sulfate and evaporating the ether, the residue was distilled in vacuo to yield 1.2 g. (66.3%) of colorless 5-exohydroxymethylnorbornene, b.p. 94-95°/11 mm., n_D^{25} 1.4972.

The 3,5-dinitrobenzoate (49) gave colorless needles from pentane-ethyl acetate, m.p. 98-99°. Its infrared spectrum is shown in Figure 14.

Anal. Calc'd for $C_{15}H_{14}O_6$: C, 56.60; H, 4.40.
Found: C, 56.45; H, 4.27.

B. Preparation of Esters

All esters were prepared in the same manner (49).

In a typical preparation, 2-endonorbornanecarbonyl chloride (1.4 g., 0.0087 mole) was added to 1.12 g. (0.0094 mole) of 2-endohydroxynorbornane in 50 ml. of carbon tetrachloride contained in a 100-ml. round-bottomed flask fitted with a reflux condenser. Pyridine (4 ml.) was added and the mixture refluxed for 2 hours on a steam bath. The reaction mixture was cooled and poured on 70 g. of ice. The mixture was extracted with ether and the ether washed successively with 3 N hydrochloric acid, 5% sodium carbonate, and finally water. After drying over magnesium sulfate and evaporating the ether, the residue was sublimed in vacuo, 110°/11 mm. The sublimate was crystallized from pentane by cooling in dry ice to yield 1.3 g. (64%) of ester, m.p. 109-110°. Its infrared spectrum is shown in Figure 17. The extinction coefficient of the 5.79 μ carbonyl band was found to be 470 l./mole-cm.

Anal. Calc'd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46.
Found: C, 76.84; H, 9.47.

The properties of the esters are summarized in Table 13, their infrared spectra are shown in Figures 15, 16, 17, and 18.

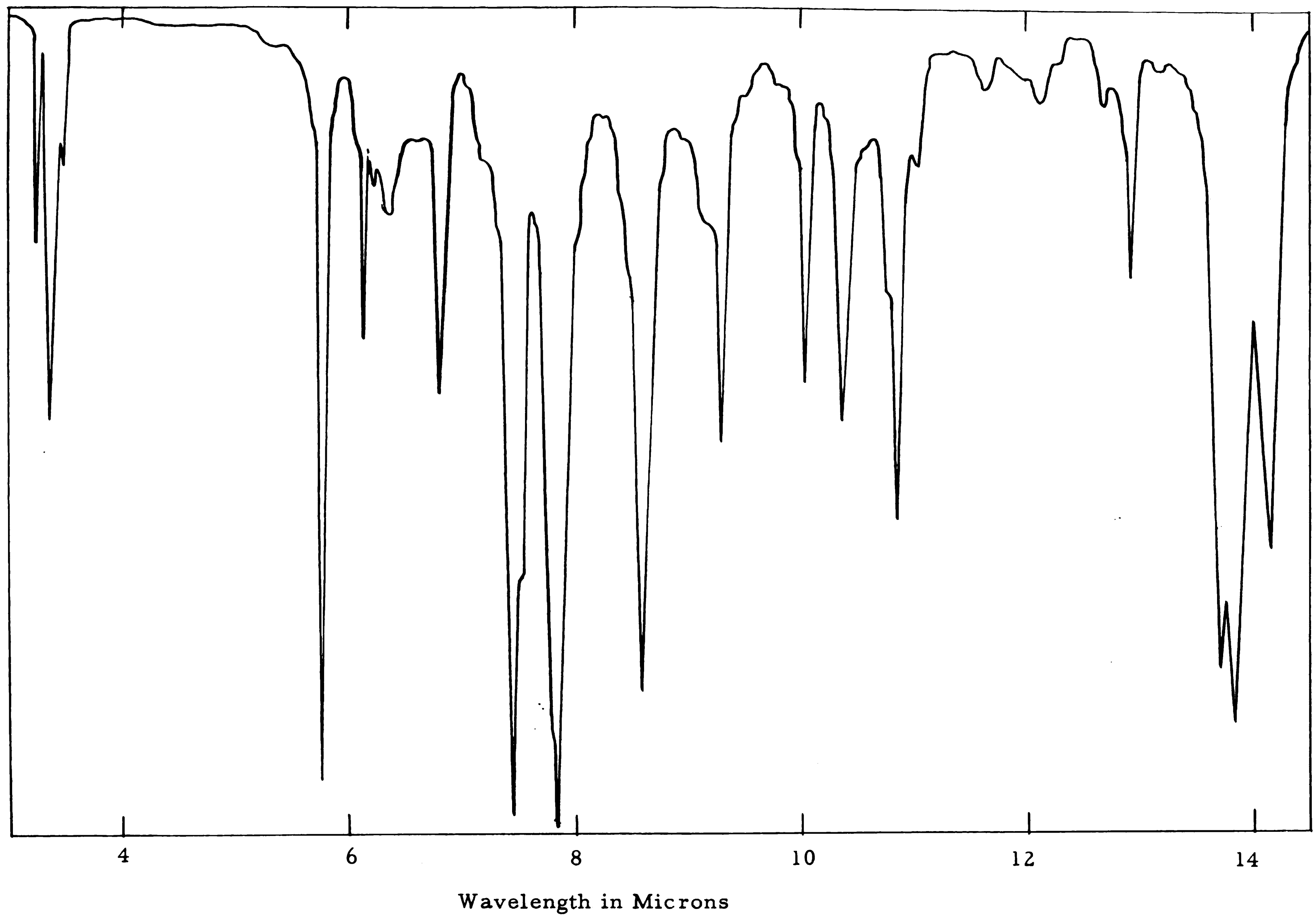
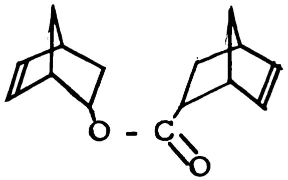
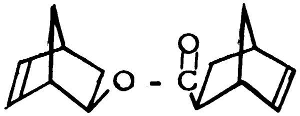
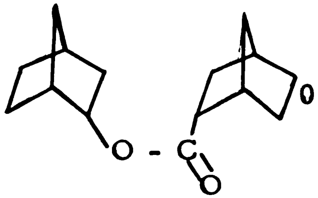
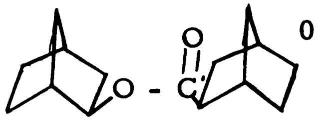


Figure 14. Infrared Spectrum of the 3, 5-Dinitrobenzoate of 5-Exohydroxymethylnorbornene.

Table 13. Yields and Physical Properties of Various Esters

Compound	Moles of Acid Chloride	Moles of Alcohol	Milliliters of Pyridine	Milliliters of CCl_4	Yield	m.p.	Extinction Coefficient of 5.77 μ band in liters/mole-cm.	Figure
	0.0033	0.0030	2	25	43.6%	60.5- 61°	409	15
	0.00725	0.0045	3	25	48.3%	72- 73°	473	16
	0.0087	0.0094	4	50	64%	109- 110°	470	17
	0.01	0.01	5	50	64%	120- 121°	489	18

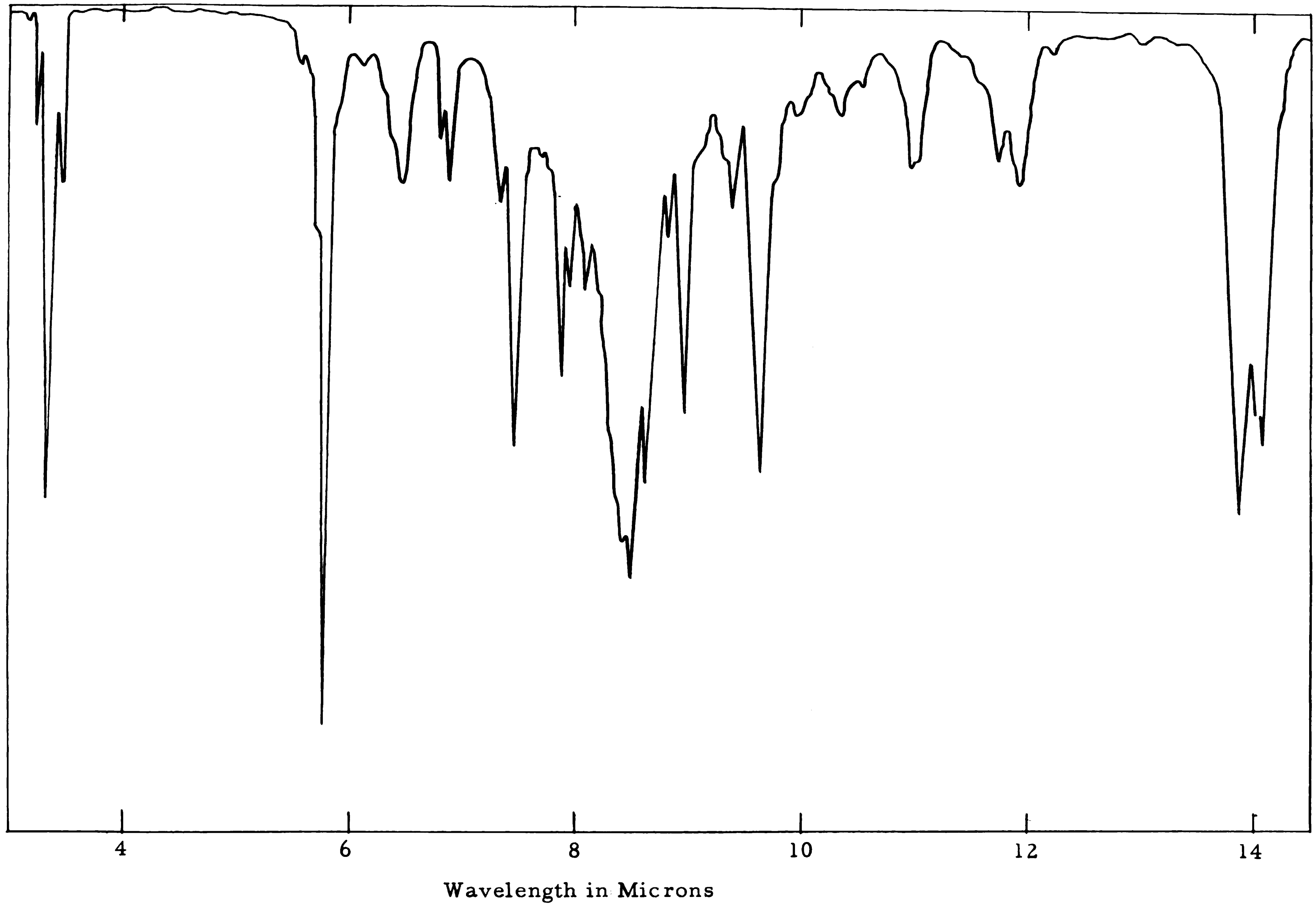


Figure 15. Infrared Spectrum of 5-Endonorbornenyl 5-endonorbornenecarboxylate.

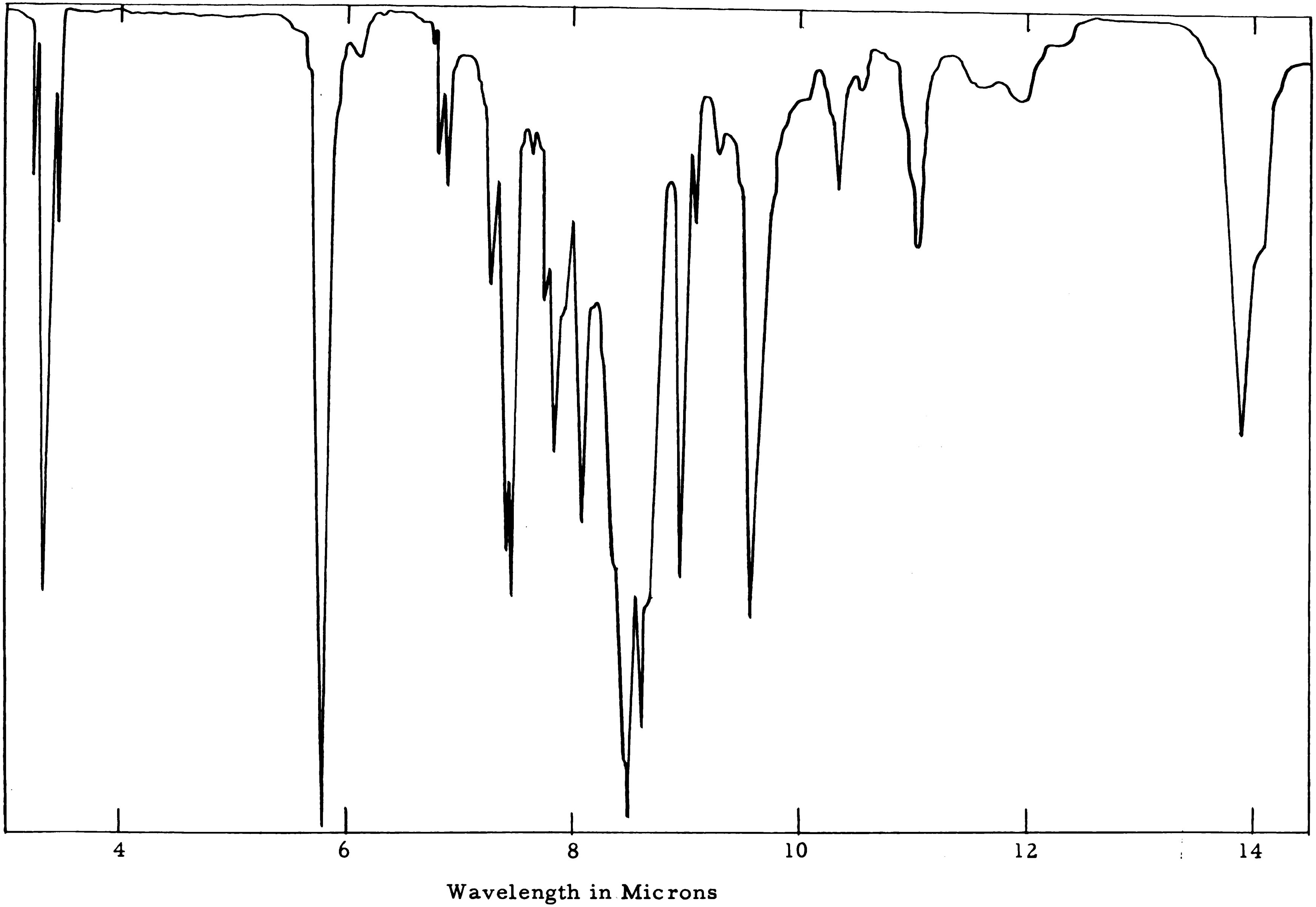


Figure 16. Infrared Spectrum of 5-Exonorbornenyl 5-Exonorbornenecarboxylate.

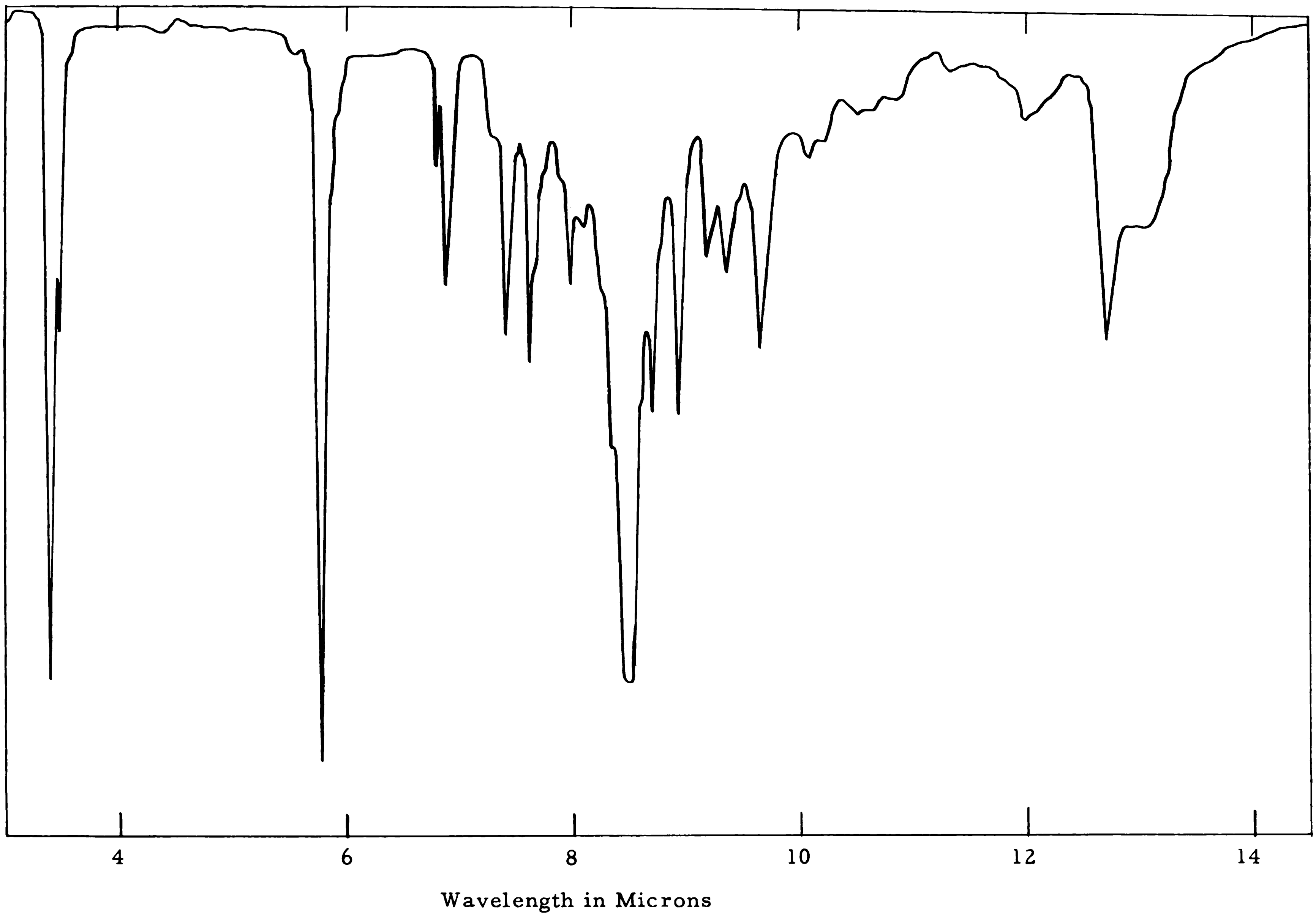


Figure 17. Infrared Spectrum of 2-Endonorbornyl 2-Endonorbornanecarboxylate.

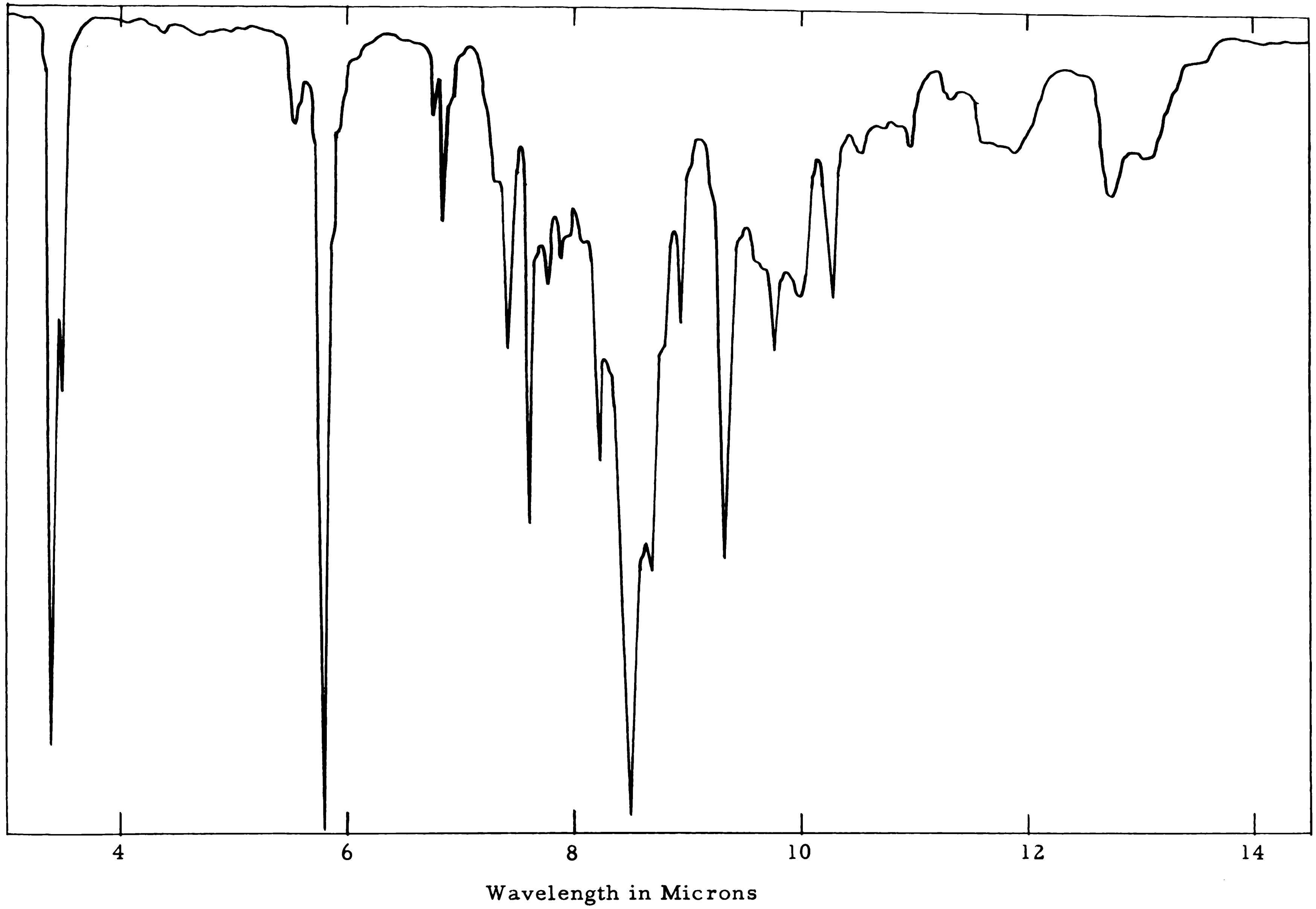


Figure 18. Infrared Spectrum of 2-Exonorbornyl 2-Exonorbornanecarboxylate.

V. Decomposition of Diacyl Peroxides

A. Identification of the Products of Decomposition

1. 2-Endonorbornanecarbonyl Peroxide Products

A 0.05 N solution of 2-endonorbornanecarbonyl peroxide in carbon tetrachloride (250 ml.) was refluxed for 24 hours. The carbon tetrachloride was removed by distillation through a 600 x 7 mm. vacuum jacketed tantalum wire spiral column (bath temperature, 85°). When no more carbon tetrachloride came over, the column was removed and the pressure was decreased gradually to 11 mm. The distillate to 80° was collected. Analysis on a Beckman GC-2 vapor phase chromatograph (retention time at 100° = 9 min.) indicated one alkyl halide. Its infrared spectrum is shown in Figure 19. This compound has been identified as 2-exochloronorbornane by virtue of its infrared spectrum (see Figure 20).

The pot residue was taken up in ether and extracted with 10% sodium hydroxide. The ether layer was dried over magnesium sulfate-norite. After evaporating the ether, the residue was sublimed, 100°/10 mm. The sublimate was crystallized from pentane by cooling in dry ice to yield a material (0.12 g.) melting at 106-108°. Its infrared spectrum is shown in Figure 21. This compound is identical to the previously prepared 2-endonorbornyl 2-endonorbornanecarboxylate.

The basic solution was acidified with 10% sulfuric acid and extracted with ether. After drying over magnesium sulfate-norite and evaporating the ether, the residue was crystallized from pentane to yield an acid melting at 60-62°. Its infrared spectrum is shown in Figure 22. This compound was found to be identical to 2-endonorbornanecarboxylic acid.

The above ester and acid were identified on the basis of melting points, mixed melting points, and infrared spectra.

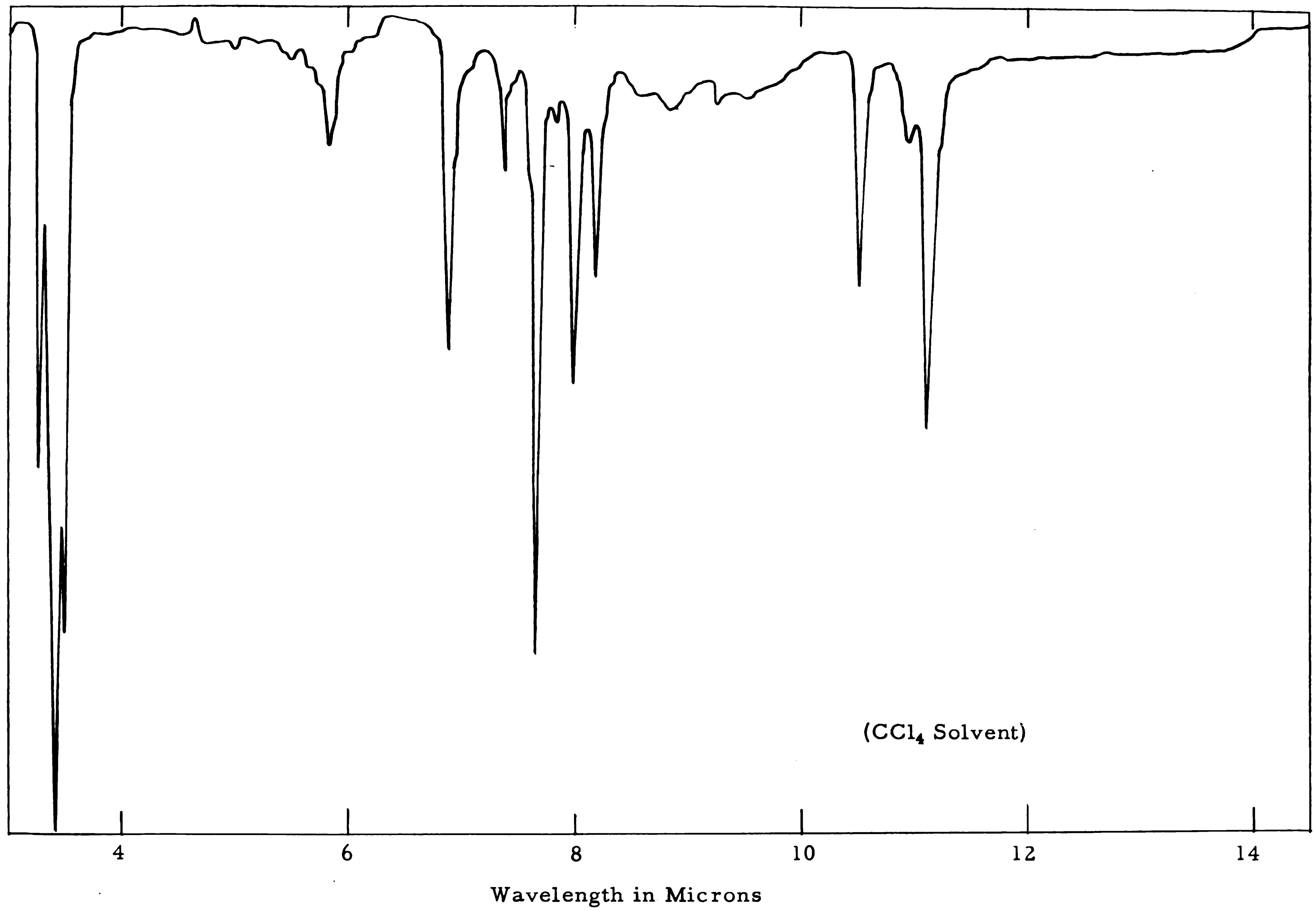
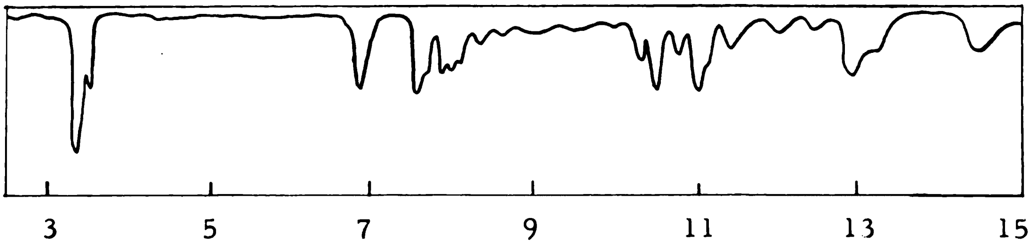
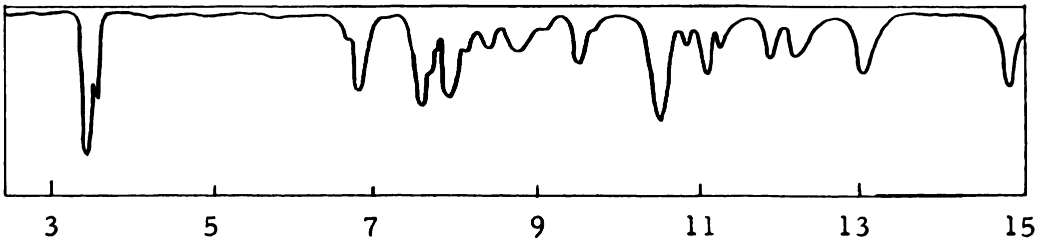


Figure 19. Infrared Spectrum of the Alkyl Halide Obtained from the Decomposition of 2-Endonorbornanecarbonyl Peroxide.



Wavelength in Microns

2-Endochloronorbornane



Wavelength in Microns

2-Exochloronorbornane

Figure 20. Infrared Spectra of 2-Exochloronorbornane and 2-Endochloronorbornane.

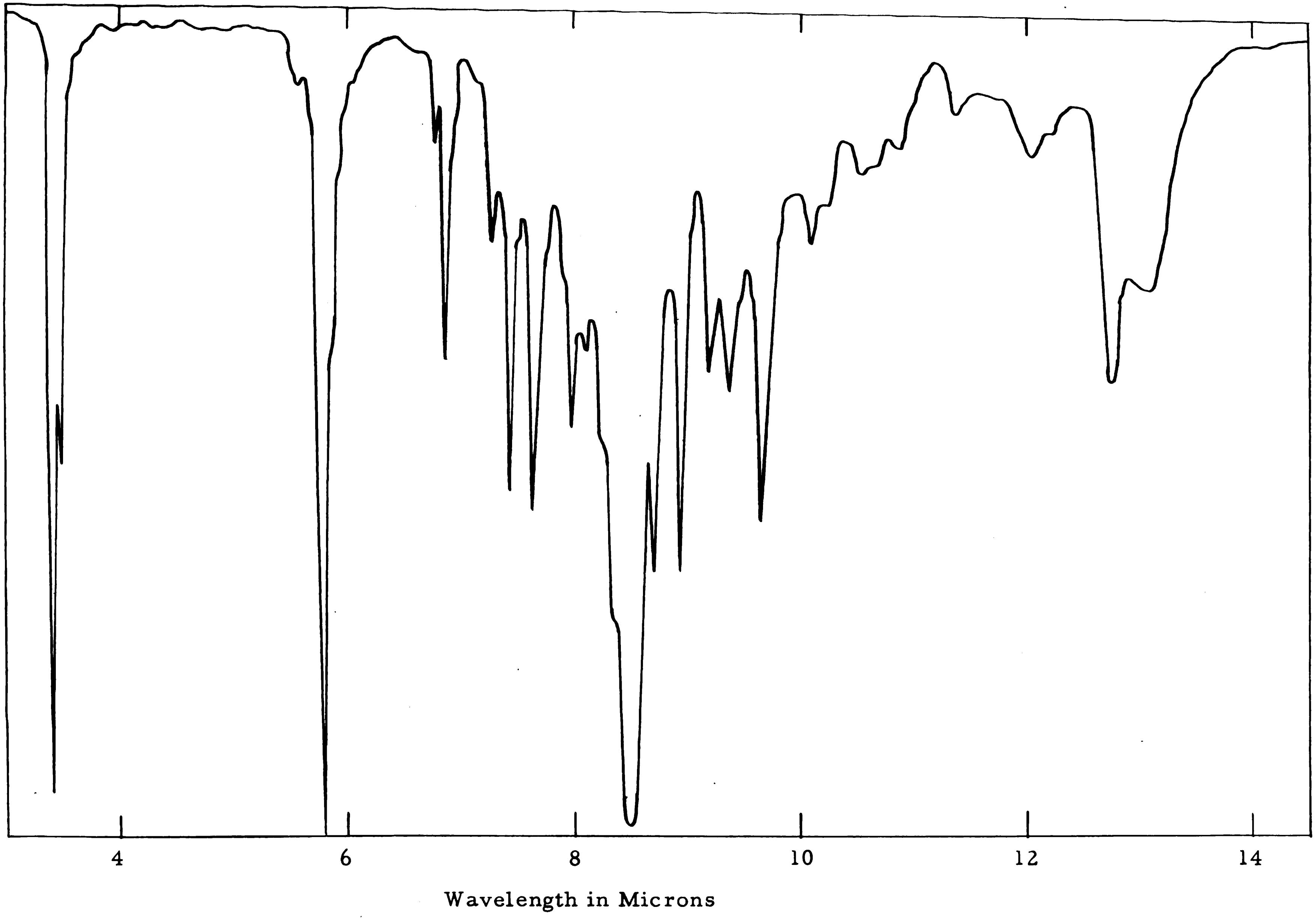


Figure 21. Infrared Spectrum of the Ester Obtained from the Decomposition of 2-Endonorbornanecarbonyl Peroxide.

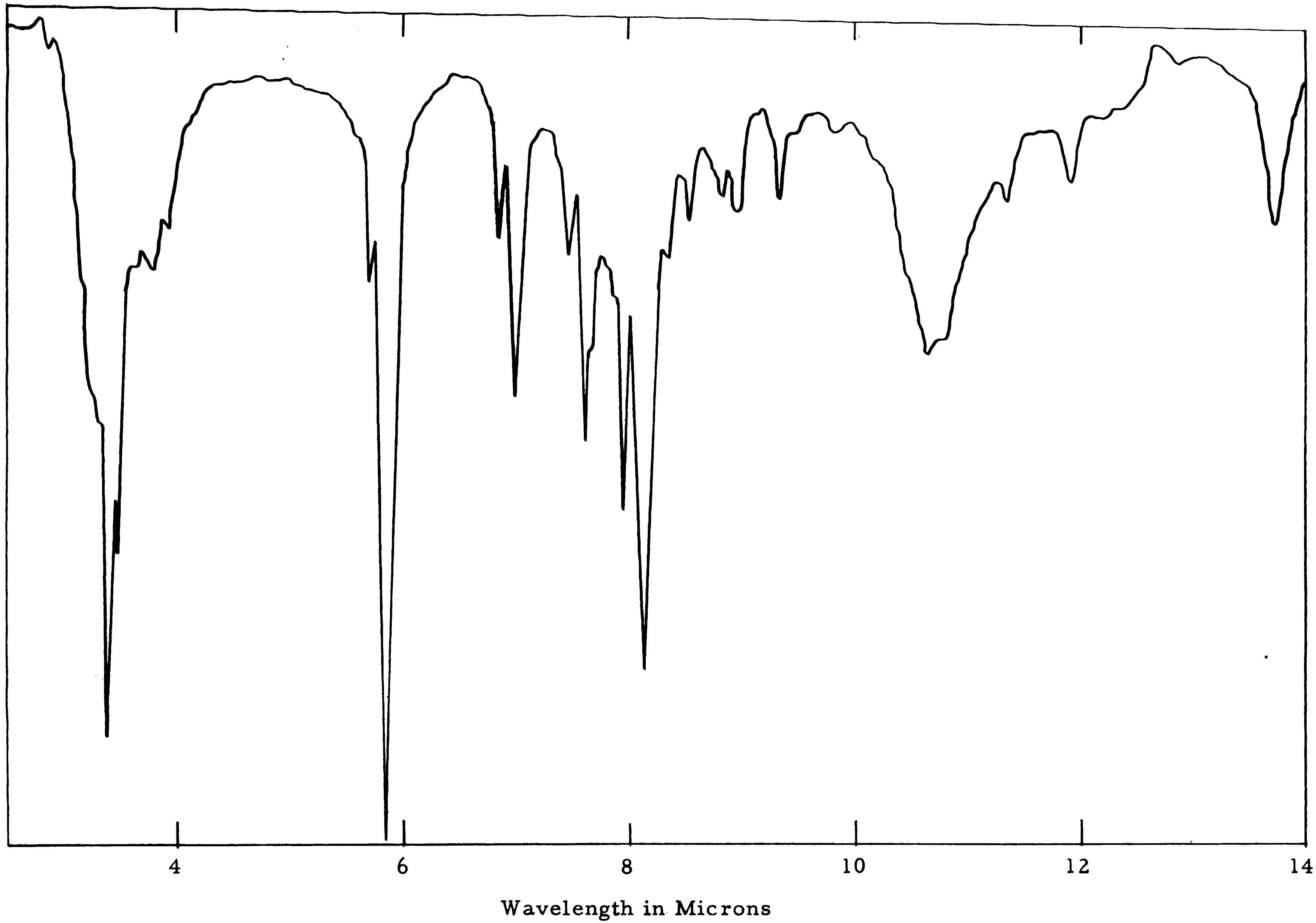


Figure 22. **Infrared Spectrum** of the Acid Obtained from the Decomposition of 2-Endonorbornanecarbonyl Peroxide.

2. 2-Exonorbornanecarbonyl Peroxide Products

The procedure in this case is identical to the 2-endonorbornanecarbonyl peroxide case. The alkyl halide was identical to the above case (see Figures 20, 23). The ester (0.15 g.) was found to melt at 118-119° (see Figure 24) and identical to 2-exonorbornyl 2-exonorbornanecarboxylate. The acid was found to melt at 50-52° (see Figure 25) and identical to 2-exonorbornanecarboxylic acid. Identifications were made on the basis of melting points, mixed melting points, and infrared spectra.

3. 5-Endonorbornenecarbonyl Peroxide Products

5-Endonorbornenecarbonyl peroxide (5 g.) was dissolved in 25 ml. of carbon tetrachloride and the solution refluxed for 24 hours. The carbon tetrachloride was removed by distillation through a 600 x 7 mm. vacuum jacketed tantalum wire spiral column (bath temperature, 85°). When no more carbon tetrachloride came over, the column was removed and the pressure dropped slowly to 15 mm. The distillate collected in this manner was concentrated by the above procedure to remove most of the carbon tetrachloride and then analyzed on a Beckman Megachrom vapor phase chromatograph at 150°. The first fraction was found to be carbon tetrachloride, the second fraction had a retention time of 20 minutes at 105°. Its infrared spectrum is shown in Figure 26. This compound has been identified at 5-exochloronorbornene by virtue of its infrared spectrum (see Figure 27).

Infrared inspection of the residue from the first distillation indicated the presence of ester and possibly lactone (5.77 μ, 5.58 μ). This material was taken up in a small amount of ether and added to 10 ml. of 5% sodium carbonate solution containing 1 pellet of sodium hydroxide. The mixture was stirred at room temperature for 16 hours and then extracted with ether. The ether solution was dried over drierite and the ether evaporated. The infrared spectrum of the material indicated the presence of ester (5.77 μ).

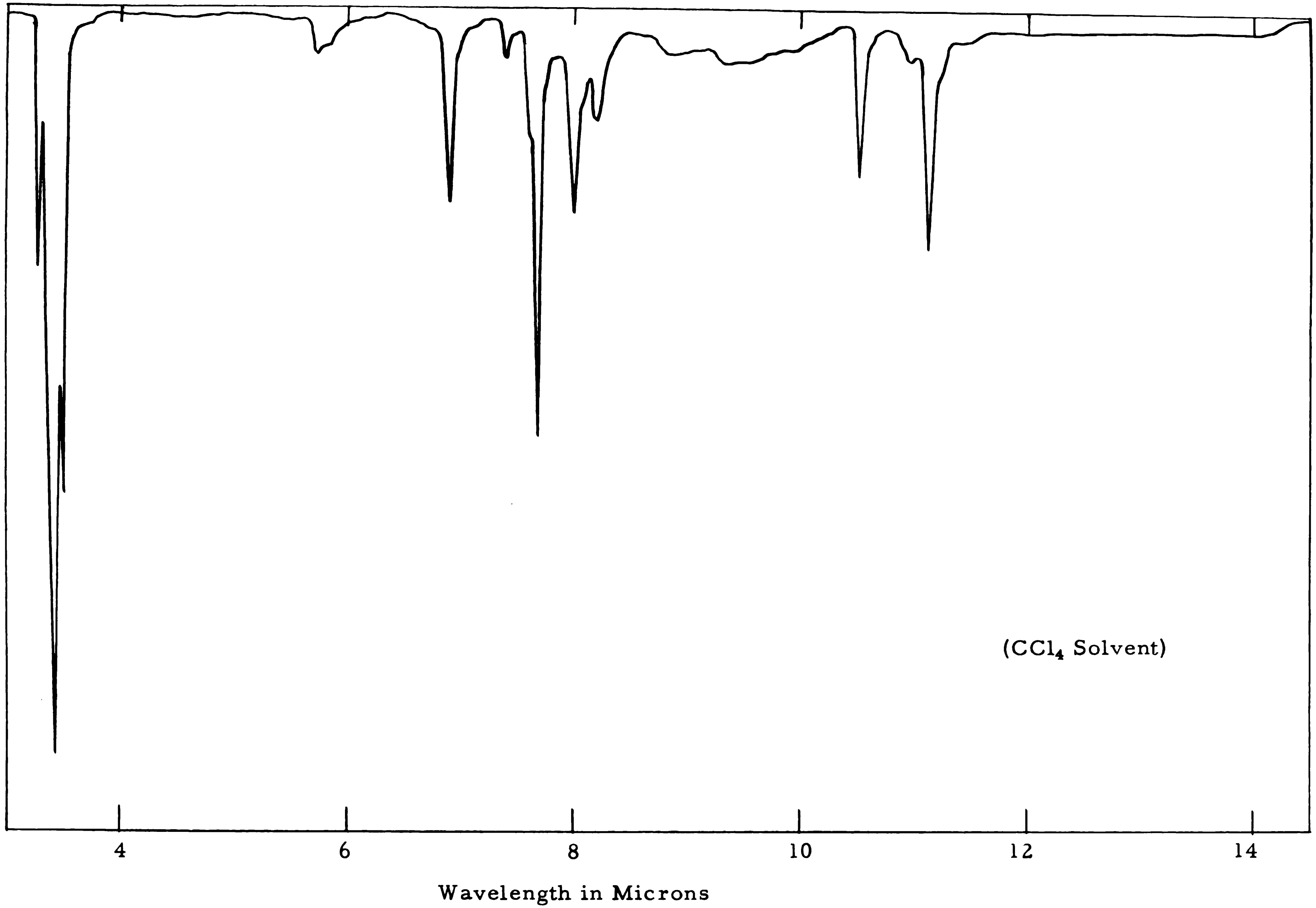


Figure 23. Infrared Spectrum of the Alkyl Halide Obtained from the Decomposition of 2-Exonorbornanecarbonyl Peroxide.

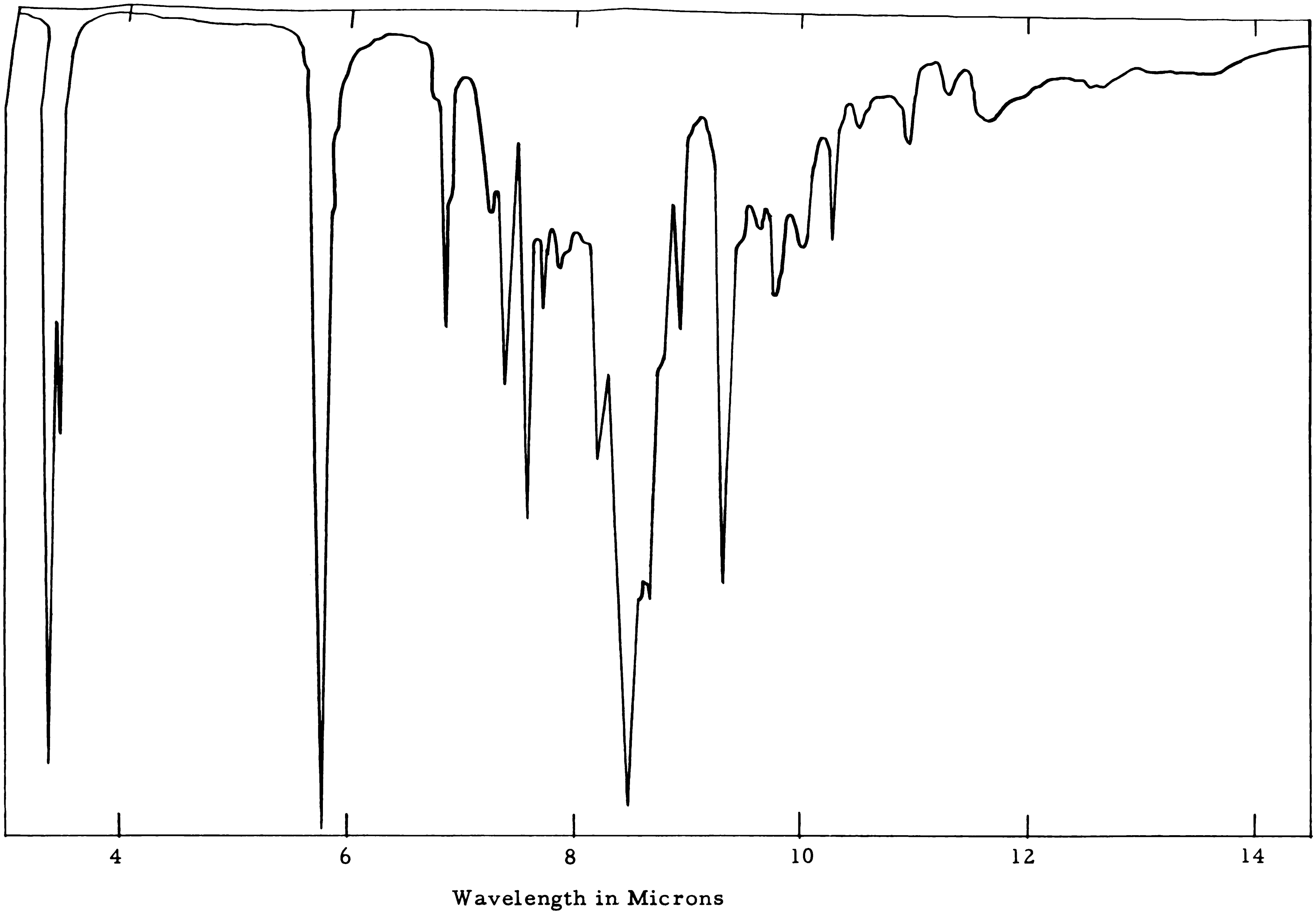


Figure 24. Infrared Spectrum of the Ester Obtained from the Decomposition of 2-Exonorbornanecarbonyl Peroxide.

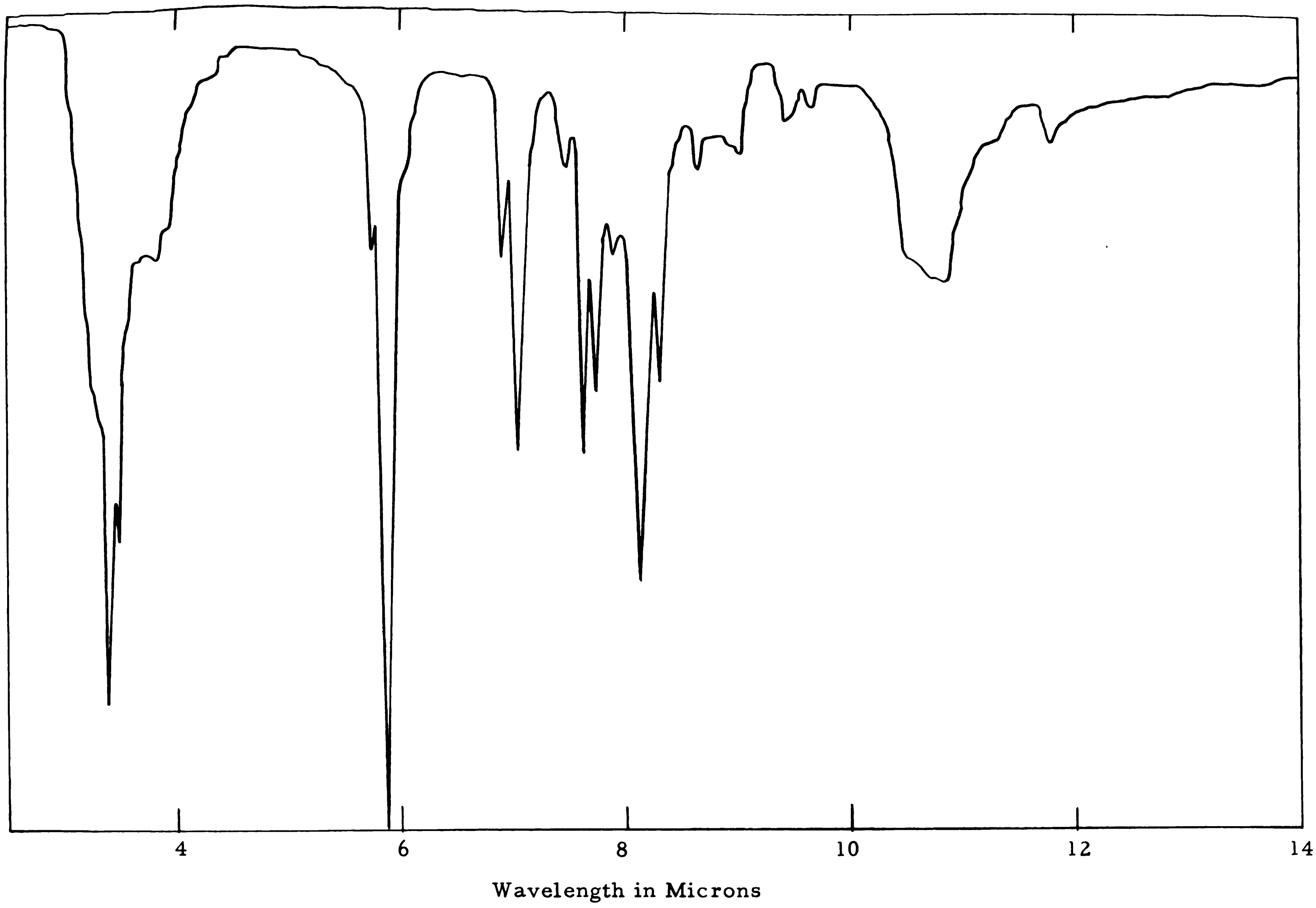


Figure 25. Infrared Spectrum of the Acid Obtained from the Decomposition of 2-Exonorbornanecarbonyl Peroxide.

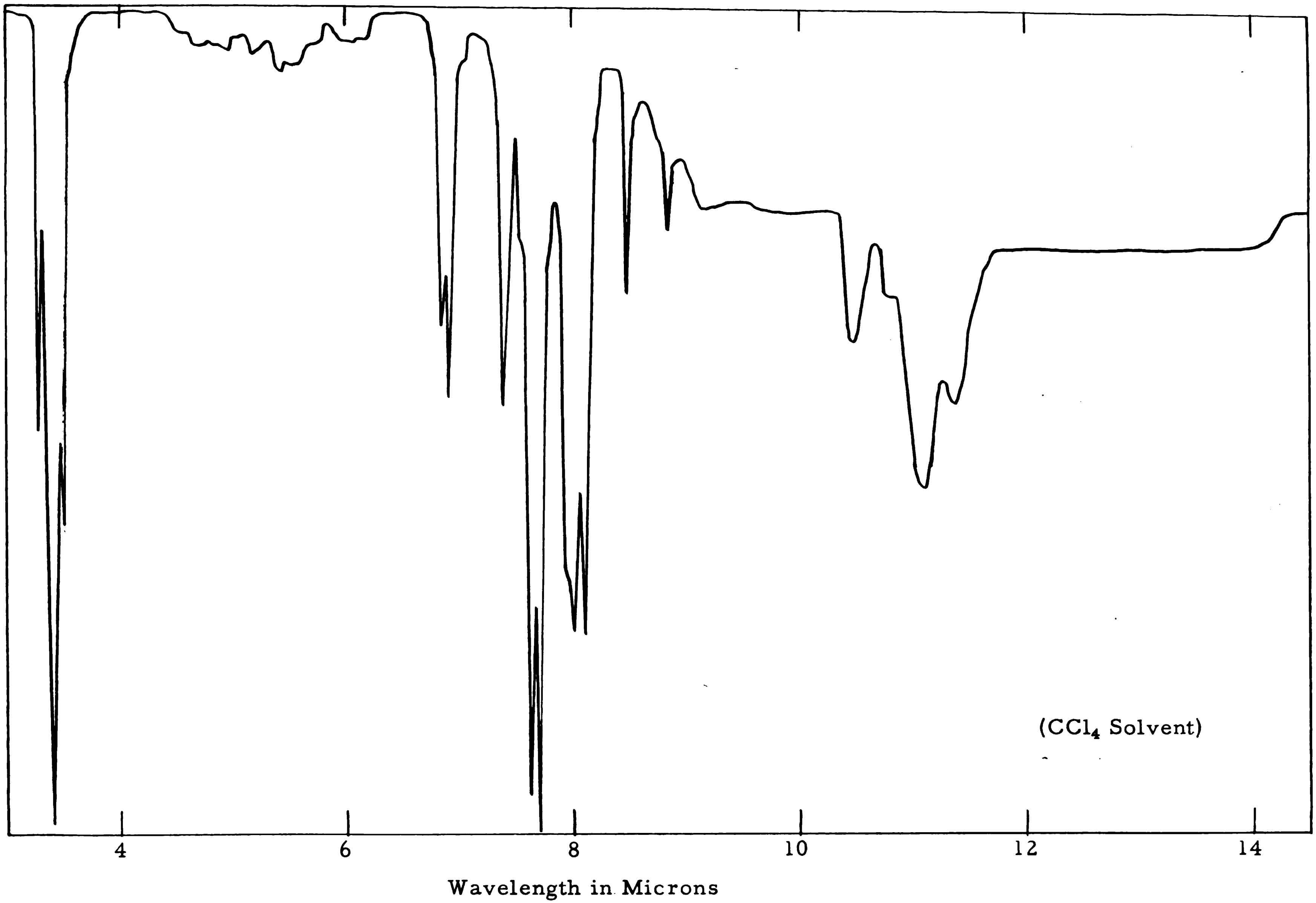
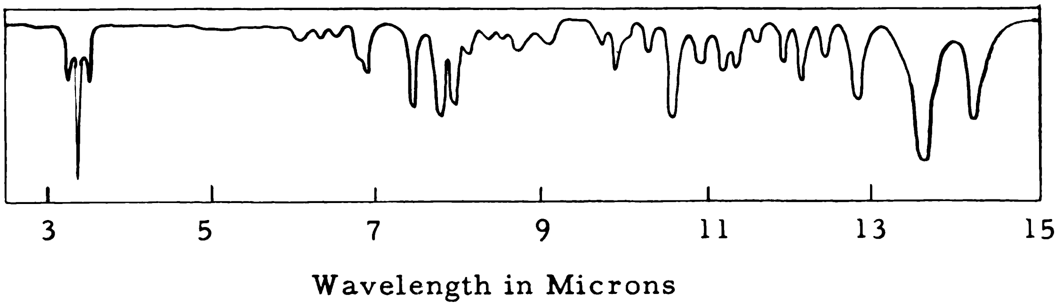
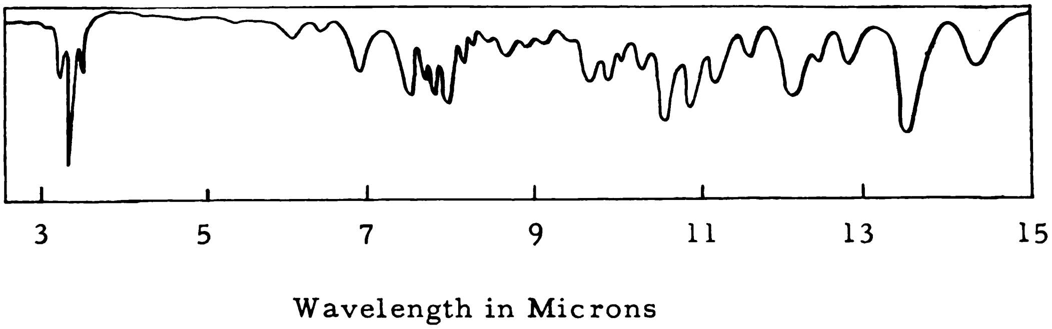


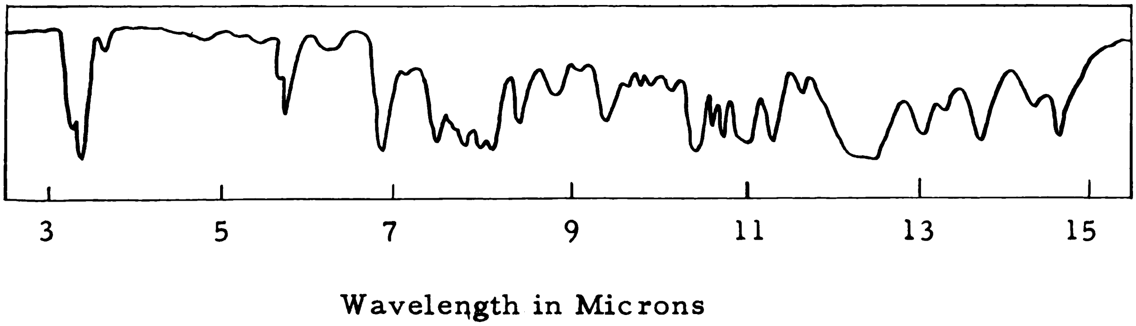
Figure 26. Infrared Spectrum of the Alkyl Halide Obtained from the Decomposition of 5-Endonorbornenecarbonyl Peroxide.



5-Endochloronorbornene



5-Exochloronorbornene



3-Chloronortricyclene

Figure 27. Infrared Spectra of 5-Exochloronorbornene, 5-Endochloronorbornene, and 3-Chloronortricyclene.

The ester-containing material was treated with 20% potassium hydroxide in aqueous dioxane at reflux for one hour. After acidification with 6 N hydrochloric acid, the solution was extracted with ether. After drying over magnesium sulfate and extracting the ether, the infrared spectrum of the residue indicated the absence of alcohol (2.7-3.0 μ) and acid (5.9 μ). The presence of the ester peak (5.77 μ) indicated that no hydrolysis had occurred.

A portion of the ester-containing material was distilled. Material boiling at 92-93°/0.07 mm. was collected. Infrared analysis (Figure 28) indicated the absence of carbonyl.

Anal. Found: C, 35.33; H, 3.68; Cl, 60.59.

The remaining portion of the ester-containing material (ca. 3 g.) was dissolved in 25 ml. of anhydrous ether and added dropwise to a suspension of 1.5 g. of lithium aluminum hydride in 50 ml. of anhydrous ether. The mixture was refluxed for 1 hour, then cooled. The excess lithium aluminum hydride was destroyed by adding small portions of ice. The insoluble basic materials were dissolved by adding 6 N hydrochloric acid. The mixture was filtered and the filtrate extracted with ether. The ether solution was washed with 5% sodium carbonate and finally with water. After drying over magnesium sulfate and evaporating the ether, the residue was distilled at 13 mm. and three fractions were collected: 30-80° (a), 80-110° (2), 110-150° (3). The three fractions and the pot residue were treated for the preparation of 3,5-dinitrobenzoate derivatives (49).

Fraction 2 gave the 3,5-dinitrobenzoate of 5-endohydroxymethylnorbornene, identified by its melting point, mixed melting point, and infrared spectrum (Figure 29). The pot residue gave the 3,5-dinitrobenzoate of 5-endohydroxynorbornene, identified by its melting point, mixed melting point, and infrared spectrum (Figure 30). Fraction 1 gave the 3,5-dinitrobenzoate of ethanol. Fraction 3 was not identified.

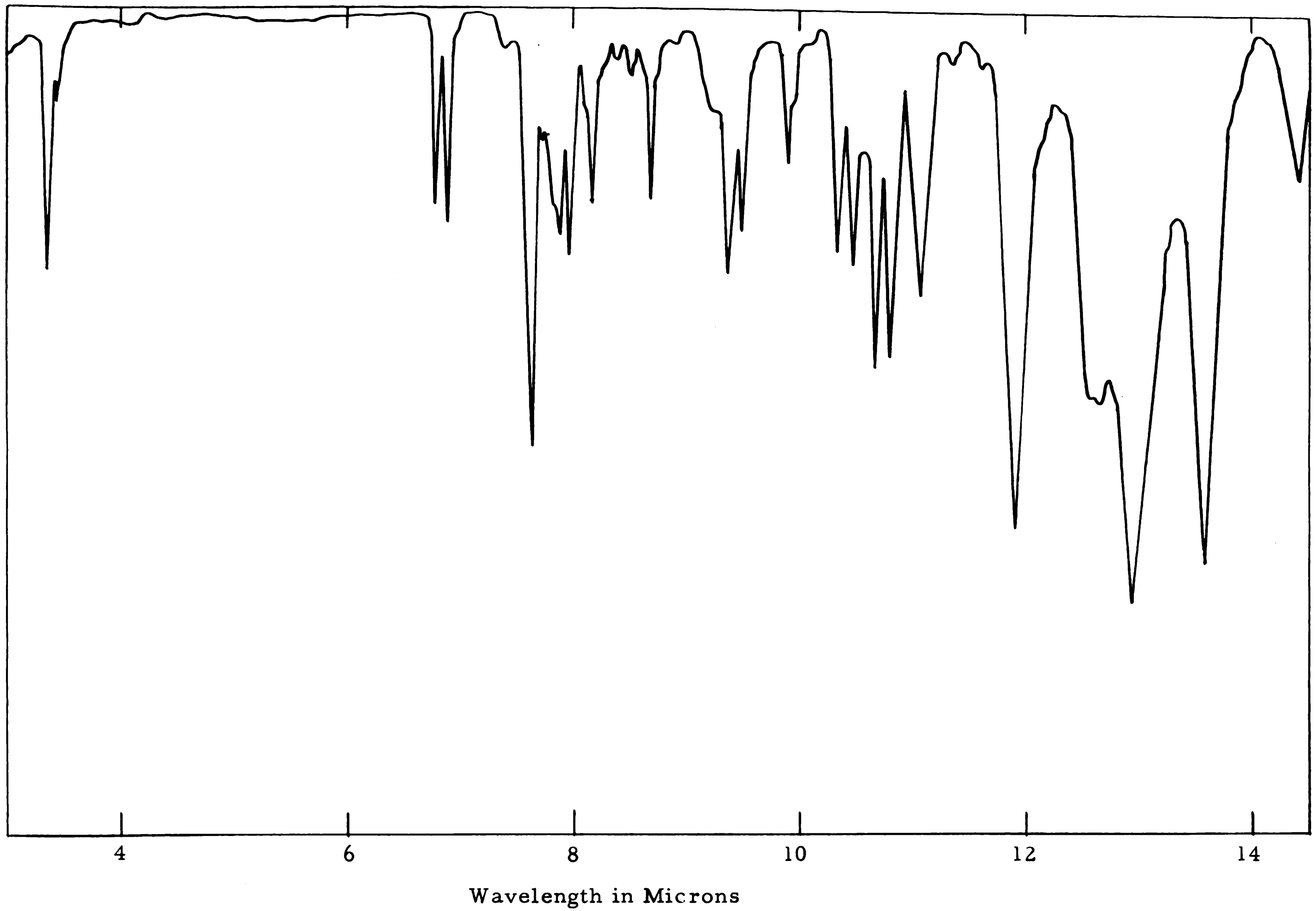


Figure 28. Infrared Spectrum of the Polychloroalkane Obtained from the Decomposition of 5-Endonorbornenecarbonyl Peroxide.

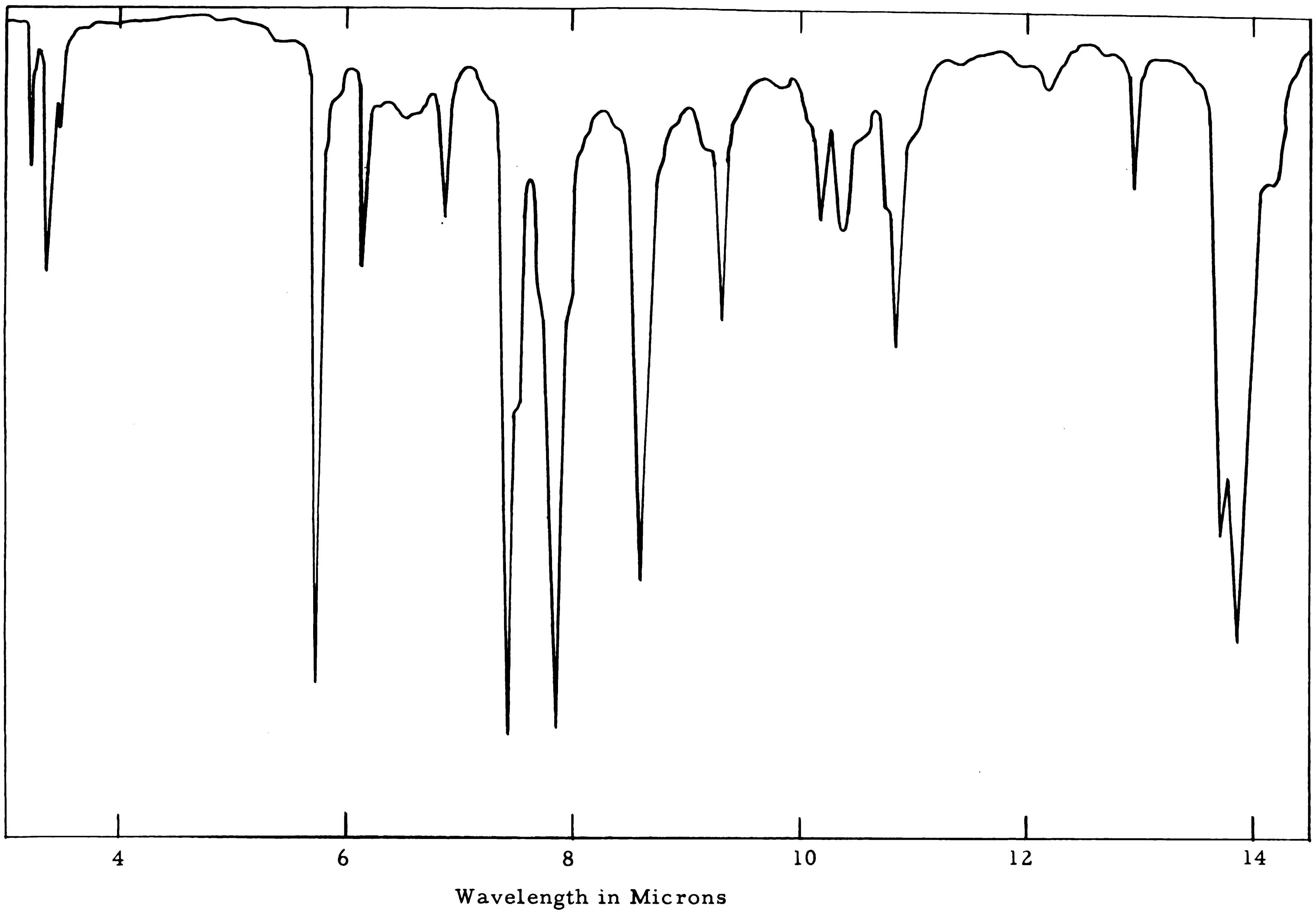


Figure 29. Infrared Spectrum of the 3, 5-Dinitrobenzoate of the Alcohol Obtained from the Decomposition of 5-Endonorbornenecarbonyl Peroxide (Distillate).

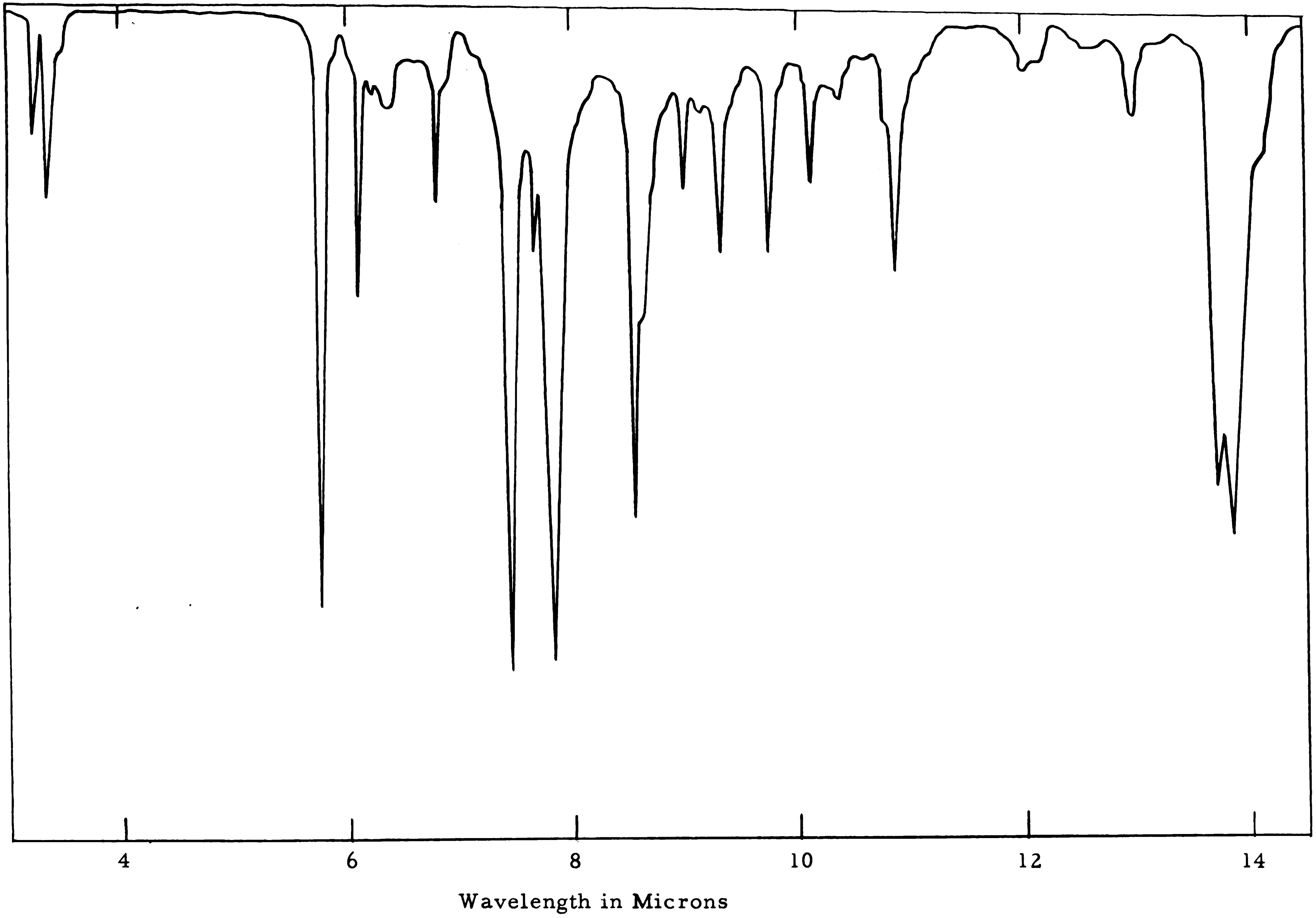


Figure 30. Infrared Spectrum of the 3, 5-Dinitrobenzoate of the Alcohol Obtained from the Decomposition of 5-Endonorbornenecarbonyl Peroxide (Pot Residue).

Number 2, 3,5-dinitrobenzoate, m.p. 80-81°.

<u>Anal</u>: Calc'd for $C_{15}H_{14}N_2O_6$: C, 56.60; H, 4.40.
Found: C, 56.70; H, 4.51.

pot residue, 3,5-dinitrobenzoate, m.p. 105-106°.

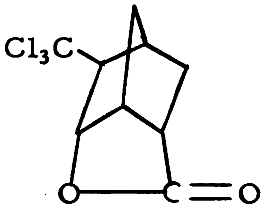
<u>Anal</u>: Calc'd for $C_{14}H_{12}N_2O_6$: C, 55.26; H, 3.94
Found: C, 55.34; H, 4.05.

Number 1, 3,5-dinitrobenzoate, m.p. 87-88°.

<u>Anal</u>: Calc'd for $C_9H_8N_2O_6$: C, 45.04; H, 3.36.
Found: C, 45.48; H, 3.41.

Number 3, 3,5-dinitrobenzoate, m.p. 183-184°.

When the pot residue from the original distillation of the decomposed peroxide solution was transferred to a molecular still (Hickman type), and the distillation continued at 115°/0.07 mm., the material lacking in carbonyl was distilled. A white substance then sublimed on the sides of the still. The white solid was dissolved in ether, the ether evaporated, and the residue sublimed, 120°/11 mm. Crystallization of the sublimed solid from ether produced a material melting at 100-101°. This material possessed a carbonyl band (Figure 31) in the infrared at 5.58 μ. The n.m.r. spectrum of this material is shown in Figure 32. This material has tentatively been given the structure:



(A)

<u>Anal</u>: Calc'd: C, 42.35; H, 3.55; Cl, 41.65.
Found: C, 42.60; H, 3.70; Cl, 41.71.

An attempt was made to hydrolyze the chlorines. The material (32 mg.) was dissolved in 25 ml. of 80% aqueous acetone. Silver nitrate (0.52 g.) was added and the mixture refluxed for 2 hours. The solution was extracted with ether. After drying over magnesium sulfate and evaporating the ether, the residue afforded 30 mg. of starting material. A method used by

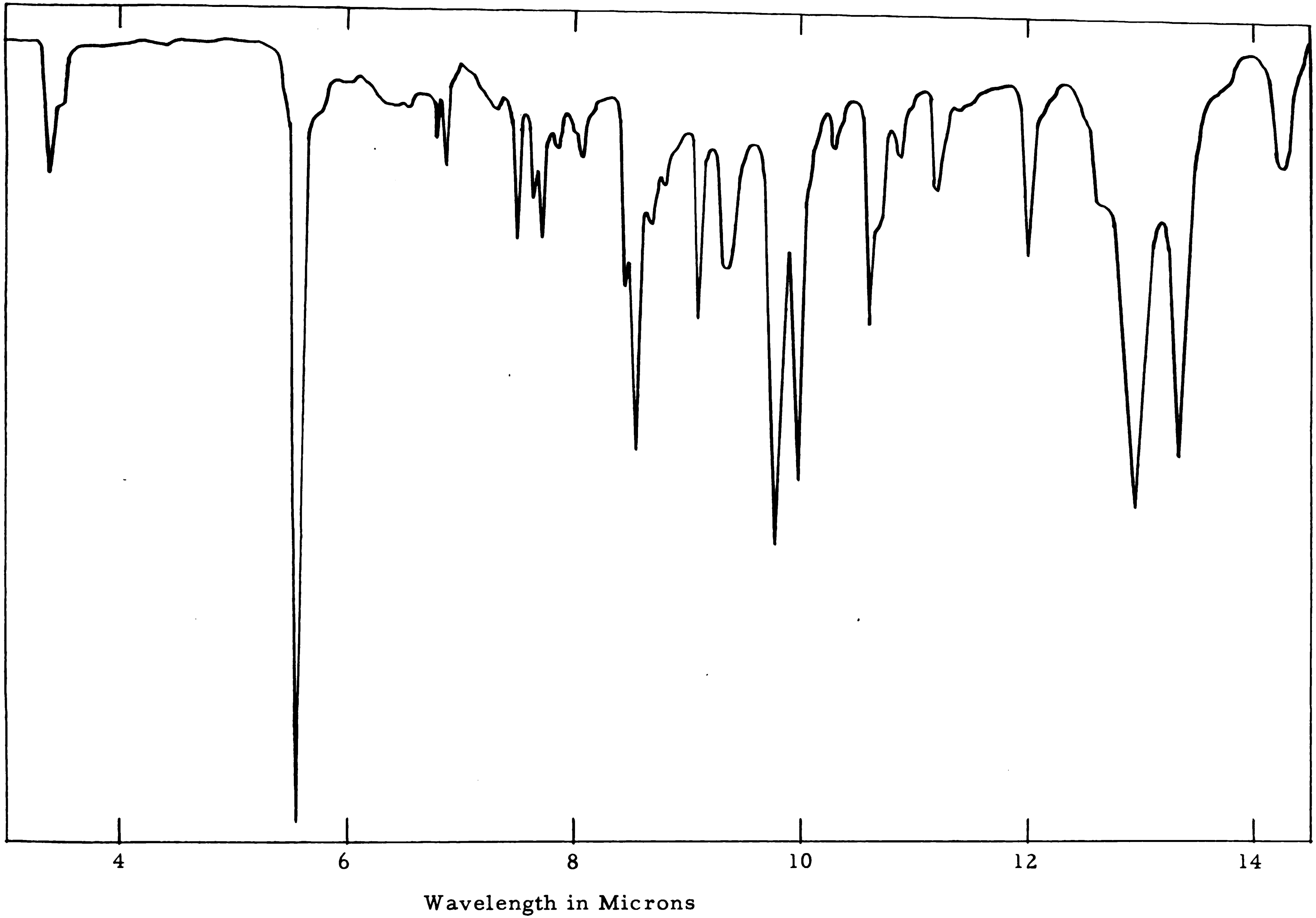


Figure 31. Infrared Spectrum of the Lactone Obtained from the Decomposition of 5-Endonorbornenecarbonyl Peroxide.

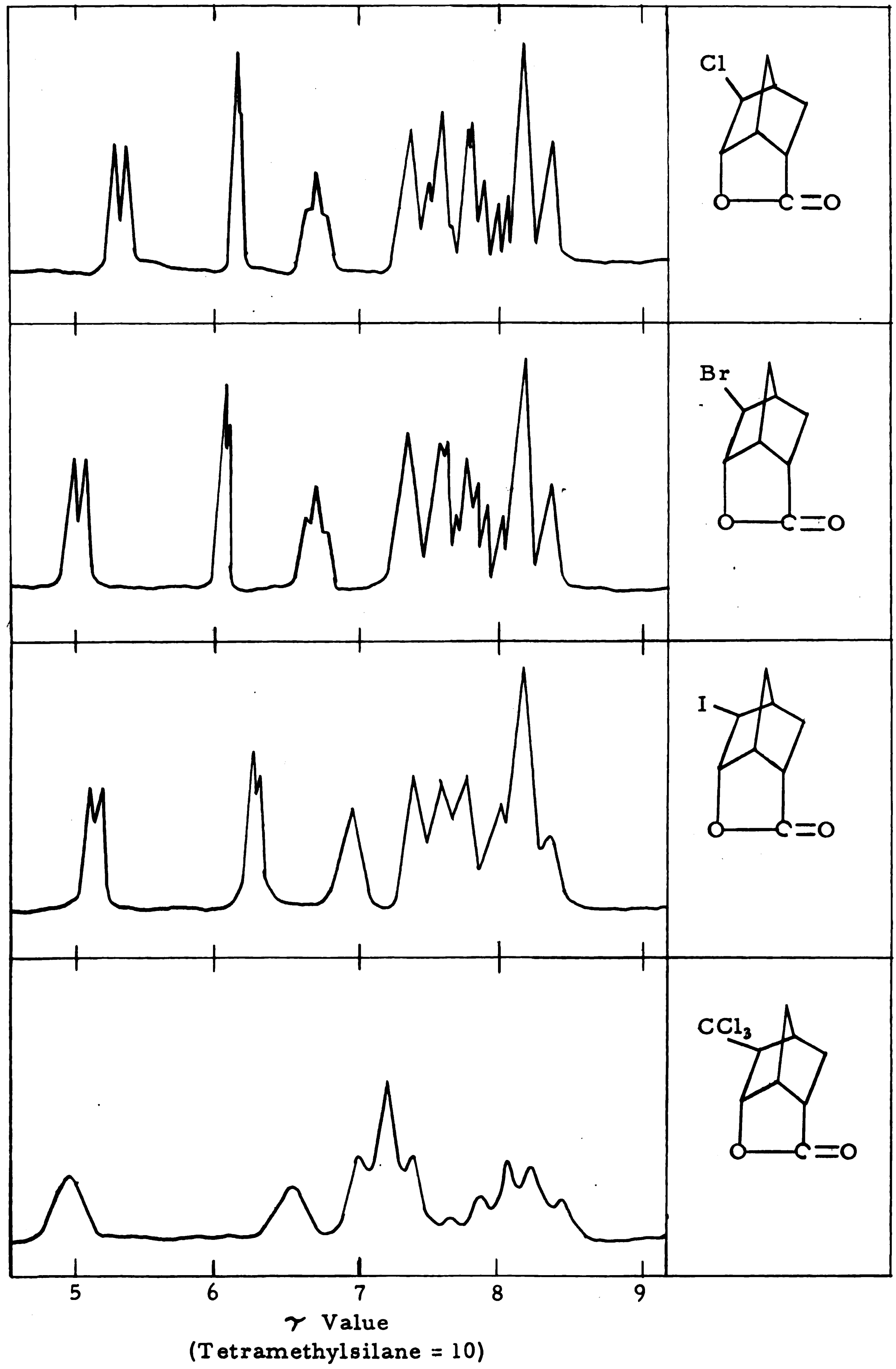
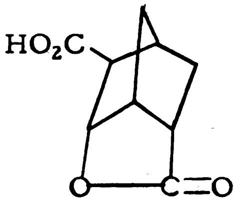


Figure 32. N.m.r. Spectra of Lactones.

Freidlina (54) was then employed. The material (0.2226 g.) was warmed on a steam bath with 0.31 ml. of fuming nitric acid for 4 hours. Fuming nitric acid (0.1 ml.) was added at 1 hour intervals. Water was then added and the mixture extracted with ether. Drying over magnesium sulfate and evaporating the ether afforded 0.2215 g. of starting material. The material (0.1 g.) was then added to 4 ml. of 80% sulfuric acid and warmed on a steam bath for 6 hours. Water was added and the mixture extracted with ether. The ether was washed once with water and after drying over magnesium sulfate, the ether was evaporated. The residue was placed in a sublimator and heated to 76°/11 mm. After 3 hours, the temperature was raised to 92° over a period of 1 hour, and then the sublimate collected at 92° was crystallized from pentane-ether. An acidic material (0.04 g.) containing no chlorine was isolated, m.p. 119-120°. This material has tentatively been given the structure:



(B)

Anal: Calc'd for: C, 59.35; H, 5.53.
Found: C, 60.68; H, 6.15.

Its infrared spectrum is shown in Figure 33.

4. 5-Exonorbornenecarbonyl Peroxide Products

5-Exonorbornenecarbonyl peroxide (5 g.) was dissolved in 25 ml. of carbon tetrachloride and the solution refluxed for 24 hours. The carbon tetrachloride was then removed by distillation through a 600 x 7 mm. vacuum jacketed tantalum wire spiral column (bath temperature, 85°). When no more carbon tetrachloride came over, the column was removed and the pressure dropped slowly to 15 mm. The distillate collected in

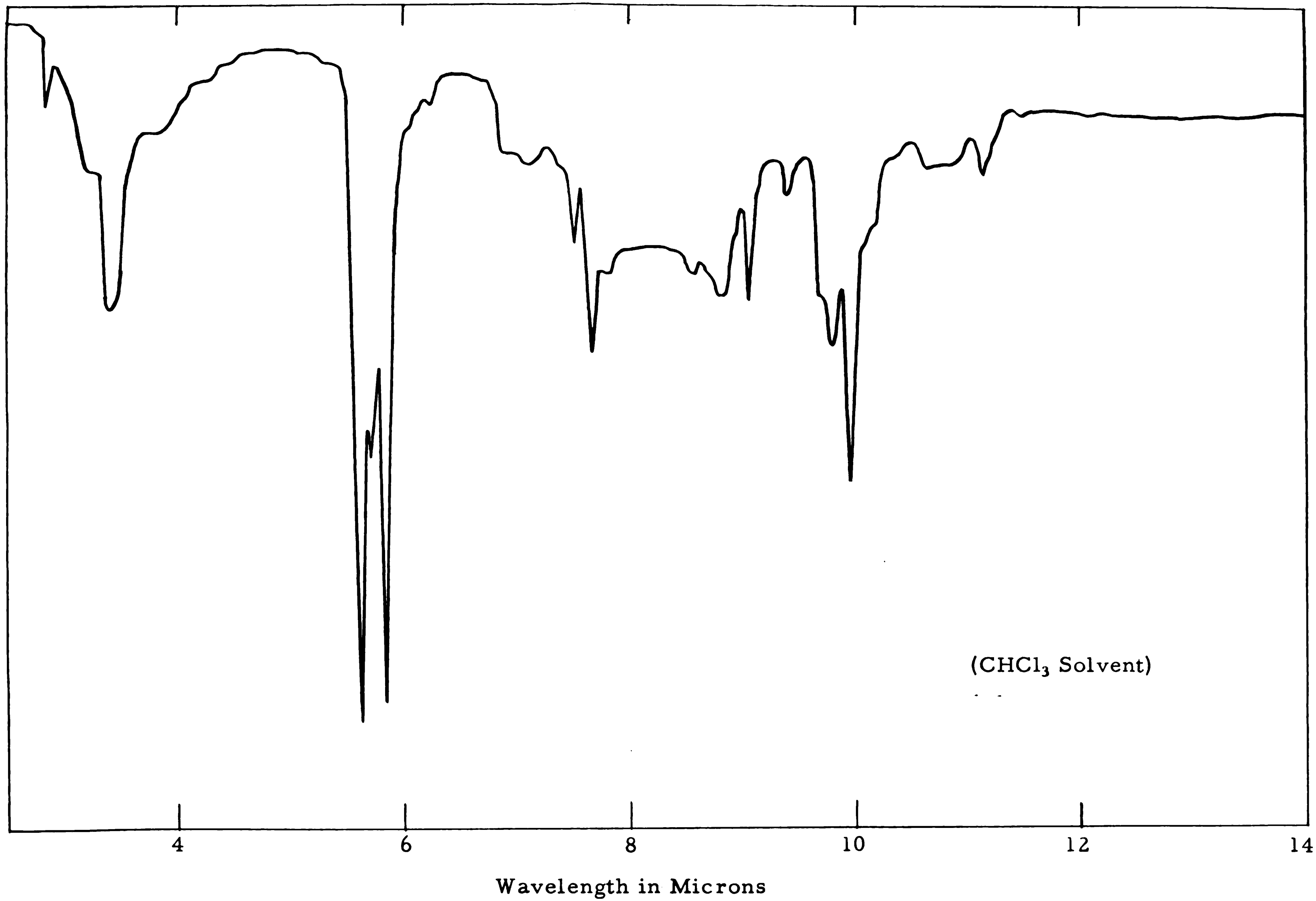


Figure 33. Infrared Spectrum of the Acid Obtained from the Hydrolysis of the Lactone Obtained from the Decomposition of 5-Endonorbornenecarbonyl Peroxide.

this manner, was concentrated by the above procedure and the residue passed through a Megachrom vapor phase chromatograph at 150°. The alkyl halide fraction was identical with the one isolated from the endo peroxide in retention time and in its infrared spectrum (Figure 34).

The infrared spectrum of the pot residue indicated the presence of ester (5.77 μ) and also a peak at 5.58 μ. This material was treated, as in the endo case, with sodium carbonate and sodium hydroxide. The ether extracts were dried over magnesium sulfate and distilled. Distillate collected to 160°/1 mm. (Figure 35) was found to be identical to the material boiling at 92-93°/0.07 mm. in the endo case (i.e. polychloroalkanes). Material boiling at 106-220°/1 mm. was also collected. Infrared analysis of this material indicated ester (5.77 μ) present. The ester-containing material (1 g.) was dissolved in 25 ml. of anhydrous ether and added dropwise to a suspension of lithium aluminum hydride in 50 ml. of anhydrous ether. The mixture was refluxed for one hour and cooled. The excess lithium aluminum hydride was destroyed by adding small portions of ice. The insoluble basic materials were dissolved by adding 6 N hydrochloric acid and the mixture filtered. The filtrate was extracted with ether and the ether washed with 5% sodium carbonate and finally water. After drying over magnesium sulfate and evaporating the ether, the residue was distilled. Distillate was collected up to 120°/11 mm. The distillate and the pot residue were each treated to prepare the respective 3,5-dinitrobenzoates (49).

The distillate was identified as 5-exohydroxymethylnorbornene through its 3,5-dinitrobenzoate and the pot residue was similarly identified as 5-exohydroxynorbornene. Identification was based on melting points, mixed melting points, and infrared spectra (see Figures 36 and 37). Distillate, 3,5-dinitrobenzoate, m.p. 96-98°.

Anal. Calc'd for $C_{14}H_{10}N_2O_6$: C, 56.60; H, 4.40.

Found: C, 56.24; H, 4.47.

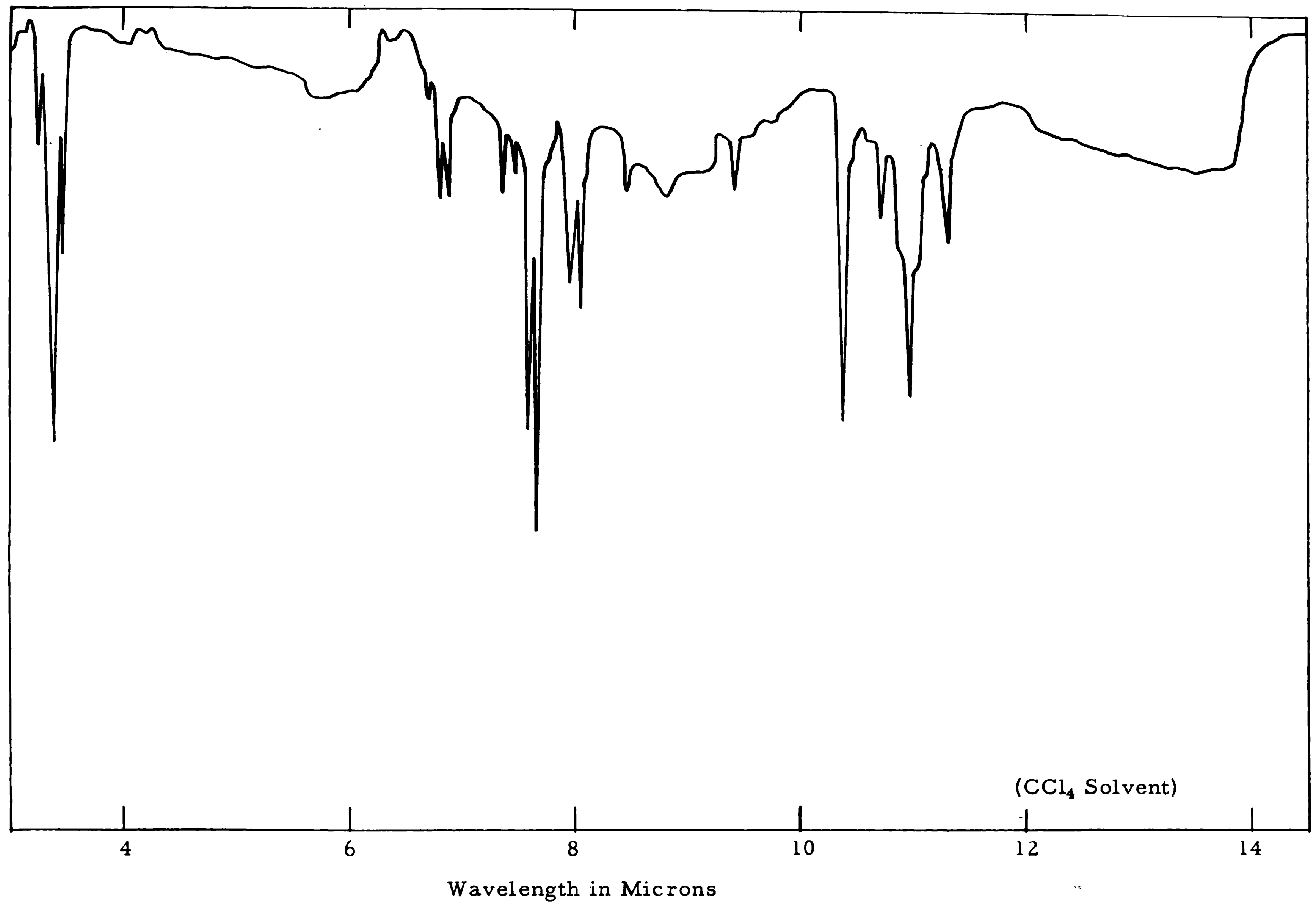


Figure 34. Infrared Spectrum of the Alkyl Halide Obtained from the Decomposition of 5-Exonorbornenecarbonyl Peroxide.

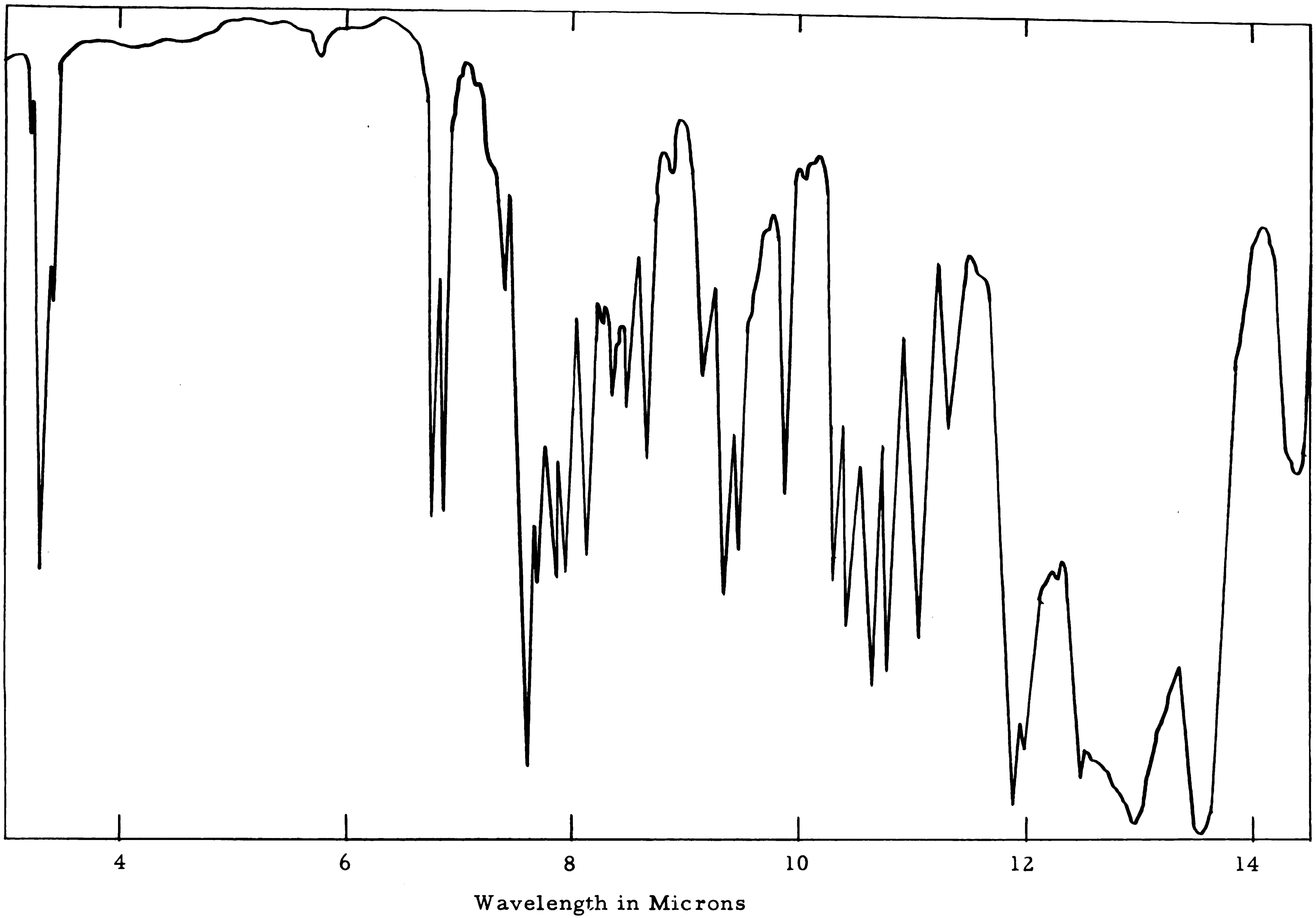


Figure 35. Infrared Spectrum of the Polychloroalkane Obtained from the Decomposition of 5-Exonorbornenecarbonyl Peroxide.

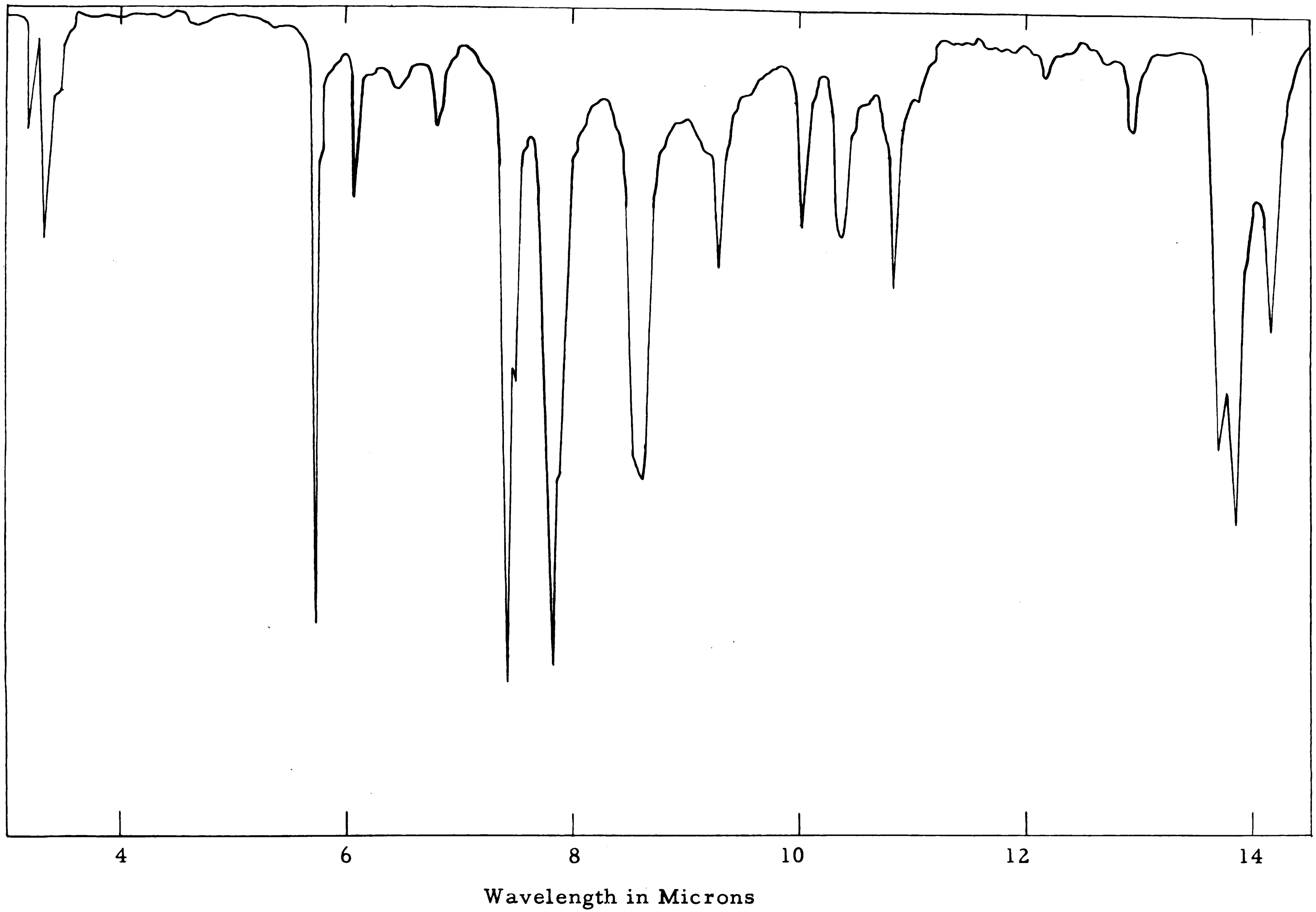


Figure 36. Infrared Spectrum of the 3, 5-Dinitrobenzoate of the Alcohol Obtained from the Decomposition of 5-Exonorbornenecarbonyl Peroxide (Distillate).

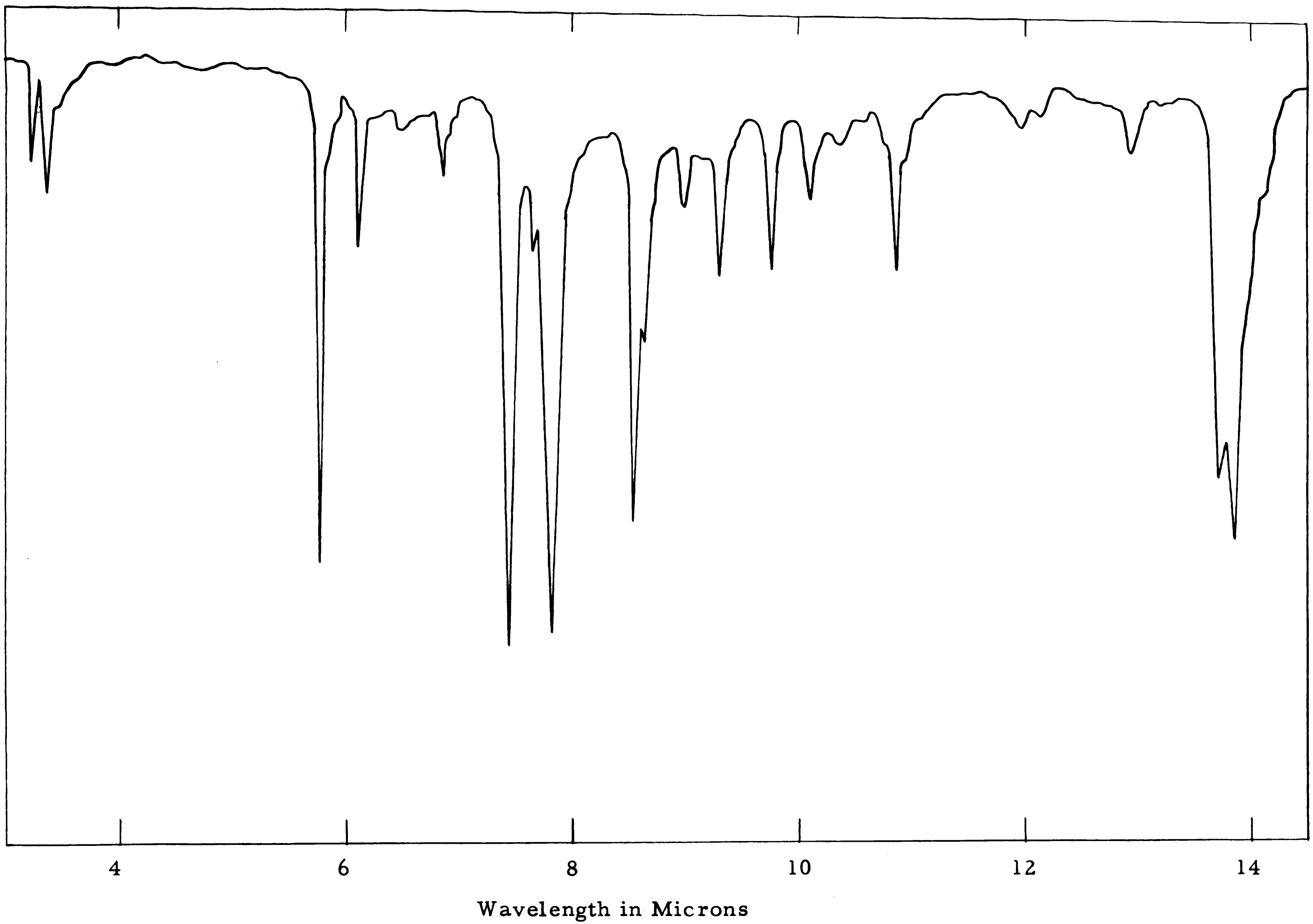


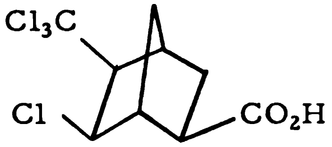
Figure 37. Infrared Spectrum of the 3, 5-Dinitrobenzoate of the Alcohol Obtained from the Decomposition of 5-Exonorbornenecarbonyl Peroxide (Pot Residue).

Pot residue, 3,5-dinitrobenzoate, m.p. 104-105°.

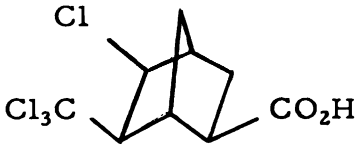
Anal. Calc'd for $C_{14}H_{12}N_2O_6$: C, 55.26; H, 3.94.

Found: C, 55.28; H, 3.99.

The water layer from the sodium carbonate-sodium hydroxide treatment was acidified and extracted with ether. After drying over magnesium sulfate and evaporating the ether, the residue was crystallized from ether to yield an acid, m.p. 176-177.5° (d 170) which was tentatively given the structures C.



and/or



(C)

<u>Anal:</u> Calc'd for $C_9H_{10}O_2Cl_4$: C, 37.00; H, 3.45; Cl, 48.60.

Found: C, 38.21; H, 3.85; Cl, 49.34.

Its infrared spectrum is shown in Figure 38.

The material containing the 5.50° μ lactone bond could not be isolated. A distillation scheme as used for the endo peroxide was unsuccessful. As described above, the alkaline extracts gave C as the only crystalline material.

B. Determination of the Products of Decomposition

1. Determination of Carbon Dioxide

Using the apparatus illustrated in Figure 1, 50 ml. of a 0.05 N solution of peroxide in carbon tetrachloride was introduced into the reaction vessel and the system swept with nitrogen for 1 hour. The absorbtion tube (2:1 ascarite-anhydrone) was then weighed and put back in the system. The solution was then refluxed for a minimum of 12 half-lives under a continuous nitrogen sweep. The heating was discontinued and the dry ice

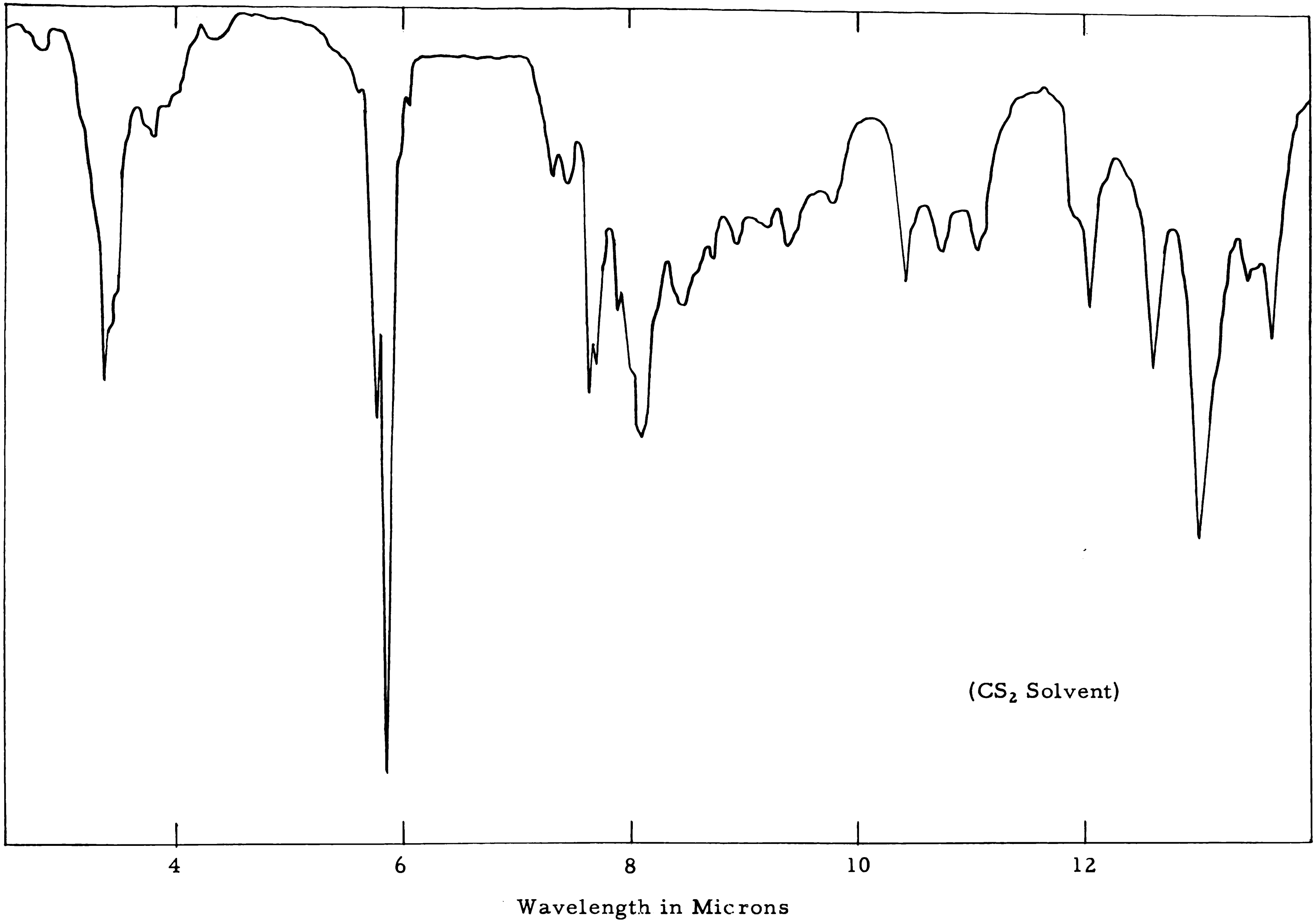


Figure 38. Infrared Spectrum of the Acid Obtained from the Decomposition of 5-Exonorbornenecarbonyl Peroxide.

traps allowed to stand at room temperature for 30 minutes; the absorbtion tube was then reweighed. The mass gained was taken as carbon dioxide liberated by the peroxide. The results are tabulated in Tables 1, 2, 3, and 4.

2. Determination of Carbonyl Containing Products

The carbonyl-containing materials that resulted from the decomposition of the various peroxides were determined by infrared spectroscopy. The results are tabulated in Tables 1, 2, 3, and 4. The amount of lactone in the case of 5-exonorbornenecarbonyl peroxide has been estimated using the extinction coefficient of the gamma-3 lactone of 2-exotrichloromethyl-3-endohydroxy-5-endonorbornenecarboxylic acid.

C. Kinetics of Decomposition

The rates of thermal decomposition of the diacyl peroxides were followed by: (1) Iodometric titration of samples of the peroxide solution.
(2) Measuring the rate of disappearance of the 5.65 μ peroxide band via a Perkin Elmer model 21 recording infrared spectrophotometer.
(3) Measuring the rate of appearance of various products in the infrared region.

The peroxide solutions were contained in 5 ml. Kimble Neutraglass ampoules. The ampoules were cleaned by immersing them in hot concentrated sulfuric acid for 12 hours. They were rinsed four times with water, given a final rinse with acetone and dried at 120° for 12 hours.

The nitrogen used to remove oxygen from the peroxide solution was purified in the same manner as in the carbon dioxide determinations.

The following experimental procedure was used in a typical kinetic determination. About 50 ml. of carbon tetrachloride solution, 0.05 N in peroxide, was purged of oxygen at room temperature by bubbling purified nitrogen into the solution for 15 minutes. The solution was then introduced as ca. 5 ml. samples into ten ampoules with a hypodermic syringe. The ampoules were sealed at -70° with an air-gas torch. They were placed in a metal cage and the cage immersed in an electrically heated mineral oil bath controlled to 0.1° by means of a Fisher-Serfass Electronic Relay. A period of two minutes was allowed for the samples to reach the temperature of the bath; zero time was thus assumed to be two minutes after the ampoules were immersed in the bath. At various time intervals an ampoule was removed from the bath and immediately quenched in ice water. The ampoules were marked and stored at -70° until completion of the run. The tips of the ampoules were broken, the ampoules drained, and 4-ml. aliquots were pipetted into 125-ml. iodine flasks. The samples were titrated as described earlier (page 34).

Using the sampling procedure described above, the rate of disappearance of the 5.65 μ peroxide band and the rate of appearance of either the 5.77 μ ester band or the 5.87 μ acid band were measured.

The data were plotted as a concentration versus time curve and the method of Guggenheim (52) employed to calculate the first order rate constants.

The energy of activation was calculated by a plot of log k versus the reciprocal of the absolute temperature employing the method of least squares to determine the slope. The entropy of activation was calculated employing the method of Foster (53).

Sample calculations for the calculation of rate constants, energies of activation and entropies of activation are given in the Appendix.

VI. Miscellaneous Experiments

A. Preparation of Galvinoxyl

Methylene-bis-para(2,5-di-t-butyl)phenol (supplied by Ethyl Corporation) was recrystallized from hexane twice. The phenol (2 g., 0.00471 mole) was dissolved in 50 ml. of anhydrous ether contained in a 125-ml. Erlenmeyer flask and 5.07 g. (0.0212 mole) of lead dioxide was added. The mixture was stirred magnetically at room temperature for 4 hours, then filtered through a sintered glass funnel. After evaporating the ether, the residue was dissolved in pentane and crystallized by cooling in dry ice. The dark blue galvinoxyl (1.1 g., 55%) was recrystallized once and dried in a vacuum desiccator for 2 hours.

B. Determination of the Purity of the Norbornenyl Acids

5-Endonorbornenecarboxylic acid and 5-exonorbornenecarboxylic acid were each treated in the following manner.

The acid (1 g.) was treated with excess diazomethane in anhydrous ether. The ether was evaporated and the ester distilled, b.p. (exo) 84-85° /15 mm., b.p. (endo) 85-86°/15 mm. The esters were analyzed on a Beckman model GC-2 gas chromatograph at 135° (20% silicone column). Methyl 5-endonorbornenecarboxylate was found to contain less than 7% of the exo isomer and methyl 5-exonorbornenecarboxylate was found to contain less than 1% of the endo isomer.

C. Attempted Preparation of the Gamma-3 Lactone of 2-Exotrichloromethyl-3-endohydroxy-5-endonorbornanecarboxylic Acid

5-Endonorbornenecarboxylic acid (5 g., 0.036 mole) was dissolved in 50 ml. of bromotrichloromethane. The mixture was irradiated with a mercury vapor lamp for 5 hours. The solvent was distilled and the residue was found to be polymeric.

Methyl 5-endonorbornenecarboxylate (5 g., 0.033 mole) was dissolved in 50 ml. of bromotrichloromethane and a small amount of benzoyl peroxide was added (ca. 0.1 g.). The mixture was refluxed for 5 hours and then the solvent was distilled. The residue was refluxed with 50 ml. of 5% sodium hydroxide and then acidified. The water solution was extracted with ether. After drying over magnesium sulfate and evaporating the ether, the residue was found to be polymeric.

D. Attempted Preparation of Syn- and Anti-7-Norbornenecarboxylic Acids

1. Preparation of 7-Syn-bromonorbornene

7-Syn-bromonorbornene was prepared by a method employed by Kwart (55). Norbornene (60 g., 0.63 mole) and 51 g. (0.63 mole) of pyridine were dissolved in 300 ml. of purified carbon tetrachloride (20). The solution was introduced into a 1-l. 3-necked round-bottomed flask equipped with a mechanical stirrer, reflux condenser, and a dropping funnel. The solution was cooled in an ice-salt bath to maintain a reaction temperature of less than 0° throughout the reaction. Bromine (102 g., 0.63 mole) was added with stirring over a period of 2 hours. The pyridinium bromide was filtered and the filtrate was washed with 200 ml. of 6 N hydrochloric acid. After drying over calcium chloride and evaporating the carbon tetrachloride, the residue was fractionated *in vacuo* to yield 74 g. (46%) of 2,7-dibromonorbornane, b.p. 100-105°/1.25 mm., n_D^{25} 1.5705 (reported (55), b.p. 70-74°/0.25-0.30 mm., n_D^{20} 1.5710).

2,7-Dibromonorbornane (24 g., 0.095 mole) was added to a solution of 3.9 g. (0.10 g.-atom) of potassium in 120 ml. of t-butyl alcohol. The mixture was refluxed for 12 hours and poured on an equal volume of water, then extracted with ether. After drying over magnesium sulfate and evaporating the ether, the residue was distilled *in vacuo* to yield 10.7 g. (58%) of syn-7-bromonorbornene, b.p. 67-70°/13 mm., n_D^{20} 1.5055 (reported (55), b.p. 68-70°/13 mm., n_D^{20} 1.5058).

2. Preparation of Syn- and Anti-7-carbomethoxynorbornene

A solution of 50 g. (0.29 mole) of syn-7-bromonorbornene in 300 ml. of dry ether was added to 22 g. (0.95 g.-atom) of magnesium under 200 ml. of ether. The addition was carried out over 32 hours under a nitrogen atmosphere at room temperature. Carbon dioxide was bubbled into the solution for 1 hour and then small portions of dry ice were added. The mixture was poured onto saturated ammonium chloride solution and acidified with cold, concentrated hydrochloric acid. The aqueous layer was extracted with ether and the ether solution was extracted with 10% potassium hydroxide solution. The basic extracts were acidified with dilute sulfuric acid and extracted with ether. After drying over magnesium sulfate and evaporating the ether, 15.8 g. of crude acid was obtained. The crude acid was treated with ethereal diazomethane, the ether evaporated, and the residue distilled *in vacuo* to yield 13.8 g. of ester, b.p. 96°/27 mm. The ester was analyzed with a Perkin-Elmer model 154 vapor phase chromatograph using a 6', 30% silicone column at 152°. Four components were observed. Analysis on 12', 20% silicone columns at 150° (Megachrom) showed only two peaks. Failure of the Megachrom at this point made the separation of the four components impractical. The overall yield of crude product is also too low to make the synthesis practical.

3. Preparation of Acetyl Bromide

Acetyl bromide was prepared employing the method of Bruton and Degering (56). Phosphorus tribromide (500 g., 1.845 moles) was introduced into a 1-l, 3-necked round-bottomed flask fitted with a mechanical stirrer, a reflux condenser, and a dropping funnel. The flask was immersed in an ice bath and 341 g. (6.92 moles) of glacial acetic acid was added over a 3 hour period. The ice bath was removed and the mixture stirred for an additional half-hour. The mixture was then distilled through a 8" Vigreux column. All of the material boiling below 76° was collected and redistilled to yield 320 g. (38%) of colorless, fuming, acetyl bromide, b.p. 74-75°/1 atm (lit. value (56), b.p. 76°).

4. Acylation of Norbornene

Anhydrous aluminum chloride (149.8 g., 1.122 moles) and 320 ml. methylene chloride was introduced into a 1-l. 3-necked round-bottomed flask fitted with a mechanical stirrer, a reflux condenser, and a dropping funnel. The flask was immersed in an ice bath and 138 g. (1.122 moles) of acetyl bromide in 160 ml. of methylene chloride was added dropwise over 2 hours. The mixture became homogeneous and light orange in color. The solution was filtered through a coarse sintered glass funnel into a similarly equipped 2-l. 3-necked round-bottomed flask. The flask was cooled in an ice bath and 94.2 g. (1 mole) of norbornene in 215 ml. of methylene chloride was added over 3.5 hours. The solution became red in color at this point. The mixture was stirred for an additional hour at room temperature, then poured on a mixture of 125 ml. of concentrated hydrochloric acid and 300 g. of ice. The aqueous layer was extracted with methylene chloride. The extracts were combined and washed successively with water, 5% sodium carbonate, and finally once more with water. After drying over magnesium sulfate and evaporating the methylene chloride, the residue was distilled *in vacuo* to yield 120 g. of a colorless liquid, b.p. 103-105°/0.8 mm. The product was found to contain bromine and had a carbonyl band in the infrared at 5.87 μ. The material decomposes on standing at room temperature. Its infrared spectrum is shown in Figure 39.

5. Haloform Oxidation of Acylation Product

Bromine (120 g., 0.75 mole) was added slowly to an ice cold solution of 100 g. (2.5 moles) of sodium hydroxide in 625 ml. of water. The resultant solution was added dropwise with stirring to 50 g. of the

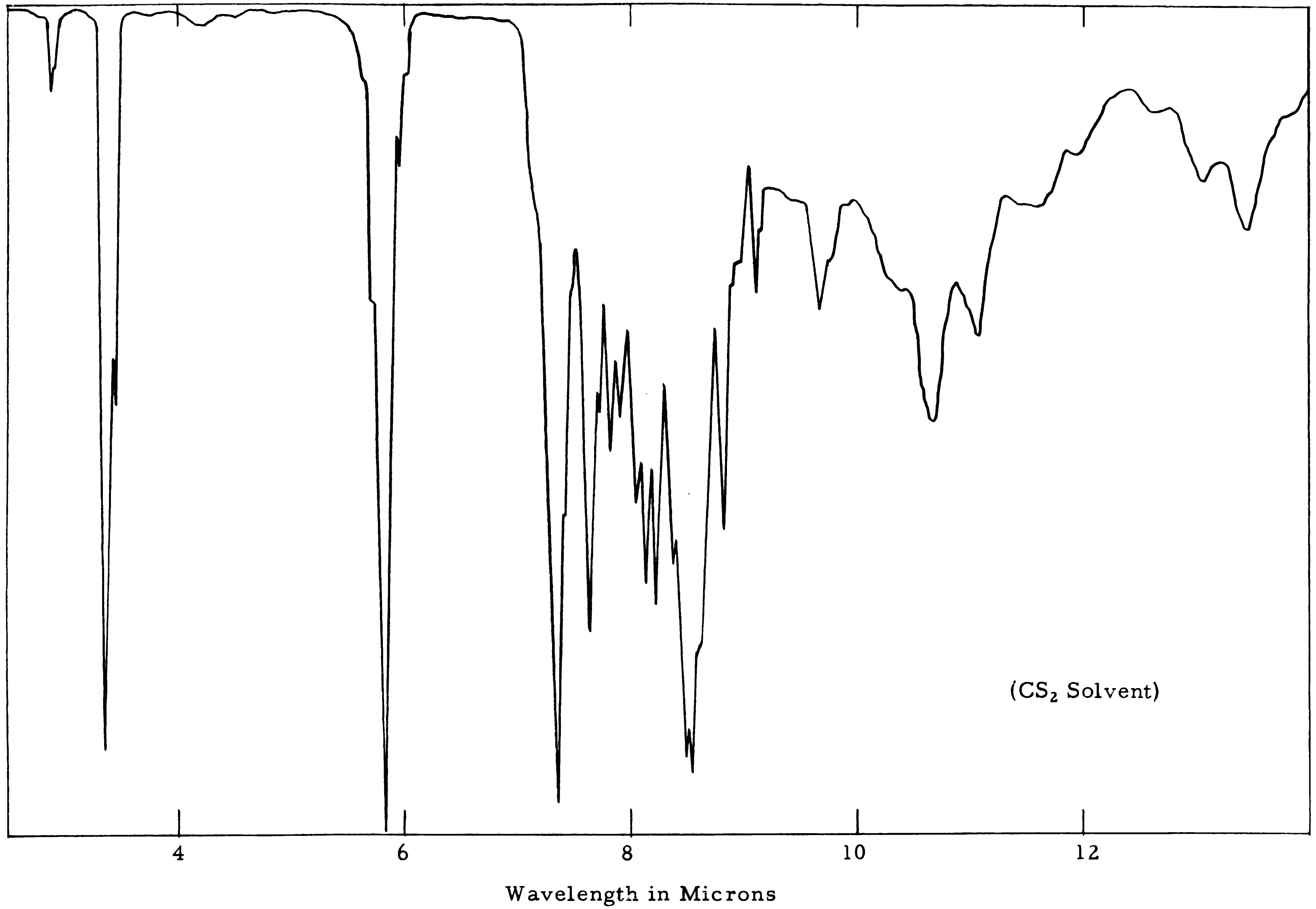


Figure 39. Infrared Spectrum of the Bromoketone Obtained from the Acylation of Norbornene with Acetyl Bromide.

bromoketone obtained from the acylation of norbornene contained in 2-l. 3-necked round-bottomed flask. The flask was fitted with a mechanical stirrer, a reflux condenser and a dropping funnel. A temperature of less than 10° was maintained over the addition period which was approximately 1 hour. After stirring for 2 hours more, the solution (now yellow) was heated at 45° until the yellow color disappeared. The solution was cooled and washed with ether. The water layer was treated with sodium bisulfite, acidified to Congo red with concentrated hydrochloric acid, and extracted with ether. The ether layers were combined, dried over magnesium sulfate, and the ether evaporated. The acidic residue (22 g.) contained bromine and had a carbonyl band in the infrared at 5.89 μ. Characteristic acid spread was noted in the carbon-hydrogen region of 3-4 μ in the infrared (Figure 40).

6. Dehydrohalogenation of Oxidation Product

Potassium metal (54 g., 0.137 mole) was added to 120 ml. of t-butyl alcohol contained in a 250-ml. round-bottomed flask fitted with a reflux condenser. The mixture was refluxed until all the potassium metal dissolved. A solution of the bromoacid (15 g.) in 20 ml. of t-butyl alcohol was added. The mixture became tan in color and material precipitated. The mixture was refluxed for 15 hours, cooled, and poured on an equal volume of ice and 5% sodium carbonate. The solution was washed with ether and treated with norite, after which it was acidified with dilute sulfuric acid and extracted with ether. After drying over magnesium sulfate and evaporating the ether, the residue was taken up in ethyl acetate and treated with norite. The ethyl acetate was evaporated to yield 8 g. of a crude acid containing no bromine. Esterification with diazomethane and distillation *in vacuo* produced an ester found to boil at 120-130°/15 mm. Syn- and anti-7-carbomethoxynorbonene has been reported to boil at 93-96°/30 mm. (57).

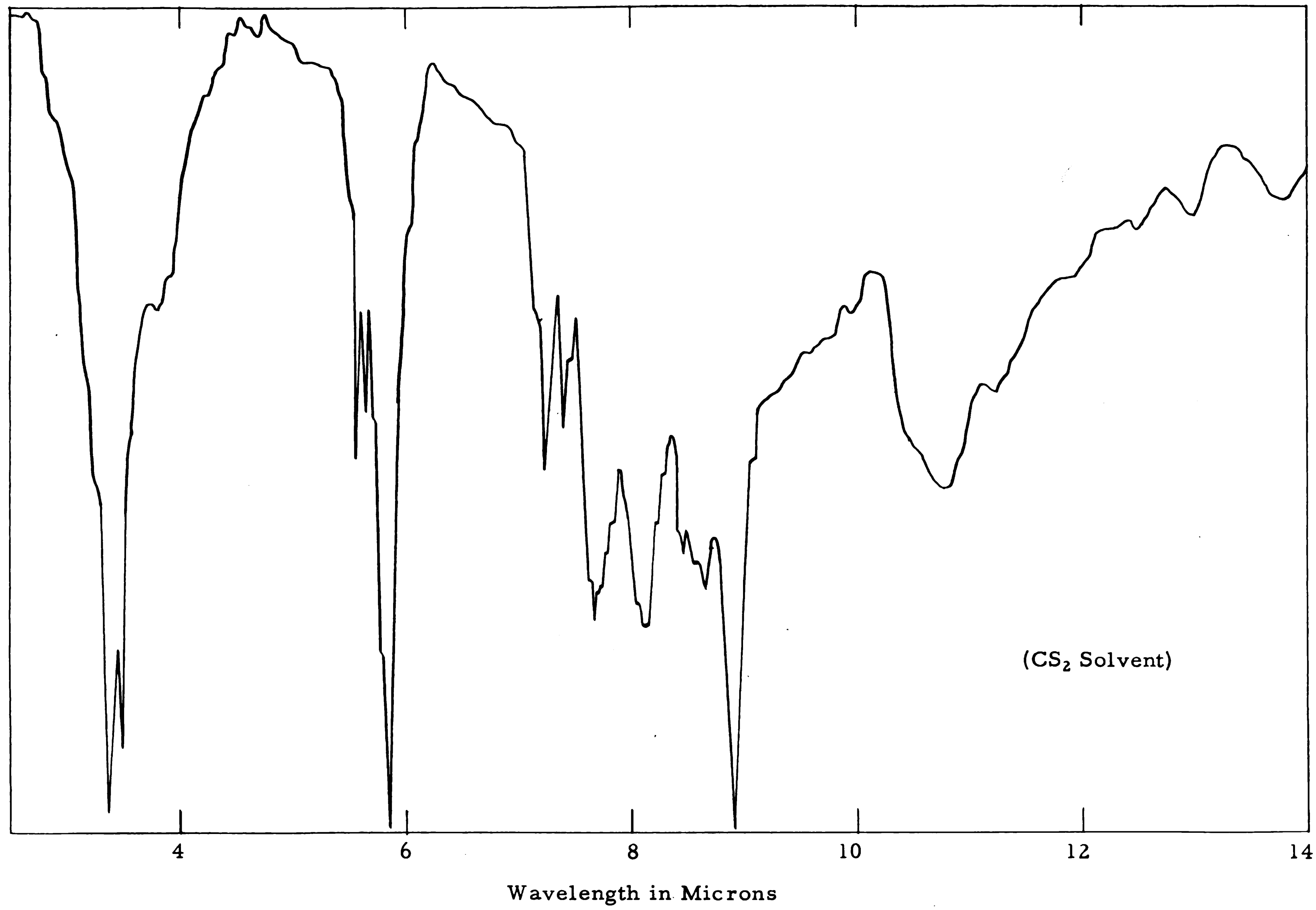


Figure 40. Infrared Spectrum of the Bromoacid Obtained from the Haloform Oxidation of the Bromoketone Obtained from the Acylation of Norbornene with Acetyl Bromide.

7. Preparation of n-Butyl Lithium

The method of Gilman (58) was employed in this preparation. Anhydrous ether (600 ml.) was introduced into a 2-l. 3-necked round-bottomed flask fitted with a mechanical stirrer, a reflux condenser, a thermometer, and a dropping funnel. The system was flushed with dry nitrogen and 22.3 g. (3.23 moles) of diced lithium metal was added. About 1 ml. of a solution of 205.5 g. (1.5 moles) of n-butyl bromide in 200 ml. of anhydrous ether was added to initiate the reaction. The mixture was cooled to -10° in dry ice-acetone and the remainder of the n-butyl bromide solution added dropwise with stirring over a 2 hour period. The blue-grey solution was stirred an additional 2 hours at -10° and then filtered.

8. Preparation of Cyclopentadienyl Lithium

The method of Kursanov (59) was employed in this preparation. Freshly distilled cyclopentadiene (79.2 g., 1.2 moles) was introduced into a 2-l. 3-necked round-bottomed flask fitted with a mechanical stirrer, a reflux condenser, a thermometer, and a dropping funnel. n-Butyl lithium solution (prepared from 1.5 moles of n-butyl bromide) was added dropwise with stirring. The temperature of the mixture was maintained at $0\text{-}5^{\circ}$ over the addition time (about 2 hours). The solution was stirred for an additional 2 hours at room temperature.

9. Preparation of the Exocyclic Enol Acetate of Acetylcyclopentadiene

Cyclopentadienyl lithium was acylated employing the method of Riemschneider (60). The above solution of cyclopentadienyl lithium was cooled to $0\text{-}5^{\circ}$ and 131 g. (1.97 moles) of acetyl chloride was added with stirring. After the addition was complete (about 3 hours), the mixture was stirred an additional hour at room temperature. The solution was then poured on ice-10% sodium hydroxide and extracted with ether. After drying over magnesium sulfate and evaporating the ether, the residue was fractionated in vacuo through a 6" Vigreux column to yield 18 g. of exocyclic enol acetate of acetylcyclopentadiene, b.p. 105-115°/15 mm. (lit. value (60), b.p. 105-115°/15 mm.).

10. Reaction of the Exocyclic Enol Acetate of Acetylcyclopentadiene with Ethylene

The enol acetate (18 g., 0.12 moles) was introduced into a steel bomb and charged with ethylene to a pressure of 500 pounds per square inch. The temperature was raised to 170° and the mixture agitated by means of an internal solenoid controlled plunger for 24 hours. The pressure rose slowly to 800 pounds per square inch and then dropped slowly to 700 pounds per square inch. The bomb was allowed to cool and a black gritty solid was removed via ether rinse. After evaporation of the ether, the residue was stirred magnetically with dilute sulfuric acid for 12 hours. The resultant solution was extracted with ether. After drying over magnesium sulfate and evaporating the ether, the remaining dark oil was dissolved in ethyl acetate and treated with norite. Evaporation of the ethyl acetate afforded 5 g. of an oily residue.

The residue (5 g.) was dissolved in 200 ml. of dioxane and 50 ml. of 10% sodium hydroxide was added. Iodine solution (a solution 0.67 M in iodine and 2 M in potassium iodide) was added until the iodine color persisted. The precipitated iodoform was filtered and the solution washed with ether. The water layer was neutralized with dilute sulfuric acid and extracted with ether. After drying over magnesium sulfate and evaporating the ether, 1.5 g. of crude acid was obtained. Esterification with diazomethane and distillation produced an ester found to boil above 110°/11 mm.

11. Acylation of Norbornene with Phosgene

A 500-ml. round-bottomed 3-necked flask was fitted with a magnetic stirrer, a gas inlet tube, and an outlet tube leading to an aniline trap.

Carbon disulfide (200 ml.) was introduced and 73.4 g. (0.55 mole) of aluminum chloride was added. The system was flushed with dry nitrogen and cooled to -20°. Phosgene (54.5 g., 0.55 mole) was then introduced. After the desired weight was attained, the system was swept with nitrogen and the gas inlet tube replaced by a dropping funnel. Norbornene (47 g., 0.5 mole) in 200 ml. of carbon disulfide was added dropwise over a 2 hour period. The resultant solution (now red-yellow) was stirred an additional hour at room temperature. After pouring on a concentrated hydrochloric acid-ice mixture, the water layer was extracted with ether. The ether was evaporated and the resultant dark oil was dissolved in dilute sodium hydroxide and treated with norite. The solution was acidified with concentrated hydrochloric acid and extracted with ether. After drying over magnesium sulfate and evaporating the ether a light yellow solid weighing 0.6 g. was obtained, m.p. 130-150°.

E. Preparation of Cyclopropaneacetyl Peroxide

1. Preparation of Cyclopropyl Lithium

The method of Hart and Holzschuh (61) was employed in this preparation. A 1-l. three-necked round-bottomed flask was fitted with a high-speed stirrer and a reflux condenser. The system was flushed with argon and closed. The system was kept under argon using a large plastic bag which acted as a pressure equalizer. Mineral oil (250 ml.) that had been dried over calcium hydride and 7.3 g. (1.06 g.-atom) of lithium were added. The flask was heated with a Fisher burner with slow stirring until the lithium melted. The mixture was then stirred vigorously until the lithium dispersed and the temperature dropped enough to prevent the lithium sand from fusing (3-5 minutes). After the mixture cooled to room temperature, the mineral oil was removed by the addition of anhydrous ether portionwise, followed by the application of suction, until 500 ml. of ether had been used.

To the lithium sand was added 250 ml. of anhydrous ether. The flask was cooled to 2° and a thermometer and a dropping funnel attached. A mixture of 46.3 g. (0.60 mole) of cyclopropyl chloride in 150 ml. of anhydrous ether was added at such a rate that the temperature of the reaction mixture never exceeded 10°. After the addition was complete (about three hours), the mixture was stirred for an additional hour. The cyclopropyl lithium was then ready for use.

2. Preparation of β-Cyclopropylethanol

To the ether suspension of cyclopropyl lithium was added a dry-ice-cold mixture of 53.2 g. (1.21 moles) of ethylene oxide in 300 ml. of anhydrous ether. The temperature of the mixture was maintained below 10° throughout the addition and then the stirring was continued for an additional hour at 2°.

The mixture was poured into water and acidified with ice-cold 10% sulfuric acid. The layers were separated and the aqueous layer saturated with sodium chloride. The water layer was then extracted with ether. After drying over potassium carbonate and evaporating the ether, the residue was distilled *in vacuo* to yield 32 g. (70%) of β-cyclopropylethanol, b.p. 70-72°/45 mm., n_D^{20} 1.4325 (lit. values (62), b.p. 73-75°/50 mm., n_D^{20} 1.4328).

3. Preparation of Cyclopropaneacetic Acid

β-Cyclopropylethanol (32 g., 0.373 mole) was added to a 1-l. three-necked round-bottomed flask fitted with a reflux condenser, dropping funnel and a mechanical stirrer. Acetone (75 ml.) was added and the mixture cooled in a water bath. A solution of 49.8 g. (0.498 mole) of chromium trioxide and 77.5 g. (0.828 mole) of sulfuric acid in 328 ml. of water was added dropwise. The addition required approximately 15 hours. Water (100 ml.) was added and the mixture stirred for an additional hour. The layers were separated and the water layer extracted with ether. After the ether was evaporated, the residue was added to 243 ml. of 4 N sodium hydroxide and the mixture refluxed for 5 hours. After the mixture cooled, it was extracted with ether.

The aqueous solution was acidified to Congo Red with 10% sulfuric acid and extracted with ether. After drying over magnesium sulfate and evaporating the ether, the residue was distilled in vacuo to yield 17 g. (46%) of cyclopropaneacetic acid, b.p. 90-94°/15 mm., n_D^{25} 1.4326 (lit. values (61), b.p. 91°/15 mm., n_D^{25} 1.4321).

4. Preparation of Cyclopropaneacetyl Chloride

A mixture of 17 g. (0.17 mole) of cyclopropaneacetic acid, 23.8 g. (0.20 mole) of thionyl chloride and 40 ml. of chloroform was refluxed for four hours. The chloroform and excess thionyl chloride were removed by distillation through a 6" Vigreux column. The fraction boiling at 131-134° was collected and amounted to 9.1 g. (45%) (lit. value (61), 132-133°).

5. Preparation of Cyclopropaneacetyl Peroxide

In a 250-ml. two-necked round-bottomed flask fitted with a thermometer and a reflux condenser there was placed 3.67 g. (0.047 mole) of sodium peroxide and 150 ml. of anhydrous ether. The reaction mixture was cooled by means of an ice bath and stirred magnetically. Cyclopropaneacetyl chloride (10 g., 0.085 mole) was added and then 1-2 drops of water. Additional drops of water were added intermittantly throughout the reaction time (5 hours). The reaction was assumed to be complete when the yellow color of the sodium peroxide was replaced by white sodium chloride.

Water was added to dissolve the sodium chloride and the layers were separated. The ether layer was washed successively with ice water, 5% sodium carbonate, and finally ice water again. After drying over magnesium sulfate and evaporating the ether, the residue was taken up in pentane.

After drying over drierite and evaporating the pentane, the residue was dissolved in 100 ml. of purified carbon tetrachloride (20).

F. Preparation of Cyclopropylcarbinyl Cyclopropaneacetate

Cyclopropaneacetyl chloride (0.7 g., 0.0059 mole) was added to 0.45 g. (0.0062 mole) of cyclopropylcarbinol in 20 ml. of carbon tetrachloride contained in a 50-ml. round-bottomed flask fitted with a reflux condenser. Pyridine (0.5 ml.) was added and the mixture refluxed for 2 hours on a steam bath. The reaction mixture was cooled and poured on 30 g. of ice. The mixture was extracted with ether and washed successively with 3 N hydrochloric acid, 5% sodium carbonate, and finally water. After drying over magnesium sulfate and evaporating the ether, the residue was distilled *in vacuo* to yield 0.5 g. (55%) of ester, b.p. 91°/14 mm., n_D^{25} 1.4431 (lit. values (47), b.p. 63-65°/2 mm., n_D^{25} 1.4475). The infrared spectrum of this compound is shown in Figure 41.

G. Preparation of Cyclobutanol

This compound was prepared by the method of Caserio, Graham, and Roberts (65). A solution of 15 g. of cyclopropylcarbinol in 140 ml. of water and 12 ml. of concentrated hydrochloric acid was heated on a steam bath for 100 minutes. The mixture was cooled and 5.5 g. of sodium hydroxide was added. Neutralization was completed by the addition of potassium carbonate. The mixture was continuously extracted with ether and the ether solution dried over magnesium sulfate. Evaporation of the ether and distillation of the residue yielded 9.1 g. (60%) of cyclobutanol, b.p. 122-124°, n_D^{25} 1.4327 (lit. values (65), b.p. 121-124°, n_D^{25} 1.4315).

H. Preparation of Cyclobutyl Cyclopropaneacetate

Cyclopropaneacetyl chloride (0.9 g., 0.0085 mole) was added to 0.55 g. (0.0077 mole) of cyclobutanol in 20 ml. of carbon tetrachloride

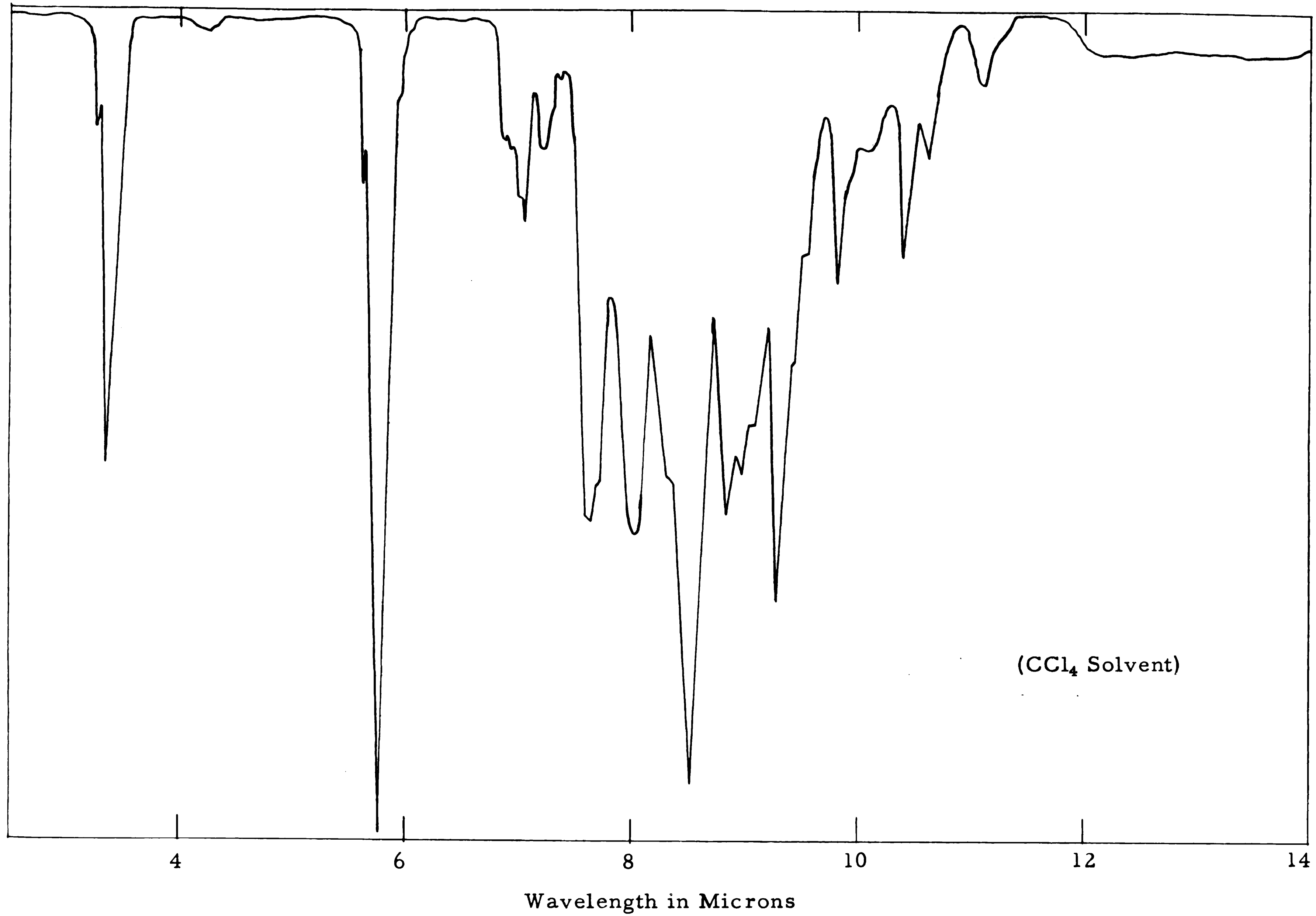


Figure 41. Infrared Spectrum of Cyclopropylcarbinyl Cyclopropaneacetate.

contained in a 50-ml. round-bottomed flask fitted with a reflux condenser. Pyridine (0.5 ml.) was added and the mixture refluxed for 2 hours on a steam bath. The reaction mixture was cooled and poured on 30 g. of ice. The mixture was extracted with ether and washed successively with 3 N hydrochloric acid, 5% sodium carbonate, and finally water. After drying over magnesium sulfate and evaporating the ether, the residue was distilled *in vacuo* to yield 0.6 g. (51%) of ester, b.p. 84°/14 mm., n_D^{25} 1.4444. The infrared spectrum of this compound is shown in Figure 42.

I. Determination of the Ester Fragment in the Decomposition of Cyclopropaneacetyl Peroxide

Cyclopropaneacetyl peroxide (ca. 5 g.) was dissolved in 100 ml. of carbon tetrachloride and refluxed for 12 hours. The carbon tetrachloride was removed by distillation through a 600 x 7 mm. vacuum jacketed tantalum wire spiral column (bath temperature, 85°). When no more carbon tetrachloride came over, the column was removed and the pressure was decreased gradually to 15 mm. The bath temperature was then raised and the distillate at 80-110°/15 mm. was collected.

The distillate was analyzed on a Beckman GC-2 vapor phase chromatograph at 135°. The chromatograph indicated five components, the major component having a retention time identical to the previously prepared cyclopropylcarbinyl cyclopropylacetate and cyclobutyl cyclopropylacetate.

The distillate was then passed through a Beckman Megachrom vapor phase chromatograph at 150° using 12', 20% silicone columns. The major component was collected and the infrared spectrum was found to be identical to cyclopropylcarbinyl cyclopropylacetate (Figure 43).

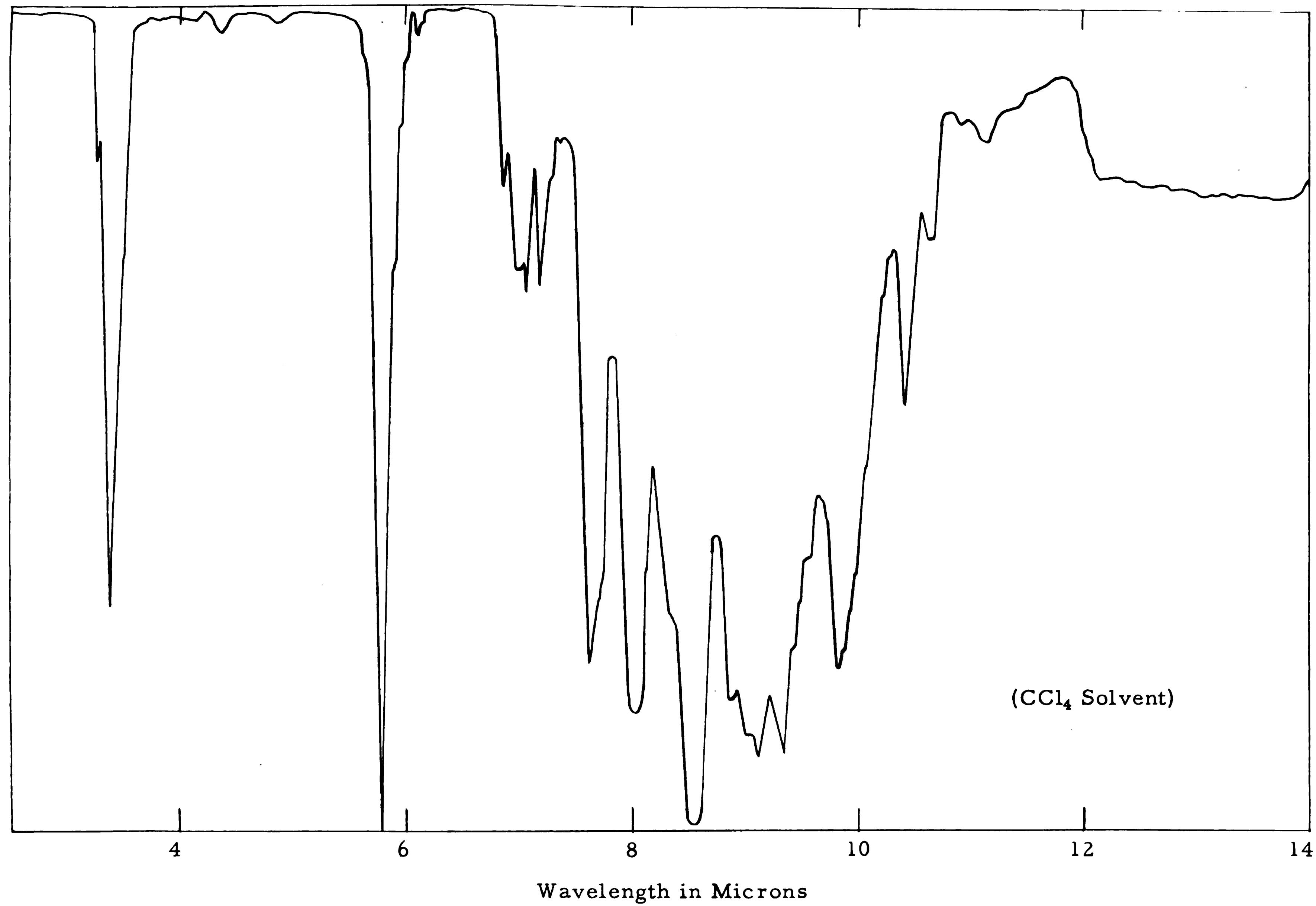


Figure 42. Infrared Spectrum of Cyclobutyl Cyclopropaneacetate.

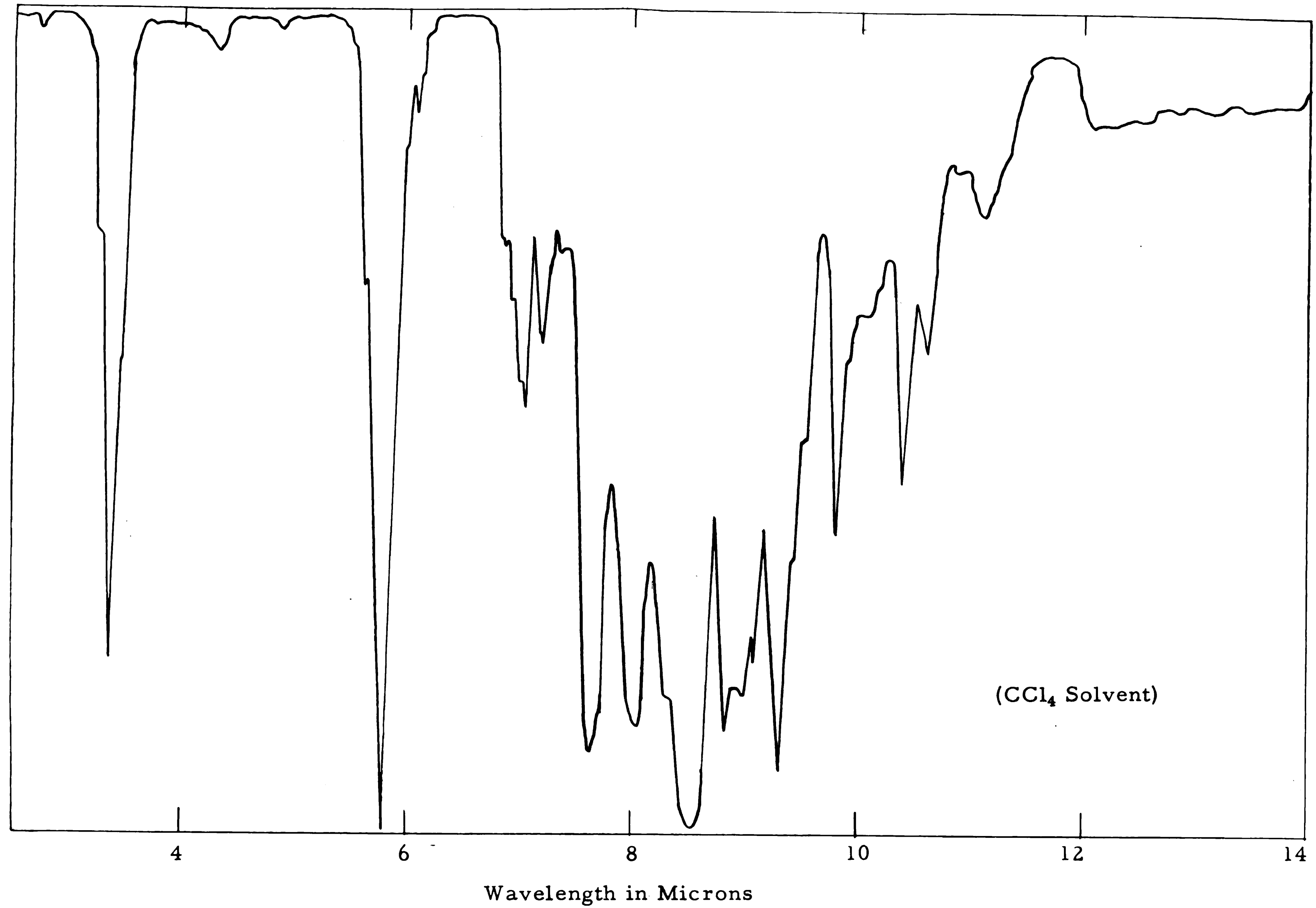


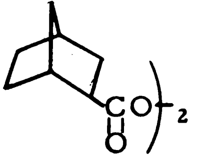
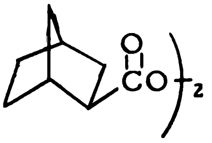
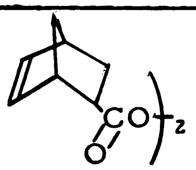
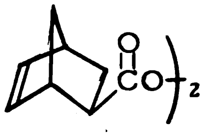
Figure 43. Infrared Spectrum of the Ester Obtained from the Decomposition of Cyclopropaneacetyl Peroxide.

SUMMARY

1. Four new diacyl peroxides, derived from 2-exo- and 2-endonorbornane carboxylic acids and 5-exo- and 5-endonorbornenecarboxylic acids were prepared, and their rates and products of decomposition in carbon tetrachloride studied.

2. The principal products from 2-endonorbornanecarbonyl peroxide were carbon dioxide (79.3%), 2-endonorbornyl 2-endonorbornanecarboxylate (10.2%), 2-endonorbornanecarboxylic acid (11.2%), and 2-exochloronorbornane (not determined quantitatively). 2-Exonorbornanecarbonyl peroxide produced carbon dioxide (73.7%), 2-exonorbornyl 2-exonorbornanecarboxylate (14.8%), 2-exonorbornanecarboxylic acid (6.2%) and 2-exochloronorbornane (not determined quantitatively). 5-Endonorbornenecarbonyl peroxide yielded carbon dioxide (48.5%), 5-endonorbornenyl 5-endonorbornenecarboxylate (9.7%), the gamma-2 lactone of 2-exotrichloromethyl-3-endohydroxy-5-endonorbornanecarboxylic acid (39%), 5-exochloronorbornene (not determined quantitatively), and polychloroalkanes (not determined quantitatively). 5-Exonorbornenecarbonyl peroxide produced carbon dioxide (56.4%), 5-exonorbornenyl 5-exonorbornenecarboxylate (14.6%), a lactone (15.3%), an acid (not determined quantitatively), 5-exochloronorbornene (not determined quantitatively), and polychloroalkanes (not determined quantitatively).

3. The relative rates of decomposition of the various peroxides at 44.5° in carbon tetrachloride, and their energies of activation are given below.

Compound				
Relative rate	1	8	10.8	11.2
Ea(kcal./mole)	32.8	27.1	24.0	24.7

4. The production of lactone from 5-endonorbornenecarbonyl peroxide represents a novel induced decomposition involving an intramolecular attack of a radical on a carboxyl group. The production of lactone from 5-exonorbornenecarbonyl peroxide is evidence for the occurrence of a free radical Wagner-Meerwein rearrangement.

5. The rates, products, and activation parameters were all consistent with a mechanism involving the formation of an alkyl radical as one of the rate-determining steps. The steric crowding in 2-endonorbornanecarbonyl peroxide appears to be significant. The rates and products from decomposition produced little or no evidence for participation in free radical reactions.

6. Several new compounds were prepared in connection with the peroxide work. These were: 2-endonorbornyl 2-endonorbornanecarboxylate, 2-exonorbornyl 2-exonorbornanecarboxylate, 5-endonorbornenyl 5-endonorbornenecarboxylate, 5-exonorbornenyl 5-exonorbornenecarboxylate, and the gamma-3 lactone of 2-exochloro-3-endohydroxy-5-endonorbornanecarboxylic acid.

7. Some miscellaneous experiments involving attempted preparations of 7-norbornenecarboxylic acids and the identification of cyclopropylcarbinyl cyclopropylacetate as the ester produced from the decomposition of cyclopropylacetyl peroxide were described.

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APPENDIX

Derivation of Equation Used in Calculating Rate Constants

The equation used to follow the decomposition of the peroxides was obtained by the following manipulations. From the equation for a first order reaction one has

$$f(C) = f(C_0)\, e^{-kt} \qquad (1)$$

where $f(C_0)$ is an appropriate function of the initial peroxide concentration and $f(C)$ is the same function at time t. If times t_1, t_2, t_3, etc., and $t_1+\Delta$, $t_2+\Delta$, $t_3+\Delta$, etc., are selected where Δ is a constant increment, then the following equations are true:

$$(f(C_1) - f(C_\infty)) = (f(C_0) - f(C_\infty))\, e^{-kt_1} \qquad (2)$$

$$(f'(C_1) - f(C_\infty)) = (f(C_0) - f(C_\infty))\, e^{-k(t_1+\Delta)} \qquad (3)$$

where $f(C_1)$ and $f'(C_1)$ are readings of the appropriate function at t_1 and $t_1+\Delta$ respectively. Similar equations for t_2, t_3, etc., would also be true. Subtracting (3) from (2) gives

$$(f(C_1) - f'(C_1)) = (f(C_0) - f(C_\infty))e^{-kt_1}\,(1-e^{-k\Delta}) \qquad (4)$$

or

$$kt_1 + \ln (f(C_1) - f'(C_1)) = \ln[(f(C_0) - f(C_\infty))\,(1-e^{-k\Delta})] \qquad (5)$$

which can be generalized by dropping the subscript 1. The right hand side of the equation is a constant. Changing to base 10 logarithms and rewriting gives

$$\mathrm{Log}(f(C) - f'(C)) = 2.303\ kt + A \qquad (6)$$

where A incorporates the right hand term of equation (5) and factor 2.303.

In this investigation, titer and absorbancy were used as $f(C)$. The rate constants were obtained by plotting $\log(f(C)-f'(C))$ versus t and multiplying the slope of the line by 2.303.

The energy of activation, Ea, was calculated using equation (7)

$$k = se^{-Ea/RT} \tag{7}$$

where k is the first order rate constant, Ea is the experimental activation energy in calories, R is the gas constant per mole (1.987 calories /°K), and s is the frequency factor. Rewriting to a more convenient form

$$\log k = \log s + Ea/2.303\ RT \tag{8}$$

and plotting log k versus 1/T, the energy of activation was obtained by multiplying the slope of the line, which was determined by the method of least squares, by -2.303 R.

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

$$k = \frac{ek'T}{h} e^{\Delta S^*/R} e^{Ea/RT} \tag{9}$$

where k is the first order rate constant, k' is Boltzmann's constant, T is the absolute temperature, h is Planck's constant, ΔS^* is the difference in entropy between initial and activated states in entropy units, E is the experimental activation energy in calories, R is the gas constant in calories per mole - °K, and e is the base of the natural logarithm system.

Combining equations 7 and 9 there is obtained

$$s = \frac{ek'T}{h} e^{\Delta S^*/R} \tag{10}$$

Taking logarithms of both sides and rearranging gives

$$\Delta S^* = R \ln s - R \ln (ek'T/h) \tag{11}$$

The entropy of activation was obtained by solving equation (8) for s at various T and k, and then using the average s in equation 11 to solve for ΔS^*.

Suitable examples of these calculations follow.

Calculation of Rate Constants for the Decomposition of 2-Exonorbornanecarbonyl Peroxide at 53.9°

Table 14. Decomposition of 2-Exonorbornanecarbonyl Peroxide in Carbon Tetrachloride at 53.9° Determined by Titrimetric Techniques

Sample	Time/min.	Titer/ml.
1	0.0	11.00
2	15.0	9.86
3	30.0	8.26
4	45.0	7.48
5	65.0	5.74
6	90.0	4.45
7	146.7	2.84
8	170.0	2.38
9	203.3	2.00
10	241.7	1.68

Table 15. Guggenheim Data for the Decomposition of 2-Exonorbornanecarbonyl Peroxide at 53.9° Determined by Titrimetric Techniques

Time/min.	V_t	$V_{t+\Delta}$	$V_t - V_{t+\Delta}$	$\mathrm{Log}_{10}(V_t - V_{t+\Delta})$
10	10.25	2.03	8.22	0.9148
20	9.34	1.92	7.42	0.8704
30	8.45	1.81	6.64	0.8221
40	7.59	1.71	5.88	0.7693
50	6.78	1.61	5.17	0.7134

Δ = 190 minutes

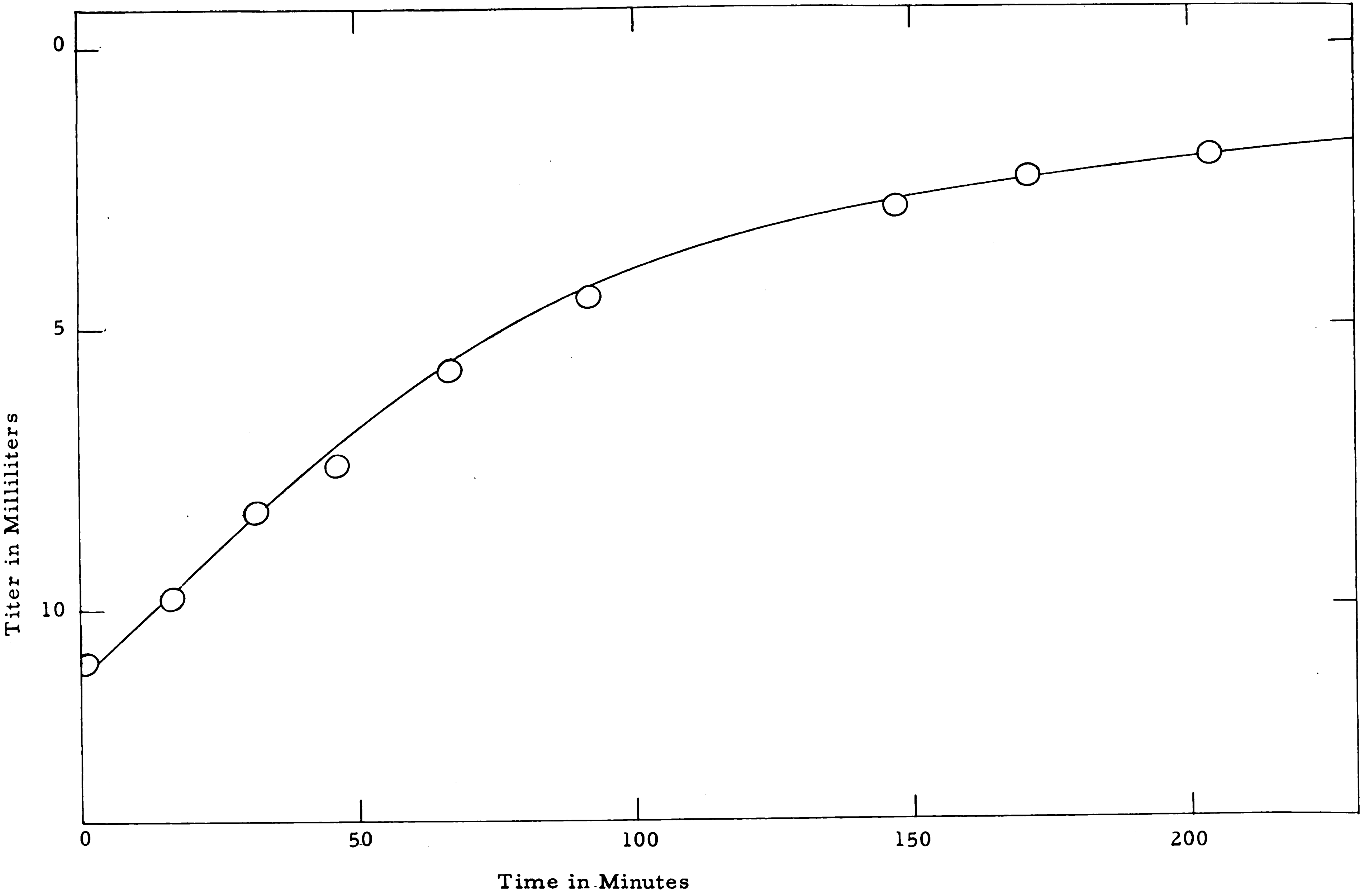

Figure 44. Titer Versus Time Plot for the Decomposition of 2-Exonorbornanecarbonyl Peroxide at 53.9°.

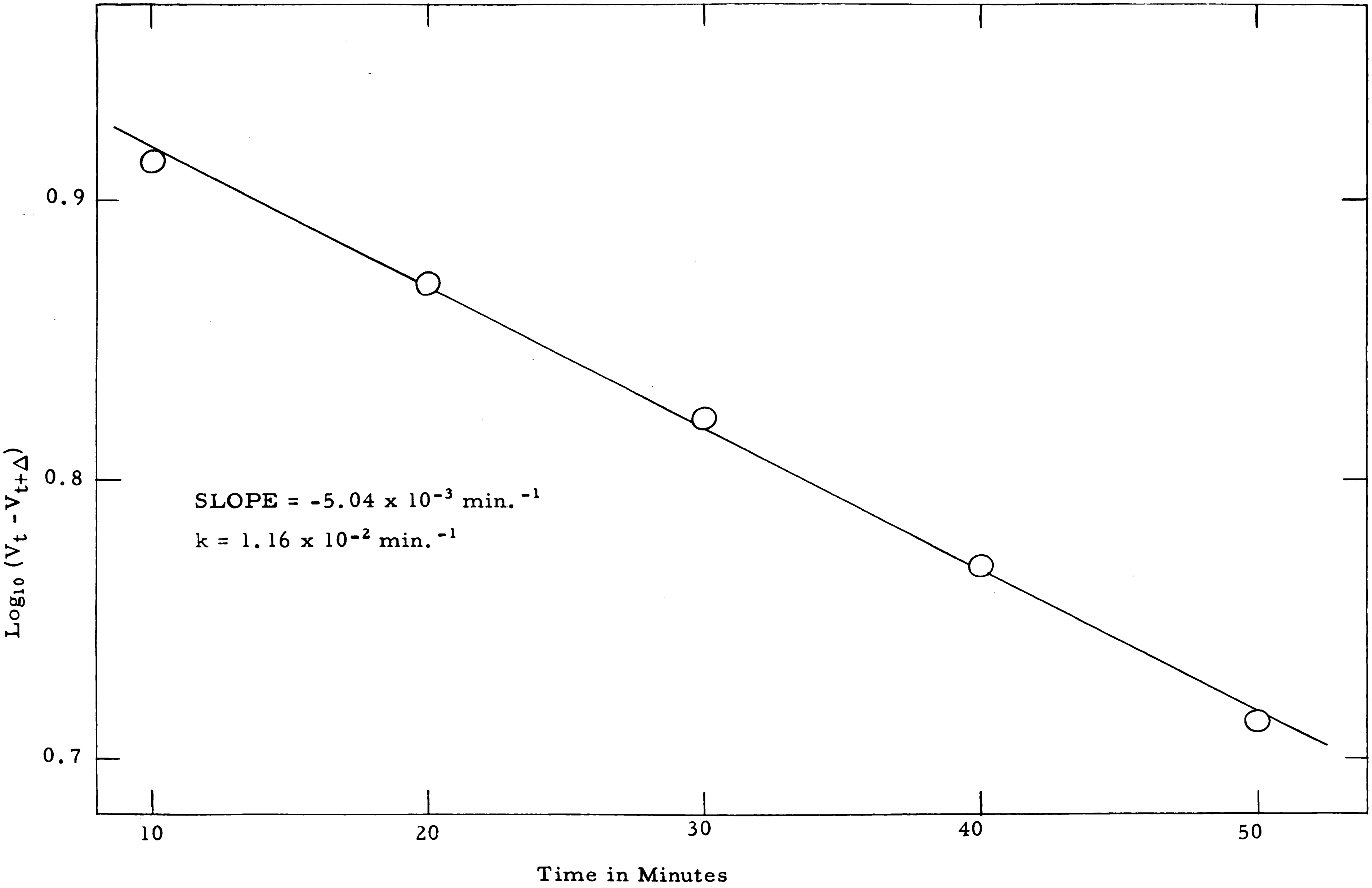

Figure 45. Guggenheim Plot for the Decomposition of 2-Exonorbornanecarbonyl Peroxide at 53.9° (Titration).

Table 16. Decomposition of 2-Exnorbornanecarbonyl Peroxide in Carbon Tetrachloride at 53.9° Determined by Infrared Techniques.

Sample	Time/min.	Absorbancy
1	0.0	0.5806
2	15.0	0.5329
3	30.0	0.4680
4	45.0	0.4076
5	65.0	0.3483
6	90.0	0.2871
7	146.7	0.2055
8	170.0	0.1858
9	203.3	0.1661
10	241.7	0.1505

Table 17. Guggenheim Data for the Decomposition of 2-Exonorbornanecarbonyl Peroxide at 53.9° Determined by Infrared Techniques.

Time/min.	A_t	$A_{t+\Delta}$	$A_t - A_{t+\Delta}$	$\text{Log}_{10}(A_t - A_{t+\Delta})$
10	0.548	0.172	0.376	-0.4248
20	0.508	0.167	0.341	-0.4672
30	0.468	0.162	0.306	-0.5142
40	0.432	0.156	0.276	-0.5590
50	0.396	0.151	0.245	-0.6108

Δ = 190 minutes

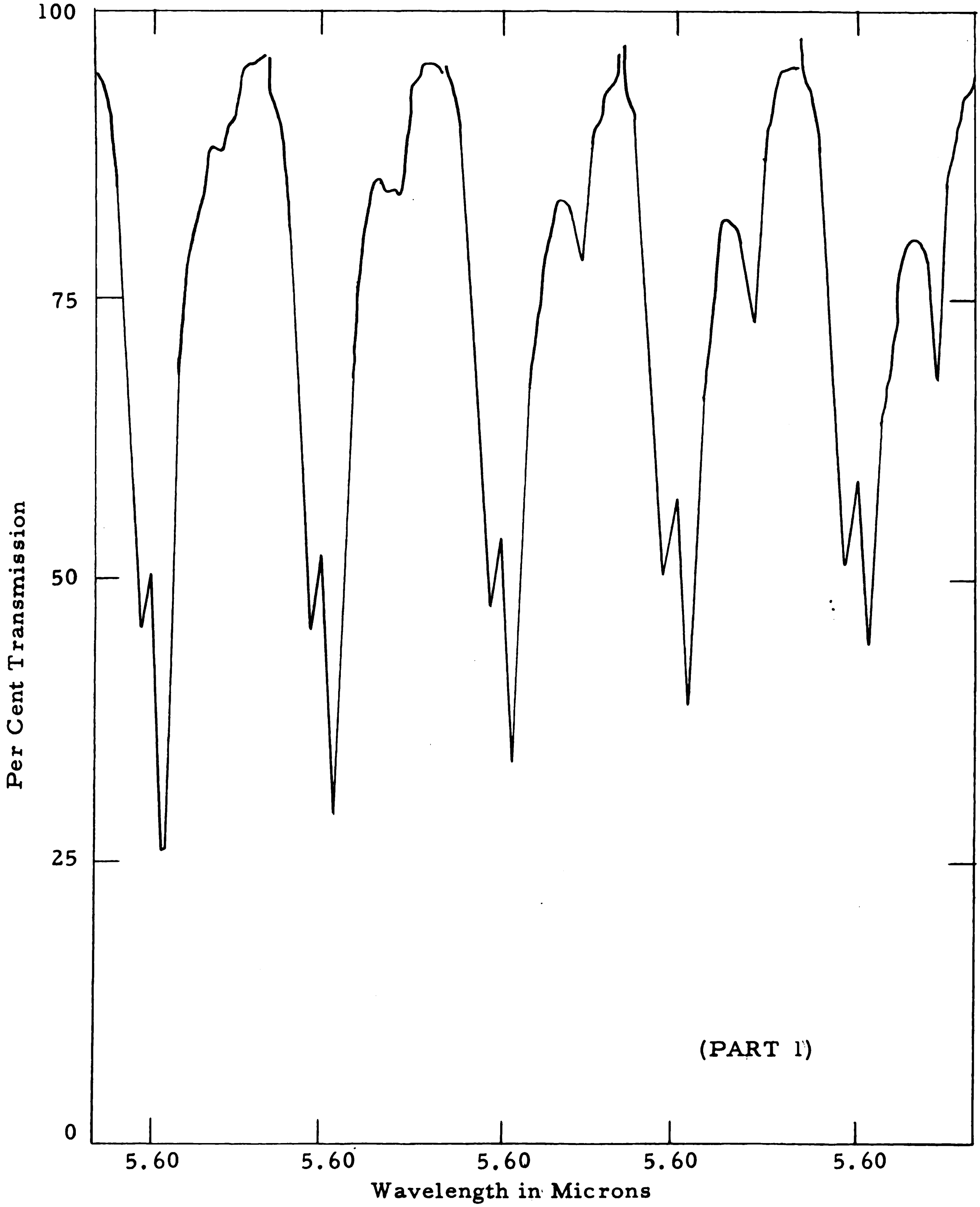

Figure 46. Quantitative Infrared Spectra of the Decomposition of 2-Exonorbornanecarbonyl Peroxide at 53.9°.

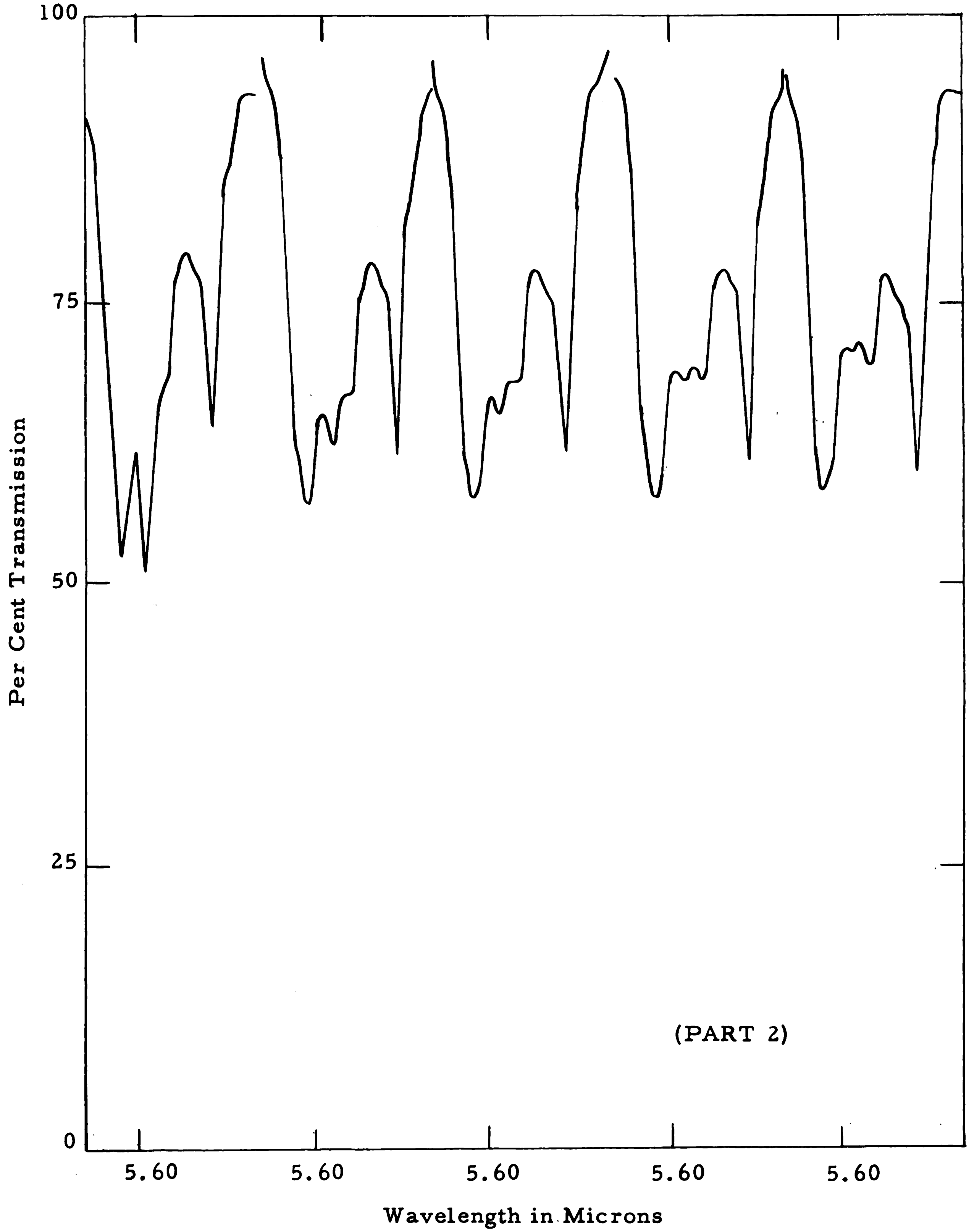

Figure 46. Quantitative Infrared Spectra of the Decomposition of 2-Exonorbornanecarbonyl Peroxide at 53.9°.

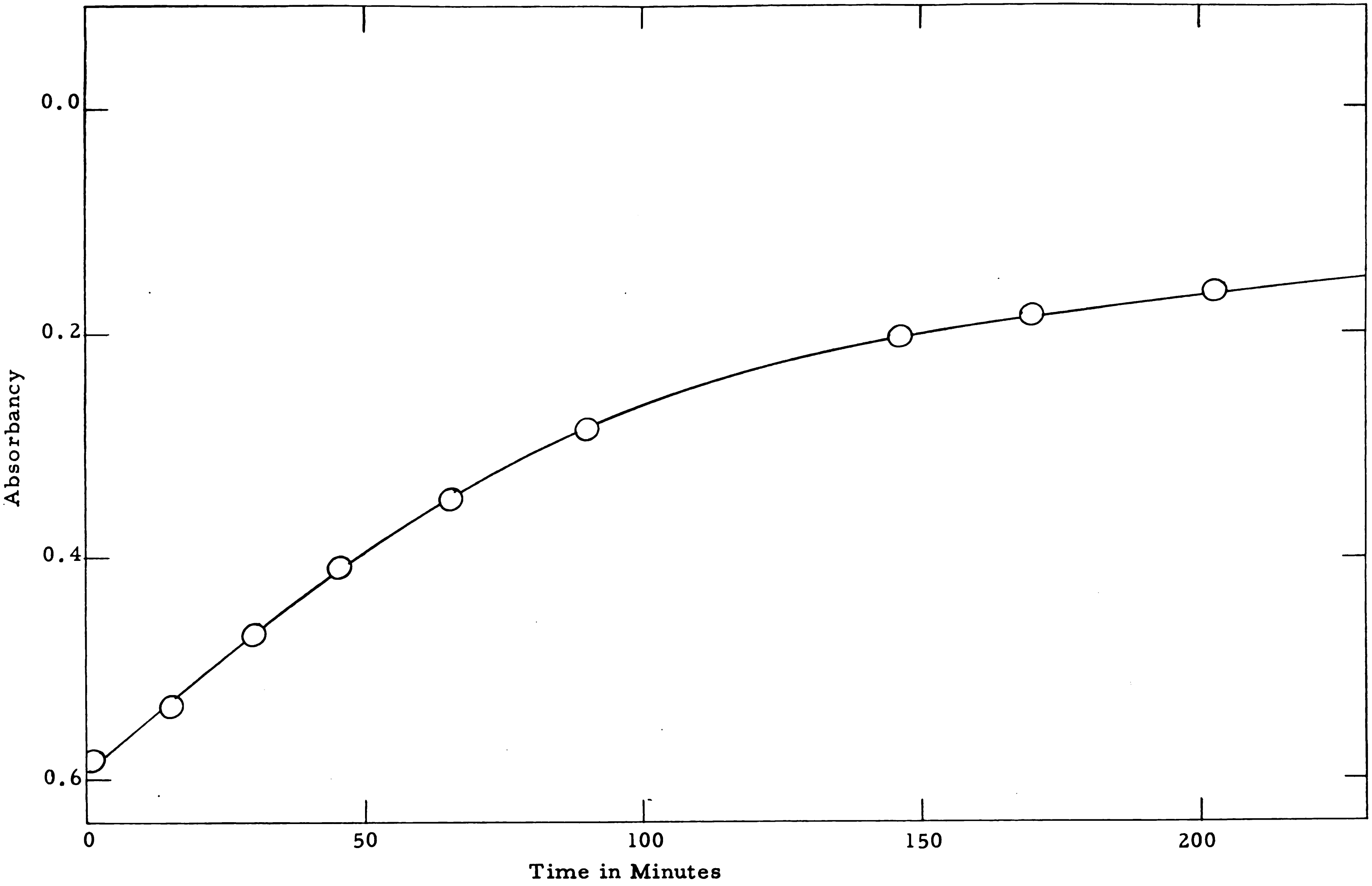

Figure 47. Absorbancy Versus Time Plot for the Decomposition of 2-Exonorbornanecarbonyl Peroxide at 53.9°.

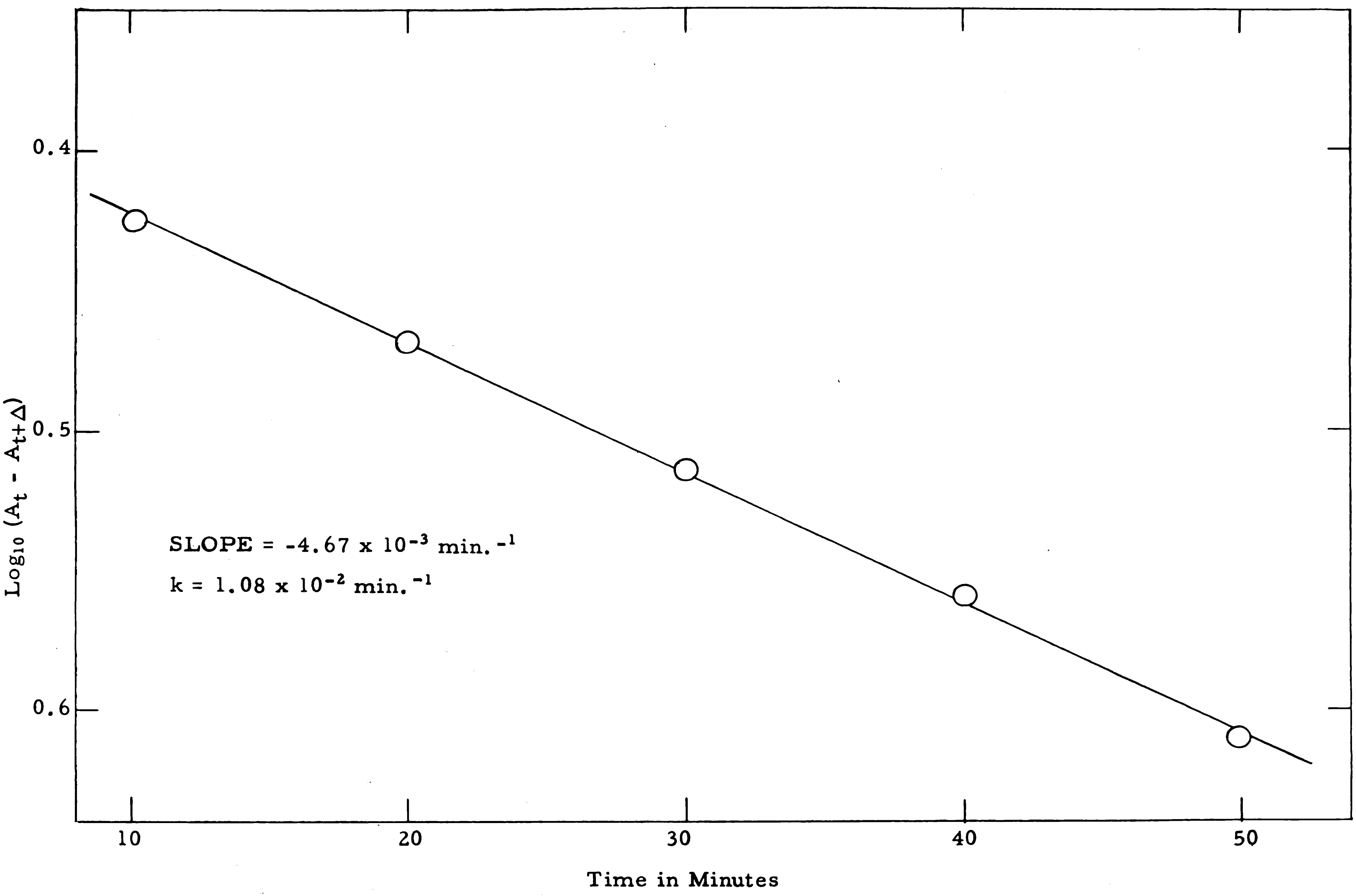

Figure 48. Guggenheim Plot for the Decomposition of 2-Exonorbornanecarbonyl Peroxide at 53.9° (Infrared).

Table 18. Appearance of Acid from the Decomposition of 2-Exonorbornanecarbonyl Peroxide in Carbon Tetrachloride at 53.9° Determined by Infrared Techniques

Sample	Time/minutes	Absorbancy
1	0.0	0.0510
2	15.0	0.0730
3	30.0	0.1021
4	45.0	0.1323
5	65.0	0.1640
6	90.0	0.1940
7	146.7	0.2097
8	170.0	0.2097
9	203.3	0.2129
10	241.7	0.2207

Table 19. Guggenheim Data for the Appearance of Acid from the Decomposition of 2-Exonorbornanecarbonyl Peroxide in Carbon Tetrachloride at 53.9° Determined by Infrared Techniques

Time/minutes	A_t	$A_{t+\Delta}$	$A_{t+\Delta} - A_t$	$\mathrm{Log}_{10}(A_{t+\Delta} - A_t)$
10	0.064	0.216	0.152	-0.8181
20	0.085	0.217	0.132	-0.8794
30	0.105	0.218	0.113	-0.9469
40	0.124	0.218	0.094	-1.0268
50	0.142	0.218	0.076	-1.1191

Δ = 190 minutes

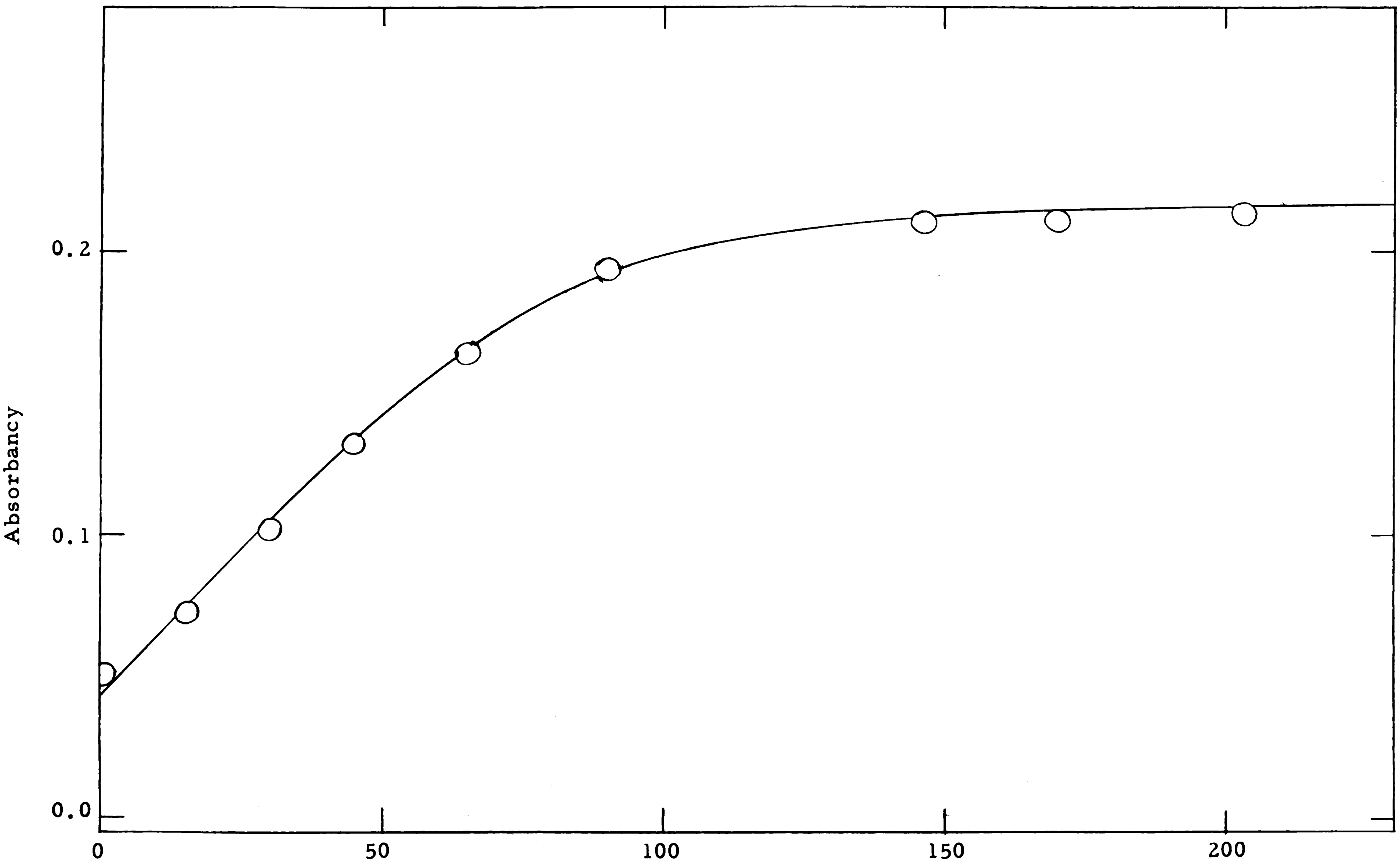

Figure 49. Absorbancy Versus Time Plot for the Appearance of Acid from the Decomposition of 2-Exonorbornanecarbonyl Peroxide at 53.9°.

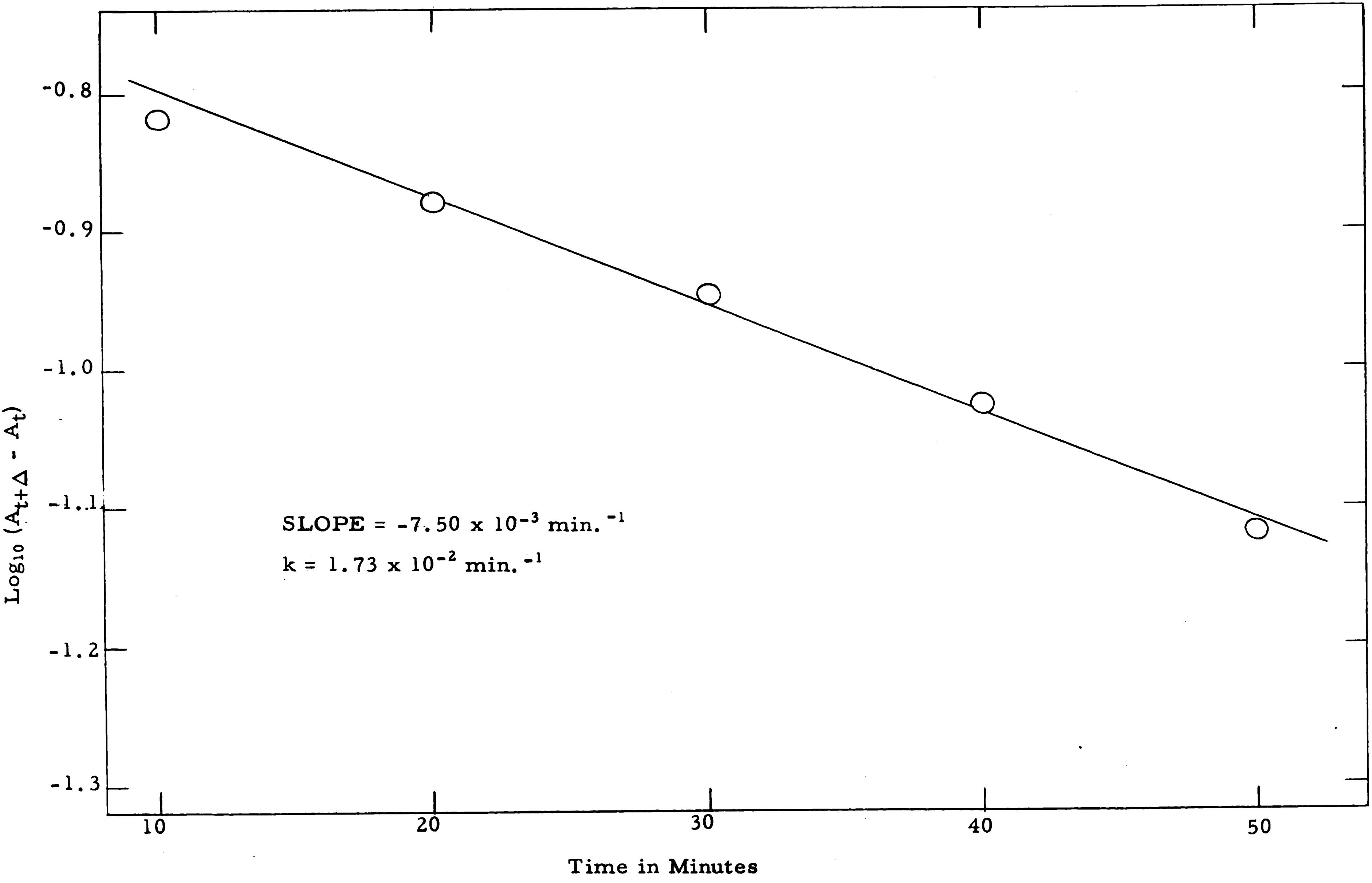

Figure 50. Guggenheim Plot for the Appearance of Acid from the Decomposition of 2-Exonorbornanecarbonyl Peroxide at 53.9° (Infrared).

Table 20. Energy of Activation for the Decomposition of 2-Exonorbornanecarbonyl Peroxide in Carbon Tetrachloride Determined by Titrimetric Techniques

T/°K	T^{-1}/°K^{-1}	k/minutes^{-1}	log$_{10}$k	Slope/°K	Ea/kcal./mole
339.05	2.9499x10^{-3}	49.1x10^{-3}	-1.30936	-6.23x10^{3}	28.5
327.05	3.0581x10^{-3}	12.3x10^{-3}	-1.91186		
317.65	3.1486x10^{-3}	2.81x10^{-3}	-2.55207		

Table 21. Entropy of Activation for the Decomposition of 2-Exonorbornanecarbonyl Peroxide in Carbon Tetrachloride Determined by Titrimetric Techniques

k/minutes^{-1}	Log$_{10}$k	Ea/2.303RT	Log$_{10}$s	Average log$_{10}$s	ΔS^* at 328.35°K/e.u.
49.1x10^{-3}	-1.30936	18.37768	17.06832	17.09082	17.49
12.3x10^{-3}	-1.91186	19.05209	17.14023		
2.81x10^{-3}	-2.55207	19.61598	17.06391		