Ozonolysis of Polycyclic Aromatics. IX.[1] Dibenz[*a,j*]anthracene[2]

EMIL J. MORICONI, BOHDAN RAKOCZY, AND WILLIAM F. O'CONNOR

Department of Chemistry, Fordham University, New York 58, N. Y.

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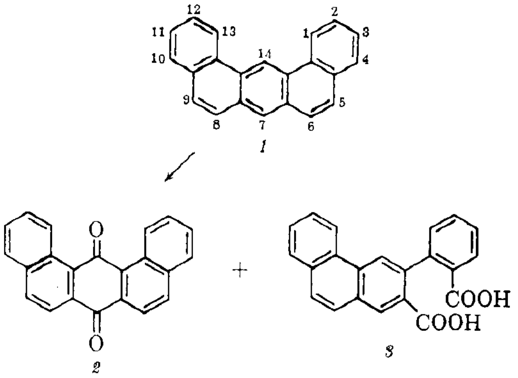
The corrected oxidation–reduction potentials of 7,14- (*2*) and 5,6-dibenz[*a,j*]anthracenediones (*5*) are, respectively, 0.452 v. and 0.405 v. Our published hypothesis predicts that ozone should therefore predominantly cleave the 5,6-bond of dibenz[*a,j*]anthracene (*1*). Ozonization of *1* in methylene chloride and 3:1 methylene chloride–methanol with one molar equivalent of ozone followed by alkaline hydrogen peroxide oxidation produced 3-(*o*-carboxyphenyl)-2-phenanthrenecarboxylic acid (*3*) in 42% yield, 7,14-dibenz[*a,j*]anthracenedione (*2*) in 10% yield; 32.5% of unchanged *1* was also recovered.

The weak carcinogen[3] dibenz[*a,j*]anthracene (*1*) represented another obvious opportunity to test our hypothesis that ozone would react predominantly at those positions in an unsubstituted polycyclic aromatic whose corresponding *o*- or *p*-quinone had the lowest corrected oxidation–reduction potential.[5] Since the corrected redox potentials for 7,14- (*2*) and 5,6-dibenz[*a,j*]anthracenediones (*5*) were recently shown to be 0.452 v. and 0.405 v., respectively,[5] ozone should therefore predominantly cleave the 5,6-bond of *1*.[6]

Experimentally, ozonization of *1* in methylene chloride and 3:1 methylene chloride–methanol at −70° with one molar ozone equivalent, followed by alkaline-peroxide oxidation gave the predicted bond cleavage product 3-(*o*-carboxyphenyl)-2-phenanthrenecarboxylic acid (*3*) in 42% yield; in addition 7,14-dibenz[*a,j*]anthracenedione (*2*) was obtained in 10% yield, and some 32.5% of unchanged *1* was also recovered. Oxygen alone had no effect on *1* under identical reaction conditions.



Compound *2* was identical with that obtained by Cook[9] on sodium dichromate–acetic acid oxidation of *1*, while *3* was independently prepared *via* peracetic acid oxidation of 5,6-dibenz[*a,j*]anthracenedione (*5*). Compounds *1*, *2*, and *3* were inert to alkaline hydrogen peroxide.

Thus, despite corrections which are in some cases greater than the measured potential differences between *o*- and *p*-quinones, *1* joins the growing list of aromatic hydrocarbons (naphthalene, anthracene, phenanthrene, benz[*a*]anthracene, picene, and dibenz[*a,h*]anthracene) whose *o*- or *p*-quinone with the lowest corrected oxidation–reduction potential corresponds to the position of predominant ozone attack.

It is also noteworthy that in the series of progressively stronger carcinogens, benz[*a*]anthracene[4b] (0),[3] *1* (+),[3] and dibenz[*a,h*]anthracene[4c] (*7*) (++),[3] ozonization under identical reaction conditions (with one molar ozone equivalent in solvents methylene chloride and 3:1 methylene chloride–methanol, at −70°) produced an increasing yield of K-region cleavage products (ozone acting as a double bond reagent) along with a decisive decrease in yield of L-region quinones (ozone acting as an electrophile). This correlation between the ozone reaction, relative carcinogenicity of unsubstituted polycyclic aromatics, and Pullmans' electronic theory of carcinogenesis[10] continues to occupy our attention, despite our recently noted apparent exception.[1]

Experimental

Melting points were determined on a Kofler micro melting point apparatus and are corrected. Infrared spectra were recorded on a Perkin-Elmer Model 21 recording spectrophotometer.

Dibenz[*a,j*]anthracene (*1*), m.p. 196–197° (lit., m.p. 197–198°),[11] was prepared using Cook and Stephenson's improved method.[11] In the oxidation step, these authors suggest oxidation of 2-methyl-1,1′-dinaphthyl ketone (*8*) to

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(1) Part VIII, E. J. Moriconi, B. Rakoczy, and W. F. O'Connor, *J. Am. Chem. Soc.*, **83**, 4618 (1961).

(2) This research was supported by a Grant C-3325 (C4) from the U.S. Public Health Service, National Cancer Institute.

(3) G. M. Badger, *Brit. J. Cancer*, **2**, 309 (1948).

(4) (a) E. J. Moriconi, W. F. O'Connor, and L. B. Taranko, *Arch. Biochem. Biophys.*, **83**, 283 (1959); (b) E. J. Moriconi, W. F. O'Connor, and F. T. Wallenberger, *J. Am. Chem. Soc.*, **81**, 6466 (1959); (c) E. J. Moriconi, W. F. O'Connor, W. J. Schmitt, G. W. Cogswell, and B. P. Furer, *ibid.*, **82**, 3441 (1960).

(5) E. J. Moriconi, B. Rakoczy, and W. F. O'Connor, *J. Org. Chem.*, **27**, 2772 (1962).

(6) In *1*, M.O. calculations predict the 7,14-positions to have the lowest *para*-localization energy,[7,8a] and the 5,6-bond to have the lowest bond localization energy.[7,8b]

(7) M. J. S. Dewar, *J. Am Chem. Soc.*, **74**, 3357 (1952).

(8) (a) R. D. Brown, *J. Chem. Soc.*, 691 (1950); (b) R. D. Brown, *ibid.*, 3349 (1950).

(9) J. W. Cook, *ibid.*, 1472 (1932).

(10) A. Pullman and B. Pullman, *Advan. Cancer Res.*, **3**, 117 (1955).

(11) J. W. Cook and E. F. M. Stephenson, *J. Chem. Soc.*, 842 (1949).

2-carboxy-1,1′-dinaphthyl ketone "by heating under pressure with aqueous selenious acid." We found it expedient to run a sealed-tube oxidation at 240–245° for 6 hr. to achieve the same result.

We feel constrained to report that the synthesis reproduced in an otherwise very useful preparative text[12] is in error.[13]

Ozonization of Dibenz[*a,j*]anthracene (*1*) to 3-(*o*-Carboxyphenyl)-2-phenanthrenecarboxylic Acid (*3*) and 7,14-Dibenz[*a,j*]anthracenedione (*2*).—A colorless solution of *1* [1.00 g., 3.6 mmoles] in 300–400 ml. of methylene chloride or 3:1 methylene chloride–methanol, was treated with 3.5 vol. % ozone at −70° until one molar equivalent (±0.1) had been absorbed. The absorption was rapid and quantitative. The resulting pale yellow solution was sparged with nitrogen to free it of excess oxygen and dissolved ozone. While the solution slowly evaporated on a hot plate, several 20-ml. portions of methanol were added to keep the volume approximately constant and to distil the more volatile methylene chloride. Ultimately the methanolic solution was treated overnight with 40 ml. of a 1:1 solution consisting of 20% aqueous sodium hydroxide and 30% hydrogen peroxide. The amber solid (450 mg.) was filtered, and the filtrate was acidified with concentrated hydrochloric acid giving 527 mg. (1.54 mmoles, 43%) of the off-white colored dicarboxylic acid *3*, m.p. 288–290° dec. One recrystallization from ethyl acetate (charcoal) yielded 517 mg. (42%) of 3-(*o*-carboxyphenyl)-2-phenanthrenecarboxylic acid (*3*), white plates m.p., 290–291° dec.; $\lambda_{C=O}^{KBr}$ 5.87 μ (s). *3* was identical (melting point and mixed melting point behavior and superimposable infrared spectra) with the dicarboxylic acid obtained from the peracetic acid oxidation of 5,6-dibenz[*a,j*]anthracenedione (*5*).

Anal. Calcd. for $C_{22}H_{14}O_4$: C, 77.18; H, 4.12. Found: C, 76.92; H, 4.34.

The amber solid was dissolved in a minimum amount of benzene and adsorbed on a 20 × 1.5 cm. alumina-packed column (Woelm's nonalkaline aluminum oxide, activity grade 1). The first blue-purple fluorescent band was eluted with benzene (5 × 50 ml. benzene). The combined fractions were evaporated to dryness to yield 326 mg. (1.17 mmoles, 32.5%) of unchanged *1*, m.p. 195–196°. The second, amber zone was eluted with two 50-ml. portions of 1:1 benzene–ethyl acetate. Evaporation of the combined fractions to dryness, and recrystallization of the residue from acetic acid gave 115 mg. (0.37 mmole, 10%) of 7,14-dibenz[*a,j*]anthracenedione (*2*), as long amber needles, m.p. 223–224° (lit., m.p. 225–226°)[9]; $\lambda_{C=O}^{KBr}$ 6.01 μ (s). *2* displayed an infrared absorption spectrum identical to, and gave no depression on admixture with, authentic *2* prepared by sodium dichromate–acetic acid oxidation of *1*.[9]

In a single experiment, ozonization of *1* (400 mg., 1.4 mmoles) in the more polar solvent dimethylformamide[18] at −35° with 1.5 molar ozone equivalents, followed by alkaline peroxide oxidation produced *3* and *2*, respectively, in 35 and 10% yields, with a 35% recovery of unchanged *1*. The work-up procedure was essentially the same as in methylene chloride and methylene chloride–methanol except that the original ozonized mixture was evaporated to dryness prior to suspension in methanol and oxidation with alkaline hydrogen peroxide.

Peracetic Acid Oxidation of 5,6-Dibenz[*a,j*]anthracenedione (*5*).—*5* was prepared by the ethyl azodicarboxylate oxidation of *cis*-5,6-dihydro-5,6-dibenz[*a,j*]anthracenediol (*4*)[11,19] To a warmed solution (85–90°) of *5* (250 mg., 0.81 mmole) in 20 ml. of *s*-tetrachloroethane and 20 ml. of acetic acid, was added dropwise 1.5 ml. of 30% hydrogen peroxide over a 15-min. period. The reaction mixture was stirred for an additional 10 hr. at 90°, after which it was cooled to room temperature, and under reduced pressure, evaporated to dryness. The residue was repeatedly extracted with boiling 10% aq. sodium carbonate solution (total 150 ml.). Acidification of the alkaline extract precipitated a pale yellow solid which on recrystallization from ethyl acetate (charcoal) gave 147 mg. (0.43 mmole, 53%) of *3*, m.p. 289–290°.

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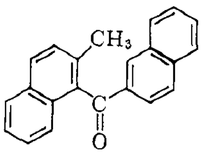
[12] D. A. Shirley, "Preparation of Organic Intermediates," John Wiley and Sons, Inc., New York, 1951, p. 100.

[13] In 1929 Clar,[14] and Fieser and Dietz[15] reported that the Elbs pyrolysis of 2-methyl-1,2′-dinaphthyl ketone (*6*) produced dibenz[*a,h*]anthracene (*7*), while 2-methyl-1,1′-dinaphthyl ketone (*8*) led to *7*. Two years later Cook[16] conclusively demonstrated that the pyrolysis products of *6* and *8* were actually identical and indeed *7*. This same author later synthesized *1* by two independent methods and a further improvement of his own synthesis has provided researchers with the only really adequate method of preparation of *1* available to date. In both editions of his classical monograph, Clar[17] formally acknowledged the intramolecular rearrangement of *8* to *6* and ultimately to *7* in the dehydration process. Unfortunately, his original, understandable error is propagated in the Shirley text and must be considered as one of the difficulties mentioned by the latter author.



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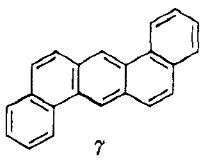

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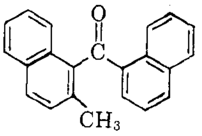

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[14] E. Clar, *Ber.*, **62**, 350 (1929).

[15] L. F. Fieser and E. M. Dietz, *ibid.*, 1827 (1929).

[16] J. W. Cook, *J. Chem. Soc.*, 487 (1931).

[17] E. Clar, "Aromatische Kohlenwasserstoffe," Springer-Verlag, Berlin, 1st ed., 1941, p. 146; 2nd ed., 1952, p. 202.

[18] We are grateful to Prof. P. S. Bailey for suggesting this solvent.

[19] The conventional oxidant sodium dichromate–acetic acid simultaneously oxidized both the diol moiety and the phenanthrene-type 8,9-bond in *4* and led to the diquinone, 5,6,7,8-dibenz[*a,j*]-anthracenetetraone, m.p. 410–411° dec. (lit. m.p. >340° dec.)[11] in 65% yield.