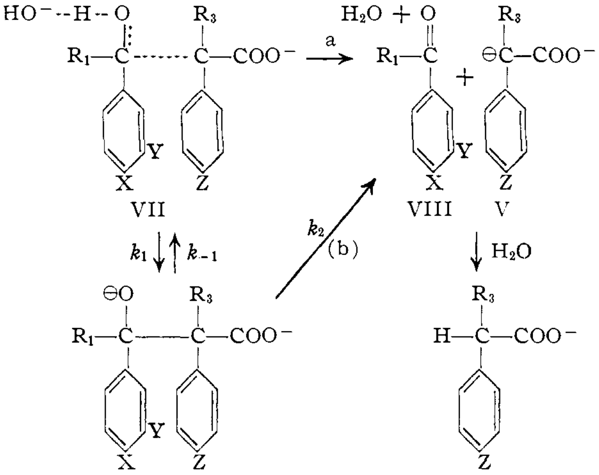
thought to proceed by removal of the proton from the β-hydroxyl group with essentially simultaneous fission of the C_α–C_β bond to form the ketone and the carbanion V (path a). The reaction is driven to completion by the irreversible acquisition of a proton from the solvent by V.



The alternative path b is deemed not to represent this reaction for the following reasons. If $k_1 >> k_{-1}$ and $k_2 < k_1$, we would have the cleavage of the C_α–C_β bond as the rate-determining step. This is the situation which obtains in the well-known dealdolization of diacetone alcohol.[26] Were this true with β-hydroxy acids, it would be difficult to see why changing the nature of the base and solvent should have such an overwhelming influence on the rate. As mentioned above, the diacetone alcohol cleavage is not nearly so sensitive to base strength. Secondly, a much smaller salt effect would have been predicted, since this rate-determining step would have involved a unimolecular dissociation of one doubly-charged anion to a second one (V) and a neutral molecule. Finally, it would be difficult to explain the effect of bulky β-substituents in decreasing the rate if the C_α–C_β bond cleavage were rate determining; the F-strain hypothesis would have led to the unqualified prediction that increasing bulk would promote dissociation.

The possibility that proton removal is rate-determining ($k_1 << k_2$) is excluded by the fact that substitution on the α-position, either an α-alkyl group or a *para*-substituent in the phenyl group, has a pronounced influence on the rate. The fairly large positive value of *rho* (2.16) shows that electron accession to C_α is involved in the transition state. This could scarcely be the case if the rate were controlled by removal of the proton from the remote β-hydroxyl group.

The arguments which show that neither separate step can be rate controlling provide powerful support for the idea that H–O and C_α–C_β bond-breaking both are important in the rate-determining step, and hence support the postulation of a synchronous mechanism.

The dealdolization of diacetone alcohol is considered to proceed by a two-step path, C–C bond cleavage being rate determining.[26] On the other hand, more complicated ketols are believed to dissociate by a concerted mechanism.[17] Perhaps someone will discover that certain β-hydroxy acids may also cleave by the two-step path.

Acknowledgment.—We are indebted to Professor F. F. Blicke for many helpful discussions.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DIVISION OF HUMBLE OIL AND REFINING CO.]

The Ozonolysis of Phenanthrene in Methanol

BY PHILIP S. BAILEY[1]

RECEIVED JANUARY 7, 1956

During ozonolysis in methanol, phenanthrene is attacked at the 9,10-double bond. The active oxygen containing ozonolysis products are characterized. The results support the Criegee mechanism for ozonolysis. The recently published Milas mechanism is criticized. By decomposition of the active oxygen containing products any one of the following substances can be obtained in good yield: 2,2′-biphenyldicarboxaldehyde, methyl 2′-formyl-2-biphenylcarboxylate, 2′-formyl-2-biphenylcarboxylic acid and diphenic acid.

This paper is the first of a series dealing with the course and mechanism of the ozonolysis reaction, especially in regard to aromatic type compounds.

The recent elegant work of Criegee and co-workers[2] concerning the mechanism of ozonolysis has dealt largely with aliphatic compounds. Wibaut and co-workers[3] have done a great deal of ozonolysis work with aromatic and heterocyclic compounds in which they have shown that the ozone attack is probably electrophilic in nature.

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(1) Address requests for reprints to the author, Department of Chemistry, University of Texas, Austin, Texas.

(2) (a) R. Criegee and G. Wenner, *Ann.*, **564**, 9 (1949); (b) R. Criegee and G. Lohaus, *Chem. Ber.*, **86**, 1 (1953); (c) R. Criegee, G. Blust and G. Lohaus, *Ann.*, **583**, 2 (1953); (d) R. Criegee and G. Lohaus, *ibid.*, **583**, 6 (1953); (e) **583**, 12 (1953); (f) R. Criegee, P. deBruyn and G. Lohaus, *ibid.*, **583**, 19 (1953); (g) R. Criegee and M. Lederer, *ibid.*, **583**, 29 (1953); (h) R. Criegee, G. Blust and H. Zinke, *Chem. Ber.*, **87**, 766 (1954); (i) G. Lohaus, *ibid.*, **87**, 1708 (1954); (j) R. Criegee, A. Kerckow and H. Zinke, *ibid.*, **88**, 1878 (1955). See also (k) P. S. Bailey, *ibid.*, **87**, 993 (1954); (l) P. S. Bailey, *ibid.*, **88**, 795 (1955); (m) J. Meinwald, *ibid.*, **88**, 1889 (1955).

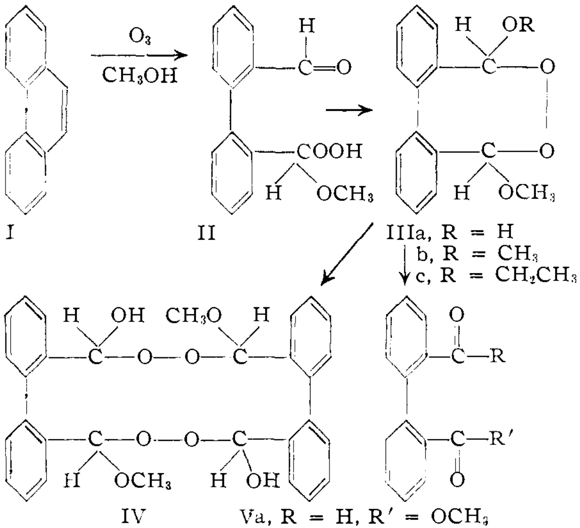
(3) P. W. Haayman and J. P. Wibaut, *Rec. trav. chim.*, **60**, 842 (1941); J. P. Wibaut and E. C. Kooijman, *ibid.*, **65**, 141 (1946); J. P. Wibaut and J. Van Dijk, *ibid.*, **65**, 413 (1946); E. C. Kooijman and J. P. Wibaut, *ibid.*, **66**, 705 (1947); J. Van Dijk, *ibid.*, **67**, 945 (1948); J. P. Wibaut, F. L. J. Sixma, L. W. F. Kampschmidt and H. Boer, *ibid.*, **69**, 1355 (1950); H. Boer, F. L. J. Sixma and J. P. Wibaut, *ibid.*, **70**, 509 (1951); F. L. J. Sixma, H. Boer and J. P. Wibaut, *ibid.*, **70**, 1005 (1951); J. P. Wibaut and F. L. J. Sixma, *ibid.*, **71**, 761 (1952); F. L. J. Sixma, *ibid.*, **71**, 1124 (1952); L. W. F. Kampschmidt and J. P. Wibaut, *ibid.*, **73**, 431 (1954); J. P. Wibaut and H. Boer, *ibid.*, **74**, 241 (1955).

They have not studied, however, the active oxygen-containing products.

As the beginning study in this program the ozonolysis of phenanthrene was undertaken. Due to the especial reactivity of its 9,10-double bond toward addition and oxidation, this substance represents an excellent bridge between the aliphatic and aromatic types and thus a good starting point in the aromatic field.

In 1905, Harries and Weiss[4] reported that the ozonolysis of phenanthrene in chloroform solution produced a crystalline explosive diozonide. They hydrolyzed the material but were unable to isolate any definite products. Very recently Schmitt, Moriconi and O'Connor[5] have repeated this work and have reported that either in chloroform or acetic acid only one mole of ozone is absorbed and a monoözonide is produced, involving the 9,10-double bond.

In the present work the ozonolysis was carried out in methanol. Here, too, only one mole of ozone per mole of phenanthrene is absorbed before appreciable amounts of ozone pass through unabsorbed. The product, which precipitates after the reaction mixture is brought to room temperature, is assigned structure IIIb on the basis of elementary analyses, molecular weight and the following facts. It gave a positive active oxygen test with potassium iodide and a negative hydroperoxide test with lead tetraacetate.[6] The infrared spectrum showed that neither carbonyl nor hydroxyl groups were present. Chemical analysis showed the presence of two methoxyl groups. When an ethanol or methanol suspension of the material was refluxed (reaction was speeded up by pyridine catalyst), methyl 2′-formyl-2-biphenylcarboxylate (Va) was produced. With sodium hydroxide in the place of pyridine the aldehydic acid (Vb) itself was the product. When both sodium hydroxide and hydrogen peroxide were employed in the reaction mixture, the product was diphenic acid (Vc).



I

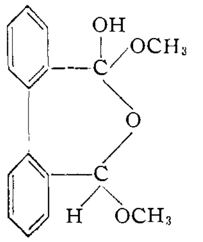
II

IIIa, R = H
b, R = CH_3
c, R = CH_2CH_3

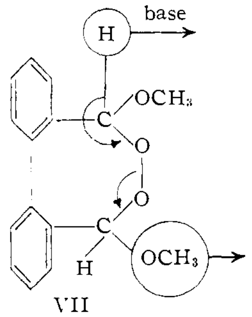
IV

Va, R = H, R′ = OCH_3
b, R = H, R′ = OH
c, R = R′ = OH
d, R = R′ = H

These decompositions of IIIb to give Va, b and c perhaps involve a rearrangement similar to that found for other peroxidic types[7] to give intermediate VI which then undergoes ring opening and loss of methanol to give Va. On the other hand, the fact that the reaction seems to be base catalyzed suggests that the changes shown in structure VII occur. Certainly, however, the facts that water is not needed and that Va is produced even in ethanol solution show that hydrolysis is not involved in the primary conversion to Va,



VI



VII

As long as the temperature of the reaction mixture is kept below 0°, the dimethoxy peroxide IIIb is not produced. The primary product, therefore, is something else which undergoes further reaction above 0° to produce IIIb. In view of Criegee's recent findings[2] and the fact that the cold reaction mixture gave a strong hydroperoxide test with lead tetraacetate, it was expected that the primary product would turn out to be the methoxy hydroperoxide II. This expectation was fulfilled by the precipitation of the crude hydroperoxide through addition of water to the cold reaction mixture.

Although the hydroperoxide II could not be purified due to its instability, it was sufficiently characterized by elementary analyses, molecular weight and methoxyl group determinations, qualitative tests and its infrared spectrum. It reacted with methanol to give the dimethoxy peroxide IIIb and with ethanol to give the corresponding ethoxymethoxy peroxide IIIc, and it was reduced with sodium iodide to give 2,2′-biphenyldicarboxaldehyde (Vd). Incidentally, reduction of the cold ozonization reaction mixture with sodium iodide also gives the dialdehyde in good yield. However, IIIb reduces only partially. During attempted reduction in a methanol–acetone mixture, IIIb largely decomposed to give the methyl ester of the aldehydic acid Va.

Besides undergoing an intramolecular hydroperoxide–aldehyde addition reaction (to give IIIa) followed by reaction with the solvent to give IIIb or IIIc, the hydroperoxide II tends to undergo the corresponding intermolecular reaction to give the di-hemiacetal IV. This dimeric product was isolated in the crystalline state only one time. However, infrared spectra and molecular weight determinations show that the monomer II is gen-

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(4) C. Harries and V. Weiss, *Ann.*, **343**, 373 (1905).

(5) W. J. Schmitt, E. J. Moriconi and W. F. O'Connor, THIS JOURNAL, **77**, 5640 (1955).

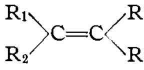
(6) R. Criegee, *Fortschr. Chem. Forsch.*, **1**, 536 (1950).

(7) R. Criegee in E. Müller, "Methoden der Organischen Chemie (Houben-Weyl)," Vol. VIII, 4th Ed., Georg Thieme Verlag, Stuttgart, Germany, 1952, pp. 54–56.

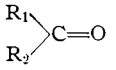
erally contaminated with the dimer IV. In some solvents the two are in equilibrium with each other; they give identical infrared spectra in bromoform, chloroform and carbon disulfide. It was necessary to take the spectra in potassium bromide pressed discs to distinguish between them. There, in contrast to the monomer II, the dimer IV showed neither a carbonyl band nor a hydroperoxy band.

Criegee[2] has proposed that the essential intermediates in the ozonolysis of a substance such as VIII are an aldehyde or ketone IX and a zwitterion X. The fate of X depends on IX and the solvent. If the solvent is inert and IX is an aldehyde, addition of X to IX to give an ozonide XI occurs; if IX is a ketone, X generally undergoes dimerization (to XII) and/or polymerization, instead. In reactive solvents, addition of the solvent to X to form hydroperoxides XIII generally occurs.

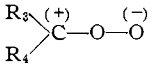
In spite of the overwhelming evidence in favor of the Criegee mechanism,[2] Milas, Davis and Nolan[8] have recently proposed a different mechanism for ozonolysis, involving primary intermediates such as XIV which are presumed to be in equilibrium with the ozonide XI.



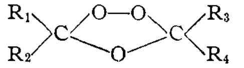
VIII



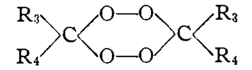
IX



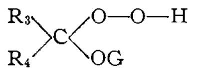
X

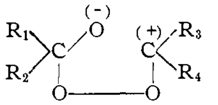


XI



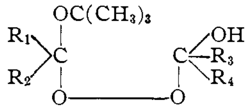
XII





XIII XIV

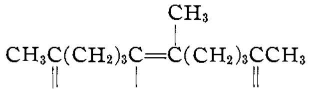
(G = H, alkyl or aryl)



XV

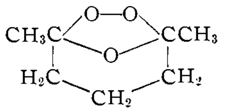
The evidence given for the Milas scheme was that ozonolyses carried out in a *t*-butyl alcohol–sulfuric acid medium at 15° produced compounds of type XV. The authors[8] assumed that these were formed by the interaction of *t*-butylcarbonium ions with zwitterions such as XIV. Hydroperoxides such as XIII were assumed to be secondary products from the breakdown of XV.

Because of the similarity of the major product IIIb to structure XV in the present research, it was necessary to consider carefully the mechanism of Milas, Davis and Nolan.[8] It seems clear, however, that the data described in the present paper are best explained by the Criegee mechanism.[2] The hydroperoxide II was obtained under much milder conditions than the compounds XV of Milas and co-workers.[8] Further, the Milas mechanism is contradictory to the following key findings of Criegee and co-workers:[2] 1. In at least one case hydroperoxides of type XIII were obtained under conditions where the ozonide was completely stable and could not be a precursor.[2e] According to the Milas mechanism[8] the ozonide ($XI \rightleftharpoons XIV$) would have to be formed first. 2. Tetramethylethylene, one of the compounds employed in the study of Milas and co-workers,[8] yields a methoxy hydroperoxide during ozonolysis in methanol under mild conditions.[2d] 3. The ozonolysis of tetramethylethylene in an inert solvent in the presence of formaldehyde gave the ozonide of isobutene instead of that of tetramethylethylene.[2h] It is difficult to reconcile this reaction other than by interaction of formaldehyde with a zwitterion of type X. 4. The ozonolysis of XVI in inert solvents does not yield the ozonide of XVI but instead ozonide XVII and 2,6-heptanedione.[2i] This reaction is not easily explained on any basis other than the intermediary formation of zwitterion XVIII.



$$\mathrm{CH_3\underset{\underset{O}{\|}}{C}(CH_2)_3\underset{\underset{CH_3}{|}}{C}=\overset{\overset{CH_3}{|}}{C}(CH_2)_3\underset{\underset{O}{\|}}{C}CH_3}$$

XVI



XVII

$$\mathrm{CH_3\underset{\underset{O}{\|}}{C}(CH_2)_3\underset{\underset{CH_3}{|}}{\overset{(+)}{C}}-O-\overset{(-)}{O}}$$

XVIII

The results of Milas, Davis and Nolan[8] are better explained on the basis of the Criegee mechanism. First a *t*-butoxy hydroperoxide (type XIII) is formed which, under the relatively drastic conditions of Milas and co-workers, undergoes hemiacetal formation with the aldehyde or ketone fragments (IX) to form type XV compounds. It is well known that hydroperoxides, like alcohols, undergo such reactions,[7] especially under acidic conditions such as employed by Milas and co-workers.[8] The reality of such a possibility is further borne out by the reactions of hydroperoxide II to give III and IV in the present investigation.

As an argument against the formation of zwitterions such as X, Milas, Davis and Nolan[8] point out that no peroxides formed by interaction of X with *t*-butylcarbonium ions were found. It seems apparent, however, that the acid-catalyzed addition of *t*-butyl alcohol to X to give XIII would be more likely to occur.

Experimental[9]

The ozonator used in this research was a Welsbach Corporation model T-23 laboratory ozonator. The determination of the quantity of ozone absorbed in each reaction was done by determining the concentration of ozone in the oxygen–ozone mixture during the reaction in terms of grams per unit volume, multiplying by the total volume of oxygen passed through the system and subtracting the quantity of ozone unabsorbed as shown in the potassium iodide trap following the reaction vessel (see Welsbach basic manual). The reaction vessel was the usual gas-absorption type with a porous fritted area at the bottom of the inlet tube to disperse thoroughly the incoming gas. The phenanthrene was Eastman Kodak Co. White Label 599. The melting point of 99–100° is indicative of its high purity. The methanol was J. T. Baker Analyzed Reagent, containing less than 0.1% water.

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(8) N. A. Milas, P. Davis and J. T. Nolan, Jr., This Journal, **77**, 2536 (1955).

(9) All melting points are corrected. Most of the microanalyses were done by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. The molecular weight determinations were run in benzene by the boiling point elevation method by Miss Jennie M. Chenet, the active oxygen determinations by Miss Marjorie T. Walker and the infrared spectra by Mr. H. W. Kinsey, all of the Humble Company.

Ozonolysis of Phenanthrene in Methanol to Give 3,8-Dimethoxy-4,5,6,7-dibenzo-1,2-dioxacycloöctane (IIIb).—A fine suspension of 5.35 g. (0.03 mole) of phenanthrene in 125 ml. of methanol (prepared by refluxing a mixture of the two until solution occurred and then cooling to the desired reaction temperature) was treated with an approximately 4% by weight ozone–oxygen mixture at a rate of 17 liters per hour and a temperature of −20 to 0° until everything dissolved. Toward the end of the reaction the ozonolysis vessel was shaken quite often in order to allow the undissolved phenanthrene to come into more intimate contact with the gas stream. Very little ozone passed through unabsorbed until most of the phenanthrene had gone into solution. A total of 1.1 to 1.2 moles of ozone per mole of phenanthrene was absorbed. The solution was then allowed to come to room temperature whereupon a colorless crystalline solid began to precipitate. After the reaction mixture had stood overnight, it was filtered, yielding 6.4 g. (78% yield) of material melting at 177–179°. Recrystallization of a small amount from methyl ethyl ketone raised the melting point to 180–181°. The material gave a slow but definite active oxygen test with potassium iodide and a negative hydroperoxide test with lead tetraacetate.[6] It was stable to shock but burned quickly in an open flame. Its infrared spectrum showed the absence of hydroxyl and carbonyl bands, but the presence of an ether band at 9.2 μ and a band at 7.5 μ which seems to be typical of methyl ethers.

Anal. Calcd. for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92; O, 23.50; methoxyl, 22.80; mol. wt., 272. Found: C, 70.53, 70.73; H, 5.75, 5.99; O, 22.75; methoxyl, 22.81; mol. wt., 260, 296.

The above preparation was carried out many times at temperatures ranging from 0 to −60° and methanol volumes of 90 to 125 ml. The yields were best under the conditions just described. The use of excess ozone lowered the yield. At low temperatures the reaction mixture became pale blue shortly after one mole of ozone per mole of phenanthrene had been absorbed. Before the precipitation of IIIb occurred, the reaction mixture gave a strong hydroperoxide test with lead tetraacetate.[6]

Although IIIb gave a qualitative active oxygen test with sodium iodide, a quantitative estimation proved impossible due, probably, to decomposition to methyl 2′-formyl-2-biphenylcarboxylate (Va). In acetic acid solution the values were 1–2% low. In an acetone–methanol solution acidified with acetic acid very little reduction occurred and a 75% yield of Va was obtained.

Ozonolysis of Phenanthrene in Methanol to Give ω-(2′-Formyl-2-biphenylyl)-ω-methoxymethyl Hydroperoxide (II).—The ozonolysis just described was repeated at a temperature of about −20°, after which the unreacted ozone was swept out by a stream of dry oxygen. While the reaction mixture was still cold, about 200 ml. of water was slowly added, accompanied by agitation and scratching on the sides of the vessel. Crystallization occurred. The colorless crystals were filtered off, washed and air-dried, 5.7 g. (74% yield), m.p. 84–88°. In cases where larger amounts of water were added the yields were higher, but the material was lower melting and darker. No solvent was found from which the material could be recrystallized. It appeared to decompose quite easily. It gave a strong active oxygen test with potassium iodide and a positive hydroperoxide test with lead tetraacetate in benzene medium. It was stable to shock but burned rapidly in an open flame. The infrared spectrum taken in a potassium bromide disc showed a broad associated hydroxyl band at 3, a carbonyl band at 5.85, an ether band at 9.2 (also the band at 7.5 which seems to be characteristic of methyl ethers) and a band at 12.05 μ, which is in the region where hydroperoxy bands normally occur (compounds IIIb, IIIc and IV show no such band in their spectra). The fact that many bands also found in the spectrum of the dimer IV were present, but in lesser intensity, indicated that the hydroperoxide was contaminated with the dimer.

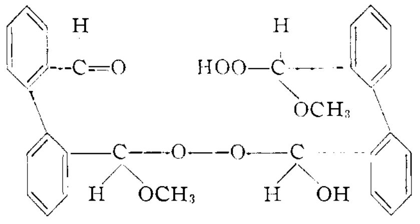
Anal. Calcd. for $C_{15}H_{14}O_4$: C, 69.75; H, 5.46; active O, 6.20; methoxyl, 12.02; mol. wt., 258. Found: C, 70.73; H, 5.22; active O, 5.02; methoxyl, 9.26; mol. wt., 342.

The molecular weight value also indicates that the material is contaminated with the dimeric peroxide IV. The material decomposes in a few days, losing methanol, as shown by analyses and infrared spectra (decrease in intensity of OH and ether bands).

The dimeric peroxide IV was obtained in the crystalline state only one time. The ozonolysis was carried out exactly as in the first experiment, after which the excess ozone was swept out by a stream of dry oxygen and the reaction mixture was set to refluxing before IIIb had a chance to precipitate. After 1.5 hr. of reflux the mixture still gave a positive active oxygen test with potassium iodide. It was then allowed to evaporate slowly. The residue was partially crystalline. Treatment with cold methanol followed by filtration gave a 40% yield of crystals melting at 87–93°. Several recrystallizations from benzene raised the melting point to 104–105°. The material gave a positive active oxygen test with potassium iodide and a negative hydroperoxide test with lead tetraacetate. It was stable to shock but burned rapidly in a flame. The analyses indicate that it is perhaps contaminated with a small amount of trimer or other polymer.

Anal. Calcd. for $C_{30}H_{28}O_8$: C, 69.75; H, 5.46; active O, 6.20; methoxyl, 12.02; mol. wt., 516. Found: C, 70.56; H, 5.66; active O, 6.16; methoxyl, 11.91; mol. wt., 592.

The infrared spectrum taken in a potassium bromide disc showed an associated hydroxyl band at 3, no carbonyl band, the ether bands at 7.5 and 9.2 mentioned earlier, and no band where the band thought to be due to the hydroperoxy group (12.1 μ) occurred in the case of the hydroperoxide II. In solution, however, the dimeric peroxide IV and the hydroperoxide II gave identical spectra (solvents: bromoform, chloroform or carbon disulfide) meaning that they must enter into equilibrium with one another. Very likely the equilibrium mixture is complex containing also the dimeric peroxide XIX. The solution spectra showed a hydroxyl band (2.8), a carbonyl band (5.8), ether bands (7.5 and 9.2) and a hydroperoxy band (12.1 μ), all of which were strong. It is noteworthy that the melting point of the dimer is lowered by treatment with the above solvents.



XIX

Attempts to repeat the crystallization of the dimer failed. The reactions behaved the same in most cases; apparently the dimer formed, but failed to crystallize from the oily peroxidic residue after evaporation of the solvent. With lesser amounts of solvent the dimethoxy peroxide IIIb precipitated as soon as the mixture neared the reflux temperature.

Ozonolyses in Methanol Using Special Working-up Procedures.—In one case the ozonolysis was carried out just as described in the first experiment, and then the reaction mixture was placed in a Dry Ice refrigerator for 4 days. A precipitate formed and was filtered off, m.p. 70–90°. The infrared spectrum in bromoform showed it to be the hydroperoxide II or its dimer (see discussion under dimer, compound IV). Judging from its melting point and behavior with solvents, it appeared to be the hydroperoxide, yield 16%. The filtrate when brought to room temperature deposited the dimethoxy peroxide IIIb in good yield.

In another experiment the ozonolysis was carried out as before, after which as much of the solvent as possible was removed at −20° and 0.01 mm. pressure; the last traces were removed between −20° and room temperature. The residue was treated with ether and filtered. The insoluble material melted at 165–175° and was shown to be the dimethoxy peroxide IIIb both by the mixture melting point method and infrared spectra; yield 37%. The ether filtrate upon evaporation yielded crystals which were shown by infrared spectrum (in bromoform) to consist to a large degree of the hydroperoxide II or its dimer.

Conversion of the Hydroperoxide II to the Dimethoxy Peroxide IIIb.—A half gram of the crude hydroperoxide II was suspended in 2 ml. of methanol and let stand an hour. Filtration yielded 0.3 g. of material melting at 167–175°. Upon trituration from methyl ethyl ketone it melted at 175–178° and showed no depression in a mixture melting point with known IIIb. Similar results were obtained when 0.5 g. of II was quickly dissolved by gentle warming in 8-

10 ml. of methanol and the mixture was allowed to stand an hour. The relatively low yields are probably due to contamination of the monomer II with the dimer IV which does not react with methanol to give IIIb.

3-Ethoxy-8-methoxy-4,5,6,7-dibenzo-1,2-dioxacycloöctane (IIIc) was obtained by suspending 1 g. of the crude hydroperoxide II in 15 ml. of absolute ethanol and letting the mixture stand overnight. Filtration gave 0.6 g. (55% yield) of material melting at 148–153°. Several recrystallizations from methyl ethyl ketone raised the melting point to 156–157°. The infrared spectrum was similar to that of IIIb, showing the absence of hydroxyl, carbonyl and hydroperoxy bands, but the presence of ether bands at 7.5 and 9.2 μ. The material gave a positive active oxygen test with potassium iodide and a negative hydroperoxide test with lead tetraacetate.

Anal. Calcd. for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34. Found: C, 71.22; H, 6.63.

2,2′-Biphenyldicarboxaldehyde (Vd).—A suspension of 2.7 g. of phenanthrene in 50 ml. of methanol was ozonized at −30 to −20° by the procedure described in the first experiment, after which dry oxygen was passed through the reaction mixture to sweep out the unreacted ozone. To the cold reaction mixture was added immediately 10 g. of sodium iodide and 10 ml. of glacial acetic acid. Immediate iodine formation accompanied by an elevation in temperature to that of the room occurred. After 30 minutes the iodine was reduced with 10% sodium thiosulfate solution and the resulting solution was placed under an air blast. A crystalline precipitate formed. After most of the methanol had been removed, water was added and the mixture was filtered, giving 2.7 g. (84% yield) of material melting at 58–60°, recrystallized from 70% ethyl alcohol, m.p. 63–64°. Kenner and Turner[10] report a melting point of 62° and Mayer[11] reports 67°.

The dioxime made by the pyridine method[12] was colorless and melted at 184–186° after recrystallization from dilute ethyl alcohol. Mayer[11] reports a yellow dioxime melting at 175–176°.

Anal. Calcd. for $C_{14}H_{12}N_2O_2$: C, 69.98; H, 5.03; N, 11.66. Found: C, 70.25; H, 5.07; N, 11.52.

A similar reduction of the crude solid hydroperoxide II using acetone solvent also produced the dialdehyde.

Methyl 2′-Formyl-2-biphenylcarboxylate (Va).—A mixture of 0.5 g. of the dimethoxy peroxide IIIb and 10 ml. of methanol was refluxed for 2 hr., during which time solution slowly occurred. When diluted with water and cooled the reaction mixture yielded 0.4 g. (91% yield) of material melting at 50–51°. When the reaction was repeated in the presence of 6 ml. of pyridine, using either methanol or ethanol solvent, solution occurred in 30 minutes to 1 hr. The product and yield were the same as before. Several recrystallizations of the material from methanol or methanol–water raised its melting point to 51–52°. The infrared spectrum showed a doublet in the carbonyl band (5.74 and 5.9 μ) as would be expected for the two different carbonyl groups. It showed a band at 9.2 μ (–C–O–C–) but none at 7.5 μ (this seems to be for methyl ethers but not esters). The material gave a negative active oxygen test with potassium iodide.

Anal. Calcd. for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03. Found: C, 75.11, 75.06; H, 4.95, 4.93.

The oxime was obtained directly from Va by the pyridine method[12] and also by carrying out the preceding reaction with IIIb in the presence of pyridine and hydroxylamine hydrochloride. Evaporation of the reaction mixture by a stream of air and crystallization of the residue from dilute ethyl alcohol gave a 96% yield of material melting at 98–100°, recrystallized from dilute ethyl alcohol, m.p. 100–101°.

Anal. Calcd. for $C_{15}H_{13}NO_3$: C, 70.57; H, 5.13; N, 5.49. Found: C, 70.22; H, 5.48; N, 5.80.

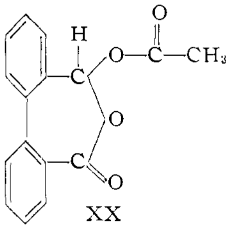
2′-Formyl-2-biphenylcarboxylic Acid (Vb).—A mixture of 2 g. of the dimethoxy peroxide IIIb, 10 ml. of 10% sodium hydroxide solution and 40 ml. of ethyl alcohol was refluxed for 15 minutes during which time solution occurred. The mixture was then acidified with dilute hydrochloric acid and diluted to cloudiness with water. Crystallization was aided by scratching on the sides of the vessel. After addition of more water and filtration, 1.4 g. (84% yield) of material melting at 134–135° was obtained. The material was also obtained from its methyl ester Va in the same manner. Several recrystallizations from dilute methanol did not change the melting point. Cook and co-workers[13] report a melting point of 132°. The material gave a negative active oxygen test with potassium bromide and was soluble in dilute sodium hydroxide and sodium carbonate solutions. The infrared spectrum showed a broad associated hydroxyl band typical of carboxylic acids and a single carbonyl band at 5.9 μ which is the position typical of aldehydes and carboxylic acids. Evidently the open chain structures (Va Vb) are correct for the acid and its methyl ester.

Anal. Calcd. for $C_{14}H_{10}O_3$: C, 74.33; H, 4.46. Found: C, 74.13; H, 4.45.

The oxime was made directly from Vb by the pyridine method.[12] It was also obtained by refluxing a mixture of 0.5 g. of IIIb, 1 g. of hydroxylamine hydrochloride, 10 ml. of 10% sodium hydroxide solution (use of only half the quantity of sodium hydroxide gave the oxime of Va instead) and 25 ml. of ethyl alcohol for 0.5 hr., acidifying with dilute hydrochloric acid and partially evaporating by a stream of air. Crystallization occurred yielding material melting at 164–171°, recrystallized from dilute ethyl alcohol, m.p. 174–175°.

Anal. Calcd. for $C_{14}H_{11}NO_3$: C, 69.70; H, 4.60; N, 5.81. Found: C, 69.97; H, 4.65; N, 5.97.

The acetate (**XX**) of the aldehyde acid Vb was made by the method of Cook and co-workers[13] with the exception that the reaction mixture was poured into water, where crystallization occurred (m.p. 134–135°). After recrystallizations from ethanol and methanol it melted at 138–139°; Cook and co-workers[13] report 125°. It was insoluble in sodium hydroxide. The infrared spectrum which showed a doublet carbonyl band at 5.7 and 5.8 μ is in line with structure XX instead of an open chain structure, since with the compounds containing an aldehyde group (Va and Vb) the carbonyl band was at 5.9 μ.



XX

Anal. Calcd. for $C_{16}H_{12}O_4$: C, 71.63; H, 4.51. Found: C, 71.55, 71.77; H, 4.69, 4.68.

Diphenic Acid (Vc).—A mixture of 1 g. of the dimethoxy peroxide IIIb, 5 ml. of 30% hydrogen peroxide, 20 ml. of 10% sodium hydroxide solution and 30 ml. of ethyl alcohol was refluxed for 30 minutes. The resulting solution was acidified with dilute hydrochloric acid, diluted with water and cooled. Crystallization occurred producing 0.75 g. (84% yield) of material melting at 216–222°. The diacid was also obtained by oxidation of the aldehyde-acid in a similar fashion (m.p. 223–228°). Vorländer and Meyer[14] report a melting point of 228–229°.

The dimethyl ester was prepared by refluxing a methanol solution of the diacid Vc containing a small amount of fuming sulfuric acid for 24 hr. Upon evaporation of the solution the ester was obtained; it melted at 73–74° after recrystallization from methanol. This is the melting point also reported by Vorländer and Meyer.[14]

Infrared spectra were determined on a Baird double beam infrared spectrophotometer using a sodium chloride prism. Except when stated otherwise the solvent was bromoform or chloroform.

Acknowledgment.—The author wishes to thank the Humble Company for inviting him to their Baytown Laboratories during the summer of 1955

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[10] J. Kenner and E. G. Turner, *J. Chem. Soc.*, **99**, 2112 (1911).

[11] F. Mayer, *Ber.*, **44**, 2304 (1911); **45**, 1107 (1912).

[12] R. L. Shriner and R. C. Fuson, "Systematic Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 202.

[13] J. W. Cook, G. T. Dickson, J. Jack, J. D. Loudon, J. McKeown, J. MacMillon and W. F. Williamson, *J. Chem. Soc.*, 139 (1950).

[14] D. Vorländer and F. Meyer, *Ann.*, **320**, 138 (1902).

and placing their research facilities at his disposal. He is especially grateful to Mr. J. A. Anderson, Jr., in whose section he worked, for expediting many things, Doctors M. A. Mosesman and L. W. Vernon for making room for him in their laboratory and office and Dr. B. H. Johnson for interpreting the infrared spectra.

BAYTOWN, TEXAS

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

The Behavior of 4-Methoxyphthalic Anhydride in Grignard Condensations

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RECEIVED MARCH 12, 1956

The reactions between 4-methoxyphthalic anhydride and the Grignard reagents from bromobenzene, α-bromonaphthalene, *m*-bromoanisole and *p*-bromoanisole have been carried out. In every case the yield of the 4-methoxy-2-aroylbenzoic acid has been found to be higher than that of the 5-methoxy isomer. If the normal reaction of a Grignard reagent with an unhindered carboxylic acid anhydride involves addition at a carbonyl group, then the yields of the keto carboxylic acids can be explained by the electron-donating effect of the 4-methoxyl group.

In 1935, Weizmann, Bergmann and Bergmann[1] carried out reactions between 4-methoxyphthalic anhydride (I) and phenylmagnesium bromide and also between I and 1-naphthylmagnesium bromide. They reported high yields (70–80%) of 4(5?)-methoxy-2-benzoylbenzoic acid and 4(5?)-methoxy-2-α-napthoylbenzoic acid, respectively. In connection with the synthesis of some methoxy derivatives of anthracene and 1,2-benzanthracene, it was necessary for the present authors to characterize the compounds reported by Weizmann, *et al.* We have found them to be the compounds where reaction has occurred at the carbonyl group in position 2, *viz.*, 4-methoxy-2-benzoylbenzoic and 4-methoxy-2-α-naphthoylbenzoic acid. The authors have also carried out reactions between I and *m*-methoxyphenylmagnesium bromide and between I and *p*-methoxyphenylmagnesium bromide with consistently higher yields of the 4-methoxy-2-aroylbenzoic acid than of the 5-methoxy isomer. Again, Bauer[2] has shown that in the reaction between I and ethylmagnesium bromide, only the carbonyl *meta* to the methoxy group is attacked with the formation of 5-methoxy-3,3-diethylphthalide.

The results of the very careful and extensive work by Newman and co-workers on the reactions of Grignard reagents with carboxylic anhydrides[3] has been interpreted by them to indicate that the normal reaction between a carboxylic anhydride and a Grignard reagent takes place by addition at a carbonyl group. In the case of hindered anhydrides it is postulated that a metathetical reaction mechanism is involved.[4]

If the normal reaction of a Grignard reagent with an unhindered carboxylic acid anhydride involves addition at a carbonyl group, then a plausible explanation for the preferential reactivity of the 2-carbonyl function of I lies in the effect of the 4-methoxyl group. With the latter group the carbonyl in position 1 is stabilized by delocalization of the unshared electron pairs on oxygen. The reaction rate at the 1-carbonyl group is therefore less than the rate at the carbonyl group in position 2.[5]

Experimental

Reactions of 4-Methoxyphthalic Anhydride. (a) With Phenylmagnesium Bromide.—The Grignard reagent from bromobenzene (22 g.) in ether (150 ml.) was added during 15 minutes and at 50–60° to a well stirred solution of 4-methoxyphthalic anhydride (24 g., m.p. 96°) in benzene (400 ml.). After stirring for 3 hr. at 50–60° the reaction mixture was decomposed with saturated ammonium chloride solution (150 ml.) and dilute hydrochloric acid (10 ml.). The ether–benzene solution of the hydrolyzed reaction products was shaken with carbonate. The carbonate extract was acidified with acetic acid and yielded 17.5 g. of 2-benzoyl-4-methoxybenzoic acid, m.p. 150–169°. After one crystallization from benzene, the yield of pure keto acid was 14 g. (m.p. 172–174°, lit.[1] 167°). The 2-benzoyl-4-methoxybenzoic acid was characterized by decarboxylating in the presence of basic copper carbonate. This afforded 3-methoxybenzophenone, which was distilled and refluxed with 55% hydriodic acid. The demethylated material was crystallized from dilute ethanol and yielded 3-hydroxybenzophenone, m.p. 115°.

The acetic acid acidified filtrate from the above keto acid was treated with hydrochloric acid. This afforded 4.6 g. of 2-benzoyl-5-methoxybenzoic acid, m.p. 140–150°. One crystallization from benzene did not change the melting point. For that reason the crude material was dissolved in concentrated sulfuric acid (10 ml.) and heated at 60–70° for 1 hr., at which time it was cooled and poured into ice and water. The reaction mixture was made basic with sodium hydroxide and any cyclized material[6] derived from the isomeric keto acid was separated. The filtrate was acidified with hydrochloric acid and afforded 2-benzoyl-5-methoxybenzoic acid. One crystallization from alcohol gave 2.7 g. of pure compound, m.p. 155–156°. It did not depress the melting point of an authentic sample made from the known 2-benzoyl-5-nitrobenzoic acid (II).[7]

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[1] C. Weizmann, E. Bergmann and F. Bergmann, *J. Chem. Soc.*, 1367 (1935).

[2] H. Bauer, *Arch. Pharm.*, **249**, 450 (1911); *C. A.*, **5**, 3802 (1911).

[3] (a) L. F. Fieser and M. S. Newman, THIS JOURNAL, **58**, 2376 (1936); (b) M. S. Newman, *ibid.*, **59**, 1003 (1937); (c) M. S. Newman and M. Orchin, *ibid.*, **60**, 586 (1938); (d) M. S. Newman, *ibid.*, **60**, 1368 (1938); (e) M. S. Newman and M. Orchin, *ibid.*, **61**, 244 (1939); (f) M. S. Newman and McCleary, *ibid.*, **63**, 1542 (1941); (g) M. S. Newman and Wise, *ibid.*, **63**, 2109 (1941); (h) M. S. Newman and Lord, *ibid.*, **66**, 733 (1944).

[4] See also the interpretation by M. S. Kharasch and O. Reinmuth in their excellent treatise, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, p. 849.

[5] The nitro group, because of electron withdrawal, would be expected to be favorable for reaction at the carbonyl group in position 1. It is therefore interesting to note that R. Goncalves, M. R. Kegelman and E. V. Brown (*J. Org. Chem.*, **17**, 705 (1952)) report a yield of 34% and 19%, respectively, for 2-(2-thenoyl)-5- and 2-(2-thenoyl)-4-nitrobenzoic acids obtained from 4-nitrophthalic anhydride and the Grignard reagent from 2-bromothiophene.

[6] The authors have found that 2-benzoyl-4-methoxybenzoic acid undergoes a slow cyclization in sulfuric acid at 60–70° to afford 2-methoxyanthraquinone, m.p. 195°. The isomeric 2-benzoyl-5-methoxybenzoic acid under these conditions affords no detectable cyclized material.

[7] W. A. Lawrence, THIS JOURNAL, **42**, 1871 (1920).