when the concept of Hammond[12] on the transition state is applied in our case. Thus, the bond-fission requirements in this case are less than those in the case of the reaction with thiosulfate ion. But in the reactions of ω-ethoxy-substituted alkyl bromides, the heat of activation decreased with the increase of the connecting methylene group as in the previous reactions with thiosulfate ion, although alternation of rates was observed in this case. The relatively small values of the heat of activations in spite of rather lower rates of reaction would probably be due to large contribution of solvation in the transition states. Solvation seems also to be responsible for the relatively large values of activation entropies.

However, in 50% ethanol solution, the rate sequence and other kinetic values of ω-ethoxyalkyl bromides were quite different from those in nitrobenzene. No alternation of rates was observed; instead, reactivity increased while heat of activation decreased with the increase of connecting methylene group between ethoxy group and halogen, as in the previous reactions with thiosulfate ion. It is known that in quaternization reactions both the heat and entropy of activation varies a great deal depending upon the solvent used.[13] For example, in the reaction of *p*-methylbenzyl bromide with pyridine the heat and entropy of activation in absolute acetone were 11.3 kcal. and −37.15 e.u., while those values in 90% ethanol were 15.4 kcal. and −22.5 e.u., respectively. Here also we found large differences of temperature coefficient values in two different solvents, *i.e.*, nitrobenzene and 50% ethanol. The differences in solvating power and in nature of solvation would be the responsible factor for these large changes from one solvent to another.[14]

Acknowledgment.—We wish to express our sincere thanks to the Ministry of Education for a Grant as well as the Grant-in-Aid for the Scientific Research and particularly to the Society of the Sigma Xi for the Grant-in-Aid which enabled us to purchase some chemicals from the United States. Our thanks are due both to Mr. Takuzo Fujino who kindly calibrated all our measuring apparatus and to Mr. Tsunehei Oki who carried out a part of the kinetic measurements.

OSAKA, JAPAN

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[12] G. S. Hammond, THIS JOURNAL, **77**, 334 (1955).

[13] J. W. Baker and W. S. Nathan, *J. Chem. Soc.*, 519, 1840 (1935).

[14] Both nitrobenzene and acetone have a rather highly negatively polarized oxygen atom in carbonyl and nitro group, which would easily solvate with positively charged quaternary nitrogen at the transition state, thus probably lowering the heat of activation; this strong solvation would also give relatively large negative values of entropy of activation. However, the oxygen atom in water or alcohol would not play such a large role.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Ozonolyses of 1,2-Dibenzoylpropene and 1,2-Dibenzoylethylene. Markownikoff's Rule and the Initial Attack of Ozone on an Unsaturated System[1]

BY PHILIP S. BAILEY AND SHEAFFERS S. BATH

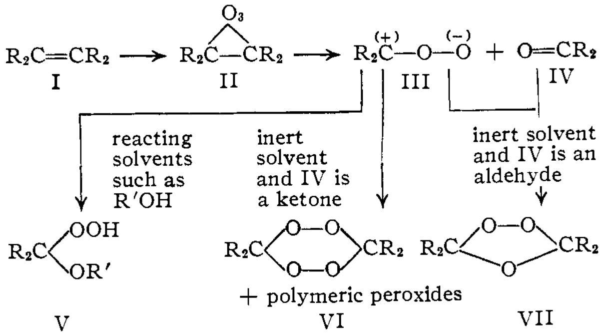
RECEIVED DECEMBER 8, 1956

The ozonolysis of 1,2-dibenzoylpropene in methanol furnishes direct evidence for the specificity previously noted in the attack of ozone on unsymmetrical olefins. The products were phenylglyoxal and α-hydroperoxy-α-methoxypropiophenone. The results are correlated with Markownikoff's rule and a mechanism is proposed which rationalizes the known facts concerning the initial attack of ozone on an unsaturated system Decompositions of α-hydroperoxy-α-methoxypropiophenone and the corresponding hydroperoxide from the ozonolysis of 1,2-dibenzoylethylene in methanol are described.

The Criegee[2] mechanism for ozonolysis has been of tremendous importance in giving a better understanding of the course of the ozonolysis reaction, in particular, the character and fate of the most important intermediate in the reaction, the zwitterion III. It leaves in doubt, however, the nature of the initial attack of ozone on an unsaturated system and of the intermediates leading to the formation of the zwitterion III and the aldehyde or ketone IV.

Recent studies have shown that ozone, like hydrogen chloride and other unsymmetrical reagents, attacks unsymmetrical olefins in a specific manner.[3] This observation furnishes an important clue to the nature of the initial ozone attack.

Criegee Mechanism



The earlier examples of this specificity of ozone attack include isobutene (VIII), which produced an ozonide (XI) as the major product when ozonized in inert solvents, and camphene (XIV) which gave rearrangement products of zwitterion XV.[2c,3] This means, in the case of isobutene, that preferential

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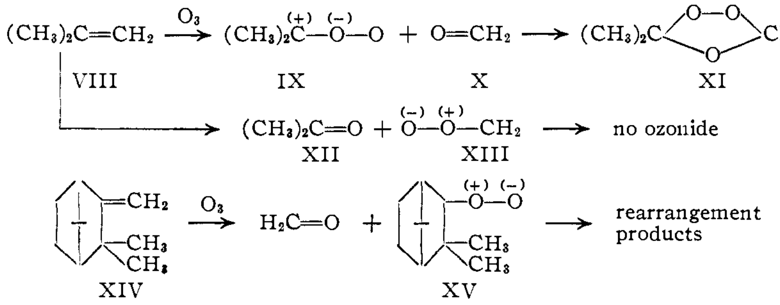
[1] A portion of this paper was presented at the International Ozone Conference, Chicago, Ill., November 28-30, 1956.

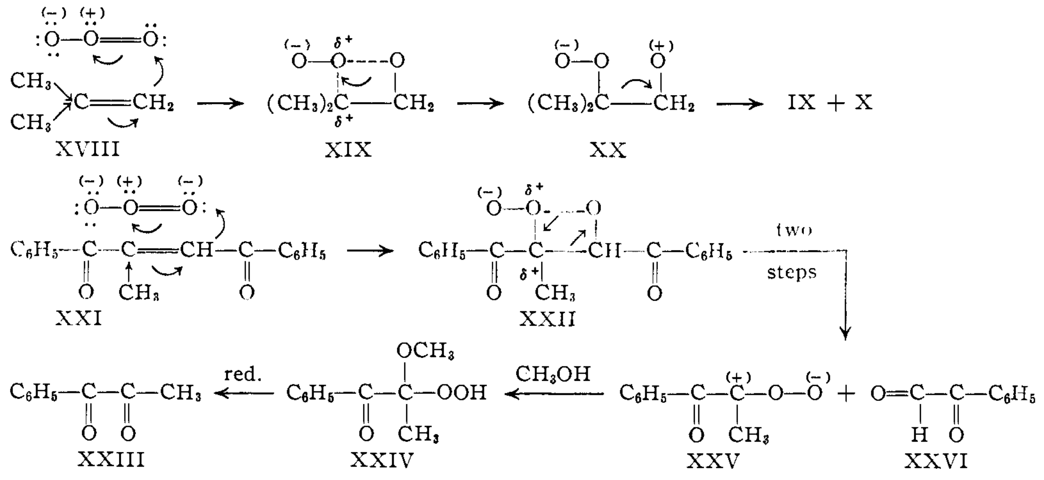
[2] (a) R. Criegee and G. Wenner, *Ann.*, **564**, 9 (1949); (b) R. Criegee and G. Lohaus, *ibid.*, **583**, 6 (1953); (c) R. Criegee, G. Blust and H. Zinke, *Chem. Ber.*, **87**, 766 (1954); (d) R. Criegee, A. Kerckow and H. Zinke, *ibid.*, **88**, 1878 (1955).

[3] P. S. Bailey, *ibid.*, **88**, 795 (1955).

cleavage of the double bond occurred to give zwitterion IX and formaldehyde, rather than zwitterion XIII and acetone.[3] This reasoning is based on Criegee's[2] finding that ozonides cannot be produced by interaction of a zwitterion and a simple ketone. In the case of camphene, preferential cleavage to zwitterion XV and formaldehyde occurred.[3]



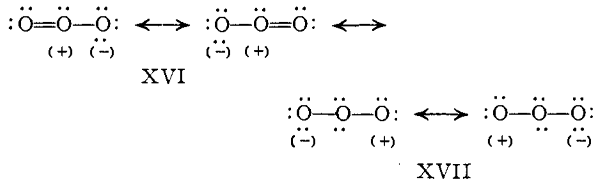
In the cases just discussed the evidence for the specificity of ozone attack was of an indirect nature. It would be much more conclusive if one could actually trap and identify the zwitterion preferentially formed. This has been done in the ozonolysis of *trans*-1,2-dibenzoylpropene (XXI) in methanol solution. The products were phenylglyoxal (XXVI) in 61% yield and α-hydroperoxy-α-methoxypropiophenone (XXIV) in 74% yield. The actual yields probably were much higher; both substances are difficult to isolate. The evidence for the structure assigned to XXIV, besides elemental analyses and the molecular weight determination, was the methoxyl group analysis, a positive lead tetraacetate test for a hydroperoxide,[4] the infrared spectrum which showed a strong carbonyl band at 5.9 μ and a hydroxyl band at 2.9 μ and reduction to 1-phenyl-1,2-propanedione (XXIII) in good yield. This reaction leaves no doubt concerning the specificity of ozone attack to produce preferentially phenyl glyoxal (XXVI) and zwitterion XXV, which was trapped through its reaction with methanol to give XXIV.



At first sight, as pointed out in the cases of isobutene and camphene,[3] these results seem to be in conflict with Markownikoff's rule, based on the usually assumed[5] electrophilic attack of the central carbon atom of the ozone molecule.

Meinwald[6] has pointed out, however, that the central oxygen atom of the ozone molecule cannot be electrophilic, since it has, in all of the structures (XVI and XVII) which make any appreciable contibution to the ozone molecule hybrid, its full quota of eight electrons. The electrophilic center in the ozone molecule, therefore, has to be a terminal atom as shown in contributing structures XVII.

On the basis of an initial terminal oxygen atom electrophilic attack and the assumption that the central oxygen atom completes the attack, the experimental results described can be correlated with Markownikoff's rule, as illustrated in the cases of isobutene (XVIII) and 1,2-dibenzoylpropene (XXI).



$$:\ddot{O}=\underset{(+)}{\ddot{O}}-\underset{(-)}{\ddot{O}}: \longleftrightarrow :\underset{(-)}{\ddot{O}}-\underset{(+)}{\ddot{O}}=\ddot{O}: \longleftrightarrow$$

XVI

$$:\underset{(-)}{\ddot{O}}-\ddot{O}-\underset{(+)}{\ddot{O}}: \longleftrightarrow :\underset{(+)}{\ddot{O}}-\ddot{O}-\underset{(-)}{\ddot{O}}:$$

XVII

The experimental results also can be explained on the basis that the second step in the ozone attack involves the other terminal atom rather than the central atom, to give intermediates of type XXVII. Although these tructures could break down in two ways, it can be argued that they would break down preferentially to give zwitterions IX and XXV, because these zwitterions should be more stable than the other two possibilities through hyperconjugation with the methyl groups.

The intermediates with the four-membered ring

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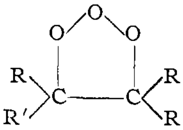
(4) R. Criegee, H. Pilz and H. Flygare, *Ber.*, **72**, 1799 (1939).

(5) (a) J. P. Wibaut, F. L. J. Sixma, L. W. F. Kampschmidt and H. Boer, *Rec. trav. chim.*, **69**, 1355 (1950); (b) F. L. J. Sixma, H. Boer and J. P. Wibaut, *ibid.*, **70**, 1005 (1951); (c) J. P. Wibaut and F. L. J. Sixma, *ibid.*, **71**, 761 (1952); (d) L. W. F. Kampschmidt and J. P. Wibaut, *ibid.*, **73**, 431 (1954).

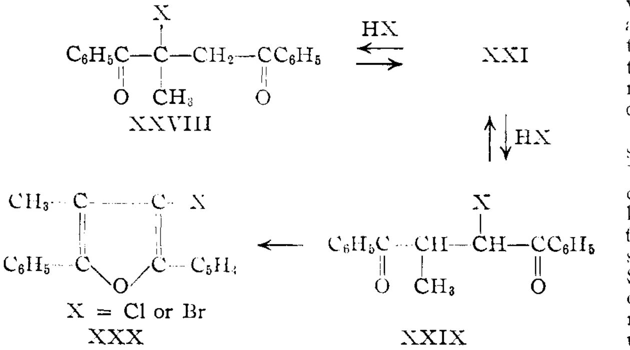
(6) J. Meinwald, *Chem. Ber.*, **88**, 1889 (1955).

(XIX and XXII) are preferred by the present author for two reasons. First, they can break down in only one way, and this gives the required zwitterions (IX and XXV) and aldehydes (X and XXVI). Second, they explain better the easy cleavage of the double bond under the extremely mild conditions of the ozonolysis reaction. These structures (XIX and XXII) are formulated as activated complexes rather than real intermediates. As such they might be expected to be formed more readily than the more stable intermediates XXVII, because the length of the oxygen–oxygen bond of the ozone molecule is almost the same as that of the carbon–carbon double bond.[7] There would be partial positive charges on the oxygen and carbon atoms shown in structures XIX and XXII because of the partially formed and broken bonds. These would cause the election shift shown to produce intermediates such as XX. The positive charge in XX weakens the remaining carbon–carbon bond causing cleavage to IX and X and to XXV and XXVI.



XXVIIa, $R = R' = CH_3$; $R'' = R''' = H$
b, $R = R'' = C_6H_5-\underset{\underset{\displaystyle O}{\|}}{C}-$; $R' = CH_3$; $R''' = H$

It is interesting to note that whereas Markownikoff's rule is followed in the ozone reaction with 1,2-dibenzoylpropene, it is not followed in the corresponding additions of hydrogen chloride and hydrogen bromide. Instead, in acetic acid solution the products are 3-chloro(or bromo)-4-methyl-2,5-diphenylfuran (XXX).[8-10] The reason for this appears to be that a complicated set of equilibria exists, part of which is shown below. The remainder is discussed elsewhere.[10] Under dehydrating conditions (glacial acetic acid) structures XXIX are trapped and converted to the corresponding furans (XXX).



trans-1,2-Dibenzoylethylene also yielded a crystalline methoxyhydroperoxide (XXXIa) upon ozonolysis in the presence of methanol. When this hydroperoxide and the one (XXXIb) from the ozonolysis of 1,2-dibenzoylpropene were heated in methanol or were treated with formic acid, sodium hydroxide or pyridine, decomposition occurred to give benzoic acid as the major product. In several instances spontaneous decompositions occurred when the ozonolysis reaction mixtures were evaporated to dryness before isolation of the hydroperoxides or when the impure hydroperoxides were allowed to stand. The pure crystalline hydroperoxides were stable at room temperature.

These decompositions to benzoic acid (and presumably methyl formate or acetate) are typical heterolytic cleavages of the peroxide group.[11] The base-catalyzed decomposition is most logically explained by a displacement type mechanism (XXXI → XXXII + XXXIII). The acid-catalyzed decomposition could also occur by a similar process (XXXIV → XXXII + XXXIII). If such a process occurred with the decompositions in warm methanol, however, the product should be largely methyl benzoate rather than benzoic acid since the displacing reagent would be, largely, methanol. This reaction, therefore, like the acid-catalyzed heterolytic decomposition of cumene hydroperoxide,[12] is best explained by a concerted rearrangement (XXXV → XXXVI → XXXII + XXXIII). This, of course, could also be the case with the acid-catalyzed decomposition. A similar rearrangement was found to occur during the ozonolysis of camphene in methanol.[3]

In two experiments small quantities of benzil were isolated. Products of this sort are typical of a competing homolytic cleavage of the peroxide group, involving changes such as shown in XXXV → XXXVII → XXXIX.

Experimental[13]

The ozonator used in this research was a Welsbach Corporation model T-23 laboratory apparatus. Oxygen dried to a dew-point of at least −60° was employed. The calculation of the quantity of ozone absorbed was done by determining the concentration of ozone in the oxygen–ozone mixture in terms of grams per liter, multiplying by the number of liters passed through the system and subtracting the quantity of ozone unabsorbed as shown in the potassium iodide trap following the reaction vessel. The reaction vessel was essentially a tube with the gas inlet at the bottom, a seal-in fritted disk just above the inlet and the outlet near the top. The *trans*-1,2-dibenzoylpropene was prepared by the method reported earlier.[14] It melted at 51–53°. The methanol and carbon tetrachloride were pure and anhydrous.

Ozonolysis of *trans*-1,2-Dibenzoylpropene (XXI).—Into a solution of 10 g. (0.04 mole) of *trans*-1,2-dibenzoylpropene, 15 ml. of methanol and 45 ml. of carbon tetrachloride, cooled to −40°, was passed at a rate of approximately 35 liters per hour a stream of oxygen containing approximately 6% ozone by weight. The reaction was stopped when the solution took on a bluish color (dissolved unreacted ozone). Some ozone passed into the potassium iodide trap during the ozonolysis. The amount of ozone used up by the reaction mixture was almost exactly 0.04 mole. A crystalline product had formed. The mixture was kept at −40° for 3-4 hr. and then filtered, yielding 5.8 g. (74% yield) of colorless crystals which melted with decomposition at 57°.

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(7) R. Trambarulo, S. N. Ghosh, C. A. Burrus, Jr., and W. Gordy, *J. Chem. Phys.*, **21**, 851 (1953).

(8) R. E. Lutz and C. E. McGinn, THIS JOURNAL, **64**, 2585 (1942)

(9) R. E. Lutz and A. H. Stuart, *ibid.*, **59**, 2316 (1937).

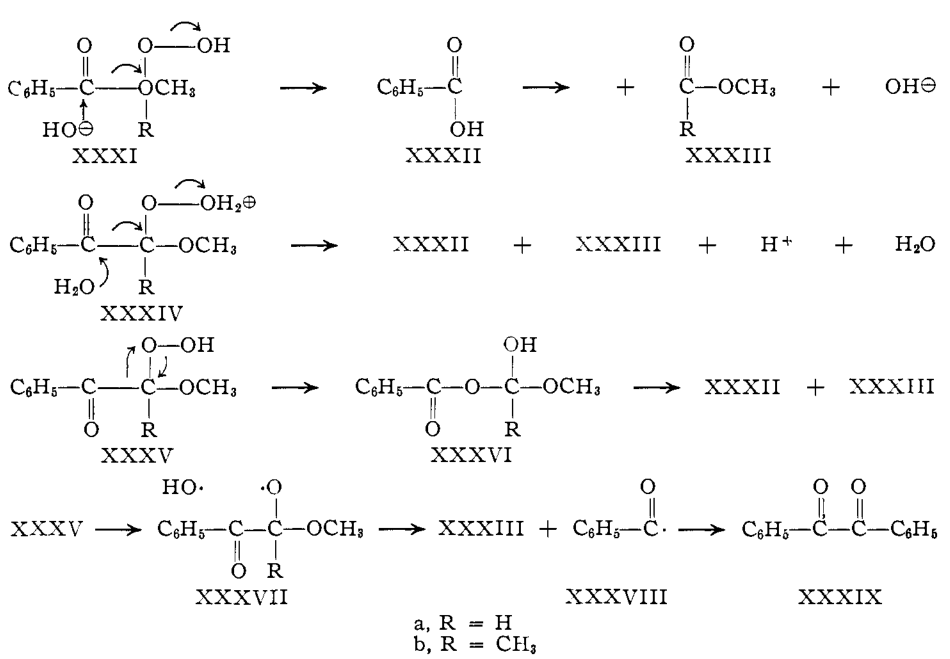
(10) P. S. Bailey and S. H. Pomerantz, *ibid.*, **75**, 281 (1953).

(11) A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954, p. 107.

(12) F. H. Seubold, Jr., and W. E. Vaughan, THIS JOURNAL, **75**, 3790 (1953).

(13) Melting points are corrected. Microanalyses were performed by the microanalytical laboratory of the University of Texas Biochemical Institute and by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. The molecular weight determination was done cryoscopically in benzene by Mr. S. B. Mainthia. The active oxygen determination was by the method of V. R. Kokatnur and M. Jelling, *ibid.*, **63**, 1432 (1941).

(14) P. S. Bailey, G. Nowlin, S. H. Pomerantz, J. V. Waggoner and E. E. Kawas, *ibid.*, **73**, 5560 (1951).



a, R = H
b, R = CH_3

Several recrystallizations by the addition of petroleum ether (b.p. 60–68°) to an ethanol solution of the material gave a good recovery of material melting at 60–61°. The material is soluble in methanol, ethanol, acetic acid and benzene, and is insoluble in petroleum ether and carbon tetrachloride. It gave a negative hydroperoxide test with lead tetraacetate in acetic acid solution but a positive test in methanol solution.[4] The infrared spectrum, taken in chloroform, showed a broad hydroxyl band at 2.8–3.1 μ and a strong carbonyl band at 5.9 μ.

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.22; H, 6.16; active O, 8.1; methoxyl, 15.82; mol. wt., 196.2. Found: C, 61.51; H, 5.65; active O, 7.7; methoxyl, 15.48, 15.66; mol. wt., 199.

The filtrate from which the hydroperoxide was originally filtered was evaporated under vacuum. The residue was warmed over a steam-bath for a few minutes to decompose any remaining peroxide material, after which it was extracted with ether and sodium bicarbonate solution. The aqueous layer was acidified and filtered, yielding 0.6 g. of benzoic acid (m.p. 120–122°, no depression in mixture melting point with an authentic sample). The ether layer was washed and evaporated. The residue was extracted several times with hot water. That which did not dissolve was treated with excess phenylhydrazine under the usual conditions; 0.2 g. of material melting at 227–228° was obtained and shown to be the phenylosazone of benzil by the mixture melting point method.[15]

The water extract was evaporated and the residue was dried, leaving 3.7 g. (61%) of colorless crystals melting at 78–85°. The material was identified as the hydrate of phenylglyoxal[15] by treating it with phenylhydrazine under the usual conditions; the osazone was obtained (m.p. 150–152°), identification was by the mixture melting point method.[15]

Ozonolysis of *trans*-1,2-dibenzoylethylene (10 g.) was carried out by the procedure described in the preceding experiment. The crude hydroperoxide XXXIa weighed 4.6 g. (60% yield) and melted with decomposition at 63–65°. Recrystallization was by addition of petroleum ether (b.p. 60–68°) to a concentrated ethyl acetate solution of the material, followed by cooling to about −15°; the pure material melted with decomposition at 68–69°. The substance was soluble in acetic acid, methanol, ethanol and ethyl acetate, insoluble in petroleum ether, benzene and carbon tetrachloride. It gave a positive lead tetraacetate test[4] in methanol solution. The infrared spectrum, taken in chloroform, showed a broad hydroxyl band at 2.9–3.0 μ and a strong carbonyl band at 5.9 μ.

Anal. Calcd. for $C_9H_{10}O_4$: C, 59.33; H, 5.53, active O, 8.78. Found: C, 59.68; H, 5.45; active O, 7.8.

The filtrate also was worked up as described in the preceding experiment, yielding 1.6 g. of benzoic acid (m.p. 120–122°), 0.5 g. of benzil phenylhydrazone (m.p. 226–228°)[15] and 4 g. (63% yield) of phenylglyoxal hydrate (m.p. 80–85°), identified through the osazone (m.p. 150–152°).[15] Identifications were by the mixture melting point method.

Reduction of α-Hydroperoxy-α-methoxypropiophenone (XXIV) to 1-Phenyl-1,2-propanedione (XXIII).—To a cold mixture of 8 g. of sodium iodide, 5 ml. of acetic acid and 10 ml. of methanol was added, slowly, 1 g. of the hydroperoxide XXIV. The mixture was allowed to come to room temperature, and the iodine thus formed was reduced with sodium thiosulfate. The resulting mixture was extracted with ether and the ether extract was washed and evaporated. The residue was treated with a solution of 0.6 g. of semicarbazide hydrochloride, 0.6 g. of sodium acetate and 5 ml. of methanol. After 30 minutes the reaction mixture was cooled and filtered, yielding 0.8 g. (75% yield) of 1-phenyl-1,2-propanedione semicarbazone (m.p. 203–205°). Recrystallization of the material from ethanol raised the melting point to 211–212°. Identification was by a mixture melting point with an authentic sample (m.p. 211–212°).[16]

Reduction of α-Hydroperoxy-α-methoxyacetophenone (XXXIa) to Phenylglyoxal.—The reduction was carried out with 1.5 g. of the hydroperoxide just as in the preceding experiment. After evaporation of the ether extract containing the reduction product, the residue was treated with 10 ml. of ethyl alcohol, 2.5 g. of phenylhydrazine and 1 ml. of acetic acid, and the mixture was refluxed for 1–2 hr. The resulting solution was diluted with water and cooled, yielding 1 g. of phenylglyoxal osazone melting at 146–149°; recrystallized from ethyl alcohol, 0.8 g., m.p. 151–153°. Identification was by the mixture melting point method.[15]

Decompositions in Alcohols. (a) **α-Hydroperoxy-α-methoxyacetophenone (XXXIa).**—A solution of 1 g. of XXXIa in 10 ml. of methanol was refluxed for 30 min., after which time it was evaporated under vacuum. The residue was extracted with sodium bicarbonate solution and ether. The aqueous fraction was acidified with hydrochloric acid and partially evaporated and cooled, yielding

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(15) The reported melting point of benzil phenylosazone is 225°. The reported melting point for phenylglyoxal hydrate is 91° and that for the phenylosazone is 152°. See R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th Ed., John Wiley and Sons, Inc., New York, N. Y., 1956.

(16) O. Diels and A. v. Dorp, *Ber.*, **36**, 3183 (1903), report a melting point of 213°.

0.57 g. (85% yield) of benzoic acid melting at 121-122°; identification was by the mixture melting point method.

(b) **α-Hydroperoxy-α-methoxypropiophenone (XXXIb).**—A suspension of 5.6 g. of XXXIb in 20 ml. of ethanol and 10 ml. of petroleum ether (b.p. 60-68°) was allowed to stand at room temperature for 5 min., during which time an exothermal reaction occurred. The solution was evaporated and the residue was extracted with ether and sodium carbonate solution. Upon acidification of the aqueous extract and partial evaporation, 2.8 g. (80% yield) of benzoic acid (m.p. 120-122°) was obtained. Evaporation of the ether extract gave a small residue which was treated with phenylhydrazine in the usual manner, yielding 0.1 g. of benzil phenylosazone (m.p. 225-227°).[15] Identifications were by the mixture melting point method.

Decompositions in Formic Acid.—In each case 1 g. of hydroperoxide (XXXIa or b) was added to 10-20 ml. of cold formic acid. An exothermal reaction ensued in case of XXXIa. The solutions were then heated on a steam-bath for 30 minutes after which they were evaporated under vacuum. The residues melted at 120-122° and were identified as benzoic acid by the mixture melting point method. The yields were 0.6 g. (90%) from α-hydroperoxy-α-methoxyacetophenone (XXXIa) and 0.52 g. (84%) from the corresponding propiophenone (XXXIb).

Decompositions in Sodium Hydroxide Solution.—In each case 1 g. of hydroperoxide (XXXIa or b) was added to 15 ml. of 10% sodium hydroxide solution. An exothermal reaction occurred in the case of XXXIa. After a few minutes it was poured into excess dilute hydrochloric acid. In the case of XXXIb the reaction mixture stood overnight before it was poured into excess dilute hydrochloric acid. Upon evaporation of these solutions and recrystallization of the residues from water, yields of benzoic acid (m.p. 120-122°) of 79% from the hydroperoxyacetophenone (XXXIa) and of 72% from the hydroperoxypropiophenone (XXXIb) were obtained. Identifications were by the mixture melting point method.

Decomposition of α-Hydroperoxy-α-methoxyacetophenone (XXXIa) with Pyridine.—To 3.8 g. of the hydroperoxide was added 15 ml. of pyridine. An exothermal reaction ensued. The mixture was then heated over a steam-bath for 20 min., after which it was evaporated by a stream of air. The residue was dissolved in ether, the ether extract was washed thoroughly and then extracted with sodium carbonate solution. Upon acidification of the aqueous layer with hydrochloric acid 1.1 g. (43% yield) of benzoic acid was obtained (m.p. 120-122°). The ether layer was evaporated and the residue was treated with phenylhydrazine in the usual way. The product was benzil phenylosazone (0.14 g., m.p. 224-226°).[16] Identifications were by the mixture melting point method.

Acknowledgment.—The authors are grateful for a grant-in-aid from the Research Corporation which made this work possible.

AUSTIN, TEXAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

Cyclic Dienes. XX. 4-*n*-Octyl-1,2-dimethylenecyclohexane[1]

BY WILLIAM J. BAILEY AND WILLIAM A. KLEIN[2]

RECEIVED OCTOBER 15, 1956

A convenient synthesis of a 2-alkyl-1,3-butadiene was developed from a commercially available alkenylsuccinic anhydride as the starting material. Thus 2-*n*-octyl-1,3-butadiene was prepared in four steps including a pyrolysis of a diacetate in an over-all yield of 53%. This 2-octylbutadiene was then converted in five steps to 4-*n*-octyl-1,2-dimethylenecyclohexane in an over-all yield of 40%. The final step in the synthesis involved the pyrolysis of a diacetate in a 55% yield. The structures of the dienes were proved by ultraviolet and infrared absorption spectra and conversion to solid Diels-Alder adducts.

A series of substituted 1,2-dimethylcyclohexanes[3–6] has been prepared in this Laboratory in an effort to determine the correlation between the molecular structure and the physical properties of the corresponding polymers. One of the objectives was the determination of the reason for the fact that the all-*cis* poly-1,2-dimethylenecyclohexane was a high melting crystalline polymer while the closely related all-*cis* natural rubber was an excellent rubber.[7] Since a methyl group located in the 4-position had very little effect on the softening point of an all-*cis* polymer, it was of interest to determine what effect a large group located in the 4-position would have on the physical properties of a poly-1,2-dimethylenecyclohexane. It had been shown previously that, as the size of the *n*-alkyl group in poly-*n*-alkyl methacrylates[8] and poly-*n*-alkylstyrenes[9] was increased, the softening point was decreased until a maximum depression occurred when the alkyl group contained eight to ten carbon atoms. Higher homologs reversed this trend and the softening points began to rise, presumably because the long alkyl side chains were capable of increasing the crystallinity of the polymers by the formation of crystallites involving only these side groups. For these reasons the synthesis of 4-*n*-octyl-1,2-dimethylenecyclohexane (I) was undertaken with the hope that a less crystalline and therefore a more rubbery all-*cis* polymer could be produced.

Since one of the key intermediates in the projected synthesis of I was 2-*n*-octyl-1,3-butadiene (II), an effort was made to find a convenient route to this diene. Previous work in this Laboratory has shown that the pyrolysis of esters is an excellent method for the preparation of unsaturated compounds and that, if charring is avoided, highly strained dienes, such as 1,2-dimethylene-4-cyclohexene, an isomer of *o*-xylene, can be prepared completely free of its aromatic isomer.[10] Marvel and

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[1] Previous paper in this series, THIS JOURNAL, **79**, 1444 (1957).

[2] Office of Naval Research Fellow, 1951-1954; Union Carbide Fellow, 1954-1955.

[3] W. J. Bailey, J. Rosenberg and L. J. Young, THIS JOURNAL, **76**, 2251 (1954).

[4] W. J. Bailey and R. L. Hudson, *ibid.*, **78**, 670, 2806 (1956).

[5] W. J. Bailey, C.-W. Liao and G. H. Coleman, *ibid.*, **77**, 990 (1955).

[6] W. J. Bailey and W. B. Lawson, *ibid.*, **77**, 1606 (1955).

[7] W. J. Bailey and H. R. Golden, *ibid.*, **76**, 5418 (1954).

[8] C. E. Rehberg and C. H. Fisher, *Ind. Eng. Chem.*, **40**, 1431 (1948).

[9] C. G. Overberger, C. Frazier, J. Mandelman and H. F. Smith THIS JOURNAL, **75**, 3326 (1953).

[10] W. J. Bailey and J. Rosenberg, *ibid.*, **77**, 73 (1955); W. J. Bailey, J. Rosenberg and L. J. Young, *ibid.*, **77**, 1163 (1955).