[CONTRIBUTION FROM THE ORGANIC PROCESS LABORATORY, FORDHAM UNIVERSITY]

The Ozonolysis of Phenanthrene[1]

BY WILLIAM J. SCHMITT,[2] EMIL J. MORICONI AND WILLIAM F. O'CONNOR[3]

RECEIVED JUNE 11, 1955

Phenanthrene has been quantitatively ozonized to a stable monoözonide. The latter has been characterized by molecular weight determination, elemental analysis, infrared spectra and by catalytic hydrogenation to 2,2'-biphenyldialdehyde. Both the monoözonide and the dialdehyde can be oxidized to 2,2'-diphenic acid. The evidence presented indicates exclusive ozonolysis of phenanthrene at the 9,10-bond. A sensitive test has been developed for the determination of glyoxal in the presence of 2,2'-biphenyldialdehyde.

Introduction

In 1905, as part of his classical work with ozone, Harries reported the ozonolysis of phenanthrene.[4] Working in a polar medium he obtained an explosive product which he identified by elemental analysis as a diozonide. He reported that he was unable to characterize the products of decomposition of this ozonide.

An examination of the resonance structures of phenanthrene reveals the strongly olefinic character of the 9,10-bond. This is supported by the chemical and infrared evidence supplied by Hunsberger and co-workers.[5] Additional evidence is indicated by the reactivity of this position with osmium tetroxide[6] and diazoacetic ester.[7] It has been pointed out that such double-bond reagents, unlike the usual electrophilic reagents, attack the most olefinic bond rather than the most reactive center in aromatic compounds.[8]

It would be expected, therefore, that ozone preferentially should attack the 9,10-bond. In addition, the resulting substituted biphenyl compound II would have a higher resonance energy than the naphthalene derivative resulting from attack at another position.

By analogy with the ozonolysis of naphthalene[9] we might expect that the monoözonide formed by reaction at the 9,10-bond would not suffer further electrophilic attack by ozone, due to the deactivation of the adjacent rings.

If, however, the reaction occurred at any other position (V), this would immediately localize another double bond in the same ring, making it very susceptible to reaction with a second molecule of ozone (VI). Finally, it is also conceivable that the unsubstituted ring of the naphthalene derivative thus formed would provide additional sites for ozonolysis. Thus, an attack on phenanthrene at any position other than the 9,10, would result in the formation of at least a diozonide, the decomposition of which would yield glyoxal.

Discussion of Results

We have carried out a study of the ozonolysis of phenanthrene to determine the nature of the ozonide and its decomposition products. At first the reaction was carried out at room temperature in the presence of 2,4-dinitrophenylhydrazine, as suggested by Gordon and his co-workers.[10] Elemental analysis of the insoluble 2,4-dinitrophenylhydrazone (VII) obtained showed that it was formed by the decomposition of a monoözonide of phenanthrene. That the ozonolysis actually did take place at the 9,10-bond was established by identifying VII as biphenyl-2,2'-dialdehyde bis-(2,4-dinitrophenylhydrazone) through an alternate synthesis.[11]

Additional proof of the main direction of the reaction was had in the quantitative ozonolysis of phenanthrene and in the isolation of the ozonide. Only one mole of ozone was absorbed per mole of phenanthrene. Elemental analysis of the isolated ozonide agreed with the theoretical values for a monoözonide. Its infrared spectrum showed strong absorption bands at 1700, 1740 and 1752 cm.$^{-1}$. Briner[12] has shown that these bands are characteristic of ozonides. An investigation of the characteristics of the spectra of homocyclic aromatic ozonides is now in progress. This substance is unique that it is the first example of a stable ozonide obtained from a homocyclic aromatic hydrocarbon. It is stable to friction, concussion, and may be heated to at least 300° without detonation. A Rast molecular weight determination has eliminated the possibility of its being a polymer.

The ozonide, when in solution, can be decomposed by water or by catalytic hydrogenation to 2,2'-biphenyldialdehyde (III). The latter method required but one mole of hydrogen per mole of ozonide. The derivatives of III are listed in Table I. Both the aldehyde and the ozonide itself can be oxidized to 2,2'-diphenic acid of very high purity.

As previously indicated, ozonolysis of any position in phenanthrene other than the 9,10, would lead to a diozonide and to the formation of glyoxal as a decomposition product. A careful search, therefore, was made for glyoxal in all ozonolysis products. In an attempt to perfect a method for determining glyoxal in the presence of biphenyldialdehyde by paper chromatography of their 2,4-dinitrophenylhydrazones, more than 70 solvent

---

(1) Presented in part before the Organic Division of the Meeting-in-Miniature of the New York Section, American Chemical Society, Feb. 26, 1955.

(2) Abstracted from a portion of a thesis submitted by William J. Schmitt, S.J., to the Graduate School of Fordham University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) To whom inquiries concerning this paper should be sent.

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

(5) I. M. Hunsberger, R. Ketcham and H. S. Gutowsky, THIS JOURNAL, **74**, 4839 (1952).

(6) R. Criegee, B. Marchand and H. Wannowius, *Ann.*, **550**, 99 (1942).

(7) R. D. Brown, *J. Chem. Soc.*, 3249 (1950).

(8) G. M. Badger and K. R. Lynn, *ibid.*, 1726 (1950).

(9) L. W. F. Kampschmidt and J. P. Wibaut, *Rec. trav. chim.*, **73**, 431 (1954).

(10) B. E. Gordon, F. Wopat, Jr., H. D. Burnham and L. C. Jones, Jr., *Anal. Chem.*, **23**, 1754 (1951).

(11) F. Weygand, G. Eberhardt, H. Linden, F. Schafer and I. Eigen, *Angew. Chem.*, **65**, 525 (1953).

(12) E. Briner, *et al.*, *Helv. Chim. Acta*, **35**, 340, 353, 2145 (1952); *ibid.*, **36**, 1166 (1953); *ibid.*, **37**, 1558, 1561 (1954); *Compt. rend.*, **234**, 1932 (1952); *ibid.*, **237**, 504 (1953).

TABLE I

Derivatives of III	Formula	M.p., °C.[14]	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
Bis-(*p*-nitrophenylhydrazone)[a,c]	$C_{26}H_{20}N_6O_4$	272–272.5	64.99	64.65	4.20	4.43	17.49	17.36
Bis-(2,4-dinitrophenylhydrazone)[a]	$C_{26}H_{18}N_8O_8$	290–291	54.73	54.64	3.18	3.71	19.6	19.7
Dioxime[b]	$C_{14}H_{12}N_2O_2$	185–186.5	69.99	69.36	5.03	5.18	11.7	11.4

[a] Not previously reported. [b] Reported by Criegee[6] and Mayer[13] as melting at 175–176°. [c] For purification see Experimental section.

systems in addition to those previously reported[15] were tried without success.[16] Alternately a simple and very sensitive analytical procedure was developed. The validity and sensitivity of the test were demonstrated by the various control experiments listed in Table II.

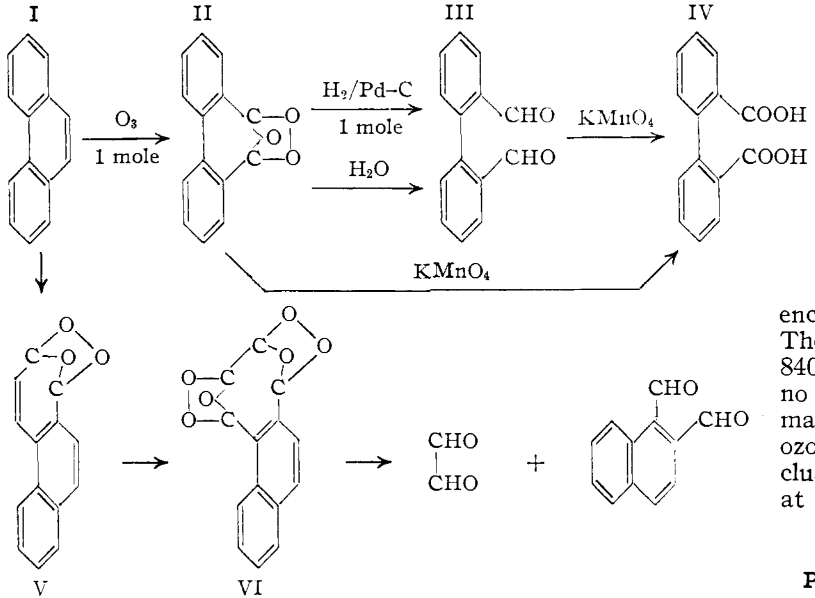

TABLE II

System tested[a]	Results
1, pure solvent	Neg.
2, solvent plus 1% glyoxal[b]	Pos.
3, reduced ozonide of I plus 1% glyoxal[c]	Pos.
4, reduced ozonide of I plus 0.5% naphthalene[d]	Pos.

[a] Based on typical run of 5 g. of phenanthrene in 120 ml. of glacial acetic acid. [b] 1% refers to amount that would be formed if 1% of the phenanthrene were attacked in a position other than the 9,10. [c] Glyoxal added after the reduction step. [d] Naphthalene added before ozonolysis.

The fourth control was employed in order to be sure that the glyoxal would show up in the reduced product and not be lost during the course of the reactions. It has been shown that naphthalene yields a diozonide which can be decomposed to *o*-phthalaldehyde and glyoxal.[9] Thus, in this control run we have glyoxal and its ozonide precursor in the same type structure as would be present should ozone attack phenanthrene to form a diozonide.

In the actual test on the reduced ozonide of phenanthrene, no evidence at all was found of the glyoxal derivative. It may be concluded, therefore, that if phenanthrene yields any diozonide, it does so in amounts less than 0.5%. It is to be noted that, since the precipitate formed during the test is so copious due to its flocculent nature, the test is certainly capable of detecting much smaller amounts of glyoxal than the 0.5% attempted in this study.

A further check on this work consisted in comparing the infrared spectra of the 2,4-dinitrophenylhydrazones of glyoxal and biphenyldialdehyde with that of the unpurified derivative obtained by ozonolysis in the presence of 2,4-dinitrophenylhydrazine. The complete absence of bands at 860, 840, 744 and 732 cm.$^{-1}$ indicated that no glyoxal derivative was present. It may be concluded, therefore, that the ozonolysis of phenanthrene yields exclusively a monoözonide by a reaction at the 9,10-bond.

Experimental

Phenanthrene.—A highly purified product was obtained by following Bachmann's procedure[17] with a chromatographic purification on activated alumina.[18] Carbon tetrachloride was the solvent used.

Ozone.—The ozone generator was an enlarged version of the one described in reference 19. Five tubes were connected in series. It delivered 0.18 mole/hour at an oxygen flow of 116 liters/hour and a secondary potential of 12,000 v. Tygon tubing was found very satisfactory for connections.

Ozonolysis Procedure.—The ozone generator was calibrated in the usual manner and the unreacted ozone was determined by passing the effluent gases through potassium iodide solution, acidifying and titrating with standard thiosulfate.[20] The ozone was absorbed almost completely and at the end of the time calculated for the formation of the monoözonide no more ozone was absorbed. When working in chloroform solution the end of the reaction was clearly seen from the deep blue color that suddenly appeared, as was noticed by Marvel and Nichols.[21]

(a) Acetic Acid Medium: Five grams (0.028 mole) of phenanthrene, dissolved in 120 ml. of glacial acetic acid, was ozonized for the calculated time. The absorption was almost quantitative. At the end of the reaction the solution had a slight yellow color. (b) Chloroform Medium: Ninety ml. of dry chloroform was used for a 5-g. run. The reaction took place in a Dry Ice–methanol-bath. The up-take of ozone was slightly less rapid than in acetic acid but just as complete. (c) In the presence of 2,4-dinitrophenylhydrazine: Five grams of phenanthrene, 11.1 g. (0.056 mole) of 2,4-dinitrophenylhydrazine, 23 ml. of sulfuric acid and 10 ml. of water were added to 200 ml. of glacial acetic acid and ozonized. The very insoluble 2,4-dinitrophenylhydra-

---

[13] F. Mayer, *Ber.*, **44**, 2304 (1911).

[14] All m.p.'s are corrected.

[15] R. G. Rice, G. J. Keller and J. G. Kirchner, *Anal. Chem.*, **23**, 194 (1951).

[16] A recent publication offers another possible method: E. W. Malmberg, THIS JOURNAL, **76**, 980 (1954).

[17] W. E. Bachmann, *ibid.*, **57**, 555 (1935).

[18] We wish to thank Dr. Douglas J. Hennessy of this University for suggesting this further step.

[19] "Organic Syntheses," Vol. 26, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 63.

[20] Reference 19, p. 68.

[21] C. S. Marvel and V. Nichols, *J. Org. Chem.*, **6**, 296 (1941).

zone precipitated continuously during the reaction. It was recrystallized from dimethylformamide.

Phenanthrene Ozonide.—The ozonide was obtained in 85% yield by pouring the acetic acid solution into very cold water. Infrequently the white colloid that first formed failed to agglutinate to yield the granular product. Vacuum removal of some of the solvent avoided this difficulty. All attempts to remove all the water from the product obtained in this way failed. However, a dry product was obtained from the chloroform solution. Most of the solvent was removed under vacuum. The concentrate was poured into absolute methanol which had been cooled in a Dry Ice-bath and the precipitate was filtered immediately, washed with more cold methanol and dried in a vacuum desiccator.

The precipitated ozonide is a white, amorphous powder that easily acquires a static charge. It burns fiercely, but is stable to shock. It softens and melts (65–90°) like a glass and, unlike most ozonides, is soluble in cold ether. Once precipitated it is stable in water and dilute acid suspension for weeks, but it decomposes in dry air.

The infrared spectra of the ozonide from chloroform and from acetic acid are essentially superimposable.

Anal. Calcd. for $C_{14}H_{10}O_3$: C, 73.33; H, 4.46; mol. wt., 226. Found: C, 73.34; H, 4.61; mol. wt. (Rast using *dl*-camphor), 223.

Ozonide Decomposition. (a) Catalytic Reduction.—Using the method of Fisher[22] but at room temperature, the theoretical amount of hydrogen was absorbed. A quantitative determination of the biphenyl-2,2'-dialdehyde thus formed[23] showed a yield of 57.5%. This low yield is understandable in the light of Fisher's experience.[22]

(b) Hydrolysis to Biphenyl-2,2'-dialdehyde.—The acetic acid solution of the ozonide was poured into four times its volume of water and the resulting colloid was let stand for two days. At the end of that time a 51% yield of the aldehyde was filtered off; m.p. 60–61°. The derivatives listed in Table I were prepared in the usual way. The *p*-nitrophenylhydrazone was purified by chromatography in a dioxane solution on activated alumina. The column was developed with 10% ethanol in dioxane, extruded and sectioned. The lower dark red band was eluted with hot dioxane and the material recrystallized from dioxane–water.

(c) Oxidation to 2,2'-Diphenic Acid.—The filtrate from the above preparation of the dialdehyde gave, on warming with potassium permanganate, a 25.5% yield of diphenic acid, m.p. 229–230°. The ozonide itself was oxidized with alkaline permanganate in the cold to an acid, m.p. 229–231°; mixed m.p. with an authentic sample of diphenic acid 229–231°; *p*-nitrobenzyl ester m.p. 184–185° (183°).[24]

Alternate Preparation of 2,2'-Biphenyldialdehyde Bis-(2,4-dinitrophenylhydrazone).—The method of Weygand[11] was used; m.p. of this 2,4-dinitrophenylhydrazone 290°; mixed m.p. with product from ozonolysis 290°. For this synthesis the N,N'-diphenyl-N,N'-dimethyl-2,2'-biphenamide was prepared according to the method of Rapson and Shuttleworth.[25] The product melted at 166–167° compared to the 160–162° reported by Weygand.

Anal. Calcd. for $C_{28}H_{24}N_2O_2$: C, 79.97; H, 5.75. Found: C, 80.06; H, 5.65.

Glyoxal Determination.—A stock solution was prepared as follows. To 2 ml. of sulfuric acid and 0.8 g. of 2,4-dinitrophenylhydrazine was gradually added 8 ml. of water. To this solution were added 50 ml. of acetic acid and 11 ml. of water. Test-tubes were prepared with 2 ml. of the stock solution diluted with 2 ml. of water. The mixture to be tested was distilled, 2 ml. of the distillate being run directly into the test-tube. Usually three samples were taken. Eleven ml. of water then was added and the mixture heated to boiling. If glyoxal were present the solution became cloudy almost immediately. On standing a flocculent precipitate formed and floated to the top as a large orange ball. The dry weight of this apparently large mass was negligible. In the control experiments the m.p. agreed with the literature value of 328° for the glyoxal derivative.

For the actual test on phenanthrene ozonide, the ozonolysis mixture was first reduced catalytically as noted above, and then directly distilled into the test-tubes. No precipitate was formed.

NEW YORK 58, N. Y.

---

[22] F. G. Fisher, H. Dull and L. Ertel, *Ber.*, **65**, 1467 (1932).

[23] H. A. Iddles, A. W. Low, B. D. Rosen and R. T. Hart, *Ind. Eng. Chem., Anal. Ed.*, **11**, 102 (1939).

[24] T. L. Kelly and M. Segura, THIS JOURNAL, **56**, 2497 (1934).

[25] W. S. Rapson and R. G. Shuttleworth, *J. Chem. Soc.*, 487 (1941).

[CONTRIBUTION NO. 1990 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

On the *cis* Forms of Some Biphenylene Derivatives of Butadiene and Hexatriene

BY EUGENE F. MAGOON AND L. ZECHMEISTER

RECEIVED MAY 26, 1955

All theoretically possible *cis* forms of 1,6-di-biphenylenehexatriene, 1-biphenylene-4-phenylbutadiene and 1-biphenylene-6-phenylhexatriene were prepared. They were characterized on the basis of their chromatographic and spectroscopic behavior as well as of their relative stabilities. The observations were in general agreement with those made in the series of α,ω-diphenyl-polyenes and symmetrical polyene-azines.

In the present paper we describe the stereochemical behavior of three compounds so far known only in the *trans* form. They are characterized by bulky end groups attached to short unsaturated systems. Di-biphenylenehexatriene has been selected because its only *cis* isomer represents a sterically "unhindered" type (Fig. 1), whereas biphenylenephenylbutadiene yields a "hindered" *cis* form (Fig. 2). Finally, biphenylenephenylhexatriene may assume the *cis* configurations B-D (Fig. 3), including a hindered mono*cis*, an unhindered mono*cis* and a hindered-unhindered di*cis* isomer. As observed earlier in the α,ω-diphenylpolyene[1] and symmetrical polyene-azine[2] series, when a terminal double bond of the open chain undergoes *trans* → *cis* rearrangement, a spatial conflict arises between a hydrogen atom of the side-chain and a ring hydrogen, with the result that the *cis* compound thus formed shows a considerably degraded spectrum. In contrast, an unhindered *cis* double bond involves a relatively slight change in the all-*trans* spectral curve.

We have now observed that the three *trans* compounds mentioned which are easily synthesized according to Kuhn and Winterstein,[3] can be rearranged to yield all expected *cis* forms (Figs. 1–3)

---

(1) A. Sandoval and L. Zechmeister, THIS JOURNAL, **69**, 553 (1947); J. H. Pinckard, B. Wille and L. Zechmeister, *ibid.*, **70**, 1937 (1948); K. Lunde and L. Zechmeister, *ibid.*, **76**, 2308 (1954); L. Zechmeister and A. L. LeRosen, *ibid.*, **64**, 2755 (1942); L. Zechmeister and J. H. Pinckard, *ibid.*, **76**, 4144 (1954); *cf.* L. Zechmeister, *Experientia*, **10**, 1 (1954).

(2) J. Dale and L. Zechmeister, THIS JOURNAL, **75**, 2379 (1953).

(3) R. Kuhn and A. Winterstein, *Helv. Chim. Acta*, **11**, 116 (1927).