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The reactivity of cyclopropane derivatives with certain free radicals

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THE REACTIVITY OF CYCLOPROPANE DERIVATIVES WITH CERTAIN FREE RADICALS

by

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Dean of Graduate College

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TABLE OF CONTENTS

Page

INTRODUCTION AND HISTORICAL BACKGROUND

In the last half century a considerable amount of evidence has been presented in favor of the theory that cyclopropane is intermediate between alkenes and alkanes. Although this hypothesis may not be entirely valid, there are certainly a number of similarities between cyclopropane derivatives and their ethylenic analogs.

If one considers first the synthesis of cyclopropane and its derivatives, one finds that practically all compounds of this type are formed as a result of elimination reactions[1,2,3]. Here, certainly, is a fundamental similarity between cyclopropanes and olefins.

Proceeding next to a comparison of reactions one sees that an overwhelming majority of both ethylenes and cyclopropanes undergo additions with a number of common reagents. One of the first comprehensive chemical studies was carried out by Kohler and Conant[4] in 1917. They noted that cyclopropane acids and ketones with carboxyl or carbonyl groups adjacent to the ring behaved like the corresponding α,β-unsaturated com-

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[1] A. Freund, Monatsh, 3, 626 (1882).

[2] J. B. Cloke and Co-workers, J. Am. Chem. Soc., 52, 2791 (1931).

[3] L. H. Sommer, R. E. Von Strien, F. C. Whitmore, J. Am. Chem. Soc., 71, 3056 (1949).

[4] E. P. Kohler and J. B. Conant, J. Am. Chem. Soc., 39, 1404 (1917).

pounds. For example they found that 2-phenyl-3 benzoylcyclopropane dicarboxylate underwent ring cleavage reactions when reduced with zinc and acetic acid[1], when attacked by strong bases[2], and when treated with HBr[3]. With these reagents, to which α,β-unsaturated systems are peculiarly sensitive, the analogous cyclopropane derivatives reacted in a similar fashion.

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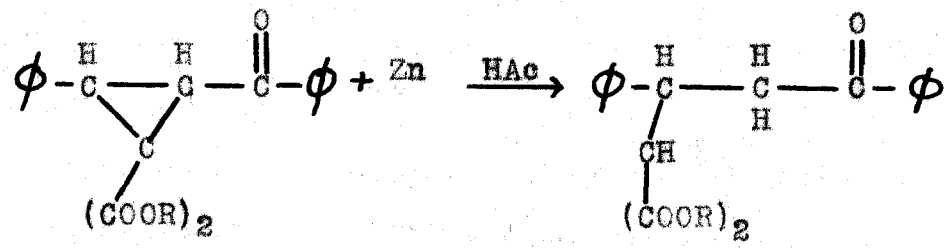

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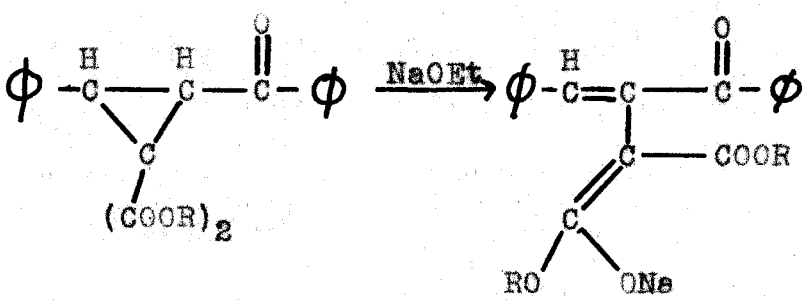

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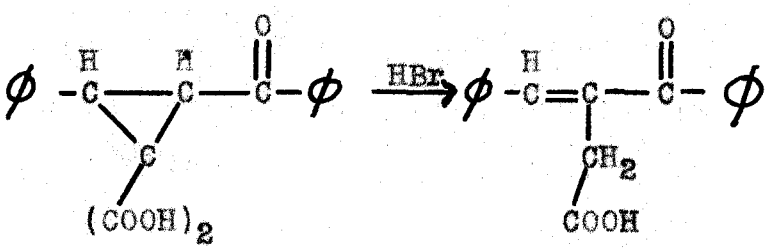
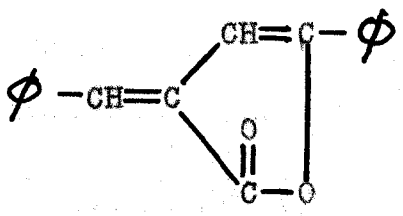
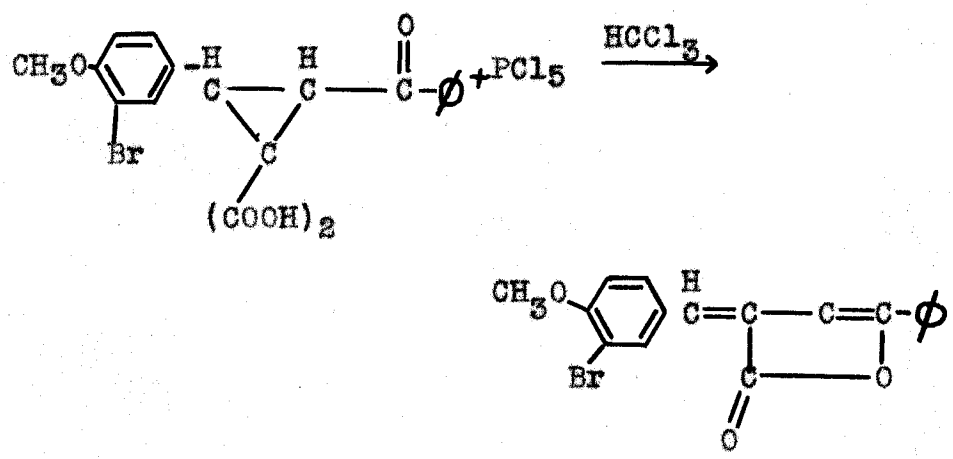




(4)



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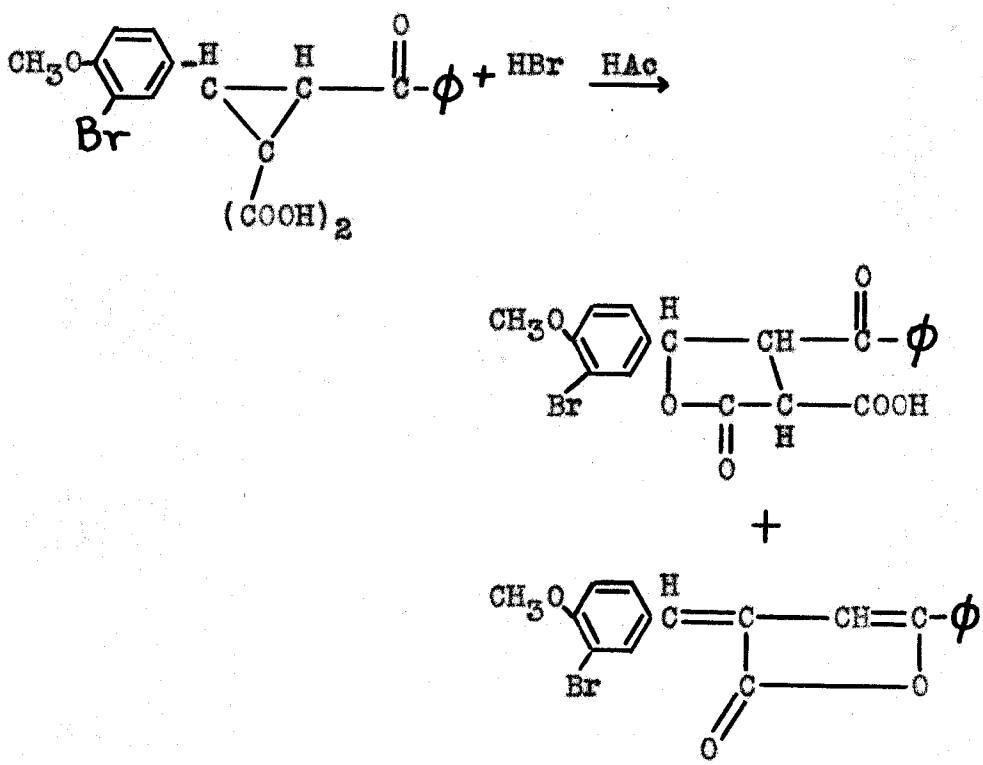

Upon further investigation[5] they found that ethyl magnesium bromide adds only across the carbonyl and not the ring in methyl-3-bromo-4-methoxyphenyl-cyclopropane-dicarboxylate, but that phenylmagnesium bromide may have cleaved the ring.

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[5] E. P. Kohler and J. B. Conant, J. Am. Chem. Soc., 39, 1699 (1917).

The diacid, but not the mono- or diester, reacted with phosporous pentachloride[4] in a manner exactly the same as that observed by Straus[6] using α,β-unsaturated ketones. Hydrogen bromide failed to react when mixed with the acid in methyl alcohol, but added readily when glacial acetic acid was employed as a solvent. The resulting products were not, however, the expected saturated products but a mixture of lactones[5]. Kohler and his co-workers[7] later isolated some of the intermediates, using an ester of slightly different structure, and proved essentially that the original products were the expected ones, but that they immediately underwent a series of rearrangements to give the final lactones. This study also showed that the cyclopropane ring was opened in two different ways by the halogen acid.

Kohler[8] next proceeded to demonstrate that the substitution of a methyl group on the same ring carbon as the benzoyl group in his original ester* prevented cleavage by basic reagents.

In a summary of the work[9], Kohler and Steele made some

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[6]F. Straus, Ann., 393, 235 (1913).

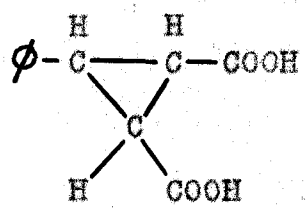
[7]E. P. Kohler, Y. A. Hill and L. A. Bigelow, J. Am. Chem. Soc., 39, 2405 (1917).

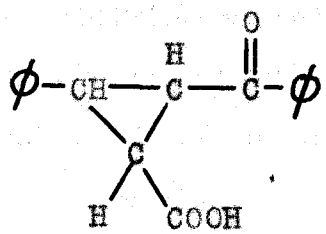
[8]E. P. Kohler and T. L. Davis, J. Am. Chem. Soc., 41, 992 (1919).

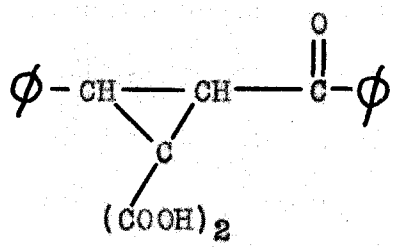
[9]E. P. Kohler and L. L. Steele, Ibid., 41, 1093 (1919).

*See p. 11.

observations on three typical cyclopropane derivatives.

I. 

II. 

III. 

Compound I behaves like a saturated compound in all respects whereas II forms an acyl chloride with thionyl chloride or phosporous pentachloride, but is inert to attack by bases. However, II reacts more readily with hydrogen bromide than III, but III is more easily lactonized by heating than II.

Allen and his co-workers[10,11,12,13] treated a similar series of cyclopropane derivatives with varying amounts of sulfuric acid in acetic acid and compared the results with hydrogen bromide addition. As was expected, the sulfuric acid was much less reactive than hydrogen bromide, and many of the

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[10] C. F. H. Allen and M. P. Bridgess, J. Am. Chem. Soc., 51, 2151 (1929).

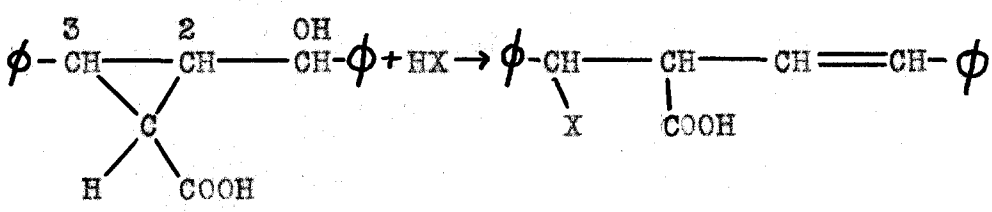
[11] C. F. H. Allen and W. E. Barker, Ibid., 54, 736 (1932).

[12] C. F. H. Allen and H. W. J. Cressman, Ibid., 55, 2953 (1933).

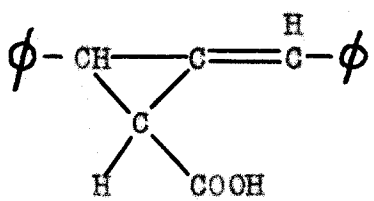
[13] C. F. H. Allen and R. Boyer, Can. J. Research, 9, 159 (1933).

compounds which Kohler was able to cleave with the halogen acid were unattacked by sulfuric acid. However, those which did react added the elements of water or acetic acid in a predictable manner i.e. the ring was broken at the same bond as with hydrogen bromide.

The one exception was found with the cyclopropane hydroxy acids in which the hydroxyl group is on a carbon adjacent to the ring. When treated with either acid alone or in solution, this type of compound yielded an unsaturated addition product according to the following scheme:



where X is bromine, hydroxyl or acetate. This discrepancy, previously reported by Stoermer[14], was explained by assuming that dehydration occurs first. The resultant molecule may be likened to an allene if one considers cyclopropane to have ethylenic properties.



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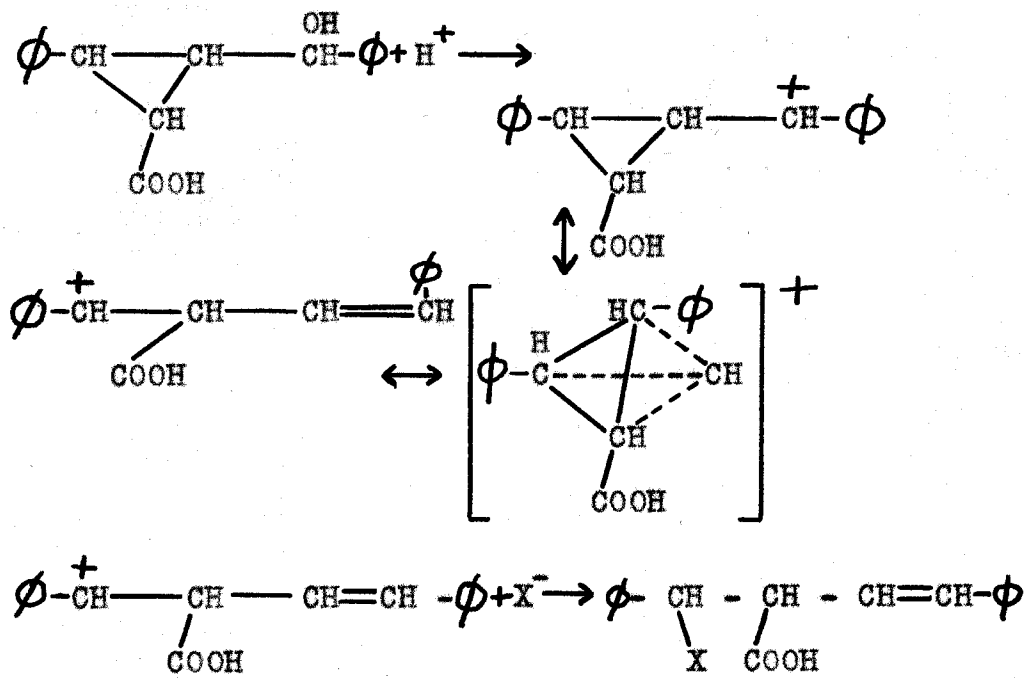
[14] R. Stoermer, F. Schenk, H. Pansegran, Ber., 60, 2566 (1927).

It has long been known that this type of compound is extremely unstable and it has also been shown that substituted allenes add in a 1,2 fashion[15].

Furthermore, the product can be predicted using the more modern mechanism shown below:



In other words, this apparent anomaly actually supports the theory of the olefinic nature of a three membered ring.

It must be pointed out at this point that although the cyclopropane derivatives used by Kohler and Allen behave like the corresponding α,β-unsaturated compounds in many respects, the reactivity seems to depend largely on the type and number of substituents on the ring. One is compelled, however, in

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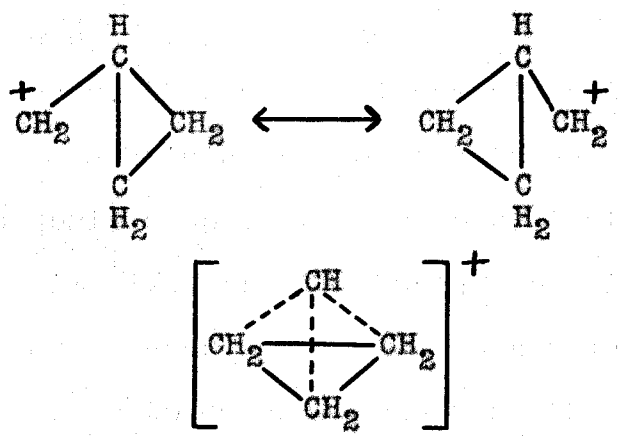
[15] W. Spatiew, J. Prakt. Chem., 55, 4 (1897).

the light of such a monumental amount of work, to accept the fact that there are certain similarities in the two systems.

A recent study by Roberts and Mazur[16] on the solvolysis of cyclopropylcarbinyl, cyclobutyl, methylallyl, allyl, and allylcarbinyl halides has yielded some rather surprising results. The rate of unimolecular solvolysis was greatest, in all cases, for the cyclopropylcarbinyl compounds.

An identical order of reactivity as observed almost simultaneously by Bergstrom and Siegel[17] who investigated the rates of solvolysis of the benzenesulfonates of cyclopropylcarbinol, allyl alcohol and 3-buten-1-ol.

This neighboring group participitation of the cyclopropane system is again well explained by the stability of the cyclopropylmethyl carbonium ion which may be stabilized by resonance as indicated by the following structures:



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[16] J. D. Roberts and R. H. Mazur, J. Am. Chem Soc., 73, 2509 (1951).

[17] C. G. Bergstrom and S. Siegel, Ibid., 74, 145 (1952).

The similarity of cyclopropane to ethylene is striking in these cases since both systems accelerate the solvolysis and both give rise to rearranged products.

On the other hand, it has been shown that vinyl and cyclopropyl halides are more resistant to solvolysis that their saturated alkyl analogs. This additional stability is probably a result of the fact that there is a certain amount of π bonding in the cyclopropane ring, as in ethylene, with the result that the carbon to halogen bond possesses more s character than the normal tetrahedral bond.

After a number of successful aromatic alkylations with olefins under the influence of typical Friedel-Crafts catalysts, Grosse and Ipatieff[18] were able to produce analogous reactions with cyclopropane as the alkylating agent. The important difference was that cyclopropane yields n-propylbenzene whereas alkylation with propane gives the isopropyl isomer.

More recent work by Fuson and Baumgartner[19] has shown that benzene and mesitylene can be alkylated with mesitylcyclopropyl ketone with the subsequent production of γ-phenyl- and γ-mesitylbutyromesitylene. The original ketone did not,

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[18] A. V. Grosse and V. N. Ipatieff, J. Org. Chem., 2, 447 (1937).

[19] R. C. Fuson and F. N. Baumgartner, J. Am. Chem. Soc., 70, 3255 (1948).

however, react with ethyl malonate or the Grignard reagent while mesitylpropenyl ketone gave the products expected from conjugate addition.

Grosse and Lind[20] added hydrogen fluoride to ethylene, propylene, cyclohexene and cyclopropane without a catalyst in the cold. In all cases they obtained the expected product, and the only side reaction of any importance was polymerization. The best yields of n-propyl fluoride were produced when the contact time was fifteen minutes. More prolonged reaction periods led to less of the desired adducts and more polymer.

Another type of reaction which may be pertinent is the polymerization of a series of hydrocarbons reported by Heisig[21] who used radon as his catalyst. It can be seen from Table I that cyclopropane once again exhibits properties intermediate between saturated and unsaturated hydrocarbons. Heisig explains the polymerizations simply as a result of the ion clusters formed by the passage of an α particle through the gases.

On the other hand, cyclopropane and its derivatives are inert to oxidation by permanganate and ozone, and has been

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[20] A. W. Grosse and C. B. Lind, J. Org. Chem., 3, 26 (1938).

[21] G. B. Heisig, J. Am. Chem Soc., 54, 2329 (1932).

shown, fail to undergo certain addition reactions if sufficiently substituted. Cyclopropyl cyanide and 1 phenyl-1 -cyanocyclopropane have been converted to their amides without cleavage, by base[22] or phosphoric acid[23].

Table I. Polymerization of Hydrocarbons by Radon

Hydrocarbon	$\frac{\text{(Vol. } H_2 \text{ and } CH_4 \text{ lost) X 100}}{\text{Vol. of hydrocarbon polymerized}}$	Molecules Condensed ion pair
Propane	82.3	1.7
Cyclopropane	20.5	3.3
Propylene	14.4	4.9
Propyne	6.1	8.3
Allene	4.9	10.4

Haller and Benoist[24] demonstrated the stability of the cyclopropane ring when they alkylated phenylcyclopropyl ketone with methyl iodide and benzyl chloride in the presence of sodium amide. Furthermore, they prepared their original ketone

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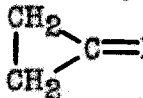
[22] P. Bruylants and A. Castille, Bull. Soi. Acad. Roy. Belg., 13, 767 (1928).

[23] E. C. Knowles and J. B. Cloke, J. Am. Chem. Soc., 54, 2028 (1932).

[24] A. Haller and E. Benoist, Ann. Chim., 17, 25 (1921).

by treating benzene with cyclopropanecarboxyl chloride and aluminum chloride. The ketone reacted with sodium amide in moist benzene to give cyclopropane and benzamide. These last examples bring to mind the unreactivity toward cleavage of the higher alicyclics and cannot be overlooked if a thorough comparison is to be made.

In his review of the chemistry of small ring rearrangements, Demjanow[25] states that cyclopropane systems are not like olefins. His reasons are (1) that the three membered ring is isomerized easily and irreversibly to a double bond and (2) that compounds of the type  are either incapable of existance or are, at best, extremely unstable. However, in an investigation of this sort, one cannot base theories on specific similarities or dissimilarities, but rather he must compare properties qualitatively and in a general sense. Thus, while Demjanow's arguments are correct, their scope is not broad enough to constitute a true comparison.

In 1917 Carr and Burt[26] presented spectroscopic results indicating that the cyclopropyl group can interact strongly when conjugated with unsaturated systems. Their theory has

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[25]N. Y. Demjanow, Uspekhi Khimii, U. S. S. R., 3, 493 (1934) C. A., 29, 458 (1935).

[26]Carr and Burt, J. Am. Chem. Soc., 40, 1590 (1918).

since been strengthened by Rogers[27] who observed shifts in the ultra-violet absorption maxima of methylcyclopropyl cyanide, phenylcyclopropane and cyclopropymethyl ketone toward longer wave lengths. The corresponding olefins produced shifts similar in direction but somewhat greater in magnitude. Corroborative evidence has also been presented by Roberts and Greene[28] in their investigation of a series of 2,4-dinitrophenylhydrazones and by Volkenburgh and his coworkers[29] who reported the spectrum of vinylcyclopropane.

Similarities in the infra-red spectra of cyclopropane and cyclobutane exist as shown by Derfer, Pickett and Boord[30] in their studies of a series of halides.

Cyclopropane is intermediate between ethylene and higher alicyclics in almost all of its physical properties including melting point, boiling point, density, parachor[31], molecular refraction, heat of combustion, heat of formation[32], bond

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[27]M. T. Rogers, ibid., 69, 2544 (1947).

[28]J. D. Roberts and Green, ibid., 68, 214 (1946).

[29]R. V. Volkenburgh, K. W. Greenlee, J. M. Dufer, C. E. Boord, ibid., 71, 3595 (1949).

[30]J. M. Derfer, E. E. Pickett and C. E. Boord, J. Am. Chem. Soc., 71, 2482 (1949).

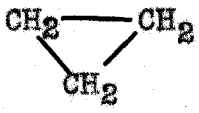
[31]G. H. Jeffrey and A. I. Vogel, J. Chem. Soc., 1804 (1948).

[32]J. W. Knowlton and F. D. Rossini, J. Research Natl. Bur. Standards, 43, 113 (1949).

order[33], bond distance[34] and thermal stability. However, the significance of these facts is somewhat dubious in view of the differences in molecular weight. and bond angle.

It should be noted that all of the chemical reactions thus far cited have been ionic in nature and that free radical reactions are conspicuously absent. One finds that the only reactions of cyclopropane with free radicals, reported in the literature, are those done in the vapor phase, and even then, only in the present of light or at elevated temperatures.

Cyclopropane is converted to 1,3-dibromopropane by bromine in sunlight but it can be substituted by chlorine in diffuse daylight to give chlorocyclopropane. The first of these reactions probably proceeds through radical addition (1), while the second involves hydrogen abstraction (2):

(1)  + $Br\cdot \longrightarrow Br(CH_2)_3\cdot$

$$Br(CH_2)_3\cdot + Br_2 \longrightarrow Br(CH_2)_3Br + Br\cdot$$

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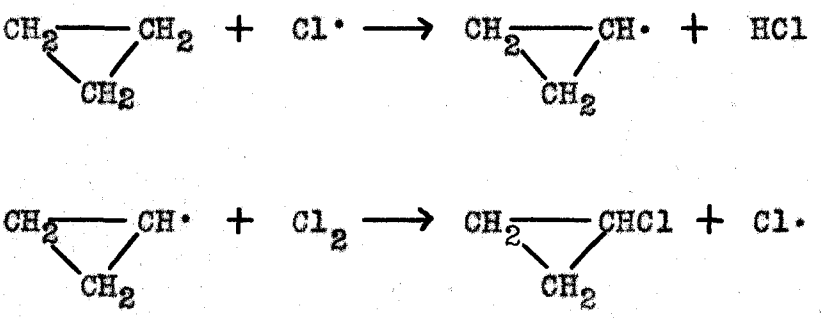
[33] G. N. Copley, Chemistry and Industry, 1941, 663.

[34] L. Pauling and L. O. Brockway, J. Am. Chem. Soc., 59, 1223 (1937).

(2) 

Both reactions are observed with ethylene and no doubt involve the same mechanisms respectively.

A radical initiated polymerization of cyclopropane has recently been reported by Scott and Gunning[35]. These authors photolysed pure cyclopropane in the presence of mercury vapor and presumably obtained a polymer of unknown constitution. Their theory, based on the absence of unsaturation, is that the product is cyclic and that the chain terminating reaction is the cyclization. The polymer is apparently a mixture of compounds of varying molecular weight, as shown by fractional distillation.

Ogg and Priest[36] studied the addition of iodine and bromine to cyclopropane and found that while iodine produced 1,3 -diiodopropane and no hydrogen iodide at 250°C. the rate of the reaction was insensitive to illumination by a tungsten lamp. Bromine and cyclopropane in visible light gave the 1,3 addition product along with some hydrogen bromide. The same

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[35] R. J. Scott and H. E. Gunning, J. Phys. Chem., 56, 156 (1952).

[36] R. A. Ogg and W. J. Priest, J. Am. Chem. Soc., 60, 217 (1938).

reaction, carried out in the dark at 250°C. yielded a large amount of hydrogen bromide and was, therefore, abandoned. Cyclopropane, when heated at 300°C. with hydrogen chloride, bromide, or iodide gave essentially no reaction.

Photochemical and thermal chlorination of cyclopropane have been shown by Roberts and Dirstine[37] to give approximately equal yields of chlorocyclopropane. The thermal reaction produces mostly allyl chloride as a by-product whereas the photochemical process gives rise to 1,1-dichlorocyclopropane along with the principal product. Roberts explains this as probably being due to the thermal instability of chlorocyclopropyl radical.

The three cyclopropane derivatives employed in the present investigation were cyclopropyl cyanide, cyclopropylmethyl ketone, and phenylcyclopropane. For each of these compounds there is a well-known, corresponding olefin, acrylonitrile, vinylmethyl ketone, and styrene respectively. It seems unnecessary to cite here the vast amount of research that has been carried out on the reactions of these olefins with various free radicals. Polymers invariably result and acrylonitrile and styrene are so sensitive that it is necessary to include a small amount of inhibitor when storing them for any length of time.

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[37] J. D. Roberts and P. H. Dirstine, ibid., 67, 1281 (1945).

In view of the extreme vulnerability of olefins to attack by free radicals, it appeared not unlikely that the same analogies in reactivity should be observed with the cyclopropyl systems as have been found in the case of ionic reagents.

EXPERIMENTAL

Materials Purchased

Acetone, Baker and Adamson reagent grade B. P. 56.5°C., was used in the styrene polymerizations without further purification.

Acetonitrile, Eastman Kodak Company B. P. 82°C., was used as obtained.

Acetyl chloride, Eastman Kodak Company B. P. 51-2°C., was taken from a sealed vessel and used immediately in the preparation of acetyl peroxide.

Benzoyl peroxide, Eastman Kodak Company M. P. 106-7°C., was used without further purification since iodine titration indicated 99.97% purity.

Cinnamaldehyde, Magnus, Mabee and Reynard Inc., U. S. P., B. P. 250°C., was considered to be of sufficient purity and was therefore used as received.

Cinnamyl alcohol, Eastman Kodak Company M. P. 33°C., was used as obtained.

Epichlorohydrin, Eastman Kodak Company B. P. 117°C., was used directly from the container.

Hydrazine Hydrate, Paragon Division of the Matheson Company, Inc., was used without further purification.

Lithium amide and sodium hydride, Metal Hydrides, Inc., were taken directly from their containers.

Styrene, Eastman Kodak Company styrene was distilled away from the stabilizer at reduced pressure*. The fraction boiling 49-50°C. at 21 mm. was used immediately after the completion of the distillation.

Toluene was distilled through a vacuum-jacketed column packed with helices, and the fraction boiling at 110°C. was used throughout the vicosity work.

Trimethylene chlorobromide, Eastman Kodak Company B. P. 142-3°C., was used without further purification.

Vinyl acetate, Eastman Kodak Company B. P. 72-3°C., was used directly even though it contained a trace of stabilizer.

Materials Synthesized

Cyclopropanol.

The preparation of cyclopropanol was carried out according to the method of Magrane and Cottle[38] with a few modifications. One mole (92 grams) of epichlorohydrin in 200 c.c. ether was added slowly to 1.1 moles of freshly prepared ethyl magnesium bromide in a two liter flask. During the addition,

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*All distillations carried out in this work were done through a vacuum-jacketed, centre-rod column (44 theoretical plates), unless otherwise specified.

[38] J. K. Magrane and D. L. Cottle, J. Am. Chem. Soc., 64, 484 (1942).

the reaction was stirred constantly and cooled in an ice-bath. To this mixture was added a second mole of freshly prepared grignard reagent in ether, sufficient to make the total volume 1500 c.c. The reaction was allowed to stand for five days after which time it was hydrolysed with a saturated ammonium chloride solution. The ether layer was separated, dried over sodium sulfate for ten days and the solvent removed by distillation. Further distillation at 35 mm. yielded about five c.c. of colorless liquid boiling at 53-60°C. The product boiled at 105-110°C. at atmospheric pressure, had a peculiar odor, turned yellow upon standing, and rapidly decolorized bromine in carbon tetrachloride. All attempts to make a 3,5-dinitrobenzoate failed.

The water layer from the hydrolysis was extracted with ether and the ether treated exactly as given above. Two ml. of liquid were recovered which appeared to be the same as the original product.

Diazomethane.

Diazomethane was prepared by the base catalysed decomposition of N-Nitrosomethylurea[39] employing a modification of the method of Arndt[40]. A two liter, three-necked, round-

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[39]F. Arndt, Org. Syn., 15, 48 (1935).

[40]Ibid., p. 3.

bottomed flask was fitted with a rubber sleeve leading from a small Erlenmeyer flask which contained the N-Nitrosomethylurea, a nickel stirrer, a pressure outlet and a condenser set for rapid distillation. The condenser outlet was placed below the surface of 100 c.c. of ether in a 1 liter erlenmeyer flask cooled in an ice-salt bath. This flask was connected in series to a similar second trap. In the round-bottomed flask were placed 120 c.c. of 70 per cent aqueous potassium hydroxide and 500 c.c. of anhydrous ether. The system was cooled to 0°C. while being stirred and 41 grams of N-Nitrosomethylurea were added through the rubber sleeve at a moderate rate. The temperature then was raised enough to distil the ether and diazomethane rapidly until two-thirds of the ether had come over. It was found that the yield of diazomethane could be increased by the addition and distillation of some fresh ether if considerable yellow color remained in the reaction vessel after the original distillation.

Attempted preparation of cyclopropyl acetate.

It was thought that the reaction between vinyl acetate and diazomethane would produce either cyclopropyl acetate or the pyrazoline which could be pyrolysed to the desire compound. Vinyl acetate, in ether solution, was added to the ether solution of diazomethane and the mixture refluxed gently for one hour. The heat was then removed and the reaction allowed to stand for two days during which the color of the diazomethane failed to disappear but a white, gelatinous

precipitate did form. This precipitate gave no test for nitrogen and had no sharp melting point, so it was considered to be a polymer arising from either the diazomethane or the vinyl acetate.

The excess diazomethane was decomposed with benzoic acid and the ether removed by distillation. The only recoverable products from the residue were methyl benzoate and vinyl acetate.

A second attempt was made to prepare cyclopropyl acetate, this time using the method of Friess[41]. A 500 c.c. Erlenmeyer flask containing .14 mole of perbenzoic acid (prepared by the method of Braun[42]), .12 mole of cyclopropylmethyl ketone, and five c.c. glacial acetic acid in 400 c.c. moist chloroform was allowed to stand for 19 days in the dark at room temperature. The disappearance of perbenzoic acid was followed by periodic titration of aliquots of the mixture iodometrically.

The mixture was washed with dilute sodium hydroxide, dried and distilled. The fraction boiling at 98°C., $n_D^{20^\circ}$ 1.3870, was considered to be the desired product, and amounted to 5.4 c.c. It showed no reaction with aqueous permanganate, but decolorized bromine in carbon tetrachloride

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[41] S. L. Friess, J. Am. Chem. Soc., 71, 14 (1949).

[42] G. Braun, "Organic Syntheses", Fifth Printing, Col. Vol. I, John Wiley and Sons, Inc., New York, 1948, p. 431.

and gave a positive ferric hydroxamate test[43]. The p-toluidide of the acid portion of this apparent ester was made by the method of Koelsch and Tenenbaum[44] and gave no depression in a mixed melting point with authentic acetyl-p-toluidine. Although the product may have been cyclopropyl acetate, it seemed impractical to make it in quantities large enough for our use, so work was discontinued.

Sodamide.

About 250 c.c. of liquid ammonia was poured into a 500 c.c. three-necked flask equipped with a stirrer and condenser and cooled in a dry ice-acetone bath. A small crystal of hydrated ferric nitrate and a 5 mm. cube of freshly cut sodium were added and the solution turned deep blue. When the color had changed from blue to gray, 8.1 grams of sodium, cut into thin strips were added rapidly and the solution again became blue. Upon the reappearance of the gray color, 100 c.c. of dry ether were added to the solution and the amonia was allowed to evaporte, leaving the desired suspension of sodamide in ether.

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[43] N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis", Thomas Y. Crowell Company, New York, 1947, p. 121.

[44] F. Koelsch and D. Tenenbaum, J. Am. Chem. Soc., 55, 3049 (1933).

Cyclopropyl cyanide.

This compound was prepared by a method similar to that of Cloke[2]. In one liter Dewar flask were placed 250 c.c. of liquid amonia and 21 grams of γ-chlorobutyronitrile (prepared by the method of Allen[45]). An ether suspension of ten grams of freshly prepared sodamide was added two or three drops at a time through a long-stemmed separatory funnel, the flask being shaken after each addition. The addition was completed in one hour and the reaction was allowed to stand for another hour with shaking every five or ten minutes.

The excess sodamide was neutralized with two to three grams of ammonium chloride to a phenolphthalein end point and 100 c.c. of dry ether was added. The ammonia was volatilized by passing dry air into the flask and the residual ether solution was filtered through a fluted filter to separate it from the inorganic salts. The ether solution was dried with calcium chloride and the solvent removed by distillation. Crude cyclopropyl nitrile was distilled at reduced pressure and the fraction boiling at 35-45°C. at 21 mm. collected as product. This was carefully redistilled at atmospheric pressure and the fraction boiling at 131.5-2°C. used throughout the experimental work. The yields were 55-66%, $N_D^{20^\circ}$ 1.4161, Sp. Gr.0.894.

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[45]C. F. H. Allen, "Organic Syntheses", Fifth Printing, Col. Vol. I, John Wiley and Sons, Inc., New York, 1948, p. 156.

One run was made using lithium amide in place of sodamide and no recoverable amount of product was obtained.

When 0.26 mole of sodium hydride was added as an ether suspension to an equimolar quantity of γ-chlorobutyronitrile in 50 c.c. of ether, no reaction was evident. After the reaction had been stirred overnight at room temperature, then at reflux for two hours without visible change, a few drops of ethyl acetate, ethyl alcohol and, finally, water were added in an attempt to initiate a reaction. When the mixture was worked up, the γ-chlorobutyronitrile was recovered almost quantitatively.

Cyclopropylmethyl ketone.

This compound was prepared according to the method of Bruylants[46] using γ-chlorobutyronitrile and two moles of methyl magnesium iodide. However, it was found that the ketone could be obtained from the Matheson Company, so large scale preparation was abandoned. The commercial material was distilled through a vacuum-jacketed column packed with helices and the fraction boiling at 110-1°C. was used throughout the experimental work.

Cinnamyl bromide.

This compound was prepared by heating and stirring one mole of cinnamyl alcohol with 3 moles of 48% hydrobromic acid

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[46]P. Bruylants, Rec. Trav. Chim., 28, 180 (1909).

for one-half hour. The solution was allowed to separate into two layers, and the product was taken up in ether. The ether solution was washed with dilute sodium carbonate, then with water, dried over calcium chloride and distilled through a Claisen head until the ether ceased coming over. Distillation was continued at five mm. and the product was collected at 103-8°C, in a 48% yield.

1-Phenyl-1,3-dibromopropane.

This compound was prepared by saturating 46.5 grams of cinnamyl bromide with hydrogen bromide at -65°C., placing the mixture in a sealed bomb, and heating for five hours at 95-105°C. The reaction mixture was distilled at 5 mm. through a Claisen head and the fraction boiling at 120-130°C. was collected as crude product. Yield 46%.

Attempted preparation of phenylcyclopropane.

This preparation involved mixing 30.6 grams of crude 1-phenyl-1,3-dibromopropane with 50 c.c. of ethyl alcohol and ten grams of powdered zinc, and refluxing for twenty minutes. At the end of this time, the solution no longer had the cloudy appearance of the original mixture, and the zinc dust and zinc salts had settled to the bottom of the flask. The mixture was filtered and poured into warm water at which time an oil separated. Treatment of the oil, suspended in a large volume of water, with 1% permanganate yielded a large amount of manganese dioxide and no product could be isolated after the oxidation.

5-Phenyl-3-pyrazoline.

This compound was prepared according to the method of Lardelli and Jeger[47]. A mixture of 80 c.c. (90 grams) of cinnamaldehyde, 50 c.c. (45 grams) of hydrazine hydrate, and 180 c.c. of absolute ethyl alcohol was refluxed for four hours. The alcohol was removed at reduced pressure and the pyrazoline subjected to a short path distillation at 14 mm. The product was collected at 138-148°C. Crude yield was 40-60% for several runs.

Phenylcyclopropane.

This compound was prepared by a modification of the method of Kishner[48]. A mixture of 118 grams of 5-phenyl-3-pyrazoline, 30 grams of pulverized potassium hydroxide, and 2.5 grmas of platinized asbestos was heated in a one liter, three-necked, round-bottomed flask equipped with a stirrer and a Claisen head set for short path distillation. The temperature was raised slowly by means of a Glas-col heating mantle and the mantle shut off at the first evidence of reaction. When the reaction had apparantly ceased, the temperature was again raised and the product was distilled as it was produced. Both the distillate

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[47]G. Lardelli and O. Jeger, Helv. Chim. Acta., 32, 1817 (1949).

[48]N. Kishner, J. Russ, Phys. Chem. Soc., 45, 949 (1913), C. A., 7, 3965 (1913).

and the residue were steam distilled, combined, taken up in ether, dried with sodium, and redistilled. The product boiled at 60-63°C. at 11 mm. (173.5°C. at atmospheric pressure) and the yield was 11.5 grams (12%), $n_D^{20°}$ 1.5320.

Platinized asbestos.

Platinized asbestos was prepared by the method of Shiels[49]. Two grams of fibrous asbestos were boiled for a short time in 100 c.c. of 5% sodium formate with occasional stirring. To this mixture was added 1.137 grams of platinum chloride in the form of a 5% aqueous solution previously neutralized with solid sodium carbonate. The whole mixture was stirred and boiled gently for ten minutes and filtered through a Buchner funnel. The crude material was washed in the funnel successively with hot 10% sulfuric acid, hot distilled water, hot 5% hydrochloric acid, and, finally, hot distilled water until the fitrate showed no chloride or sulfate ions to be present. The product was dried overnight in an oven at 110°C.

Phenylethyl carbinol.

This compound was prepared in normal fashion by the action of phenyl magnesium bromide on acetaldehyde. The product boiled at 108-110°C. at 15 mm. and was used after a single distillation.

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[49] D. O. Shiels, J. Phys. Chem., 33, 1167 (1929).

β-Methylstyrene.

This compound was prepared by the dehydration of phenylethyl carbinol with phosporic acid according to the method of Dehn and Jackson[50]. The product distilled at 53-6°C. at 11 mm., $n_D^{20°}$ 1.5461.

Experimental Techniques

Decomposition of benzoyl peroxide in cyclopropyl cyanide.

In a large test tube were placed 10.582 grams of cyclopropyl cyanide and .529 grams of benzoyl peroxide. The tube was cooled in a dry ice-acetone bath, evacuated, and sealed. After being heated in a constant temperature bath at 82°C. for twenty-four hours, the contents of the tube were distilled at atmospheric pressure. The distillate proved to be pure cyclopropyl cyanide and recovery was essentially quantitative.

An equimolar amount of benzoyl peroxide (20.13 grams) was added to 11.098 grams of cyclopropyl cyanide in a 500 c.c. flask with 250 c.c. of carbon tetrachloride as a diluent. The flask was sealed and heated as in the previous case. When the system was opened, there was evolution of a considerable amount of gas which was assumed to be carbon dioxide. Distillation gave a 10 c.c. fraction boiling at 126-7°C. and left a residual solid which consisted mostly of p-trichloromethyl-

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[50] W. M. Dehn and K. E. Jackson, J. Am. Chem. Soc., 55, 4285 (1933).

benzoic acid as shown by a mixed melting point with an authentic sample.

The liquid product had an ultra-violet spectrum quite different from that of pure cyclopropyl cyandie and gave a positive Beilstein test for chlorine. It was found that a mixture of five c.c. each of chlorobenzene and cyclopropyl cyanide behaved, in all respects, like the liquid from the reaction during distillation. We concluded, therefore, that our product was only an azeotrope of the nitrile and chlorobenzene.

Decomposition of azo-bisdiethylacetonitrile in cyclopropyl cyanide[51].

Pure cyclopropyl cyanide (8.907 grams) and .917 grams of azo-bisdiethylacetonitrile were heated together in a constant temperature bath at 82°C. under a nitrogen atmosphere for twenty-two hours. Distillation of the mixture produced only one liquid fraction which had the boiling point and refractive index of cyclopropyl cyanide. A solid remained in the flask which after a single recrystallization, gave no depression of melting point when mixed with authentic bisdiethylsuccinonitrile.

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[51]The author would like to thank George B. Lucas of Iowa State College for making available generous quantities of azobisdiethylacetonitrile and bisdiethylsuccinonitrile.

Decomposition of acetyl peroxide in cyclopropyl cyanide.

Acetyl peroxide (.67 mole in 95 c.c. carbon tetrachloride prepared by the method of Kharasch[52]) was added through a long-stemmed separatory funnel to 5 c.c. of cyclopropyl cyanide heated at 90-100°C. The resultant mixture was heated for one-half hour after the addition, washed with dilute sodium hydroxide dried and distilled. After the solvent had come over and three c.c. of nitrile had been collected, a solid was formed at the bottom of the column, so the distillation was discontinued and the solid product worked up. The compound was found to be hexachloroethane, and no other products could be isolated.

When a similar decomposition of the peroxide was carried out in acetonitrile, a small but definite yield of succinonitrile resulted.

Reaction of cyclopropyl cyanide with triphenylmethyl.

Pure cyclopropyl cyanide (five c.c.) was added to triphenylmethyl (prepared by the method of Hammond[53]) and the mixture was allowed to stand at room temperature in a sealed system for five days. Iodometric titration of the radical at the beginning and end of this period indicated no appreciable decrease in radical concentration, and the color of the

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[52]M. S. Kharasch et al, J. Am. Chem. Soc., 63, 526 (1941).

[53]G. S. Hammond, J. T. Rudesill and F. J. Modic, Anal. Chem., (in press 1951).

solution, characteristic of the radical, failed to disappear. Stirring in the presence of air produced triphenylmethyl peroxide which melted at 182-4°C.

Polymerization of styrene in the presence of cyclopropyl cyanide.

Equal volumes (10 c.c.) of cyclopropyl cyanide and styrene were mixed, evacuated and sealed. The mixture was heated for twenty hours at 78°C., then distilled at 23 mm. Fraction I came over at 41-41.5°C. and had a refractive index of 1.4655. A second fraction distilled at 41.5-44°C. and its refractive index was 1.4826. In view of the fact that the total volume of the two fractions exceeded that of the original cyclopropyl cyanide, and that their refractive indices were midway between those of styrene (1.5449) and the nitrile (1.4161), the product was considered to be an azeotropic mixture of starting materials.

The infra-red spectrum of the polymer isolated from a second sample, prepared and treated in exactly the same way, failed to indicated an absorption in the region of 4.5 microns, the typical frequency for the nitrile linkage.

The polymerization of styrene in the presence of cyclopropylmethyl ketone.

Approximately equimolar quantities of styrene and cyclopropylmethyl ketone were mixed with a catalytic amount of benzoyl peroxide. The mixture was divided into seven parts and placed in large test tubes (22x175 mm.) whose necks had

been previously constricted. The separate ampules were cooled to -75°C. in a dry ice-chloroform-carbon tetrachloride mixture and evacuated for a short time. The systems were closed with stopcocks and allowed to warm to room temperature at which time the freezing and evacuation was repeated. After this procedure had been carried out three times, the cooled ampules were sealed with a torch and were heated at 78°C. in a constant temperature bath. Periodic determination of the styrene and peroxide concentrations by iodometric titration (described below) served as a method of following the course of the reaction. All runs, including the controls with acetone in place of cyclopropylmethyl ketone, were carried out in the above manner.

Analytical procedure for benzoyl peroxide.

An aliquot of known volume (usually 10 c.c.) was withdrawn from the reaction vessel as soon as it had been opened. To this aliquot, in a 500 c.c. Erlenmeyer flask, were added 30 c.c. of glacial acetic acid, 2 c.c. of saturated aqueous potassium iodide, and several small pieces of dry ice. The system was allowed to stand for ten minutes with occasional swirling and addition of more dry ice. At the conclusion of this time, the system was diluted with 100 c.c. of distilled water and the liberated iodine was titrated with standard sodium thiosulfate solution to a starch end-point.

Analytical procedure for styrene.

A small sample from each ampule was weighed directly into a 100 c.c. volumetric flask, following the withdrawal of the aliquot for the peroxide determination. The sample was diluted to 100 c.c. with carbon tetrachloride and mixed thoroughly. A 10 c.c. aliquot from the carbon tetrachloride solution and 25 c.c. of standard bromide-bromatic solution were placed in a 300 c.c. Erlenmeyer flask equipped with a three-way inlet funnel connected through a standard taper joint. The system was partially evacuated and two to three c.c. of 6N sulfuric acid and 10 c.c. of glacial acetic acid were added through the funnel. After the flask had been shaken for two to three minutes, two c.c. of saturated aqueous potassium iodide were added and oxidized to iodine by the excess bromine. The iodine was titrated with standard sodium thiosulfate to a starch end-point as before.

Determination of polymer molecular weights.

Polystyrene resulting from several typical polymerizations in the presence of cyclopropylmethyl ketone or acetone was precipitated by pouring the reaction mixture slowly into 100 c.c. of methanol with vigorous stirring. After being filtered and dried the polymers were dissolved in benzene and lyophilized for further purification. They were used, in this condition, for the determination of their average molecular weights.

The average molecular weights of the polymers were calculated from the viscosities of their toluene solutions at various concentrations, using the Staudinger relationship $[\eta]=KM^{\alpha}$ where $[\eta]$ is the intrinsic viscosity, K and α are suitable constants, and M is the average molecular weight. The intrinsic viscosity, defined as $\lim_{C \to 0} \eta_r-1 /C$ where η_r is the relative viscosity, and C is the concentration in grams of polymer/100 c.c. of solution, is determined by plotting η_r-1 vs. concentration and extrapolating to $C = 0$. The constants, K and α were those reported by Pepper[54] for unfractioned polystrene in toluene.

The results of the molecular weight determinations are shown in Table II (Discussion of Results).

The infra-red spectra of the polymers were practically identical with that of polystyrene prepared by bulk polymerization.

Decomposition of benzoyl peroxide in cyclopropylmethyl ketone and acetone.

Mixtures of benzoyl peroxide and either cyclopropylmethyl ketone or acetone were placed in separate ampules and sealed using a procedure exactly the same as that used in the styrene polymerization experiments. The samples were heated at 78°C.

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[54]D. C. Pepper, J. Polymer. Sci., 7, 347 (1951).

and the course of the peroxide decomposition was followed by periodic iodometric titration as before. These kinetics, when treated by the method of Bartlett and Nozaki[55] indicated that there is little or no greater amount of chain decomposition of the benzoyl peroxide in one solvent than the other.

Decomposition of acetyl peroxide in cyclopropylmethyl ketone.

Freshly prepared acetyl peroxide was decomposed in a 10 - 20 fold excess of cyclopropylmethyl ketone according to the method of Kharasch[56]. The methyl acetate, acetic acid and excess ketone were distilled at 50 mm. and the residue at two mm. About two c.c. of liquid boiling at 35°-40°C. (174°-5°C. at atmospheric pressure) were isolated. This product gave a positive test with 2,4-dinitrophenylhydrazine solution and a weak iodoform test. The infra-red spectrum of the product showed absorption in the regions 3.2 to 3.3, 9.8 and 10.9 to 11.7 microns.

Decomposition of benzoyl peroxide in cyclopropylmethyl ketone.

A mixture of ten grams of benzoyl peroxide and twenty c.c. of cyclopropylmethyl ketone was sealed in an evacuated 250 c.c. flask and heated at 78°C. for twenty hours. Upon distillation, 11.5 c.c. of cyclopropylmethyl ketone were recovered and the residue darkened considerably. The residue was extracted with

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

[56] M. S. Kharasch, J. Am. Chem. Soc., 65, 15 (1943).

five percent aqueous sodium hydroxide which, in turn, was extracted with ether. Evaporation of the ether produced a small amount of oily material. When the aqueous phase was acidified, another oil separated, from which benzoic acid could be sublimed. The oil from the acidification finally solidified to an amorphous material which, when recrystallised from an ethyl alcohol - water mixture , darkened at 189°C. and melted with decomposition at 192°-6°C. The solid gave a questionable phenylhydrazone test and its infra-red absorption spectrum indicated only a carbonyl linkage and a carboxyl group. The spectrum did, however, compare closely with that of one of the products of benzoyl peroxide decomposition in phenylcyclopropane.

Decomposition of benzoyl peroxide in phenylcyclopropane.

Ten c.c. of impure phenylcyclopropane was heated overnight at 78°C. with .5 gram of benzoyl peroxide in a sealed, evacuated tube. The mixture was distilled at 11 mm. and 8.5 c.c. of phenylcyclopropane came over at 60°C. leaving a residue of benzoic acid and about one c.c. of liquid, presumably a mixture of phenylcyclopropane and β-methylstyrene, possibly in the form of a low polymer.

A second decomposition was carried out, this time using 20 c.c. of phenylcyclopropane and 10 grams of benzoyl peroxide in a 250 c.c. system, evacuated and sealed before use. The mixture was heated for 20 hours at 78°C., then distilled

at 9 mm. Fifteen c.c. of phenylcyclopropane was recovered before distillation was discontinued. The residue was extracted with five percent aqueous sodium hydroxide and chloroform. When the aqueous layer was acidified with hydrochloric acid, 4.5 grams of benzoic acid contaiminated with some phenylcyclopropane, and some other material, precipitated. Evaporation of solvent from the chloroform layer left an oily residue which solidified on cooling. The material did not burn cleanly and failed to melt sharply, hence it was considered to be either a polymer of β-methylstyrene or a mixture of decomposition products of benzoyl peroxide. The infra-red absorption spectrum was very similar to that of the solid isolated from the decomposition of benzoyl peroxide in cyclopropylmethyl ketone and indicated no cyclopropyl linkage. Although the solid was undoubtedly a mixture or products, comparison of the two spectra with that of pure benzoic acid demonstrates that the amount of benzoic acid is probably small. (See Plate III).

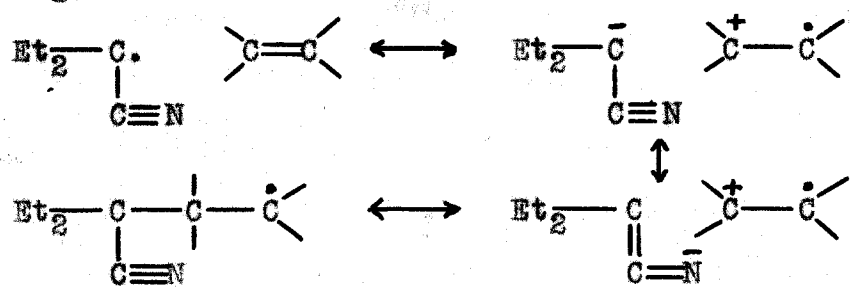
Finally, 11 c.c. of phenylcyclopropane, recovered from the previous run and considered to be of high purity, was treated with 5.5 grams of benzoyl peroxide using the same procedure as before. After being heated for twenty hours, the reaction mixture was distilled at 12 mm. and 8.5 c.c. of phenylcyclopropane, boiling at 61°-62°C., was recovered. A 0.5 c.c. fraction was collected between 62° and 120°C. and

had a refractive index identical to that of pure phenylcyclopropane (1.5316). The residue was extracted as before and acidification of the basic extract yielded over one gram of benzoic acid, along with a small amount of a rather amorphous, water insoluble, substance from which benzoic acid could be sublimed. After recrystallization from ethyl alcohol the solid melted at 206°-210°C. and gave no melting point depression when mixed with the solid resulting from the decomposition of benzoyl peroxide in cyclopropylmethyl ketone.

DISCUSSION OF RESULTS

In their determination of the monomer reactivities of various substituted styrenes and vinyl heterocycles Walling and his co-workers[57] have defined styryl as an electron donor radical and methacrylyl as an electron acceptor radical. These terms, previously employed by Bartlett and Nozaki[58] with reference to styrene and maleic anhyride, respectively, are concerned with the contribution of non-bonded resonance structures to the transition state of the reaction between two monomers in a copolymerization.

Of the radicals used in our work, one finds three of the electron acceptor type. They are bonzoate, acetate and diethylcyanomethyl. Each of these, when undergoing chemical reaction, should gain considerable stability from structures typified by the following:



As an example of an electron donor radical, it is clear

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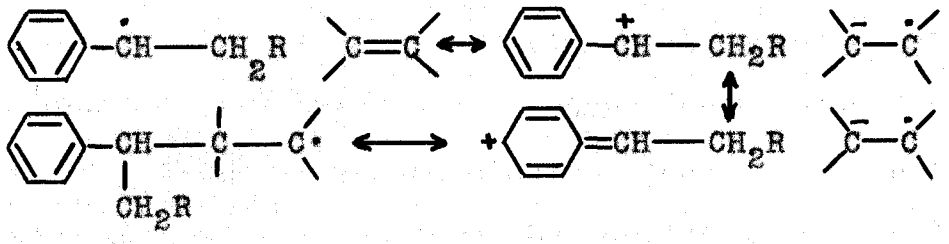
[57] C. Walling, E. Briggs, K. Wolfstein and F. Mayo, J. Am. Chem. Soc., 70, 1537 (1948).

[58] P. D. Bartlett and K. Nozaki, ibid., 68, 1495 (1946).

that the growing styryl radical is stabilized by structures involving electron transfer from the radical.



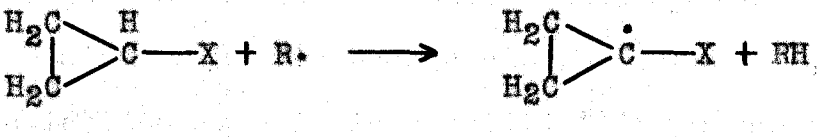
An olefin is convenient to use as a point of attack in these cases because it can act as either an electron acceptor or donor molecule.

Triphenylmethyl radical should be classed as a donor radical, although it is somewhat weaker than styryl in this respect. Despite the high resonance energy of the triphenylcarbonium ion, the inherent stability of the radical itself makes it reluctant to lose its unpaired electron.

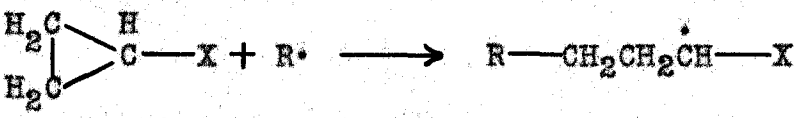
During the first part of this work, acetate, benzoate and diethylcyanomethyl radicals exclusively were used to test the reactivities of our cyclopropene derivatives. It became apparent, however, that this would involve an attack by an acceptor radical on molecules which should, themselves, be electron acceptors. Hence we chose to investigate the reactivities of the cyclopropanes toward the growing styryl radical.

If radicals were to attack the cyclopropane system one would expect to observe oneof two possible reactions. The first of these is hydrogen abstraction which has been found to occur between many different radicals and the solvents in which

they are produced. This type of reaction is particularly prevalent with saturated hydrocarbons although hydrogen abstraction from aromatic systems is not uncommon.



The alternate reaction would be one involving radical addition to the cyclopropane derivative with simultaneous ring cleavage.



Addition reactions are frequently observed between free radicals and a variety of unsaturated systems. It is interesting to note that all three of the olefins analogous to the cyclopropane derivatives employed in this study undergo reactions of the addition type with great facility.

Cyclopropyl cyanide is completely insensitive to all radicals used in the experimental work, as witnessed by the fact that all of the original nitrile could be accounted for in every case (allowing for losses during the process of working up the reaction mixture). One might expect a certain amount of added stability as a result of the deactivation by the substituent on the ring, but the fact remains that acrylonitrile exhibits no such unreactivity.

That benzoate radicals do not attack cyclopropyl cyanide

is demonstrated by the fact that no isolable amount of product, apart from the original nitrile and benzoic acid, could be recovered from the decomposition of benzoyl peroxide in this solvent. Further indication of the insensitivity of the nitrile is the preferential attack of the benzoate radical on carbon tetrachloride when the latter was used as a diluent for the reaction. The products found, p-trichloromethylbenzoic acid, carbon dioxide and chlorobenzene, are known to be the normal ones arising from the decomposition when it is carried out in pure carbon tetrachloride[59].

Other work in our laboratory has shown that a high yield of bis-diethylsuccinonitrile from the decomposition of azo-bis-diethylacetonitrile is indicative of the unreactivity of the solvent in which the decomposition is carried out[60]. Since no product except the substituted succinonitrile and the original cyclopropane derivative could be found, one must conclude that there is no reaction between the diethylcyanomethyl radical and cyclopropyl cyanide.

The failure of acetate radical to attack cyclopropyl cyanide is, perhaps, not too surprising in view of the fact that the yield of the dimer from the control run with acetoni-

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[59]S. Kambara and T. Futsu, J. Chem. Soc. Japan, Ind. Chem. Sect., 51, 113 (1948).

[60]Unpublished observations of George B. Lucas, Iowa State College.

trile was extremely small. On the other hand we may not be working with acetate radicals in this case, but actually with methyl radicals. At any rate, none of the radicals produced by the decomposition of acetyl peroxide appear to be sufficiently reactive to affect the nitrile.

As far as electron donor radicals are concerned, neither triphenylmethyl nor growing styryl radicals undergo any reaction with cyclopropyl cyanide. The fact that there was no appreciable change in radical concentration during the reaction period and the isolation of triphenylmethyl peroxide after exposure to the air are sufficient proof that the nitrile is not attacked by triphenylmethyl. Although cyclopropyl cyanide was recovered from the reaction with styrene only as an azeotrope with the monomer, the infra-red spectrum[61] of the resultant polymer shows no absorption in the region of 4.5 microns. Since the nitrile linkage has a very sharp band in this region, we can say that no copolymerization or chain transfer has taken place during the reaction.

Since the mechanism and the kinetics of styrene polymerization have been treated so exhaustively in the literature, it seemed logical to study the reactivity of cyclopropylmethyl ketone toward the growing styryl radical from a kinetic

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[61]We are indebted to the Institute of Atomic Research for use of their Baird Infra-red Spectrophotometer and in particular to Richard M. Hedges who ran all of the spectra reported in this thesis.

point of view. The method used was particularly convenient since the titration of both species to be determined was carried out iodometrically. Typical plots used to calculate the rate of consumption of peroxide and polymerization of styrene are shown in Figures I and II. Data for several typical runs are compiled in Table II.

Table II. Kinetic Data from Styrene Polymerization

Run	Mole Fraction Solvent	P_o	k_1	K'	$K' \times k_1^{\frac{1}{2}}$
7	.501	.00788	.1314	16.50	5.98
8	.501	.00864	.1425	13.81	5.22
9	.501	.00444	.1164	19.25	6.57
10	.484	.00482	.1248	15.40	5.44
11	.498	.00892	.1473	11.85	4.55
12	.553[a]	.0218	.2250	10.50	5.09
13	.553[a]	.00784	.1433	13.44	5.98

[a]Runs with acetone

In deriving the kinetic law, P is defined as the peroxide concentration, M as the monomer concentration, k_1, k_2, k_3, and k_4 as the rate constants for the initiation, propogation, transfer, and termination of the chain, respectively, and K' is the overall rate constant for the polymerization process.

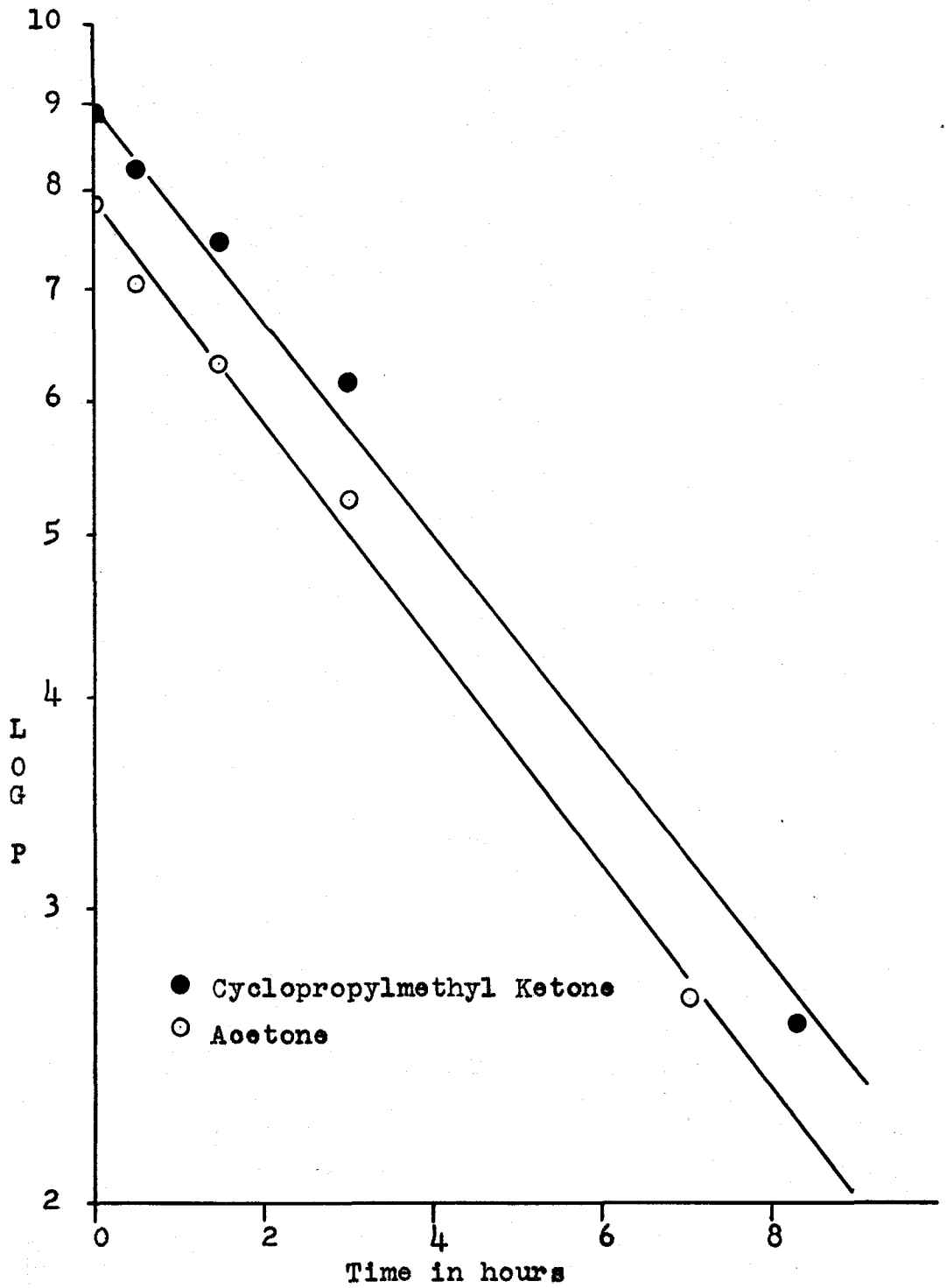

Figure I. Rate of consumption of peroxide

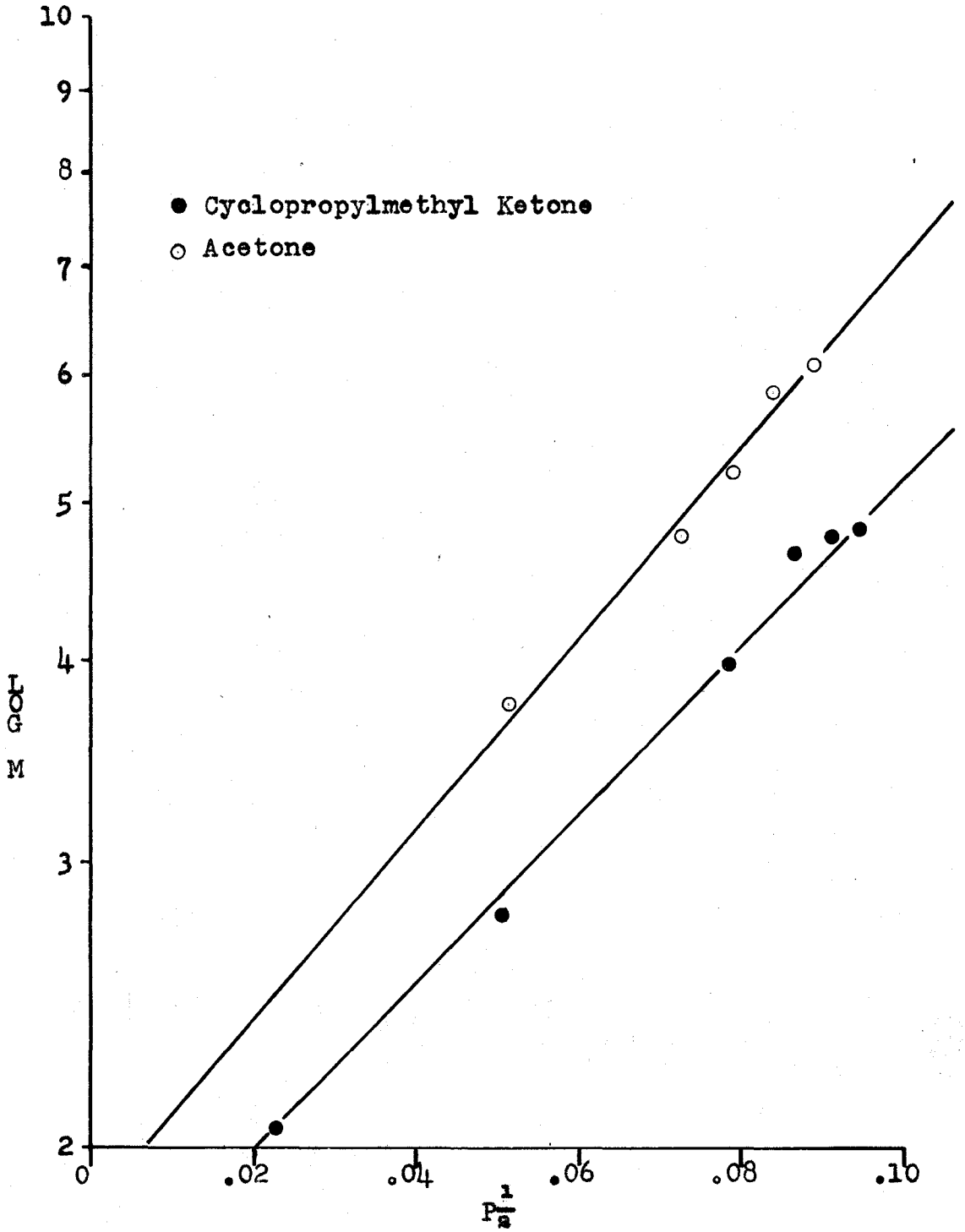

Figure II. Overall rate of polymerization

$$P \xrightarrow{k_1} 2R\cdot$$

$$R\cdot + M \xrightarrow{k_2} R\cdot$$

$$R\cdot + SH \xrightarrow{k_3} RH + S\cdot$$

$$2R\cdot \xrightarrow{k_4} R{-}R$$

$$\frac{d[R\cdot]}{dt} = 2k_1[P] + 2k_4[R\cdot]^2 \cong 0$$

Assuming a steady state for R·,

$$[R\cdot] = \left(\frac{k_1}{k_4}[P]\right)^{\frac{1}{2}}$$

and

$$-\frac{d[M]}{dt} = k_2[R\cdot][M]$$

$$\frac{\ln[M]}{2} = k_2\left(\frac{[P]}{k_1 k_4}\right)^{\frac{1}{2}} + C$$

$$\frac{K'}{2} = k_2\left(\frac{1}{k_1 k_4}\right)^{\frac{1}{2}}$$

Assuming that k_4 is approximately equal for all runs, it follows that k_2 is proportional to the product of K' and $k_1^{\frac{1}{2}}$. Although the range of calculated values, as shown in Table II, is fairly large, it should be noted that the value of $K' \times k^{\frac{1}{2}}$ for the control runs with acetone are straddled by those for the runs using cyclopropylmethyl ketone as the solvent. The most probable explanation for the failure of the above relation-

ship to hold more rigorously is that there is a certain amount of chain decomposition of benzoyl peroxide by the growing styryl radicals. A side reaction of this type would increase the rate of disappearance of peroxide without changing k_2 appreciably. A variation in the amount of chain decomposition is not unlikely since the initial peroxide concentrations differed, in some cases, by a factor of almost ten.

From the viscosities of some of the polymers resulting from the styrene polymerizations it was possible to calculate their intrinsic viscosities, $[\eta]$, graphically, as shown in Figure III. These were, in turn, used in the Staudinger equation to calculate the average molecular weights, $\overline{M}$, of the polystyrene.[54]

$$[\eta] = K \quad \overline{M}^{\alpha}$$

$$K = 4.37 \times 10^{-4}$$

$$\alpha = 0.66$$

Table III. Average Molecular Weight Data

Solvent			
Cyclopropylmethyl ketone	0.019	7,800	0.013
Acetone	0.021	10,800	0.0096
Acetone	0.015	12,450	0.0084
Acetone	0.017	16,000	0.0064
Cyclopropylmethyl ketone	0.004	27,500	0.0026

Determination of the average molecular weights of the polymers enable us to calculate the degree of polymerization, $\overline{P}$. Kinetically this is defined by the equation

$$\overline{P} = \frac{k_2 [R\cdot] [M]}{k_3 [R\cdot] [SH] \; k_4 [R\cdot]^2} \tag{1}$$

where

$$[R\cdot] = \left(\frac{k_1}{k_4} [P]\right)^{\frac{1}{2}} \tag{2}$$

Inverting one finds that

$$\frac{1}{\overline{P}} = \frac{k_3 [SH]}{k_2 [M]} + \frac{k_1^{\frac{1}{2}} k_4^{\frac{1}{2}} [P]^{\frac{1}{2}}}{k_2 [M]} \tag{3}$$

It is interesting to note from Table III that the degree of polymerization increases as the initial concentration of peroxide decreases.

This sensitivity of molecular weight to peroxide concentration, coupled with the assumption that k_4 is approximately the same for all runs, indicates that the term $\frac{k_3 [SH]}{k_3 [M]}$ in equation (3) is necessarily small. Since the solvent to monomer ratio in every case was close to 1:1, one can say qualitatively that the k_3's for acetone and cyclopropylmethyl ketone are, probably, small and approximately equal in magnitude. The only conclusions that can be drawn from these data are that both ketones are poor chain transfer agents, and,

therefore, that the cyclopropane ring undergoes hydrogen abstraction with difficulty, if at all.

Perhaps the most conclusive evidence against either chain transfer or copolymerization is the infra-red spectra of some of the polymers. Examination of Plate I reveals that not only does the spectrum fail to indicate a carbonyl band, but that it is virtually identical with the spectrum of polystyrene prepared by bulk polymerization.

Since vinylmethyl ketone is known to copolymerize smoothly with styrene[62], here is one more example of dissimilarity in behavior of cyclopropane and ethylene derivatives.

The kinetics of the decomposition of benzoyl peroxide in both acetone and cyclopropylmethyl ketone were studied and treated by the method of Bartlett and Nozaki[55]. This treatment was proposed as a means of studying the chain decomposition of benzoyl peroxide in various solvents. The rate law is derived in the following way, using the same nomenclature as that employed for the kinetics styrene polymerization.

$$P \xrightarrow{k_1} 2R\cdot$$

$$R\cdot + P \xrightarrow{k_3} Y + R\cdot$$

$$2R\cdot \xrightarrow{k_4} R{-}{-}R$$

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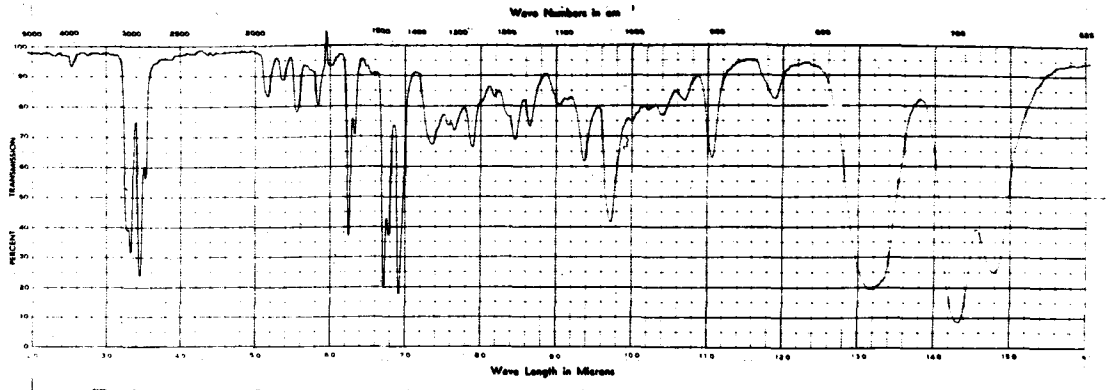
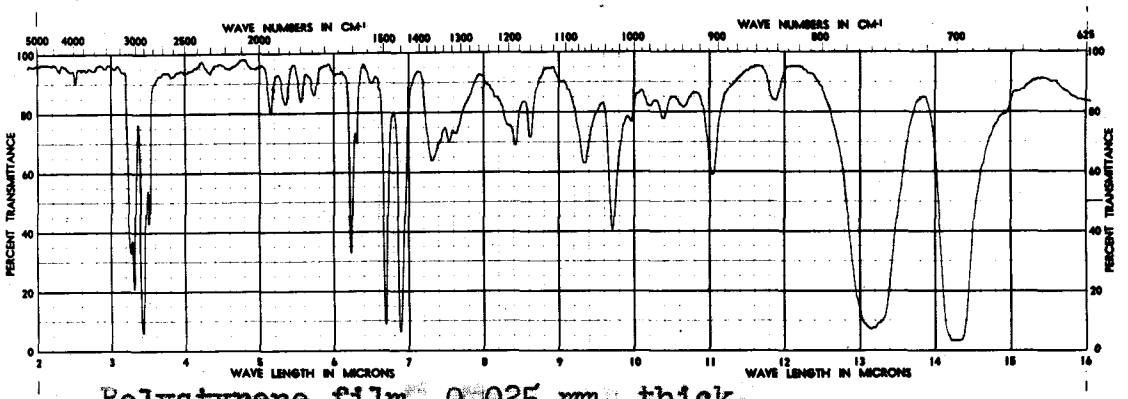
[62] A. D. McLaren and C. J. Seiler, Paper Trade J., 126, TAPPI, sect. 95 (1948).



Polymer from typical run evaporated on a plate from benzene solution.



Polystyrene film, 0.025 mm. thick.

Plate I. Comparison of isolated polystyrene with sample prepared by bulk polymerization.

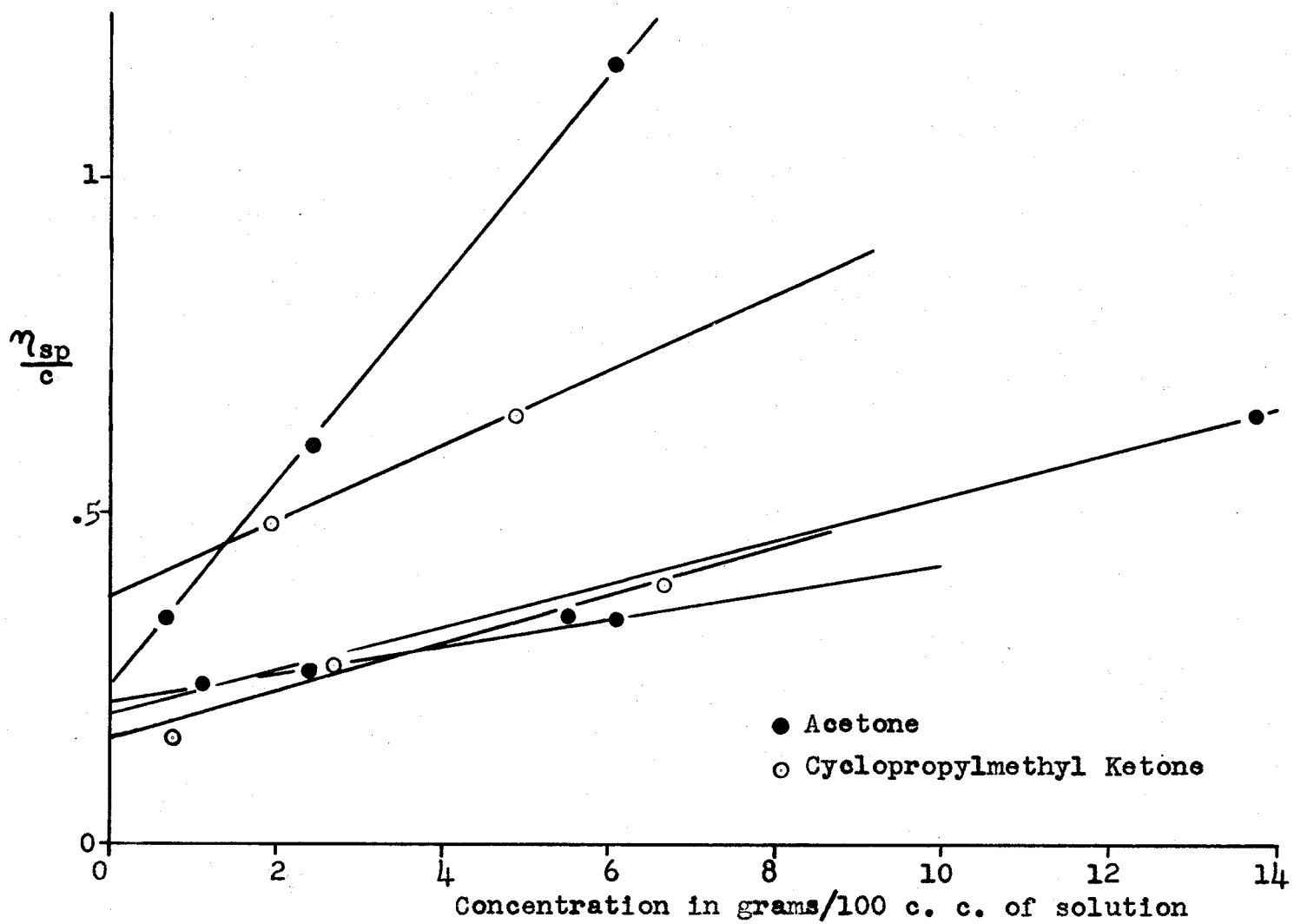


Figure III. Determination of intrinsic viscosities

At the steady state

$$\frac{d[R\cdot]}{dt} = 2k_1[P] - 2k_4[R\cdot]^2 \cong 0$$

$$[R\cdot] = \left(\frac{k_1[P]}{k_4}\right)^{\frac{1}{2}}$$

The rate of peroxide decomposition is then

$$-\frac{d[P]}{dt} = k_1[P] + k_3[P][R\cdot]$$

$$= k_1[P] + k_3\left(\frac{k_1}{k_4}\right)^{\frac{1}{2}}[P]^{3/2}$$

$$= k_1[P] + k_i[P]^{3/2}$$

where

$$k_i = k_3\left(\frac{k_1}{k_4}\right)^{\frac{1}{2}}$$

and may be considered the rate constant for induced decomposition. Integration of this expression gives

$$\ln \frac{a + P^{\frac{1}{2}}}{P^{\frac{1}{2}}} - \ln \frac{a + P_o^{\frac{1}{2}}}{P_o^{\frac{1}{2}}} = k_1 t \qquad (4)$$

where

$$a = \frac{k_1}{k_i}$$

It can be seen that if the peroxide concentrations are measured at equal reaction times for any two runs, the equation (4) above takes the form

$$\ln \frac{a + P_1^{\frac{1}{2}}}{P_1^{\frac{1}{2}}} = \ln \frac{a + P_2^{\frac{1}{2}}}{P_2^{\frac{1}{2}}} + \ln C, \quad (5)$$

which may, in turn, be converted to

$$\frac{1}{P_1^{\frac{1}{2}}} = \frac{C}{P_2^{\frac{1}{2}}} + \frac{C - 1}{a} \quad (6)$$

Plots of $\frac{1}{P_1^{\frac{1}{2}}}$ vs. $\frac{1}{P_2^{\frac{1}{2}}}$ should give straight lines from which C and a can be calculated. Figure IV shows three such lines, where X is an arbitrary constant to reduce the size of the graph.

Similarly, a plot of $\frac{a + P^{\frac{1}{2}}}{P^{\frac{1}{2}}}$ against time, as shown in Figure V, should give a straight line if equation (4) is valid.

The fact that the curves are linear for both acetone and cyclopropylmethyl ketone indicates that a certain amount of chain decomposition does occur when benzoyl peroxide is decomposed in these solvents. However, since the results are similar for both ketones, one can say that the cyclopropane derivative exhibits essentially no greater activity in this type of reaction than does acetone. Even if chain decomposition does occur, there is no evidence that reaction takes place on the cyclopropane ring.

Although the decomposition of acetyl peroxide in cyclopropylmethyl ketone yielded a small amount of product, the reaction appears to have taken place at the methyl group rather

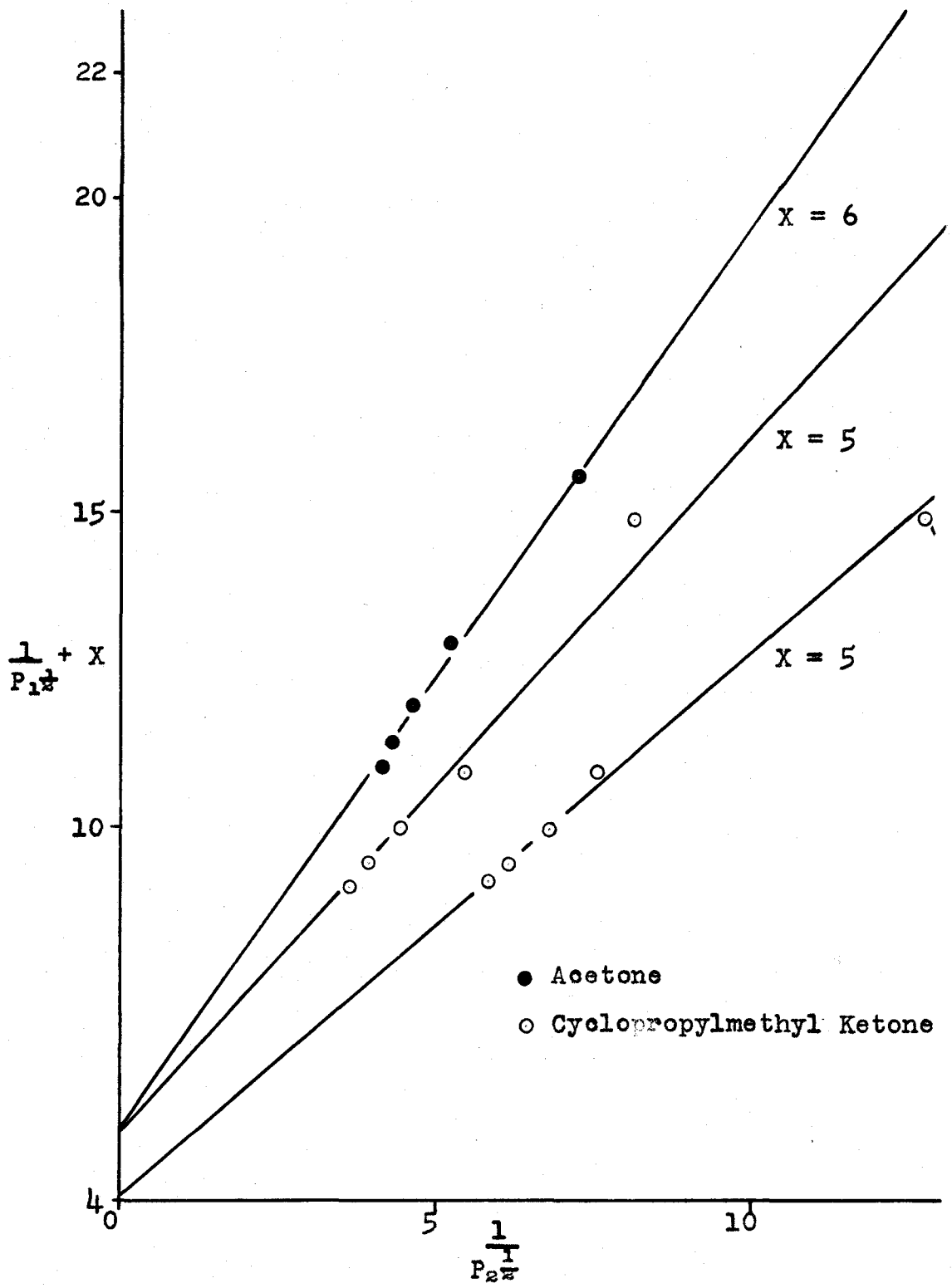


Figure IV. Graphic determination of C and a

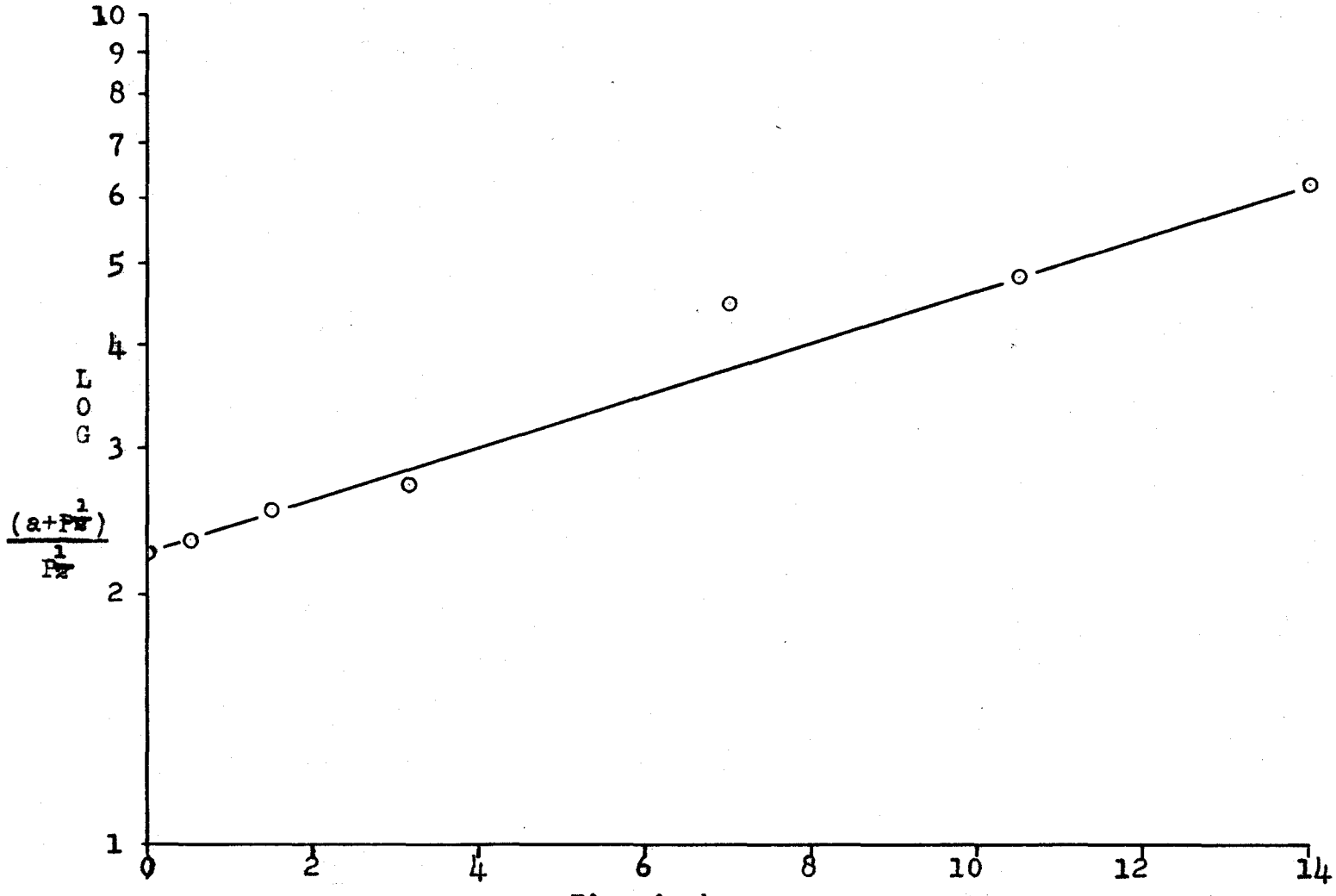


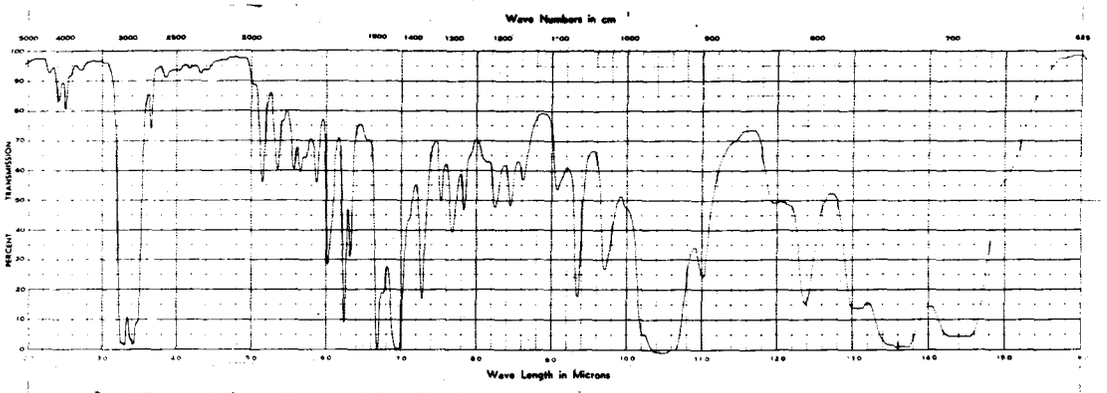
Figure V. Test of agreement with Bartlett and Nozaki kinetics

than the ring. This hypothesis is supported by the fact that the liquid showed absorption of infra-red radiation in regions typical of the cyclopropane moiety and the carbonyl group. The small yield indicates that reaction, if any, must be slow and certainly not a chain reaction.

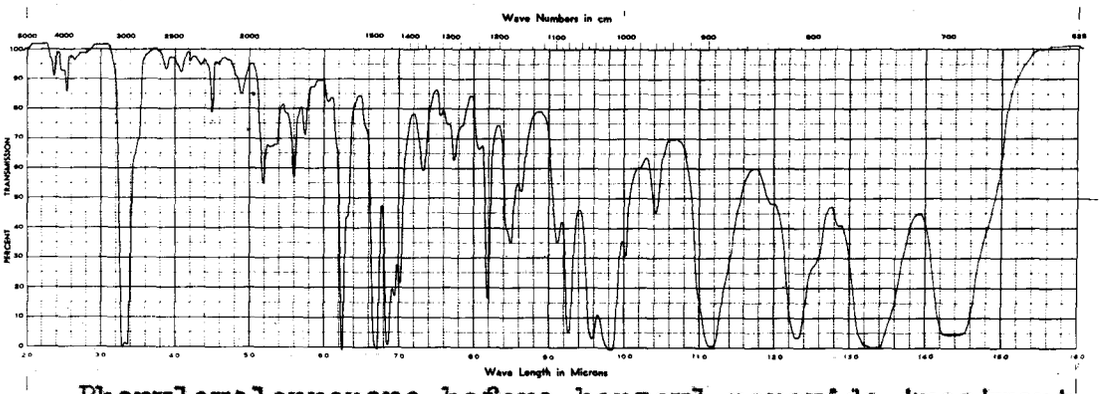
If was found that the phenylcyclopropane prepared by the pyrolysis of 5-phenyl-2-pyrazoline, even after exhaustive fractionation, contained a small amount of β-methylstyrene. When the mixture was heated overnight with a catalytic amount of benzoyl peroxide the phenylcyclopropane was recovered in a somewhat purer state as shown by the infra-red spectrum. When the treatment was repreated with a larger amount of benzoyl peroxide a product was recovered whose infra-red spectrum indicated no β-methylstyrene whatsoever (see Plate II). There was also found in each case a considerable yield of benzoic acid contaminated with a substance which may be polymerized -methylstyrene. Further reaction of this purest phenylcyclopropane with benzoyl peroxide did not change its refractive index or its infra-red spectrum.

Plate II demonstrates clearly the disappearance of the vinyl absorption, due to β-methylstyrene, in the region of 10.4 - 10.5 microns, with successive benzoyl peroxide treatments.

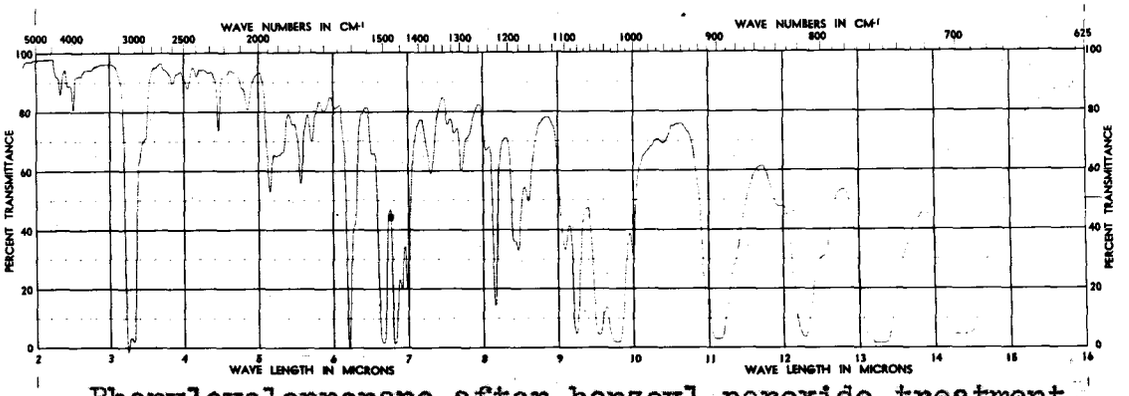
The fact that virtually all of the phenylcyclopropane can be accounted for after being used as a solvent for the



Authentic β-methylstyrene.



Phenylcyclopropane before benzoyl peroxide treatment.



Phenylcyclopropane after benzoyl peroxide treatment.

Plate II. Purification of phenylcyclopropane.

decomposition of a large amount of benzoyl peroxide is conclusive evidence that the cyclopropane is completely unreactive toward benzoate radicals. The fate of the benzoyl peroxide is somewhat in doubt, but it may react with itself to give a mixture of products.

At least one of these products has also been isolated from benzoyl peroxide decomposition in cyclopropylmethyl ketone as witnessed by the similarity of the infra-red spectra shown in Plate III and the failure of the mixed melting point to be depressed. It seems highly improbable that such agreement in physical properties is merely coincidental. The implication is, of course, that the benzoate radical attacks a peroxide molecule in preference to either phenylcyclopropane or cyclopropylmethyl ketone.

The failure of free radicals to abstract hydrogen from the cyclopropane ring was predicted, at least in part, by H. C. Brown[63] during his study of I-strain. Using his approach to the matter, one would say that removal of a hydrogen atom from a ring carbon would change the coordination number of that carbon from two to three. Since there is already considerable I-strain caused by the shrinkage of the bond angle from 109° 28' to 60°, a coordination number of three, requiring an angle of 120°, would serve only to increase the strain.

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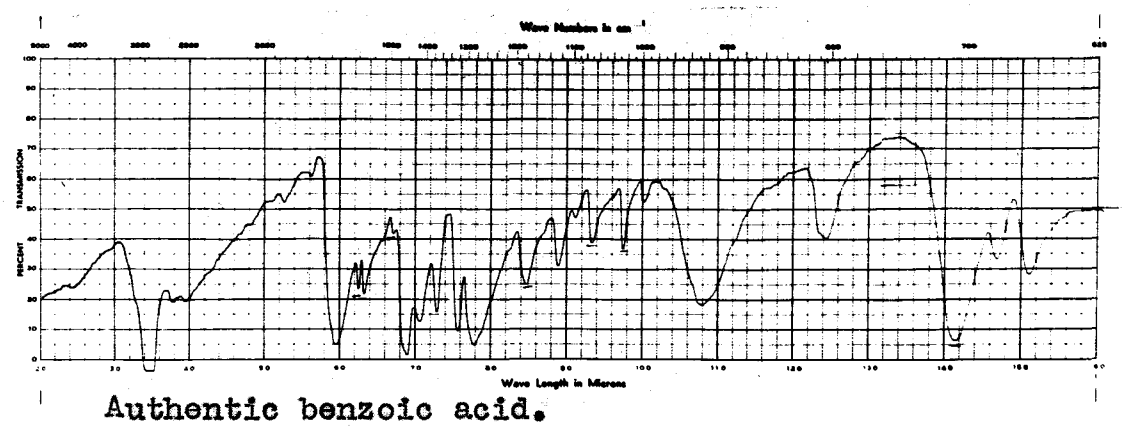
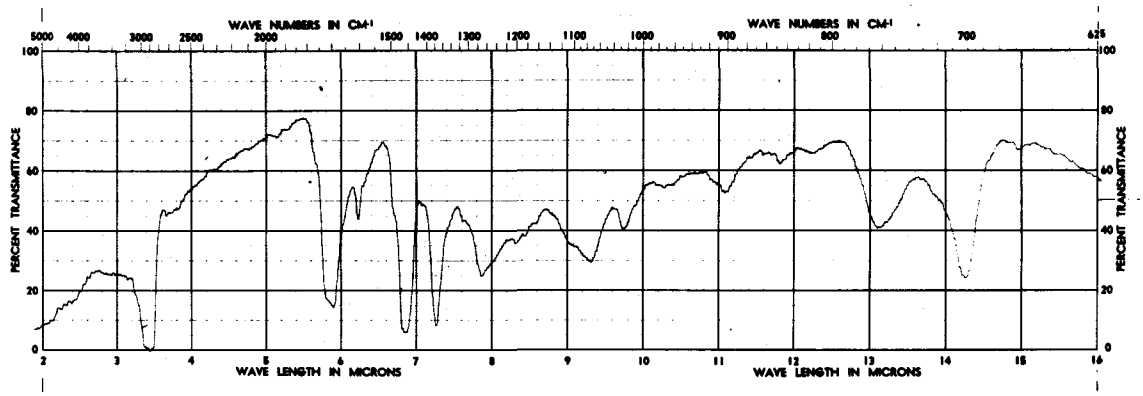
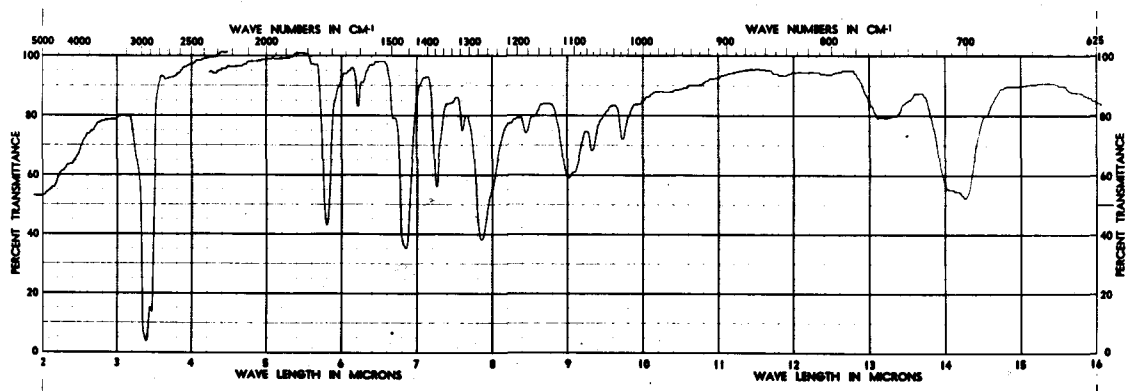
[63]H. C. Brown and M. Gernstein, J. Am. Chem. Soc., 72, 2926 (1950).



Authentic benzoic acid.



Solid from benzoyl peroxide and cyclopropylmethyl ketone.



Solid from benzoyl peroxide and phenylcyclopropane.

Plate III. Comparison of solids from two reactions.

Coulson and Moffitt[64] have discussed strained ring systems using the molecular orbital treatment. They stated that since there are six carbon to carbon bonding orbitals in the plane of the cyclopropane ring, there is probably an appreciable error in calculating the resonance energy by the conventional methods. Using the methylene diradical as a model for comparison, they calculated a resonance energy of about one electron-volt per methylene group in cyclopropane. This value is approximately the same as the one calculated for ethylene using the ethylene diradical as a comparison.

The authors went on to say:

> We can now see how the relatively high degree of delocalization which we have been led to associate with the C-C bonding electrons manifests itself in the behaviour of cyclopropane. We should expect such effects to include a capacity for conjugating with neighbouring unsaturated groups of favourable symmetry as well as for giving the cyclopropyl system an electrophilic character.

Thus, cyclopropane maintains its similarity to ethylene as far as hydrogen abstraction is concerned, since both types of molecules resist the removal of a hydrogen atom by homolytic cleavage. Why, then, should not ring opening occur with at least comparable ease?

It has been shown repeatedly that such ring opening can be effected by a number of acidic and basic reagents, although the reaction usually tends to be slower with cyclopropanes.

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[64] C. A. Coulson and W. E. Moffitt, Phil. Mag., 40, 1 (1949).

One should remember, however, that most acids and bases can exist as such in solution for, essentially, an infinite time. This is certainly not the case with free radicals whose half lives can be, at most, only a fraction of a second.

Therefore, despite the fact that ring opening by radicals may be energetically just as feasible with cyclopropane as it is with ethylene, the energies of activation for the two reactions must differ considerably. The highly reactive free radical, during its brief existence, must attack some species, other than cyclopropane, in a reaction which requires less energy to reach the transition state.

In conclusion, one can say that the data indicate a pronounced difference in the reactivities of cyclopropane and ethylene derivatives toward free radicals. Although there is not unequivocal proof that the cyclopropane moiety is entirely insensitive to radical attack, we can state without fear of contradiction that any reaction which takes place does so at a rate much slower than the rates observed in similar reactions with olefinic molecules.

SUMMARY

A review has been made of the literature since 1900 concerning the comparison of cyclopropane derivatives with analogous ethylenes and higher alicyclics. It has been found that the three-membered ring resembles ethylene closely in physical properties and in reactions with a number of ionic reagents. An attempt has been made to show whether this analogy can be extended to reactions with free radicals.

Cyclopropyl cyanide has been shown to be completely insensitive to attack by benzoate, acetate, triphenylmethyl, diethylcyanomethyl, and growing styryl radicals.

A study of the kinetics and products of styrene polymerization in the presence of cyclopropylmethyl ketone has indicated no copolymerization or chain transfer with solvent. Decomposition of benzoyl peroxide in both acetone and cyclopropylmethyl ketone, when followed kinetically and treated by the method of Bartlett and Nozaki, have shown that a certain amount of induced decomposition of the peroxide does occur. The reaction has been considered to take place at the methyl rather than the cyclopropyl group. Acetyl peroxide has been decomposed in cyclopropylmethyl ketone, and the small yield of product has been found to contain the cyclopropane ring, again indicating reaction at the methyl group.

Phenylcyclopropane has been purified by repeated heating with benzoyl peroxide. An impure product has been isolated

from these treatments whose infra-red spectrum shows no cyclopropyl group, but is very similar to that of a product of the decomposition of benzoyl peroxide in cyclopropylmethyl ketone. It has been concluded, therefore, that benzoate radicals react with benzoyl peroxide in preference to cyclopropane derivatives.

The theories of H. C. Brown and of Coulson and Moffitt have been discussed since these workers have predicted or implied that hydrogen abstraction by free radicals would be difficult in a cyclopropane system. These predictions have been shown, experimentally, to be correct.

An attempt has been made to rationalize the failure of ring cleavage to occur by assuming a higher activation energy for the reaction than for the corresponding addition to ethylene.

ACKNOWLEDGMENT

The author finds it difficult to express fully his gratitude to Dr. George S. Hammond. A true educator in every respect, Dr. Hammond has given generously of his time and knowledge, and has been a constant stimulus during this work.