The tan solution was examined by visible–ultraviolet spectroscopy and shown to contain 0.99 mmole of tricyanovinyl alcohol (λ_{max} 297 mμ, ϵ 11,300) and 0.01 mmole of 1,1,2,3,3-pentacyanopropene (λ_{max} 397 and 414 mμ, ϵ 22,600 and 22,100, respectively).

When a solution of 0.81 g. (5.9 mmoles) of tricyanovinyl chloride in 4 ml. of tetrahydrofuran was treated with 2 ml. of water, a rapid (45 seconds) exothermic reaction took place with evolution of carbon dioxide (identified by the white precipitate it gave with lime water). The addition of 1.0 g. of tetramethylammonium chloride in 15 ml. of water followed by the removal of the tetrahydrofuran under vacuum gave 0.364 g. (51%) of tetramethylammonium pentacyanopropenide, m.p. 310–312°. The ultraviolet-visible spectrum was identical with that of an authentic sample.

Reaction of Tricyanovinyl Chloride with Tricyanovinyl Alcohol.—A mixture of 1.37 g. (0.01 mole) of tricyanovinyl chloride, 1.92 g. (0.01 mole) of the tetramethylammonium tricyanoethenolate and 15 ml. of tetrahydrofuran was heated under reflux on a steam-bath for 4 hours. The solid that separated weighed 2.35 g. It was shown to contain 0.0068 mole of pentacyanopropenide anion by spectroscopic examination. The filtrate yielded 0.45 g. (33%) of unreacted tricyanovinyl chloride after concentration and sublimation.

Reaction of Tricyanovinyl Ethyl Ether with N,N-Dimethylaniline.—A solution of 1.47 g. (0.01 mole) of tricyanovinyl ethyl ether in 5 ml. of N,N-dimethylaniline was heated in a boiling water-bath for 30 minutes. The resultant deep red solution was taken up in 30 ml. of methylene chloride and extracted successively with two 25-ml. portions of cold 2 *N* hydrochloric acid, 25 ml. of water and 10 ml. of saturated sodium chloride solution. The organic layer was then concentrated and chromatographed on acid alumina (Woelm) using ethyl acetate–acetone for elution. The deep-red gummy solid weighed 0.95 g. and contained 0.74 g. (34% yield) of N,N-dimethyl-*p*-tricyanovinylaniline as shown by the visible absorption intensity at 515 mμ. The infrared spectrum of this gum indicated the absence of N,N-dimethyl-*p*-(2,2-dicyano-1-ethoxyvinyl)-aniline.[13]

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS, AUSTIN 12, TEX.]

The Initial Attack of Ozone on Unsaturated Systems. Ozonolyses of Unsymmetrical Derivatives of 1,2-Dibenzoylethylene[1]

BY PHILIP S. BAILEY, SHASHIKANT B. MAINTHIA AND CLAUDE J. ABSHIRE

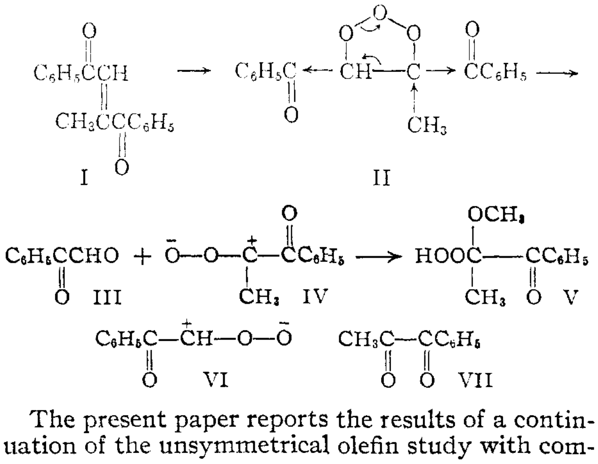
RECEIVED MARCH 26, 1960

The study of the specificity of ozone attack on unsymmetrical olefins is continued with *cis*-1,2-dibenzoylpropene, *cis*-1,2-dibenzoyl-1-methoxyethylene, *cis*-1-amino-1,2-dibenzoylethylene and *cis*- and *trans*-1,2-dibenzoylstyrene. The results of this study and of studies made elsewhere make it clear that there is no single type of initial ozone attack, nor is there a single route to peroxidic and non-peroxidic ozonation products after the inital ozone attack. With most olefinic double bonds, however, it appears that a five-membered ring intermediate is produced *via*, at least in protolytic solvents, a π-complex involving the terminal electrophilic atom of the ozone molecule.

Introduction

The Criegee mechanism[2,3] for ozonolysis does not attempt to elucidate the manner in which ozone initially attacks an unsaturated system. Various suggestions and discussions concerning this problem can be found in the literature.[3-7]

One approach to the problem of the initial ozone attack has involved the identification of the zwitterion and carbonyl moieties which are predominantly found during ozonolyses of unsymmetrical olefins.[8,9] For example, ozonolysis of *trans*-1,2-dibenzoylpropene (I) in the presence of methanol gave preferentially phenylglyoxal (III) and zwitterion IV (isolated as the methanol adduct V) rather than moieties VI and VII.[9] This result, as well as most other examples of the specificity of ozone attack reported up to the present time, can be explained by any of three ways: (1) a two-step addition in accordance with Markownikoff's rule to give a four-membered ring intermediate,[3,9] (2) the collapse of a five-membered ring intermediate (*e.g.*, II → III + IV) formed either by a one-step or a two-step ozone attack,[3,9-12] (3) an ozone attack which leads to no addition intermediate, but produces through an activated complex the more stable of the two possible zwitterion intermediates.



The present paper reports the results of a continuation of the unsymmetrical olefin study with com-

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[1] A portion of this work was presented at the 132nd Meeting of the American Chemical Society, Organic Chemistry Division, Symposium on Mechanisms of Oxidation Reactions, New York, N. Y., September, 1957.

[2] (a) R. Criegee and G. Wenner, *Ann.*, **564**, 9 (1949); (b) R. Criegee, *ibid.*, **583**, 1 (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); (e) R. Criegee, *Record Chem. Progr. Kresge-Hooker Sci. Lib.*, **18**, 111 (1957).

[3] P. S. Bailey, *Chem. Revs.*, **58**, 925 (1958).

[4] P. S. Bailey, *Chemistry & Industry*, 1148 (1957).

[5] E. A. Blair and A. Maggiolo, Abstracts of Papers presented at the 134th Meeting of the American Chemical Society, Chicago, Ill., September, 1958, p. 6 P.

[6] F. T. Wallenberger, *Tetrahedron Letters*, No. 9, August, 1959. p. 5.

[7] (a) E. J. Moriconi, W. F. O'Connor and L. Taranko, *Arch. Biochem. and Biophys.*, **83**, 283 (1959); (b) E. J. Moriconi, W. F. O'Connor and F. T. Wallenberger, THIS JOURNAL, **81**, 6466 (1959).

[8] P. S. Bailey, *Chem. Ber.*, **88**, 795 (1955).

[9] (a) P. S. Bailey and S. S. Bath, THIS JOURNAL, **79**, 3120 (1957); (b) P. S. Bailey, S. S. Bath and J. B. Ashton, *Advances in Chem. Ser.*, **21**, 143 (1959).

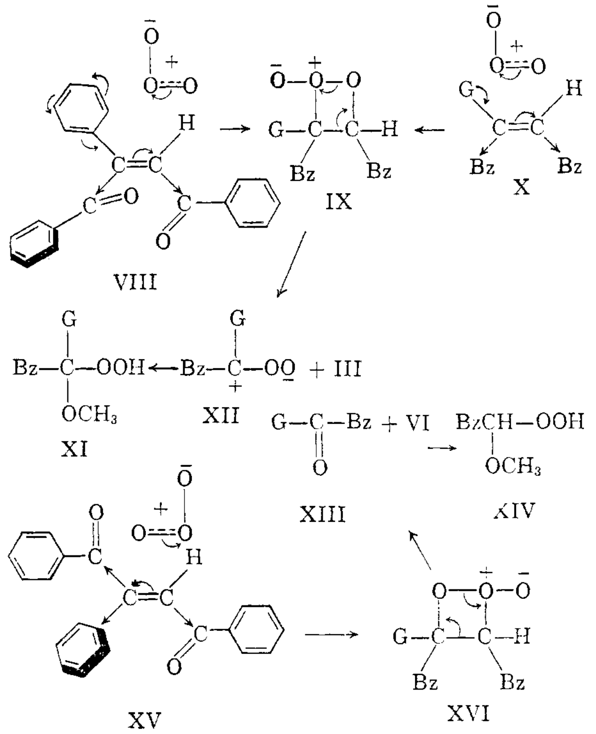
[10] L. A. Subluskey, G. C. Harris, A. Maggiolo and A. Tumolo, *ibid.*, **21**, 149 (1959).

[11] R. Criegee, private discussions.

[12] A. Maggiolo, "Organic Ozone Reactions and Techniques," The Welsbach Corp., Ozone Processes Div., Philadelphia, Pa., 1957

pounds chosen for the purpose of deciding which, if any, of the three described types of ozone attack actually occurs. The compounds studied were *cis*-1,2-dibenzoylpropene (Xd), *cis*-1,2-dibenzoyl-1-methoxyethylene (Xc), *cis*-1-amino-1,2-dibenzoylethylene (Xb) and *cis*- (VIII) and *trans*-1,2-dibenzoylstyrene (XV). The *trans*-amino- and methoxydibenzoylethylenes are not known.

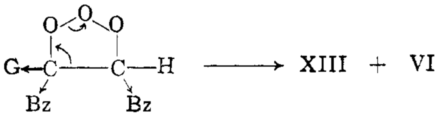
The two-step attack leading to a four-membered ring would be controlled predominantly by the resonance effects of the groups around the olefinic double bond.[3,9] La Pine and other molecular models show the benzalacetophenone system of *cis*-1,2-dibenzoylstyrene (VIII) to be in one plane, with the other benzoyl group out of this plane. Physical and chemical evidence is consistent with this picture.[13]



(a) G = phenyl, (b) G = $-\ddot{\text{N}}\text{H}_2$, (c) G = $-\ddot{\underset{\cdot\cdot}{\text{O}}}\text{CH}_3$, (d) G = $-\text{CH}_3$, Bz = benzoyl throughout

Thus, the course of the addition should be as shown in VIII to give IXa which must break up to give moieties XIIa and III. By this mechanism the results with Xb, Xc and Xd should be similar, since molecular models show that the amino, methoxyl and methyl groups can always be planar with the olefinic double bond whether or not the benzoyl groups are, and because the resonance effects of these groups (and also the inductive effect of the methyl group) is electron releasing. In the case of *trans*-1,2-dibenzoylstyrene (XV), the 1,2-dibenzoylethylene system is planar, but the other phenyl group is out of this plane, as shown both by molecular models and by physical and chemical data.[13] Thus, by the mechanism leading to a four-membered ring, the phenyl group attached to the olefinic double bond can affect the addition only inductively, leading to XVI and moieties XIII and VI.

The direction of cleavage of the five-membered ring intermediate XVII can be influenced by the inductive effects of the substituents, but not by their resonance effects. Thus with VIII, Xb, Xc and XV, where the inductive effects of the phenyl, amino and methoxyl groups are all electron withdrawing, the ring cleavage (in XVII) should lead preferentially to moieties XIII and VI. Compound Xd, however, should behave like the *trans* isomer (*i.e.*, Xd → II → III + IV).



XVII, (a) G = phenyl, (b) G = $-\text{NH}_2$, (c) G = -OCH
Bz = benzoyl throughout

By the mechanism leading to the most stable zwitterion, each of the substances under consideration should give moieties XII and III, since the resonance effects of all four groups G (phenyl, amino, methoxyl and methyl) would be to stabilize zwitterion XII.

Results

Ozonolysis of *cis*-1,2-dibenzoylpropene (Xd) in the presence of methanol produced the same cleavage moieties (III and IV) as were obtained from the *trans* isomer.[9] Along with phenylglyoxal (III, 57% yield) and α-hydroperoxy-α-methoxypropiophenone (V, 59% yield), however, was obtained benzoic acid in 33% yield. The greater decomposition of IV or V to benzoic acid in the case of the *cis* isomer than in the case of the *trans* isomer was perhaps due to the fact that the *cis* isomer reacted more slowly than did the *trans* isomer, thus requiring that more ozone be passed through the system.

Ozonolysis of *cis*-1,2-dibenzoyl-1-methoxyethylene (Xc) in the presence of methanol gave methyl phenylglyoxalate (XIIIc) in 74% yield and α-hydroperoxy-α-methoxyacetophenone (XIV) in 84% yield. The latter was identified by its analyses, reduction to phenylglyoxal, and by comparison of its infrared spectrum with that of the same material obtained from ozonolysis of *trans*-1,2-dibenzoylethylene under the same conditions.[9a] An 11% yield of benzoic acid also was obtained. Lutz, Wilder and Parrish[14] had previously ozonized Xc in chloroform. The products were benzoic acid (62% yield), phenylglyoxalic acid (6% yield) and methyl phenylglyoxalate (XIIIc) in 88% yield. Thus, it appears that XIIIc and zwitterion VI also are formed preferentially in non-protolytic solvents.

Phenylglyoxamide (XIIIb) in 88–95% yield was obtained from ozonolysis of *cis*-1-amino-1,2-dibenzoylethylene (Xb) in the presence of methanol. Attempts to isolate hydroperoxide XIV failed because of difficulty in separating it from XIIIb and to its tendency to decompose to benzoic acid[9a] in the presence of XIIIb. Benzoic acid was isolated in 78–81% yields. The same cleavage moieties (XIIIb and VI) seem to be produced in non-protolytic solvents. The products reported from ozonoly-

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[13] (a) L. P. Kuhn, R. E. Lutz and C. R. Bauer, THIS JOURNAL, **72**, 5058 (1950); (b) R. E. Lutz and C. R. Bauer, *ibid.*, **73**, 3456 (1951); (c) C. R. Bauer and R. E. Lutz, *ibid.*, **75**, 5997 (1953).

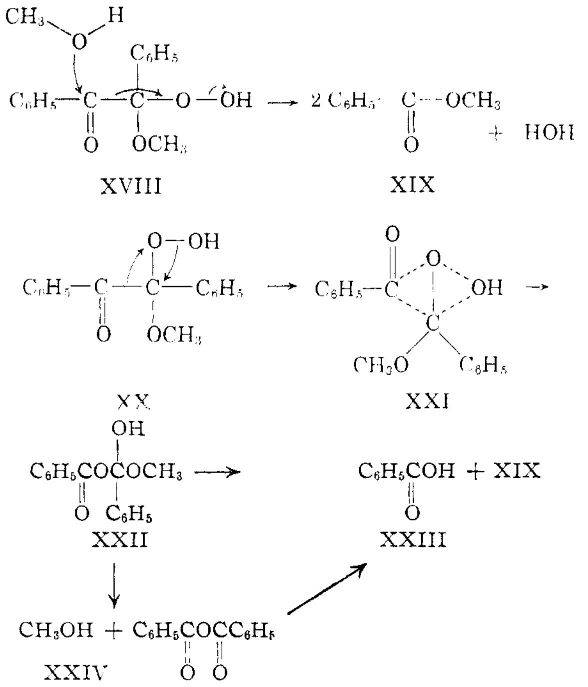
[14] R. E. Lutz, F. N. Wilder and C. I. Parrish, *ibid.*, **56**, 1980 (1934).

sis of Xb in chloroform were benzoic acid (82% yield), phenylglyoxalic acid (12% yield) and phenylglyoxamide (XIIIb) in 43% yield.[14]

It also proved impossible to isolate the hydroperoxide moiety from ozonolyses of *cis*- and *trans*-1,2-dibenzoylstyrene (VIII and XV) in the presence of methanol, although its presence was indicated by a positive lead tetraacetate test.[15] The hydroperoxide in each case was shown to be largely XIa by the fact that whereas a reductive work-up procedure gave 91–97% yields of benzil (XIIIa from reduction of XIa) and 54–59% yields of phenylglyoxal (III, isolated as mandelic acid), a decomposition work-up procedure gave only a 2% yield of benzil (XIIIa) along with a 20–25% yield of phenylglyoxal (III) and a 95% combined yield of benzoic acid and methyl benzoate based on an expected 2 moles of the two from one mole of XIa. The low yield of phenylglyoxal apparently was due both to its further oxidation by ozone to benzoic acid and methyl benzoate (which was shown to occur readily in the methanol–carbon tetrachloride medium) and to polymerization (which would be greatest during the heat induced decomposition work-up procedure). The proportion of methyl benzoate (XIX) to benzoic acid (XXIII) obtained by the decomposition procedure was always considerably greater than one to one. This could be due partially to a solvolytic decomposition of XIa, as shown in XVIII, or to esterification of benzoic acid (XXIII) produced by rearrangement of XX, as proposed earlier for such hydroperoxides,[3,9a] (XX → XXI → XXII and XXII → XXIII + XIX or XXII → XXIV → XXIII + XIX). A thorough study of the decomposition of hydroperoxides such as XIa is in progress. Some of the XXIII and XIX obtained probably came from ozonation of phenylglyoxal and perhaps from decomposition of minor amounts of hydroperoxide XIV. Benzil (XIIIa), however, was shown not to be appreciably attacked by ozone under the conditions of the ozonolysis.

Ozonolysis of *cis*-1,2-dibenzoylstyrene (VIII) in carbon tetrachloride gave inconclusive results. Judging from the low yield (*ca.* 25%) of benzil obtained, it would appear that zwitterion XIIa also was formed predominantly in this case. However, it should be pointed out that this yield is considerably higher than that obtained in methanol. The relatively high yield of benzoic acid and derivatives obtained indicates that these substances were formed both from decomposition of zwitterion XIIa and ozonation of phenylglyoxal (III). *trans*-1,2-Dibenzoylethylene was ozonized for comparison; the results were similar to those with VIII, but involving moieties III and VI.

It is evident that these results are consistent with none of the mechanisms suggested in the Introduction. The results with the isomeric 1,2-dibenzoylpropenes (I and Xd) can be explained by any of the three mechanisms, the results with *cis*-1,2-dibenzoylstyrene (VIII) can be accounted for either by the two-step mechanism leading to a four-membered ring or by the mechanism leading to the more stable of the two possible zwitterions, the results with *cis*-1-amino-1,2-dibenzoylethylene (Xb) and with *cis*-1,2-dibenzoyl-1-methoxyethylene (Xc) can be accounted for only by the mechanism involving the five-membered ring intermediate, and the *trans*-1,2-dibenzoylstyrene (XV) results can be explained only by the mechanism leading to the more stable of the two possible zwitterion moieties.



Discussion

The results just described, along with other data in the literature, suggest that the type of ozone attack varies with the nature of the compound undergoing attack. Ozone is a highly energetic and versatile reagent and apparently can attack organic groupings in the following ways: (1) an electrophilic attack on a nucleophilic atom with the formation of a σ-complex or some comparable species[3,12]; (2) an electrophilic attack on a carbon–carbon double bond to produce a π-complex[3,4]; (3) a four-center reaction on a carbon–carbon double bond; (4) a nucleophilic attack on an electrophilic atom[16]; (5) a radical attack on certain saturated groupings.[13]

With most carbon–carbon double bonds, at least in protolytic solvents, the predominant initial ozone attack seems to be type 2 to give a π-complex (XXV or XXVI) followed, contrary to our original suggestion[4] by electron shifts 1 and 2 (in XXVI) to produce the five-membered ring intermediate XXVIII. The so-called complex XXVII suggested recently by Blair and Maggiolo[5] as the initial ozone adduct probably is the transition state in this transformation. In non-protolytic solvents perhaps a competing four-center ozone attack occurs to give XXVII and XXVIII directly.[17,18]

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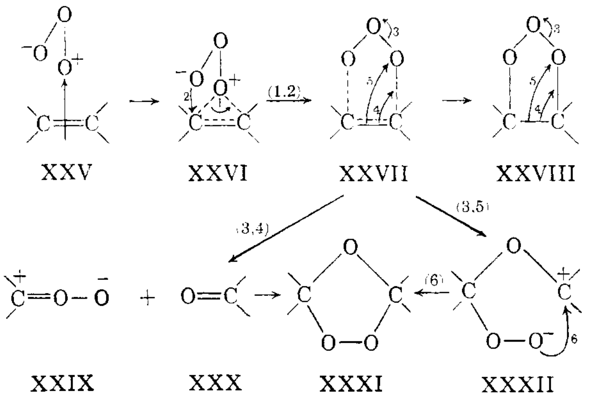
(15) R. Criegee, H. Pilz and H. Flygare, *Ber.*, **72**, 1799 (1939).

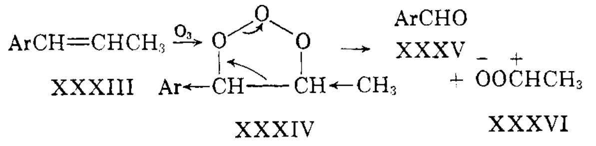
(16) A. H. Riebel, R. E. Erickson, C. J. Abshire and P. S. Bailey, This Journal, **82**, 1801 (1960).

(17) F. Dobinson and P. S. Bailey, *Tetrahedron Letters*, No. **13**, 14 (1960).

(18) Kinetic studies have not been made with ozonolyses of olefinic double bonds because the reactions are so fast. However, kinetic studies with aromatic compounds carried out by F. L. J. Sixma, H. Boer and J. P. Wibaut, *Rec. trav. chim.*, **70**, 1005 (1951), under heterogeneous conditions, and by T. W. Nakagawa, L. J. Andrews and R. M.

The specificity of ozone attack with most olefins, except the 1,2-dibenzoylstyrenes (VIII and XV), can be explained on the basis of the intermediate five-membered ring, the direction of cleavage of which is controlled by the inductive effects of the substituents on the ring. This includes the observations of Briner and co-workers[19] that during ozonolyses of compounds XXXIII, the aromatic aldehyde XXXV is present in greater amounts than is the aliphatic aldehyde.

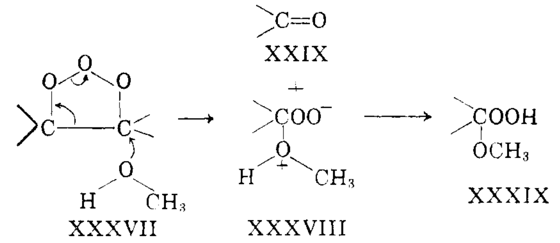




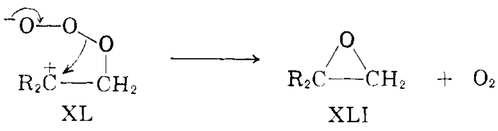
As pointed out earlier by Blair and Maggiolo,[5] steric factors can make it difficult or impossible for transition state XXVII (in which the carbon atoms still have their Sp^2 hybridization) to be formed. This apparently is the case with the 1,2-dibenzoylstyrenes (VIII and XV); electron shifts 1 and 2 (in XXVI) are immediately followed by electron shifts 3 and 4 (in unstable XXVII), before XXVIII can ever be produced, to give the more stable pair of zwitterion (XXIX) and carbonyl (XXX) moieties.

In other instances, where less stable cleavage moieties (XXIX and XXX) are possible and the solvent is inert (toward zwitterion XXIX, etc.), electron shifts 3 and 5 (in XXVII) followed by 6 (in XXXII) might occur in a concerted process to give an ozonide (XXXI). This essentially, is the mechanism for ozonide formation suggested by Criegee[20a] and by Leffler,[20b] before Criegee proposed his presently accepted mechanism, and more recently by Lutz.[20c] Something of this sort competing with complete cleavage at either stage XXVII or XXVIII is necessary in order to explain the recently reported findings of Criegee[21] that *trans*-1,2-di-*t*-butylethylene forms a primary ozonide (presumably type XXVIII) which is stable at low temperatures, whereas no such intermediate is observable with the *cis* compound, which produces a true ozonide (type XXXI) in high yield. Decomposition of the primary ozonide in the case of the *trans* isomer gave lower or no yields of the true ozonide in various inert solvents, accompanied by polymeric material (probably polymers of zwitterions of types XXIX or XXXII). Similarly, Briner[19] has shown that ozonolyses of *cis* and *trans* isomers in inert solvents do not produce the same proportions of ozonide XXXI on the one hand and of XXX and polymers of XXIX and XXXII on the other hand.

In reactive (toward zwitterion XXIX etc.) solvents such as methanol, complete cleavage usually occurs[3,21] and there appears to be little or no competition from the concerted rearrangement process. This is understandable on the basis that the solvent enters the reaction at stage XXVII or XXVIII in the manner illustrated in XXXVII to give XXIX, XXXVIII and finally XXXIX. A similar action by excess formaldehyde in the reaction mixture could account for the unique ozonide formation reported earlier by Criegee, Blust and Zinke.[22]



When steric hindrance occurs on one side only of a double bond, epoxide formation rather than double bond cleavage often occurs during ozonations.[3,5] It appears likely that in these cases the preponderance of bulky groups on one carbon atom of the double bond causes σ-complex formation (XL) instead of π-complex formation or a four-center reaction to occur. Loss of oxygen, analogous to that with sulfide and tertiary amine ozonations,[3] rather than ring closure, hindered by the bulky groups, would give the epoxide XLI.



It is to be emphasized that the reaction mechanisms described here are highly competitive and that minor variations in structure, reaction medium and conditions might cause one to be favored over another. This is due to the facts that not only ozone, but also the initial ozone–organic adducts are highly energetic and go to products quickly.

During the study of the unsymmetrical 1,2-dibenzoylethylene derivatives, the ozonolysis of *cis*-1-chloro-1,2-dibenzoylethylene was attempted. After passage of 6 moles of ozone per mole of starting material through the reaction mixture, a 70% recovery of starting material was made. This

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Keefer, This Journal, **82**, 269 (1960), under homogeneous conditions, show the reactions to be second order. The mechanisms described here are consistent with these kinetics.

(19) E. Dallwigk and E. Briner, *Helv. Chim. Acta*, **39**, 1826 (1956); (b) E. Briner, E. Dallwigk and M. Ricca, *ibid.*, **41**, 1390 (1958); (c) E. Briner and M. Ricca, *ibid.*, **41**, 2178 (1958); (d) E. Briner, S. Flisgar and M. Ricca, *ibid.*, **42**, 749 (1959); (e) E. Briner and S. Flisgar, *ibid.*, **42**, 1310 (1959); (f) **42**, 2063 (1959).

(20) (a) R. Criegee, *Ann.*, **560**, 131 (1948); (b) J. E. Leffler, *Chem. Revs.*, **45**, 399 (1949); (c) R. E. Lutz and C. K. Dien, *J. Org. Chem.*, **23**, 1861 (1958).

(21) (a) R. Criegee, Paper presented at the 136th National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1959; (b) R. Criegee, *Chem. Ber.*, **93**, 689 (1960).

(22) R. Criegee, G. Blust and H. Zinke, *ibid.*, **87**, 766 (1954).

deactivation of carbon–carbon double bonds to ozone attack by chloro groups has been noted previously by Noller.[23] In the present work the ozonolyses of several other halogen-substituted olefins were attempted: *cis*- and *trans*-1,2-dibromo-1,2-diphenylethylene, *trans*-1,2-dichloro-1,2-diphenylethylene and 2,3-dibromo-1,4-diphenyl-2-butene. In all of these cases the ozone attack was extremely slow. This deactivation by halogen could be due to either or both electrical and steric factors and is consistent with π or σ-complex formation or with a four-center ozone attack.

Experimental[24]

The ozonator, ozonation flasks and ozonation procedure were described in earlier publications.[9a,25] The methanol and carbon tetrachloride were pure and anhydrous.

Starting Materials.—*trans*-**1,2-Dibenzoylethylene** (m.p. 109–110°) was supplied by the National Aniline Division of Allied Chemical and Dye Corp. It was converted to *meso*-**1,2-dibenzoyl-1,2-dibromoethane** (m.p. 177–178°) by the method of Lutz.[26] *cis*-**1,2-Dibenzoyl-1-methoxyethylene** (Xc), (m.p. 108–109°) was prepared from *meso*-1,2-dibenzoyl-1,2-dibromoethane in 83% yield by the method of Conant and Lutz[27] (using, however, commercial sodium methoxide in place of sodium and methanol). *cis*-**1-Amino-1,2-dibenzoylethylene** (Xb, m.p. 141–142°) was prepared from *meso*-1,2-dibenzoyl-1,2-dibromoethane in 90% yield by the method of Lutz, Amacker, King and Shearer.[28] **3-Chloro-2,5-diphenylfuran** (m.p. 74–75°) was prepared in 55% yield from *trans*-1,2-dibenzoylethylene by the procedure of Lutz.[29] This was converted to *cis*-**1-chloro-1,2-dibenzoylethylene** (m.p. 69–70°)[27] by the characteristic nitric acid oxidation[30] in 62% yield. *cis*-**1,2-Dibenzoylstyrene** (VIII, m.p. 129–130°) was prepared in 90% yield by the method of Allen and Rosener,[31,13c] using commercial sodium methoxide in place of sodium and methanol. This was converted to *trans*-**1,2-dibenzoylstyrene** (XV, m.p., 126–127°) by the method of Oliveri-Mandala.[32,13c] *trans*-**1,2-Dibenzoylpropene** (I, m.p. 50–52°) was prepared by the method of Bailey, Nowlin, Pomerantz, Waggoner and Kawas.[33] It was converted to **3-methyl-2,5-diphenylfuran** (m.p. 59–60°) by the reductive cyclization procedure[34] and on to *cis*-**1,2-dibenzoylpropene** (Xd, m.p. 66–68°) by nitric acid oxidation.[30,34] **1,2-Diphenylacetylene** (m.p. 60–61°) was prepared by the procedure of Smith and Falkof[35] and was converted to *cis* and *trans*-**1,2-dibromo-1,2-diphenylethylene** (m.p. 210–211° for *trans* and 66–68° for *cis*) by the method of Il'ichev.[36] *trans*-**1,2-Dichloro-1,2-diphenylethylene** (m.p. 151–152°) was also prepared as described by Il'ichev.[36] **2,3-Dibromo-1,4-diphenyl-2-butene** (m.p. 97–98°) was prepared from 2,3-dibromo-2-butene-1,4-diol[37] by the method of Dupont, Dulou and Lefebvre.[38]

Ozonolysis of *cis*-**1,2-Dibenzoyl-1-methoxyethylene (Xc).** (a) α-**Hydroperoxy**-α-**methoxyacetophenone** (XIV).—Into a cold (−25°) suspension of 2 g. of 1,2-dibenzoyl-1-methoxyethylene (Xc) in 3 ml. of methanol and 12 ml. of CCl_4 was passed an ozone–oxygen stream containing 62 mg. of ozone per liter at a rate of 17 l. per hour. The ozone reacted slowly and it was necessary to pass 1.7 mole-equivalents through the reaction mixture before one mole equivalent was absorbed. The reaction mixture was swept with dry oxygen for a short time and then cooled to −35°. After a half-hour, the precipitate which formed was filtered off and washed with carbon tetrachloride; 0.8 g., m.p. 80° dec. Partial evaporation of the filtrate gave more of the material; total yield 1.15 g. (84%); recrystallized from ethyl acetate by addition of ligroin, m.p. 83° dec.

Anal. Calcd. for $C_9H_{10}O_4$: C, 59.33; H, 5.53; active O, 8.78. Found: C, 58.97; H, 5.72; active O, 8.55.

Since the material melted higher than that obtained earlier (m.p. 68–69°-dec.) by ozonolysis of *trans*-1,2-dibenzoylethylene,[9a] the latter preparation was repeated. The hydroperoxide melted at 82° dec. Infrared spectra showed the two samples to be identical. The hydroperoxide was further characterized by sodium iodide reduction[9a] to phenylglyoxal in 70% yield (isolated as the phenylosazone, m.p. 151–153°).

(b) **Methyl Phenylglyoxalate (XIIIc).**—The filtrate from which the above hydroperoxide was separated was warmed to decompose any remaining hydroperoxide and was evaporated under vacuum. The residue was shaken with sodium bicarbonate solution and ether (extract I). The bicarbonate solution was acidified and extracted with ether (extract II). From ether extract II was obtained 0.1 g. (11% yield) of benzoic acid melting at 121–122°. Ether extract I was washed and evaporated and the residue was dissolved in ethanol and treated with 40 ml. of 2,4-dinitrophenylhydrazine reagent.[39] The yield of methyl phenylglyoxalate 2,4-dinitrophenylhydrazone melting at 173–174° was 1.9 g. (74%).[40] Identifications were by mixture melting points with authentic samples.

In another instance the residue from evaporation of ether extract II was distilled. The yield of methyl phenylglyoxalate boiling at 99° (1 mm.) was 61%. It was identified through its 2,4-dinitrophenylhydrazone, m.p. 173–174°.[40]

Ozonolysis of *cis*-**1-Amino-1,2-dibenzoylethylene (Xb).** (a) **Phenylglyoxamide (XIIIb).**—Into a solution of 3 g. of *cis*-1-amino-1,2-dibenzoylethylene (Xb) in 5 ml. of methanol and 10 ml. of carbon tetrachloride cooled to −30° was passed an ozone–oxygen stream containing 68 mg. of ozone per liter, at a rate of 27 l. per hour. The reaction occurred slowly and it was necessary to employ 1.4 mole-equivalents of ozone in order for one mole-equivalent to be absorbed. Fifteen milliliters of carbon tetrachloride was added in order to increase the carbon tetrachloride–methanol ratio and the mixture was partially evaporated under vacuum. By three sucessive filtrations and partial evaporations, a total of 1.7 g. (95% yield) of phenylglyoxamide (m.p. 74–79°) was obtained; recrystallized from ethanol, m.p. 77–78°; the semicarbazone prepared in aqueous solution melted at 232–233°.[41]

(b) **Attempted Isolation of** α-**Hydroperoxy**-α-**methoxyacetophenone (XIV).**—Evaporation of the filtrate from the above phenylglyoxamide separation gave a gummy, peroxidic residue. Attempts to crystallize the material failed. Similar attempts also failed with reaction mixtures using pure methanol and 1 part methanol to 4 parts carbon tetrachloride as the solvent. The ozonolysis was then repeated in pure methanol at −60° and the reaction mixture was reduced immediately with sodium iodide. Titration of the released iodine with standard sodium thiosulfate showed an active

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[23] C. R. Noller, J. F. Carson, H. Martin and K. S. Hawkins, THIS JOURNAL, **58**, 24 (1936).

[24] Melting points are corrected. Microanalyses were performed by the microanalytical laboratory of the University of Texas Biochemical Institute, the Schwartzkopf Microanalytical Laboratory, Woodside, N. Y., and the Huffman Microanalytical Laboratories, Wheatridge, Colo. The active oxygen determinations were by the method of R. Criegee, G. Blust and G. Lohaus, *Ann.*, **583**, 4 (1953), with the exception that the iodide reduction was carried out at −20° in order to prevent peroxide decomposition from giving low values.

[25] P. S. Bailey, THIS JOURNAL, **78**, 3811 (1956).

[26] R. E. Lutz, *ibid.*, **49**, 1109 (1927).

[27] J. B. Conant and R. E. Lutz, *ibid.*, **47**, 888 (1925).

[28] R. E. Lutz, T. Amacker, S. M. King and N. H. Shearer, *J. Org. Chem.*, **15**, 191 (1950).

[29] R. E. Lutz, THIS JOURNAL, **48**, 2916 (1926).

[30] (a) R. E. Lutz and F. N. Wilder, *ibid.*, **56**, 978 (1934); (b) **56**, 1193 (1934).

[31] C. F. H. Allen and H. B. Rosener, *ibid.*, **49**, 2110 (1927).

[32] E. Oliveri-Mandala, *Gazz. chim. ital.*, **45**, II, 138 (1915); *C. A.*, **10**, 1517 (1916).

[33] P. S. Bailey, G. Nowlin, S. H. Pomerantz, J. V. Waggoner and E. E. Kawas, THIS JOURNAL, **73**, 5560 (1951).

[34] R. E. Lutz and C. E. McGinn, *ibid.*, **64**, 2585 (1942).

[35] L. I. Smith and M. M. Falkof in E. C. Horning, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 350.

[36] A. M. Il'ichev, *Zhur. Obshchei Khim.*, **18**, 1121 (1948); *C. A.*, **43**, *1755 (1949); E. Bergmann, J. Chem. Soc.*, 402 (1936).

[37] R. Lespieau, *Ann. chim. phys.*, [8] **27**, 172 (1912).

[38] G. Dupont, R. Dulou and G. Lefebvre, *Bull. soc. chim. France*, 653 (1954).

[39] R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th Edition, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 111.

[40] H. H. Schlubach and V. Franzen, *Ann.*, **578**, 223 (1952), report a melting point of 174°.

[41] R. E. Lutz, F. N. Wilder and C. I. Parrish (ref. 14) report melting points of 76–77° and 233–234° for phenylglyoxamide and its semicarbazone, respectively.

oxygen content of 0.5 mole equivalent. In another run the reduction was carried out after evaporation of the solvent under reduced pressure at room temperature. The active oxygen content was only 0.15 mole equivalent.

(c) **Decomposition of the Hydroperoxide.**—The ozonolysis was carried out as before using 2.5 g. of Xb, 5 ml. of methanol and 10 ml. of carbon tetrachloride. The solution was evaporated to dryness under reduced pressure and the residue was warmed (to decompose any remaining peroxide) and extracted with sodium bicarbonate solution and ether. Acidification of the bicarbonate layer gave 0.95 g. (78% yield) of benzoic acid (m.p. 121–123°). Evaporation of the ether layer gave a 88% yield of phenylglyoxamide, isolated as the semicarbazone; m.p. 233–234° after recrystallization from ethanol.[41]

In another instance the ozonolysis was carried out in methanol, after which the reaction mixture was refluxed for one hour to decompose the hydroperoxide. The solvent was evaporated under reduced pressure and the residue was treated as described in the preceding paragraph. The yield of benzoic acid (m.p. 122–123°) was 81% and that of phenylglyoxamide (isolated as the semicarbazone, m.p. 227–230°) was 54%. Identifications were by mixture melting points with authentic samples.

Ozonolysis of *cis*-1,2-Dibenzoylstyrene (VIII) in a Polar Solvent. (a) Attempted Isolation of Peroxidic Product.—An ozone–oxygen mixture containing 66 mg. of ozone per liter was passed at a rate of 27 l. per hour into a cold (−30°) suspension of 2 g. of *cis*-1,2-dibenzoylstyrene (VIII) in 3 ml. of methanol and 25 ml. of carbon tetrachloride. About 2 moles of ozone per mole of starting material was required to order to cause 1 mole equivalent to react. The reaction mixture gave a positive lead tetraacetate test for a hydroperoxide. No crystalline hydroperoxide could be obtained, however, by keeping the reaction mixture at −35 to −60°, even after partial evaporation.

(b) **Decomposition Products.**—A suspension of 10 g. of *cis*-1,2-dibenzoylstyrene (VIII) in 35 ml. of methanol and 80 ml. of carbon tetrachloride was treated with 1.5 mole equivalents of ozone as described in the preceding experiment. Filtration of the reaction mixture at −35° gave 2.7 g. (27% recovery) of starting material. The filtrate was diluted with 60 ml. of methanol and was refluxed for 2 hours, after which time it no longer gave an active oxygen test with sodium iodide. Evaporation under reduced pressure gave a yellow oil which was dissolved in ether. The ether solution was extracted with sodium carbonate, from which extract a 55% yield of benzoic acid melting at 122° was obtained. Extraction of the ether solution with 20% sodium hydroxide solution, neutralization of the basic layer with hydrochloric acid, extraction of the resulting solution with ether and evaporation of the ether extract gave an oil which crystallized from benzene, yielding 0.7 g. (20%) of DL-mandelic acid (m.p. 118°). Evaporation of the original ether extract and distillation of the residue gave 4.2 g. (1.32 mole equivalents) of methyl benzoate (b.p. 95–100° (15 mm.), n^{16}_{D} 1.51780)[42] and a viscous liquid boiling at 100–190° (15 mm.). The liquid crystallized on standing to give 0.12 g. (2% yield) of benzil melting at 93–95°. The ester was identified by a quantitative saponification to benzoic acid (m.p. 122°) and by transesterification with 3,5-dinitrobenzoic acid to methyl 3,5-dinitrobenzoate (m.p. 105–107°).[43] Identifications of all crystalline products were by the mixture melting point method.

In another experiment phenylglyoxal was concentrated by distillation (contaminated with methyl benzoate) and identified through its phenylosazone (m.p. 151–153°). In a third experiment, using as the solvent a solution of 5 ml. of methanol and 80 ml. of carbon tetrachloride, decomposition of the peroxidic ozonolysis product occurred during evaporation of the reaction mixture. The yield of methyl benzoate was much lower and a 36% yield of benzoic anhydride was obtained.

(c) **Reduction Products.**—The ozonolysis was carried out as described in the preceding experiment and the cold reaction mixture was swept with oxygen and filtered into a cold (−30°) mixture of 20 g. of sodium iodide, 40 ml. of methanol and 10 ml. of acetic acid. In the funnel was a 21% recovery of starting material. After an hour the liberated iodine in the reduction medium was titrated with sodium thiosulfate; the presence of 1.2 gram atoms of peroxidic oxygen per mole of reacting starting material was indicated. The reaction mixture was extracted several times with carbon tetrachloride. The carbon tetrachloride extract was evaporated and the residue was dissolved in ether. At this point benzoic acid (6% yield, m.p. 120–121°) and mandelic acid (59% yield, m.p. 117–118°) were isolated as described in the preceding experiment. Evaporation of the ether solution after these separations yielded 4.83 g. (91% yield) of benzil (crystallized from ethanol, m.p. 94–95°).

Ozonolysis of cis-1,2-Dibenzoylstyrene (VIII) in Carbon Tetrachloride. (a) Decomposition.—Twelve liters of an ozone–oxygen stream containing 0.06 g. of ozone per liter was passed through a solution of 5 g. of VIII in 100 ml. of carbon tetrachloride cooled to 0°. One mole equivalent of ozone reacted. A yellow explosive precipitate was present. The reaction mixture was carefully refluxed in a round-bottom flask for 3 hours, after which time it gave only a faint peroxide test with iodide ion. The solvent was evaporated under reduced pressure, the residue dissolved in 100 ml. of dry methanol, the resulting solution refluxed for 2 hours and evaporated, the residue dissolved in ether, and the ether solution (A) extracted five times using 10 ml. of 14 % sodium carbonate solution each time. The sodium carbonate extract was acidified with concd. hydrochloric acid, cooled and filtered, yielding 1.35 g. (0.8 mole-equivalent) of benzoic acid melting at 120–121°. Sodium bisulfite and 30% sodium hydroxide extractions of ether solution A gave nothing. Evaporation of solution A gave an orange-colored oil which crystallized from ethanol solution on cooling, yielding first 0.84 g. of starting material (m.p. 128–129°) and second, on further cooling, 0.36 g. of unknown colorless crystals melting at 135–145°. After four recrystallizations (70% recovery) from ethanol, the material melted sharply at 158°; infrared spectra showed no hydroxyl or carbonyl bonds.

Anal. Found: C, 77.09; H, 5.99; 0, 17.06; mol. wt., 419 (in bromoform).

Evaporation of the filtrate from crystallization and recrystallization of the material above gave a yellow oil which was distilled at 14 mm. pressure, giving 0.51 g. (0.33 mole equivalent) of methyl benzoate boiling at 90–95° and 0.58 g. (0.21 mole equivalent) of benzil boiling at 130–200° and melting at 93–95°. Identifications of known crystalline materials were by the mixture melting point method and identification of methyl benzoate was as described previously.

(b) **Reduction.**—The ozonolysis was carried out as described in the preceding experiment, with the absorption of 1.38 mole equivalents of ozone. The ozonized solution was poured into a reducing solution consisting of 40 g. of sodium iodide, 75 ml. of methanol and 18 ml. of glacial acetic acid. Titration with 0.1 *N* thiosulfate showed 1 mole-equivalent of peroxidic oxygen. The carbon tetrachloride layer was separated, the aqueous layer was extracted with carbon tetrachloride and the combined carbon tetrachloride solutions were worked up as described in the preceding experiment. The products were as follows: 0.75 mole-equivalent of benzoic acid (m.p. 120–121°), 0.05 mole-equivalent of mandelic acid (from the 30% sodium hydroxide extraction, m.p. 117–118°), a small amount (0.5 g. from 10 g. of VIII) of the unknown material melting at 158°, 0.14 mole-equivalent of methyl benzoate (90–95° (14 mm.)) and 0.28 mole-equivalent of benzil (m.p. 93–95°). Identifications were by mixture melting point determinations or by previously described methods.

Ozonolysis of *trans*-1,2-Dibenzoylethylene in Carbon Tetrachloride.—The ozonolysis and decomposition was carried out as described for VIII, except that the reflux procedure in the presence of methanol was omitted. The products were benzoic acid (0.88 mole-equivalent, m.p. 120–121°), benzil (0.04 mole-equivalent, m.p. 93–95°) and an undetermined amount of an anhydride thought to be benzoic anhydride. When the decomposition was carried out in the presence of methanol (100 ml. added immediately after the ozonolysis), the products were benzoic acid (0.18 mole equivalents, m.p. 119–121°), methyl benzoate (0.95 mole equivalent, b.p. 90–95° (14 mm.)), and benzil (0.10 mole equivalent, m.p. 93–95°).

When the ozonolysis reaction mixture was worked up by

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[42] "Handbook of Chemistry and Physics," 39th Edition, Chemical Rubber Publishing Co., Cleveland, Ohio, 1957, p. 793, reports n^{16}_{D} 1.51810.

[43] A. I. Vogel, "Practical Organic Chemistry," 3rd Ed., Longman, Green and Co., London, 1956, p. 393.

the reductive process as described for VIII, the active oxygen content was shown to be 0.21 mole equivalent, and the products were benzoic acid (0.72 mole-equivalent, m.p. 119–121°), mandelic acid (0.03 mole-equivalent, m.p. 117–118°), methyl benzoate (0.21 mole-equivalent, b.p. 90–95° (14 mm.)) and benzil (0.09 mole-equivalent, m.p. 93–95°).

Ozonolysis of *trans*-1,2-Dibenzoylstyrene (XV) in Polar Solvent. (a) **Attempted isolation of the peroxidic ozonolysis products** as described earlier for the *cis* isomer yielded only a small amount of benzoic acid. The ozone absorption was slightly faster and more complete than in the case of the *cis* compound.

(b) **Decomposition Products.**—The ozonolysis, decomposition and work-up was as described for the *cis* compound except that an approximately 50–50 mixture of methanol and carbon tetrachloride was used as the solvent and, due to its low solubility, a 40% recovery of starting material was made after the absorption of 1.6 mole-equivalents of ozone. The yields of benzoic acid (m.p. 120–121°), mandelic acid (m.p. 117–118°) and methyl benzoate (b.p. 95–100° (15 mm.)) were 79, 25 and 111%, respectively, based on an expected one mole per mole of starting material reacting. No benzil was isolated. Products were identified as described in the case of the *cis* isomer.

(c) **Reduction Products.**—The ozonolysis and work-up were carried out as described in the case of the *cis* compound except that the starting material was completely in solution (1.6 g. of XV, 20 ml. of methanol and 30 ml. of carbon tetrachloride) and the reaction went to completion, involving one mole of ozone per mole of XV. Iodometric titration showed 1 gram-atom of peroxidic oxygen per mole of starting material and the products were mandelic acid (54% yield, m.p. 117–118°) and benzil (97%, m.p. 94–95°). No benzoic acid was isolated. Identifications were by the mixture melting point method.

Conversion of phenylglyoxal to DL-mandelic acid was shown to occur in 80% yield when an ether solution of freshly prepared phenylglyoxal[9a] was extracted with 30% sodium hydroxide solution and the basic extract was worked up in the usual manner.

Conversion of benzoic acid to methyl benzoate occurred in only 14% yield when a solution of 10 g. of benzoic acid, 100 ml. of methanol and 100 ml. of carbon tetrachloride was refluxed for 18 hours. In a similar experiment 99% of the benzoic acid was recovered after 4 hours of reflux. The work-up procedure was as described in the ozonolysis experiments.

Ozonation of Phenylglyoxal.—Forty-five liters of an ozone–oxygen mixture containing 0.069 g. of ozone per liter was passed through a solution of 4 g. of phenylglyoxal in 35 ml. of methanol and 50 ml. of carbon tetrachloride at −35°. Ozone was slowly absorbed to the extent of 1.33 mole equivalents. The reaction mixture was refluxed for 3 hours (no longer peroxidic) and was evaporated under reduced pressure. The residue was dissolved in ether and the ether solution was extracted with sodium carbonate solution. From the latter by the usual method was obtained a 23% yield of benzoic acid (m.p. 120–121°). Nothing was obtained from the ether solution by sodium bisulfite or sodium hydroxide extractions. Evaporation and distillation of the residue gave a 25% yield of methyl benzoate (b.p. 95–100° (15 mm.)). Identifications were as described in preceding experiments.

After a similar **ozonation of benzil** a near quantitative recovery of starting material was obtained.

Ozonolysis of *cis*-1,2-Dibenzoylpropene (Xd). (a) **α-Hydroperoxy-α-methoxy-propiophenone (V).**—A solution of 1.4 g. of *cis*-1,2-dibenzoylpropene (Xd) in 2 ml. of methanol and 10 ml. of carbon tetrachloride was treated with an ozone–oxygen mixture at −25° as described in earlier experiments. A total of 1.8 mole-equivalents of ozone was required in order for one mole-equivalent to be absorbed. The reaction mixture was kept at −35° for 3 hours and filtered. Thus was obtained 0.65 g. (59% yield) of material melting at 62° dec.; recrystallized from ethyl acetate by addition of ligroin, m.p. 69° dec.

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.21; H, 6.17; active O, 8.16. Found: C, 61.12; H, 6.59; active O, 8.05.

Infrared spectra showed the material to be the same as that obtained by ozonolysis of the *trans* isomer[9a]; the earlier material, however, appeared to be contaminated slightly with starting material and/or decomposition products. The hydroperoxide was reduced, as before,[9a] with sodium iodide to 1-phenyl-1,2-propanedione (m.p. of disemicarbazone, 240–241°)[44] in 50% yield.

Anal. Calcd. for $C_{11}H_{14}N_6O_2$: C, 50.4; H, 5.5. Found: C, 50.5; H, 5.3.

(b) **Phenylglyoxal.**—The filtrate and washings from the hydroperoxide separation were combined and heated to decompose any remaining peroxidic material and then shaken with ether and sodium bicarbonate solution. The ether extract was evaporated and the residue was extracted with hot water. The undissolved portion was shown to be benzil (30 mg.) by conversion to its phenylosazone (m.p. 225–226°). The hot water layer was evaporated, treated with phenylhydrazine, ethanol and a drop of acetic acid and refluxed for 1–2 hours. One gram of phenylglyoxal phenylosazone (57% yield, m.p. 151–153°) was obtained. The bicarbonate layer was acidified and extracted with ether. Evaporation of the ether layer gave 0.23 g. (33% yield) of benzoic acid (m.p. 121–122° after recrystallization from water). Identifications were by mixture melting points with authentic samples.

Attempted Ozonolyses of Halogen Substituted Olefins.—These were all carried out at −30° as described in preceding experiments. The solvent was methanol; excess ozone was employed in all cases. Identifications were by the mixture melting point method.

(a) ***cis*-1-Chloro-1,2-dibenzoylethylene.**—Six mole-equivalents of ozone was used, 2.7 of which was absorbed by the reaction mixture (methanol perhaps reacted). Sodium iodide reduction and titration of the released iodine with thiosulfate showed 1.7 mole-equivalents of active oxygen to be present. A 70% recovery of starting material was made.

(b) **2,3-Dibromo-1,4-diphenyl-2-butene.**—Seven mole equivalents of ozone was used, 5.2 of which was absorbed. Sodium iodide treatment showed 1.8 mole equivalents of active oxygen (methanol perhaps reacted). A 71% recovery of starting material was made. This was partly due to low solubility of the starting material.

(c) ***trans*-1,2-Dibromo-1,2-diphenylethylene.**—Nine mole-equivalents of ozone was employed, most of which was recovered in the sodium iodide trap. This was partly due to the low solubility of the starting materials. A 93% recovery of starting material was made upon partial evaporation of the solution. Further evaporation led to an explosion.

(d) ***cis*-1,2-Dibromo-1,2-diphenylethylene.**—Five mole-equivalents of ozone was employed. Cooling of the reaction mixture led to a 50% recovery of starting material.

(e) ***trans*-1,2-Dichloro-1,2-diphenylethylene.**—Six mole-equivalents of ozone was employed, most of which passed into the sodium iodide trap. Cooling of the reaction mixture gave a 45% recovery of starting material.

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(44) K. V. Auwers, *Ber.*, **50**, 1612 (1917), reports the melting point as 229–232°. However, a sample made from authentic 1-phenyl-1,2-propanedione showed the same melting point as, and gave no depression in a mixture melting point with, the above sample. The previous monosemicarbazone sample[9a] also was converted to the disemicarbazide, which was shown to be identical to that just described by a mixture melting point.