[CONTRIBUTION FROM THE ESSO RESEARCH LABORATORIES, HUMBLE OIL & REFINING CO.]

Free Radical Reactions of Dimethoxymethane

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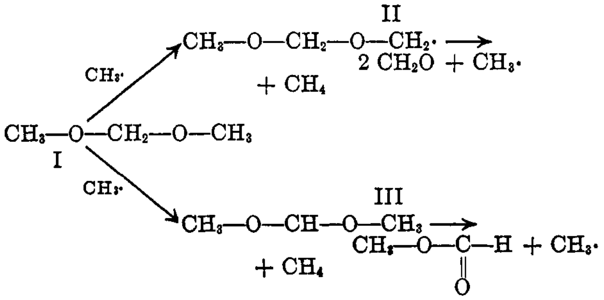
Abstraction of hydrogen from dimethoxymethane by alkyl radicals occurs at least 20% on a methyl carbon and no more than 80% on the methylene carbon. $CH_3—O—CH_2—O—CH_2\cdot$ (II) is relatively stable and maintains its existence until it attacks another molecule. $(CH_3—O)_2CH\cdot$ (III) decomposes to methyl formate and a methyl radical. Exchange of II to III occurs.

Free radical reaction of dimethoxymethane (I) with ethylene has been reported in the literature.[1] The product was described as comprising higher acetals derived from radical attack on the methylene carbon. In this previous work the products were of such high molecular weight that it is difficult to draw reliable conclusions about the point of free radical attack and the mechanism of the reaction. Hence, we have undertaken a study of the reaction of pure I with free radicals and the trapping of the intermediate radicals derived from I by reaction with ethylene. Conditions were such as to yield products low enough in molecular weight to allow identification.

Free radical abstraction of a hydrogen—*e.g.*, by a methyl radical—from I can occur at two nonequivalent positions. The intermediate radicals II and III thus generated might be expected ultimately to decompose into fragments as indicated.



In the one case formaldehyde and methane should be formed and in the other methyl formate and methane. In each case the decomposition should comprise a free radical chain since the methyl radical is regenerated at each step.

Experiments in which dimethoxymethane is treated with a catalytic amount of di-*t*-butyl peroxide at 200° show that a free radical chain decomposition does indeed occur. The products are exclusively those derived from III (see Table I). Thus, either free radical attack generates III exclusively or II is stable under these conditions and in turn generates III—*e.g.*, by abstraction of a hydrogen from another dimethoxymethane molecule.

To test which of these conditions applies the reaction was carried out in the presence of ethylene in order to trap the intermediate radicals as reported by Peterson and Weber.[1] Products are listed in Table II. The sequence of reactions outlined in Fig. 1 accounts for these products.

Among the higher molecular weight molecules

TABLE I

PRODUCTS RESULTING FROM FREE RADICAL DECOMPOSITION OF DIMETHOXYMETHANE

Product	Moles/Mole of Initiator	Analytical Methods[a]
Methane	12.5	I.R., M.S.
Methyl Formate	12.7	I.R., G.C., titration
Formaldehyde	0	Titration, G.C.

[a] I.R. = infrared spectroscopy; M.S. = mass spectroscopy; G.C. = gas chromatography.

TABLE II

PRODUCTS RESULTING FROM FREE RADICAL REACTION OF DIMETHOXYMETHANE IN THE PRESENCE OF ETHYLENE

Charge: 1000 ml. dimethoxymethane, 0.0257 mole di-*t*-butyl peroxide. Conditions: 200°, 370 p.s.i.g. ethylene partial pressure

Product	Mole/Mole of Peroxide	Analytical Methods[a]
Volatile products		
Methane + propane	8.99	I.R., M.S.
Methyl formate	16.01	I.R., G.C., titration
Ethylene addition products		
Dimethyl acetal of Alkylaldehyde	0.03	I.R., hydrolysis
Alkoxymethoxymethane	4.88	I.R., methanol exchange
Higher formate ester	0.47	I.R., saponification, methanol exchange
Paraffin	7.51	I.R., H_2SO_4 extract, M.S.
Olefins	0.54	I.R.
Initiator decomposition products		
t-Butyl alcohol	0.47	I.R., G.C.
Acetone	1.27	I.R., G.C.
Trace compounds	0.10	I.R.

[a] I.R. = Infrared spectroscopy; M.S. = mass spectroscopy; G.C. = gas chromatography.

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[1] M. D. Peterson and A. G. Weber, U. S. Patent 2,395,292, Feb. 19, 1946.

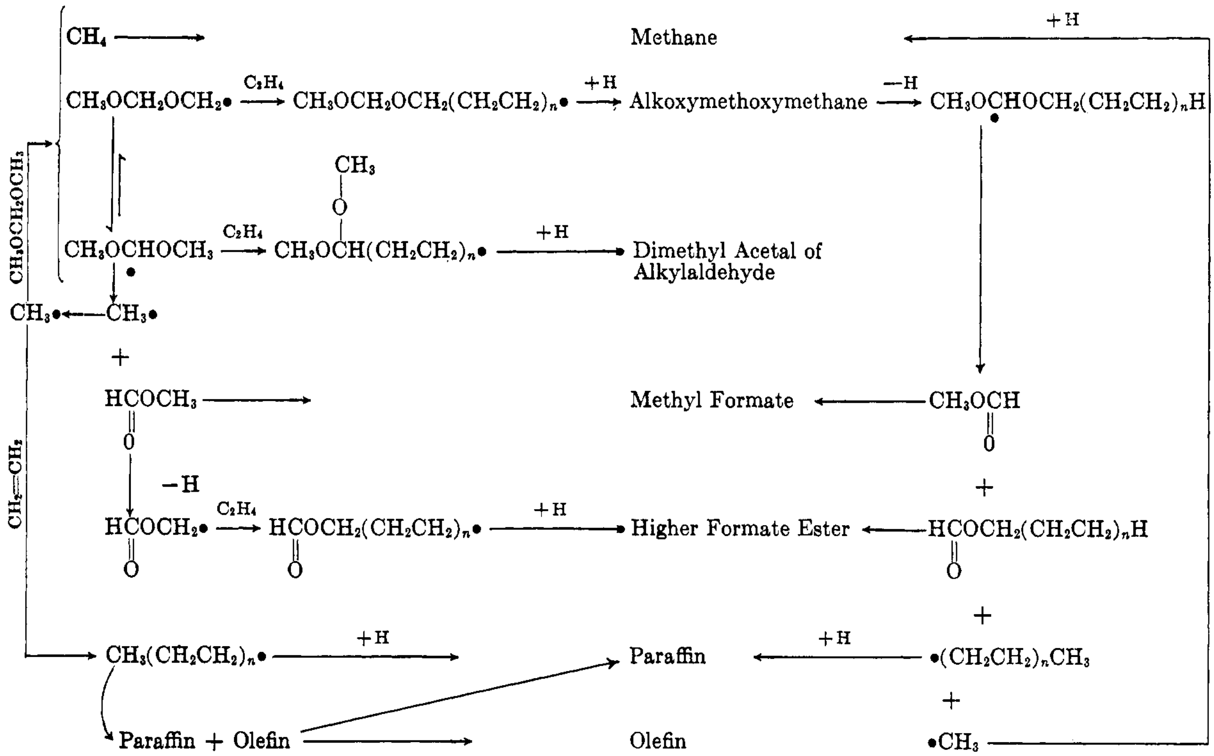

Fig. 1. Mechanism of free radical reaction of dimethoxymethane with ethylene 200°, 0.0257 mole di-*t*-butyl peroxide l., 370 p.s.i.g. ethylene partial pressure

derived from intermediate radicals the oxygenated products consisted almost exclusively of alkoxymethoxy methanes derived from II, although a trace of acetal derived from III appears to be present as well. Thus, it is shown that II is formed under these conditions. A small amount of higher formate esters is formed doubtless via free radical decomposition of the alkoxymethoxymethanes analogous to that demonstrated for dimethoxymethane, or *via* radical attack on the methyl formate formed in the reaction. Methyl esters, such as Urry and Huyser[2] found in the free radical reaction of methyl formate with ethylene at lower temperature, were not detected in this product. Negligible traces of other carbonyl compounds were also found in the higher molecular weight product. These compounds are not accounted for in the proposed mechanism and are probably derived from decomposition products of the peroxide initiator.

The distribution of products shows that considerable decomposition of the intermediate radical, III, occurs even in the presence of ethylene. The proposed mechanism (Fig. 1) requires that the yield of paraffin be equal to that of formate ester. This requirement is met (Table III).

When ethylene is present the methyl radicals liberated by decomposition of III lead to formation of the higher paraffins as well as methane. Paraffins may also be formed to a small extent by decomposition of higher alkoxymethoxymethanes as shown in Fig. 1. These paraffins comprise the homologous series of odd carbon numbers as required by the proposed mechanism. After extraction of other materials from the higher molecular weight fraction with sulfuric acid, mass spectroscopic analysis showed only peaks corresponding to the odd carbon paraffins.

TABLE III

PRODUCTS RESULTING FROM FREE RADICAL DECOMPOSITION OF DIMETHOXYMETHANE IN THE PRESENCE OF ETHYLENE

Paraffin, Mole/Mole of Initiator		Formate Ester, Mole/Mole of Initiator	
Methane + propane	8.99	Methyl formate	16.01
Higher paraffins	7.51	Higher formates	0.47
	16.50		16.48

These experiments in the presence and the absence of ethylene together demonstrate that radical II can give rise to III by hydrogen exchange. In view of the rapid decomposition of III it is unlikely that it can give rise to II by the reverse isomerization. With this assumption a lower limit can be placed on the ratio of attack on methyl and methylene groups in dimethoxymethane. Under conditions employed this ratio is 0.25.

On the basis of these experiments it is possible to

$$\text{Methyl/methylene attack} > \frac{\text{alkoxymethoxymethane}}{\text{methyl formate + higher formate + acetal}}$$

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[2] W. H. Urry and E. S. Huyser, *J. Am. Chem. Soc.*, 75, 4876)1953).

conclude that radical abstraction of hydrogen occurs on both the methyl and methylene carbons of dimethoxymethane to yield II and III, respectively. It can also be concluded that radical exchange, either intra- or intermolecular, occurs between these two positions. Radical III is so unstable that it decomposes before reacting with ethylene under these conditions. Radical II is stable enough so that it attacks another molecule, according to opportunities afforded it, before it decomposes.

EXPERIMENTAL

Materials. Practical grade (Eastman) dimethoxymethane was purified by treating 3 l. of the material with 100 g. of sodium dispersed in 300 ml. of decahydronaphthalene. Dimethoxymethane was distilled from the mixture through a 30-plate Oldershaw column; the center cut was collected and further treated with 10 g. of sodium hydride. A second distillation yielded a mid-cut, b.p. 41.0–41.1° (uncorr.), n^{20}_{D} 1.3535.

Commercial grade di-*t*-butyl peroxide was obtained from Shell Chemical Corp. *p*-Toluenesulfonic acid, isobutyl formate, and 1,4-dioxane were Eastman white label grade. 1-Heptanol was redistilled Eastman white label grade, b.p. 176.0°. *n*-Heptane (99 mole %) and 2-methyl-1-pentene (95 mole %) were obtained from Phillips Petroleum Co. Sodium methoxide was obtained from Matheson Coleman and Bell. Ethylene glycol was Baker Analyzed Reagent grade. All inorganic reagents were C.P. grade.

Hexoxymethoxymethane. A mixture consisting of 152.2 g. (2.0 mole) of dimethoxymethane, 408.7 g. (4.0 mole) of 1-hexanol, and 3.80 g. (0.02 mole) of *p*-toluenesulfonic acid was heated for 4 hr. at 115° in a 2-l. Parr autoclave. Subsequent distillation of the reaction mixture yielded a fraction of pure hexoxymethoxymethane, b.p. 167.6 (uncorr.) n^{25}_{D} 1.4032.

Titrimetric procedures. The quantitative determination of formaldehyde by the sodium sulfite method described by Walker[3] was modified to include the quantitative determination of both components of a mixture of formaldehyde and methyl formate. The latter was found to hydrolyze rapidly and completely in the presence of excess strong base. To a mixture of formaldehyde and methyl formate dissolved in dimethoxymethane was added a measured quantity of aqueous 0.100*N* sodium hydroxide. Excess base, indicated by the persistent blue color of thymolphthalein indicator, was back titrated with 0.100*N* hydrochloric acid to the colorless endpoint. Sodium sulfite solution was added to the neutral solution, and formaldehyde was determined by the normal procedure. The lower detectable limit of formaldehyde was 5 mg. per 50 ml. of solution.

Carboxylic acid content was determined by nonaqueous titration with 0.100*N* sodium methoxide solution by the method described by Fritz.[4] Formate esters are not affected by this titration.

Infrared spectra. Infrared spectra were obtained using a Beckman IR-5 Spectrophotometer. Analyses for specific types of compounds were based upon the absorption peaks of the standard materials listed below.

Type Compound	Absorption Peaks	Standard
Dialkoxymethane	1044 cm.$^{-1}$	Hexoxymethoxymethane
Formate ester	1735 cm.$^{-1}$	Isobutyl formate
Olefin	1091 cm.$^{-1}$	2-Methyl-1-pentene
Alcohol	3650 cm.$^{-1}$	1-Heptanol

Free radical decomposition of dimethoxymethane. Dimethoxymethane (897.7 g., 11.8 moles) was charged to an evacuated 2-l. stainless steel Parr stirred autoclave. The reactor was heated to 200° and 3.76 g. (0.0257 mole) of di-*t*-butyl peroxide dissolved in 52 ml. of dimethoxymethane was injected into the system with nitrogen over a 4.5-hr. period. Following the reaction period the autoclave was cooled and 24.95 l. (corr.) of gas containing 7.13 l. (0.318 mole) of methane was passed through a Dry Ice-acetone trap and collected.

Upon distillation of the liquid reaction mixture through a 12 mm. × 25 cm. Helipak column, the bulk of the material was collected at b.p. 34–44° and contained 19.55 g. (0.326 mole) of methyl formate, together with unaltered dimethoxymethane.

After the addition of 50 ml. of *n*-heptane to the distillation residue, a second distillation fraction (7.96 g., b.p. 46–97°) was collected which contained 1.82 g. (0.0239 mole) of dimethoxymethane, 1.36 g. (0.0234 mole) of acetone, 2.03 g. (0.0274 mole) of *t*-butyl alcohol, 2.57 g. of *n*-heptane, and 0.18 g. of unidentified materials.

No evidence for the presence of formaldehyde was indicated by infrared or mass spectroscopic analyses of the gaseous product from the reaction or by titrametric and infrared analyses of the liquid reaction mixture.

Free radical reaction of dimethoxymethane in the presence of ethylene. Dimethoxymethane (897.7 g., 11.8 moles) was charged to an evacuated 2-l. stainless steel Parr stirred autoclave. At the reaction temperature of 200° the autoclave was pressured to 880 p.s.i.g. with ethylene, and 3.76 g. of di-*t*-butyl peroxide dissolved in 24 ml. of dimethoxymethane was injected into the autoclave with ethylene pressure. An average ethylene partial pressure of 375 p.s.i.g. (880 psig. total) and temperature of 200° were maintained throughout the reaction period of 4.5 hr. At the end of this period the autoclave was cooled to room temperature and the products recovered as described below.

Analysis of products. Investigation and identification of the reaction products is illustrated by the sequence outlined in Fig. 2. Materials outside the boxes were separated and determined quantitatively.

A total of 41.4 l. (corr.) of gas was collected from the autoclave. Condensable vapors were removed from the gas by passage through a Dry Ice–acetone trap. The noncondensable gas contained 4.75 l. (0.211 mole) of methane (IV) and 0.45 l. (0.020 mole) of propane (V) as determined by infrared and mass spectra.

Distillation of the liquid through a 12 mm. × 25 cm. Helipak column yielded an initial fraction (870 g., b.p. 37–44°) containing in addition to recovered dimethoxymethane 24.7 g. (0.410 mole) of methyl formate (VI).

A second distillation fraction (7.47 g., b.p. 44–85°) contained 1.89 g. (0.0326 mole) of acetone, 0.89 g. (0.012 mole) of *t*-butyl alcohol, and 4.69 g. of dimethoxymethane as determined by infrared and gas chromatography.

The distillation residue (VII) weighed 66.9 g. and had an average molecular weight of 192 as determined by the freezing point depression of benzene. These ethylene addition products were determined by the reaction sequence outlined in Fig. 2 and described below.

Acid content of VII, XI, *and* XIII was determined by nonaqueous titration and found to be negligibly small and constant throughout the analytical workup.

Acid and ester content of VII *by saponification.* A 10-ml. aliquot of a standard solution of 1.00*N* potassium hydroxide in ethylene glycol was added to 20.0 g. of product VII dissolved in 50 ml. of dioxane. The mixture was heated at reflux for 2 hr. and then cooled, and excess base was titrated with 0.200*N* acid. Total ester and acid content was 3.9 mole %.

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(3) J. Frederic Walker, *Formaldehyde*, Reinhold, New York, 1944, pp. 257–258.

(4) James S. Fritz, *Acid-Base Titrations in Nonaqueous Solvents*, G. Frederick Smith Chemical Co., Columbus, Ohio.

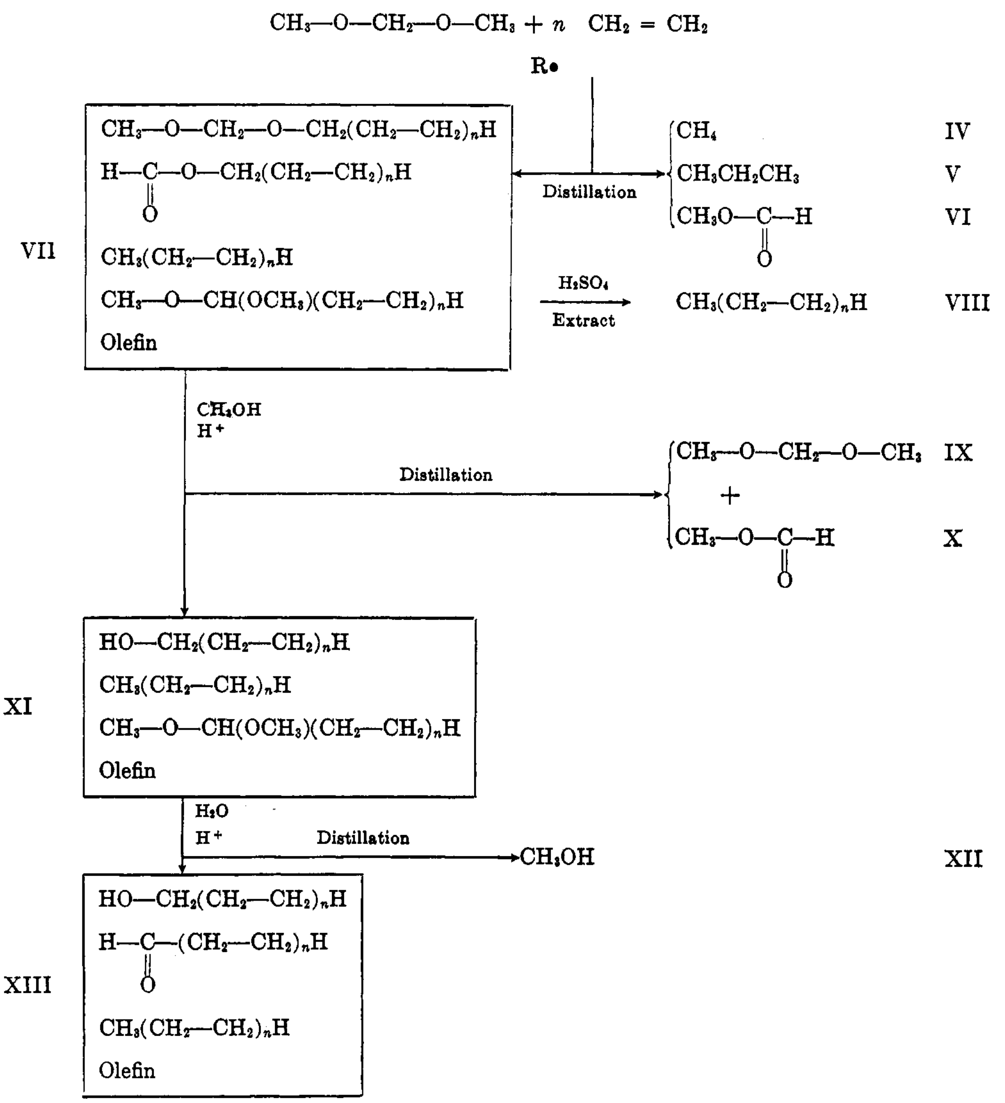

Fig. 2. Analytical sequence for dimethoxymethane-ethylene reaction product characterization

Paraffin in VII *by sulfuric acid extraction.* A 2-ml. portion of VII was repeatedly extracted in a glass stoppered graduated centrifuge tube with 4-ml. portions of concd. sulfuric acid until the volume of the insoluble organic phase remained constant. The sulfuric acid layer was removed each time with a fine gauge hypodermic needle. The organic phase comprised 55 wt. % of VII. The C_{11} and higher portion of the paraffin was analyzed by mass spectroscopy and was found to consist of paraffins with odd numbers of carbon atoms. No detectable amounts of even carbon numbers were present. This range of molecular weights was chosen for convenience in analysis; the C_4 to C_{10} range was not analyzed.

Formate ester and dialkoxymethane content by methanol exchange. Under the following conditions a mixture of *n*-butyl formate and hexoxymethoxymethane was shown to undergo quantitative exchange with methanol to evolve methyl formate and dimethoxymethane.

In a 1-l. autoclave, 20.0 g. (0.104 mole) of product VII, 600 ml. of methanol, and 0.38 g. (0.0022 mole) of *p*-toluenesulfonic acid were heated at 115° for 4 hr. Distillation of the mixture yielded 14.3 g. of initial fraction containing 0.211 g. (0.0035 mole) of methyl formate X and 2.50 (0.0329 mole) of dimethoxymethane IX as determined by titration and gas chromatography, respectively. Methanol was then distilled from the mixture until approximately 30 ml. of residue remained. This residue XI was dissolved in 100 ml. of benzene and was washed with 50 ml. of saturated sodium chloride solution, 50 ml. of 5% sodium carbonate solution, and 50 ml. of saturated sodium chloride solution. Benzene and traces of water and methanol were removed by distillation leaving product XI.

Acetal content by acid hydrolysis. Product XI was dissolved in 76 g. of dioxane to which was added 3.0 g. of water and 2 drops of concd. hydrochloric acid. The mixture was refluxed for 3 hr. Distillation of the reaction mixture yielded volatile materials—water, dioxane, a trace of methanol (XII, 0.016 g., 0.0005 mole)— and a residue, XIII.

Product XIII after this acid hydrolysis showed a slight increase in the carbonyl absorption of the infrared spectrum confirming the liberation of a small quantity of aldehyde. Total carbonyl absorption of product XIII was less than 2 mole % and was attributed to the aldehyde, acid, and a trace (less than 1 mole %) of ketonic component probably arising from ethylene addition to initiator decomposition products.

Elemental analysis of product VII. The over-all composition of product VII as determined above is 36 mole % alkoxymethoxymethane, 3.5 mole % formate ester, 4.0 mole % olefin, 55.5 mole % paraffin, and 1 mole % miscellaneous oxygenated.

Anal. Calcd. for this mixture: C, 78.98; H, 14.18; O, 6.84. Found: C, 78.96; H, 13.91; O, 7.17.

Acknowledgment. We are indebted to Mr. D. R. McAdams of these laboratories for mass spectroscopic analyses and to Dr. Earl S. Huyser for helpful suggestions concerning certain aspects of mechanism.

BATON ROUGE, LA.

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Small-Ring Compounds. XXXVII. Free Radical Decarbonylation of Some Cyclopropanecarboxaldehydes[1]

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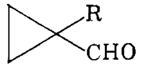
The di-*t*-butyl peroxide initiated decarbonylations of cyclopropanecarboxaldehyde and 1-methyl- and 1-phenylcyclopropanecarboxaldehyde have been studied. The first of these did not undergo decarbonylation to a measurable extent, while the substituted aldehydes reacted without ring opening to give methyl- and phenylcyclopropane, respectively.

Cyclopropyl radicals have been generated under a variety of conditions, and the extent of ring opening has been determined in each case. Only unrearranged cyclopropyl products were reported from photochemical chlorination[3] and vapor-phase nitration[4] of cyclopropane, brominative decarboxylation of silver cyclopropanecarboxylate,[5] and decomposition of biscyclopropanecarboxylic acid peroxide in carbon tetrachloride.[6] Exclusively open-chain products, structurally derived from the allyl radical, were formed in the Kolbe electrolysis of potassium cyclopropanecarboxylate[7] and the photolysis of methyl cyclopropyl ketone,[8] while mixtures of allyl and cyclopropyl chloride were obtained on thermal chlorination of cyclopropane.[3] Apparently, products in which the intermediate cyclopropyl radical has maintained its structural identity are obtained exclusively when the radical is generated at temperatures below 175–200° while at higher temperatures varying amounts of ring opening occur. The results of the photolysis of methyl cyclopropyl ketone[8] have been interpreted in terms of a concerted ring-opening reaction in which cyclopropyl radicals do not appear to be involved as intermediates.

It is relatively difficult to generate cyclopropyl radicals as compared with other hydrocarbon radicals.[9] For example, Trotman-Dickenson and Steacie[9a] report cyclopropane to be less reactive toward methyl radicals than a large number of other hydrocarbons studied. Only benzene was less reactive than cyclopropane.

As part of a study of a number of small-ring radicals as generated by the free radical decarbonylation of the corresponding aldehydes, we have studied the decarbonylation of the aldehydes I (R = H, CH_3, and C_6H_5) initiated by di-*t*-butyl peroxide. Because of the volatility of cyclopropanecarboxaldehyde and 1-methylcyclopropane carboxaldehyde under the usual decarbonylation conditions (130–140°), the reactions were carried out in diphenyl ether. The decarbonylation of 1-phenylcyclopropanecarboxaldehyde was run without solvent. The homogeneity and identity of the products were determined by means of vapor-phase chromatography, infrared spectroscopy, NMR, and by comparison with authentic samples. The extents of decarbonylation at 135–145°, calculated as a maximum value on the assumption that all the noncondensable gas evolved was carbon monoxide, were: 15% for cyclopropanecarboxaldehyde, 59% for 1-methylcyclopropanecarboxaldehyde and 97% for 1-phenylcyclopropanecarboxaldehyde. However, infrared analysis of the gas evolved with cyclo-



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[2] National Science Foundation Predoctoral Fellow, 1956–1960.

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[7] F. Fichter and H. Reeb, *Helv. Chim. Acta*, **6**, 450 (1923). However, note that this reaction is suspect as a free radical process, see E. J. Corey and co-workers, *J. Am. Chem. Soc.*, **82**, 2645 (1960).

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[9] (a) A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 329 (1951); (b) G. S. Hammond and R. W. Todd, *J. Am. Chem. Soc.*, **76**, 4081 (1954); (c) J. R. McNesby and A. S. Gordon, *J. Am. Chem. Soc.*, **79**, 825 (1957).