of acid, m.p. 43–46° and 4.8 g. of soft solid and oil. The principal products from ultraviolet-initiated addition, therefore, were a mixture of unsaturated esters including $CF_3CF_2CF_2CH{=}CH(CH_2)_8COOC_2H_5$ formed by the dehydroiodination of the intermediate iodo-addition compound and isomerization of ethyl 10-hendecenoate.

Thermally-induced Addition of Iodoperfluoroalkanes to Ethyl 10-Hendecenoate. (a). At 215° for 6 Hr.—Reaction of 150 g. (0.5 mole) of 1-iodoperfluoropropane and 125 g. (0.59 mole) of ethyl 10-hendecenoate at 215° for 6 hr. in a 400-ml. Hastelloy C-lined shaker tube gave 11.0 g. of volatile gas and 261 g. of fluid product which contained both the acid and the ester groups according to infrared analysis. Zinc reduction and distillation gave a black tarry residue (20.5 g.) and a partly crystalline distillate (163.8 g.). Fractionation in column A gave impure ethyl 12,12,13,13,14,14,14 - heptafluorotetradecanoate, b.p. 166–174°/20 mm.; $n^{25}D$ 1.4036 to 1.3888; 120 g. (62% yield, crude) which contained liquid isomeric unsaturated compounds (infrared absorption band at 5.77 μ) which were not completely separated by distillation in a 4-ft. by 0.5-in. Podbielniak column. Unchanged ethyl 10-hendecenoate been rearranged to an internal olefinic ester (10.30-μ absorption band; no 6.05-μ band) as in ultraviolet light-induced reaction. Pure $CF_3(CF_2)_2(CH_2)_{10}COOC_2H_5$, m.p. 30–30.5°, was obtained by pressing out the oil from the impure product. When ethyl acetate (1.5 moles) was used as a coreactant, the amount of tar formed was less than 1% and 95% of distilled products were obtained (see Table II).

Preparation of 8,8- to 14,14,14-Pentadecafluorotetradecanoic Acid *via* the Nitrile.[27]—Reaction of 4.9 g. (0.0086 mole) of 7,7- to 13,13,13-pentadecafluoro-1-iodotridecane[28] (b.p. 130°/9 mm.; m.p. 38–40°) and 1.5 g. (0.023 mole) of potassium cyanide in 15 cc. of 95% alcohol gave the nitrile which was hydrolyzed directly to the acid, m.p. 79.5–80°; f.p. 78°; 4.4 g. (90%); recrystallized in methylene chloride solution at 5°. Analyses are in Table II.

16-Heptadecenoic Acid. (a). 7-Keto-16-heptadecenoic Acid.—2-(10-Undecenoyl)-1-cyclohexanone[13] (b.p. 145°/0.5 mm.; $n^{25}D$ 1.4938, 67.0 g.; 0.25 mole) was stirred with a steel rod at 100° in a steel beaker while a solution of 40 g. (0.71 mole) of potassium hydroxide in 28 g. of water was added. The liquid became thick and pasty in 3 to 5 min. as the temperature rose to 130° and fell. A solution made in 2 l. of water was acidified with concentrated hydrochloric acid at 40–45°; the precipitated acid was collected and washed with water. The yield was 68 g. (100%) of crude 7-keto-16-heptadecenoic acid, m.p. (sinter 58°) 62–67°. The reaction was repeated five times with identical results. Recrystallization of 136.3 g. of the keto acid from 1 l. of petroleum ether and hexane gave 101.7 g. (72%); m.p. (sinter 68°) 68.5–69.5°; 13.0 g. (9%), m.p. (60.5°) 61.5–66°; and 1.2 g., m.p. (54°) 59–62°. An infrared spectrum showed a COOH band at 5.82 μ; $H_2C{=}CH$ band at 6.03 μ; bands at 7.04, 7.68, 10.06, and 10.90 μ (CH deformation bands of $CH_2{=}CH{-}$); and two bands not in 16-heptadecenoic acid (see below) at 7.98 and 8.28 μ.

Anal. Calcd. for $C_{17}H_{30}O_3$: C, 72.3; H, 10.7. Found: C, 72.0; H, 10.6.

(b) **Wolff-Kishner Reduction.**—A mixture of 135 g. (0.25 mole) of the crude potassium salts of 7-keto-17-heptadecenoic acid (above), 400 ml. of diethylene glycol and 25 ml. of hydrazine hydrate was heated to 137° (caution: foaming occurred). Hydrazine hydrate (25 ml.) was added after 2 hr. and refluxing was continued at 137° for 2.5 hr. The condenser was removed and vapors driven off up to 185° in 43 min. The temperature was kept at 185–195°. A sample, when acidified, gave solid acid, m.p. (sinter 45.5°) 53–58.5°; recrystallized from acetone, m.p. (55°) 60.5–62.5°. It contained unreduced keto acid (infrared analysis). A sample after 2 hr. had m.p. 47.5–51°, and after 3 hr., m.p. 48–52°. Infrared analysis showed no unreduced keto acid was present and was identical to a recrystallized sample of 16-heptadecenoic acid. The mixture was cooled and worked up as above. The acid was recrystallized from 300 cc. of acetone and 30 cc. of water; total yield, 58 g. (88%) based on crude potassium salt mixture. When a longer heating time (14 hr.) at 195° was employed, as is customary,[13] isomerization of part of the product to 15-heptadecenoic acid occurred (infrared analysis). Attempts to separate the acids by fractional crystallization from alcohol failed.

In a second experiment twofold amounts were used. Samples taken after 1.5 hr. at 192–195° showed some unreduced keto acid, but after 3.0 hr. no keto acid and no isomerized olefinic acid. 16-Heptadecenoic acid, m.p. (54°) 55–56°; 124.5 g. (93%), was recrystallized after treatment with decolorizing carbon in petroleum ether, m.p. 57–58°.

Anal. Calcd. for $C_{17}H_{32}O_2$: C, 76.1; H, 12.0. Found: C, 75.7; H, 12.0.

An infrared spectrum showed COOH (bonded OH) band, $C{=}O$ band at 5.82 μ, $CH_2{=}CH$ (stretch) band at 6.08 μ and associated deformation bands at 7.06, 7.68, 10.08, and 11.0 μ. There were also present new bands not in 7-keto-16-heptadecenoic acid at 8.05, 8.20 (8.32), and 8.43 and 10.65 μ. These bands were useful in studying mixtures. There was no 10.36 μ band of $-CH{=}CH-$ (*trans*) which was present in the infrared spectra of the mixtures of unsaturated acids prepared by 14 hr. refluxing at 195°.

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[27] A. H. Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1946, p. 292.

[28] Prepared by heating $CF_3(CF_2)_6I$ with an excess of ethylene at 200°; *cf.* R. N. Haszeldine, *J. Chem. Soc.*, 2856 (1949); 3761 (1953); and T. N. Bell, *ibid.*, 4973 (1961).

Ozonolysis of Dihydropyran. Reactions of 4-Hydroperoxy-4-methoxybutyl Formate

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Ozonolysis of dihydropyran in methanol readily afforded 4-hydroperoxy-4-methoxybutyl formate (II). The latter could be reduced smoothly to 4-formoxybutyraldehyde (VI) or dehydrated to methyl 4-formoxybutyrate (III). Products arising from thermal and ferrous ion-catalyzed decomposition of II have been determined.

The primary peroxidic product arising from the ozonolysis of cyclohexene in methanol has been shown by Bailey[1] to be essentially the aldehyde-hydroperoxide predicted by the Criegee[2] mechanism. A monomeric product could not be isolated as such because of facile intermolecular self-

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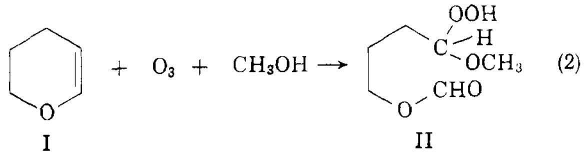
[1] P. S. Bailey, *J. Org. Chem.*, **22**, 1548 (1957).

[2] See P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958).

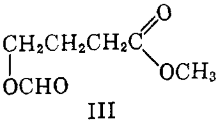
condensation giving low polymeric peracetals as the isolable products of the reaction. A further complication arose in that aldehyde end groups in the polymeric peracetals were partially converted to acetals by the methanol solvent.

One would expect, on the basis of the Criegee mechanism[2] and some knowledge of the way in which unsymmetrical carbon–carbon double bonds are split by ozone[3,4] that a modified "cyclohexene" such as 3,4-dihydro-2H-pyran (I) would be cleaved in the presence of methanol to give a simple monomeric product, namely 4-hydroperoxy-4-methoxybutyl formate (II), uncomplicated by further intermolecular condensations. As a previous investigation indicated, this expectation was fulfilled; several hydroperoxy formates analogous to II but with different alkoxyl moieties were obtained by ozonizing dihydropyran in the presence of various common alcohols.[5,6] These sirupy liquids appeared to be monomeric and reasonably homogeneous. Nevertheless, complete purification and characterization by preparation of solid derivatives was not achieved. Catalytic reduction and various decomposition reactions gave mixtures of nonperoxidic products which at that time could not be satisfactorily separated. A re-examination of some of the reactions of II with the aid of gas chromatography has now given a clearer picture of the transformations involved.

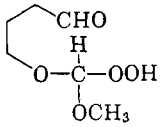


I II

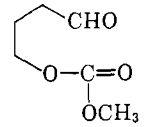
Despite the apparent success of Rieche and Bischoff[7,8] in using a dihydroquinoline pseudo-base to prepare a solid derivative of a secondary hydroperoxy ether, we were unable to utilize this reagent. Attempts to acylate the hydroperoxy function resulted only in loss of water and formation of methyl 4-formoxybutyrate (III). Dehydration in this manner with p-toluenesulfonyl chloride and pyridine proved to be an exceptionally clean preparation of III (80% yield). γ-Butyrolactone (VII, 4%) and the formoxy aldehyde (VI, 2%) were the only significant by-products obtained in the distillable fractions. The relatively high yield of III coupled with the essentially monomeric nature of II indicated that ozone cleavage of the double bond in dihydropyran did not occur extensively counter to that indicated by reaction 1. Alternate rupture would be expected to yield the hydroperoxide IV which could either self-condense, as in the case of cyclohexene,[1] or dehydrate to ester V.



III



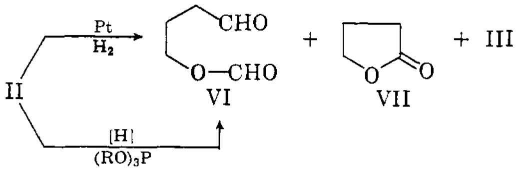
IV



V

No evidence for carbonates was found. Only minor amounts of polymeric IV could be present in crude II and still give the results observed.

That II was easily dehydrated by acylating agents was not unexpected in view of the facile decomposition of primary and secondary hydroperoxy esters noted by Mosher and co-workers.[9] Catalytic hydrogenation of II resulted in uptake of only 62% of the calculated amount of hydrogen.



The expected product, 4-formoxybutyraldehyde (VI), was obtained in only 42% yield along with III (21%) and γ-butyrolactone (VII) in 9% yield. On the other hand, reduction of II at −40° with tributyl phosphite gave VI in 80% yield with only minor amounts of III and lactone as by-products. This result again demonstrates the efficacy of the phosphite reduction method.[10]

Ferrous ion-induced cleavage of secondary α-hydroperoxy ethers has been shown by Milas[11] and others[12] to result in over-all loss of water forming the corresponding ester as a major product. That this is not the sole reaction is indicated by De LaMare and co-workers,[13,14] who demonstrated the intermediacy of R· radicals by isolation of coupling and other products derived from the alkyl radical fragments. These pathways are summarized on p. 4500, top of col. 1.

Our results are in accord with this interpretation. Decomposition of II with ferrous ion gave III,

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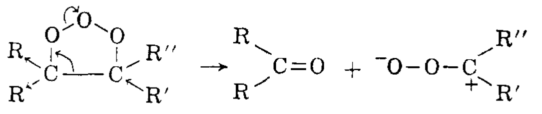
[3] A convenient although somewhat oversimplified generalization is that cleavage of an unsymmetrical olefin occurs to give a carbonyl derived from the olefinic carbon having the stronger electron-withdrawing groups attached to it and the zwitterion fragment arises from the (other) carbon to which are bonded the more electron-donating groups. See P. S. Bailey, S. B. Mainthia, and C. J. Abshire, *J. Am. Chem. Soc.*, **82**, 6136 (1960), for a recent discussion of this problem.



[4] See V. Schmidt and P. Grafen, *Angew. Chem.*, **72**, 579 (1961), for ozone cleavage of some carbocyclic enol ethers.

[5] Q. E. Thompson, U.S. Patent 2,973,372.

[6] R. Zelinski and H. J. Eichel, *J. Org. Chem.*, **23**, 462 (1958), attempted ozonolysis of 2-hydroxymethyl-3,4-dihydro-2H-pyran with uncertain results. We have ozonized other 2-substituted dihydropyrans and, although reaction with ozone was facile and quantitative, the subsequent chemistry appeared to be quite complex. Additional investigation was not pursued.

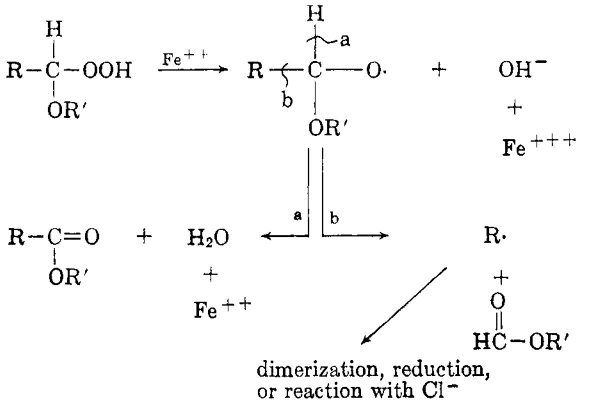
[7] A. Rieche and C. Bischoff, *Ber.*, **94**, 2722 (1961).

[8] A. Rieche, E. Schmitz, and P. Dietrich, *ibid.*, **92**, 2239 (1959).

[9] L. S. Durham, L. Glover, and H. S. Mosher, *J. Am. Chem. Soc.* **82**, 1508 (1960).

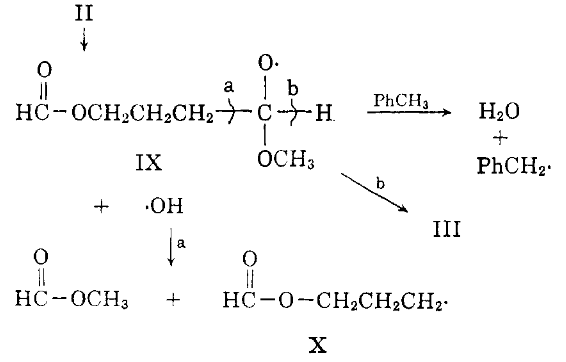
[10] W. S. Knowles and Q. E. Thompson, *J. Org. Chem.*, **25**, 1031 (1960).

[11] N. A. Milas, R. L. Peeler, and O. L. Mageli, *J. Am. Chem. Soc.*, **76**, 2322 (1954).

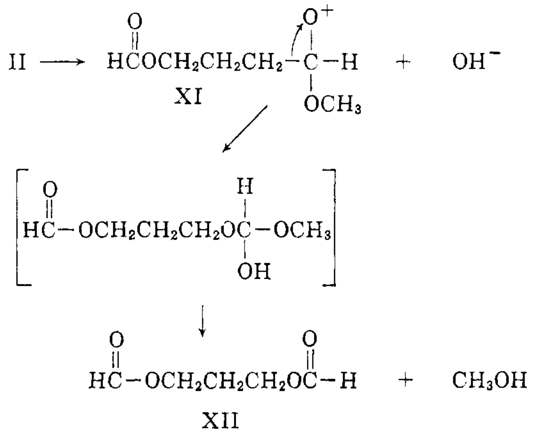


(25%) and the expected radical coupling product, $(HCOOCH_2CH_2CH_2)_2$ (VIII, 34%). Yields of each appeared to be fairly independent of reaction conditions.

Because the hydroperoxide II and its higher alkoxyl homologs[6] were excellent catalysts for styrene or styrene–maleic ester polymerizations, investigation of its thermal decomposition in toluene was undertaken. As anticipated, a wide variety of products resulted. These are listed in Table I (Experimental). Examination of the relatively small amount of gaseous materials produced indicated that hydrogen was the largest single gaseous component accompanied by smaller amounts of carbon dioxide, carbon monoxide, possibly oxygen and traces of hydrocarbons. The low over-all yield of hydrogen (10% based on hydroperoxide), however, indicated that the interesting hydrogen-forming pathway observed recently by Mosher and co-workers[15] was of minor importance here. While it is not necessary to speculate in detail concerning the genesis of each decomposition product, it is apparent that most are readily accountable on the basis of the expected homolytic cleavage of the RO—OH bond of II. Degeneration of the initially formed radical IX



via cleavage of bond a would yield the trimethylene formoxy radical X. With the exception of trimethylene glycol diformate (XII) all identified products are logically traceable to IX, X, benzyl and hydroxyl radical precursors. Despite the fact that trimethyleneglycol diformate could arise by homolytic rearrangements of IX, its complete absence in the ferrous ion-catalyzed decomposition of II suggests an ionic pathway for the formation of this particular product.



It is also possible that III and VI may be formed in part by ionic processes involving XI.

Experimental

Apparatus, Procedures.—Ozone was generated using a Welsbach T-23 laboratory ozonizer. The reactor, the standardization of the ozone stream, and determination of ozone absorbed have been previously described.[16] The bulk of the gas chromatography was done using an Aerograph Model A-90C instrument attached to a 1-mv. Brown recorder equipped with a disk chart integrator. A 2-m., 0.25-in. column with 20% LAC-3R-728 polyester[17] as stationary phase supported on siliconized Chromsorb "W" was used as column packing.

Preparative gas chromatography was done using a Beckman Megachrom instrument also with 20% LAC-3R-728 column packing.

Routine infrared spectra were obtained with a Perkin-Elmer Infracord, but where wave number data are reported here or where particularly careful comparisons were indicated, a Perkin-Elmer Model 221 instrument was employed. Melting points are uncorrected.

Preparation of 4-Hydroperoxy-4-methoxybutyl Formate (II).—Dihydropyran (8.4 g., 100 mmoles) in 80 ml. of dry methanol was cooled to −60°. A standardized ozone–oxygen stream (0.7 mmole/min. addition rate) was conducted through the solution held at −60°. Ozone absorption was complete until 100 mmoles of ozone had been added whereupon uptake ceased abruptly. The mixture was allowed to warm to room temperature. Methanol was removed under water pump vacuum with a rotating evaporator followed by 1 hr. at oil pump vacuum. Care was taken during solvent removal to keep the liquid temperature below 30°. The clear colorless sirup, amounting to 15.9 g. (97%), was soluble in water and most organic solvents. The product showed a strong hydroxyl absorption at 3400 cm.$^{-1}$, a sharp carbonyl band at 1725 cm.$^{-1}$, and a fairly broad band centered at 1190 cm.$^{-1}$ characteristic of formate esters among others. Of

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(12) D. Sharp and T. M. Patrick, *J. Org. Chem.*, **26**, 1389 (1961).

(13) J. Kumamoto, H. E. De LaMare, and F. F. Rust, *J. Am. Chem. Soc.*, **82**, 1935 (1960).

(14) H. E. De LaMare, J. K. Kochi, and F. F. Rust, *ibid.*, **83**, 2013 (1961).

(15) See L. J. Durham and H. S. Mosher, *ibid.*, **82**, 4537 (1960), for leading references.

(16) Q. E. Thompson, *ibid.*, **83**, 845 (1961).

(17) Cambridge Industries Co., Inc., 101 Potter St., Cambridge Mass.

particular significance was the absence of absorption at 2720–2730 cm.$^{-1}$ characteristic of aldehydic $-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{H}$ stretching.[18]

The following analysis was typical of the crude hydroperoxy ester.

Anal. Calcd. for $C_6H_{12}O_5$: C, 43.89, H, 7.37; CH_3O—, 18.90; active O, 9.75; mol. wt., 164.2. Found: C, 42.89; H, 6.92; CH_3O—, 19.90; active O, 9.30; mol. wt. 178 (cryoscopic in ethylene dibromide).

Attempted distillation of a 15-g. sample resulted in extensive decomposition, loss of vacuum, and finally violent explosion at about 150°.

Reduction of 4-Hydroperoxy-4-methoxybutyl Formate (II) (a) Catalytic Hydrogenation.—Dihydropyran (16.8 g.) was ozonized in 150 ml. of methanol as previously described. After warming to 0°, the methanol solution of IV was transferred to a low pressure hydrogenation bottle along with 100 mg. of platinum oxide catalyst and pressurized to 60 p.s.i. with hydrogen. On shaking, hydrogen uptake became very rapid at about 20°. Reaction ceased after uptake of 0.125 moles of hydrogen. Separation of catalyst and removal of solvent on a rotating drier gave 18.8 g. of colorless oil. The gas chromatogram of this material showed it to contain, in addition to some trace volatile materials, three major components. These were readily separated by gas chromatography and subsequently identified as 4-formoxybutyraldehyde (VI, 42%), methyl 4-formoxybutyrate (III, 21%), and γ-butyrolactone (VII, 9%) (all yields based on dihydropyran).

The aldehyde VI, b.p. 44° (0.75 mm.), n^{25}_{D} 1.4234, showed aldehydic absorption at 2730 cm.$^{-1}$, strong carbonyl absorption at 1725 cm.$^{-1}$, and a broad C—O stretching band at 1180 cm.$^{-1}$.

Anal. Calcd. for $C_5H_8O_3$: C, 51.72; H, 6.96. Found: C, 51.60; H, 7.11.

Treatment with *p*-nitrophenyhydrazine or 2,4-dinitrophenylhydrazine afforded the corresponding phenylhydrazones. The *p*-nitrophenylhydrazone, m.p. 109–109.5°, was obtained as yellow needles from methanol.

Anal. Calcd. for $C_{11}H_{13}O_4N_3$: C, 52.59; H, 5.22; N, 16.73. Found: C, 52.85; H, 5.32; N, 17.00.

The 2,4-dinitrophenylhydrazone, m.p. 108–109°, was similar in appearance and solubility.

Anal. Calcd. for $C_{11}H_{12}O_6N_4$: C, 44.60; H, 4.08; N, 18.91. Found: C, 44.71; H, 4.00; N, 18.72.

The infrared spectra of both derivatives were consistent with their structure and showed the formate ester function to be intact.

Methyl ester III, b.p. 43° (0.3 mm.), n^{24}_{D} 1.4186 exhibited a sharp carbonyl stretching band at 1728 cm.$^{-1}$ with a shoulder at 1735 cm.$^{-1}$ as well as the C—O stretching band at 1177 cm.$^{-1}$.

Anal. Calcd. for $C_6H_{10}O_4$: C, 49.31; H, 6.90. Found: C, 49.31; H, 6.72.

γ-Butyrolactone was easily identified by comparison of its gas chromatographic retention time and infrared spectrum with that of authentic material.

(b) **Phosphite Reduction.**—Hydroperoxide II prepared by ozonolysis of 0.2 mole of dihydropyran as in (a) was reduced with 50 g. of tri-*n*-butyl phosphite by a previously described procedure.[10] Reduction was extremely exothermic beginning at about −40°. The temperature was kept in the −40 to 0° range by strong cooling and slow addition of the phosphite over about 15 min. The reaction mixture was then warmed to room temperature and solvent was removed at 30–40° under reduced pressure (50–100 mm.). The colorless oil remaining (75 g.) was shown by gas chromatography to be essentially the desired aldehyde (VI) and tri-butyl phosphate. Fractional distillation afforded 18.6 g. (80% from dihydropyran) of aldehyde, b.p. 43–45° (0.75 mm.), which was identical to VI prepared as in part (a) and approximately 40 g. (75%), b.p. 94–96° (0.2 mm.), n^{25}_{D} 1.4225 (lit.,[19] n^{25}_{D} 1.4224), of tri-*n*-butyl phosphate.

Methyl 4-Formoxybutyrate (III).—Crude 4-hydroperoxy-4-methoxybutyl formate (II) (67 g.) dissolved in 100 ml. of dry methylene chloride was added slowly over 30 min. to a cold solution of 84 g. of *p*-toluenesulfonyl chloride and 79 g. of dry pyridine dissolved in 600 ml. of methylene chloride while keeping the reaction temperature about 10°. The cooling bath was removed and the temperature rose to 33° spontaneously whereupon it gradually subsided. After 6 hr., work-up was effected by addition of 250 ml. of water and subsequent washing of the organic layer with two 100-ml. portions of 1 *M* hydrochloric acid to remove excess pyridine. After a final water wash, the methylene chloride solution was dried with anhydrous calcium sulfate and the solvent was removed *in vacuo* leaving 61 g. of a pale yellow oil. Gas chromatography indicated the following approximate per cent composition: volatile materials 5%; pyridine, 3.6%; aldehyde (VI, 1.4%); methyl 4-formoxybutyrate (III, 86.4%); and γ-butyrolactone (VII, 3.6%). Vacuum distillation gave a main cut of III, b.p. 50–54° (0.4 mm.), amounting to 50 g. and consisting of approximately 97 wt. per cent III with 1% VI and 2% VII as impurities. Thus, the over-all yield of III was approximately 80% based on crude II starting material. Careful fractionation of crude III provided material free of aldehyde, but it was necessary to resort to gas chromatography to obtain III completely free of γ-butyrolactone. Chromatographic retention times and infrared spectra showed this material to be identical to

TABLE I

SUMMARY OF DISTILLABLE PRODUCTS OBTAINED BY THERMAL DECOMPOSITION OF HYDROPEROXIDE II IN TOLUENE

Cut no.	Components present[a] (wt. present or wt. % of cut)	Method of identification[b]
1	Methyl formate 2 g. total	A, B, C[c]
	n-Propyl formate 5 g. total	A, B, C[d]
2	Benzaldehyde, 12%	A, B
(25 g.)	Benzyl alcohol, 1.4%	A
	1,3-Propanediol diformate (XII), 12%	A, B, C[e]
	Methyl 4-formoxybutyrate (III), 40%	A, B
	Benzyl formate, 4%	A, B[f]
	γ-Butyrolactone, 33%	A, B
3	Methyl 4-formoxybutyrate, 15%	A
(4 g.)	γ-Butyrolactone, 20%	A
	1,6-Hexanediol diformate VIII, 5%	A[g]
	Bibenzyl, 10%	A, B
	Benzoic acid, 20%	A, B
	Five additional minor components	Unidentified

[a] Listed in approximate order of increasing retention time on polyester column. See Experimental. [b] Method A, comparison of g.l.c. retention time with an authentic sample and, in addition, added authentic material to mixture to observe peak height increase of unknown in question. Method B, isolated unknown by gas chromatography and compared infrared spectrum with that of an authentic sample. Method C, additional identification as specified. [c] B.p. 30–32°, reported in Lange's Handbook, 10 ed., b.p. 30.8°. [d] B.p. 80.5°, reported 80.9°. [e] B.p. 75° (10 mm.) n^{25}_{D} 1.4162. *Anal.* Calcd. for $C_5H_8O_4$: C, 45.45; H, 6.10. Found: C, 45.50; H, 6.10. [f] Retention time identical to III but isolated from the latter by gas chromatography using a less polar column. [g] Could not be isolated in pure form from this mixture. Appeared to be contaminated with another unidentified formate ester. Identification of VIII tenuous at best.

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[18] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y., 1958.

[19] G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley & Sons, Inc., New York, N. Y., 1950, p. 259.

III obtained as a by-product in the catalytic hydrogenation of IV.

Decomposition of II by Ferrous Ion.—A solution of 16.4 g. of II in 30 ml. of water was treated dropwise with 28 g. of ferrous sulfate heptahydrate dissolved in 85 ml. of water while keeping the temperature in the 20–25° range. Decomposition of peroxides appeared to be complete when approximately half of the ferrous sulfate solution had been added as evidenced by lack of temperature effect during the last half of the addition. A clear oily layer had separated. When addition of ferrous ion was complete (45 min.), 100 ml. of ether was added. The aqueous phase was extracted twice with 50-ml. portions of ether. The ether layers were combined, washed, dried with calcium sulfate, and the solvent was removed leaving 7.5 g. of clear oil. Gas chromatography showed the mixture to be composed of about 7% unidentified volatile products, 50% methyl 4-formoxybutyrate (III), about 3% aldehyde VI (both identified by their g.l.c. retention times and infrared spectra) and about 40% of a higher ester component which was subsequently identified as 1,6-hexanediol diformate (VIII). Over-all yields based on crude II were 25 and 34% for esters III and VIII, respectively.

A second ferrous ion-induced decomposition of II in which 16.4 g. of the hydroperoxide was added slowly to a 1 *M* sulfuric acid solution of ferrous sulfate (28 g. heptahydrate in about 80 ml. of water) at 0–5° gave essentially the same results as in the first experiment. Gas chromatography of the crude esters (6.4 g.) showed 44% III and about 48% VIII present as the major components giving over-all yields of 19 and 35% respectively, from hydroperoxide II.

The identity of VIII was conclusively established by distillation of 13 g. of the combined crude esters giving 4.3 g. of crude VIII, b.p. 78–83° (0.5 mm.). Redistillation gave 1.0 g., b.p. 68–70° (0.28 mm.), $n^{25}\text{D}$ 1.4289. Pure VIII prepared by esterification of 1,6-hexandiol with formic acid gave b.p. 68–69° (0.28 mm.), $n^{25}\text{D}$ 1.4289 and was identical in all respects with ester VIII prepared by the ferrous in decomposition of II.

Thermal Decomposition of 4-Hydroperoxy-4-methoxybutyl Formate (II) in Toluene.—A solution of 66 g. (0.4 mole) of II in 250 ml. of toluene was heated under gentle reflux using a water separator in the return line. Provision was made for collecting any gaseous products (b.p. below −75°). Reflux was continued for 13 hr. until a negative potassium iodide test indicated destruction of peroxides. During this interval approximately 2.1 l. of gas (corrected for water vapor and reduced to standard conditions) was obtained. A rough analysis of the gas mixture by infrared and mass spectroscopy indicated that it was approximately 42% hydrogen while carbon dioxide (10%), carbon monoxide (5%), air, and relatively minor amounts of methane and ethane made up the remaining components. Based on moles of II being decomposed the yield of hydrogen appeared to be slightly less than 10%.

After destruction of peroxide, toluene and volatile products were collected by distillation at atmospheric pressure (cut 1). A straw-colored liquid amounting to 35 g. remained. This was subjected to vacuum distillation giving 25 g., b.p. 65–95° (12 mm.) (cut 2). From the dark oily high boiling material remaining an additional 4 g. of oil, b.p. 100–185° (1.8 mm.), was collected (cut 3). Each of these fractions was examined by gas chromatography, and with the exception of cut 3, all products present in $> 1\%$ concentration were identified. These results are summarized in Table I. The dark residue remaining was discarded.

Intramolecular Reactions of Some Cyclic β-Diketones[1]

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The reaction of 2-(4,4-dimethyl-2,6-dioxocyclohexyl)succinic acid with acetic anhydride resulted in an unusual decarboxylation and rearrangement reaction. This paper describes this reaction and discusses certain other reactions of β-diketones.

Although acetic anhydride frequently has been employed to convert carboxylic acids into their corresponding anhydrides, it has been observed that the reaction at times can take an entirely different course. For example, when phenylacetic acid was heated with acetic anhydride and sodium acetate, a good yield of phenylacetone was obtained.[3] In the synthesis of strychnine,[4] one of the key steps was the conversion of a carboxylic acid into a methyl ketone by means of acetic anhydride and sodium acetate. We have now observed this unusual decarboxylation and certain other reactions on a β-diketo acid, 2-(4,4-dimethyl-2,6-dioxocyclohexyl)succinic acid (I).

When I was allowed to react with acetic anhydride, a neutral compound was obtained, which has lost the elements of carbon dioxide and water and has been substituted by an acetyl group. On the basis of its elemental analysis, ultraviolet and infrared spectra, this compound could have either structure IIa or IIb. A conclusion as to which of these represents the actual structure has been drawn from studies of model compounds VII and VIII, whose structures are similar to that of IIb. The model compound VII was prepared by the action of acetic anhydride on 2-(2-carboxyethyl)-5,5-dimethylcyclohexane-1,3-dione; this model (VII) exhibited strong infrared absorption at 1795 cm.$^{-1}$ and 1660 cm.$^{-1}$. The product obtained from the reaction of I with acetic anhydride exhibited infrared absorption at 1805 cm.$^{-1}$ and 1645 cm.$^{-1}$. However, one would expect three peaks in the infrared spectrum of IIb, but only two peaks

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