Communications TO THE EDITOR

Ozonization of Anthracene[1]

Sir:

Badger[2] has classified ozone as a "double bond reagent" and Brown[3] has assumed that it makes a one-step attack of both reactive centers on both reactive centers of the unsaturated molecule, rather than a two-step attack. If so, it should attack anthracene at the 1,2-bond, because this bond, according to the molecular orbital theory, has the lowest "bond localization energy."[3,4]

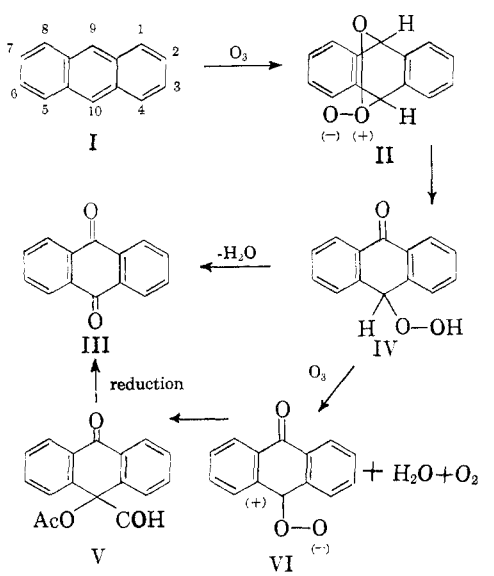
If the attack is by the two-step process, however, it should occur at the 9 and 10 positions, because these have the lowest "atom localization energies."[3,4] Diels-Alder type reagents also would attack at the 9 and 10 positions, even by a one-step mechanism, but ozone can probably be excluded from this category since it does not behave as such with ordinary conjugated systems.

The ozonization of anthracene in acetic anhydride to give anthraquinone has been reported.[5] The yield was not given, however, nor was it shown that ozone instead of oxygen actually was the reactant. We have ozonized anthracene in acetic acid at 10° with 5% ozone and have found that the ozone is readily absorbed. The reaction is complete after three moles per mole of anthracene react. Anthraquinone is produced in 69% yield. Some anthraquinone (28%) precipitates during the reaction. The remainder is produced by sodium iodide or bisulfite reduction of the peroxidic filtrate. Ozone rather than oxygen was shown to be the attacking agent not only by the fact that far more than catalytic amounts were absorbed but also by passing the same volume of 0.5–1% ozone through the reaction mixture and showing that the amount of anthraquinone produced was directly proportional to the amount of ozone employed.

These results are important for two reasons. This is the first established instance in which ozone has attacked the ends of a conjugated system rather than a specific double bond. The geometry of the system is such that the ozone molecule can reach across the ends of the system, i.e., from C-9 to C-10. Further, this is excellent evidence for the two-step mechanism and corroborates Wibaut's[6] experiments which indicate that the initial attack is electrophilic. Such can be the case only with the two-step mechanism.[3]

The following suggested mechanism for the anthracene reaction explains the essential fact that anthraquinone is produced both during the ozonolysis (presumably by decomposition of a peroxidic intermediate, e.g. IV) and by reduction of a peroxidic intermediate. Evidence for IV is the isolation of some anthrahydroquinone by sodium iodide reduction. Since anthraquinone is the principal reduction product, however, oxidation of IV to VI is proposed. This is to be expected since IV would be in equilibrium with a perhydroquinone structure.

The suggested mechanism does not explain the requirement of three moles of ozone per mole of anthracene. It seems likely that the 31% of anthracene which did not produce anthraquinone reacted by the one-step mechanism. This should result in destruction of both outer rings and account for a large portion of the total three moles of ozone.



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(1) Included in part in a paper presented before the International Ozone Conference, Chicago, Ill., November 28–30, 1956.

(2) Badger, *Quart. Revs.*, **5**, 155 (1951).

(3) (a) Brown, *Quart. Revs.*, **6**, 63 (1952). (b) Brown, *J. Chem. Soc.*, 3249 (1950).

(4) Dewar, *J. Am. Chem. Soc.*, **74**, 3357 (1952).

(5) Roitt and Waters, *J. Chem. Soc.*, 3060 (1949).

(6) For leading references see Bailey, *J. Am. Chem. Soc.*, **78**, 3811 (1956).

1,5-Diaryl-2,3-pyrrolidinediones. VII. Reassignment of Structure

Sir:

Since Schiff and Gigli[1] first reported the preparation of 1,5-diphenyl-2,3-pyrrolidinedione (Ia) a

(1) R. Schiff and L. Gigli, *Ber.*, **31**, 1306 (1898).

large number of 1,5-diaryl-2,3-pyrrolidinediones has been synthesized, and several curious aspects of their chemical behavior have been studied in this laboratory.[2-6]

Previous evidence to the contrary notwithstanding,[4,7] we now wish to report conclusive proof that the structures of such compounds have been incorrectly assigned. Addition of *p*-anisidine to β-(*p*-methoxybenzoyl)-acrylic acid affords α-(*p*-anisylamino)-β-(*p*-methoxybenzoyl)-propionic acid, m.p. 144.5–145.0° dec.

Anal.[8] Calc'd for $C_{18}H_{19}NO_5$: C, 65.64; H, 5.80; N, 4.25. Found: C, 65.69; H, 5.79; N, 4.25.

Treatment of this ketoacid with sodium borohydride, followed by benzoyl chloride in pyridine yielded α-(N-benzoyl-*p*-anisylamino)-γ-*p*-anisyl-γ-butyrolactone, m.p. 164.5–165.5°.

Anal.[8] Calc'd for $C_{25}H_{23}NO_5$: C, 71.95; H, 5.55; N, 3.36. Found: C, 71.82; H, 5.53; N, 3.37.

This substance was shown by identity of infrared spectra and mixture melting point determination to be identical with the benzoyl derivative of the cyclic reduction product obtained by Vaughan and Peters[3] by catalytic hydrogenation and benzoylation of β-(*p*-anisylidine)-α-(*p*-anisylimino)-propionic acid (IIb), reacting as its proved cyclic tautomer, then presumed to be Ib, 1,5-dianisyl-2,3-pyrrolidinedione (enol form).

The absorption band in the high frequency range of the infrared spectra of substances previously held to be the enolic forms of 1,5-diaryl-2,3-pyrrolidinediones[7] is now assigned to N—H rather than O—H, since the treatment of Ia with sodium nitrite in glacial acetic acid affords an N-nitroso derivative whose infrared spectrum is transparent in the N—H region. The nitroso compound melts with decomposition at 216.0–216.5°.

Anal.[8] Calc'd for $C_{16}H_{12}N_2O_3$: C, 68.56; H, 4.32; N, 10.00. Found: C, 68.71; H, 4.17; N, 10.14.

The original substance thus has an endocyclic double bond which is evidently in the α,β-position (as in an enamine form), since the carbonyl absorption at 1736 cm.$^{-1}$ is at a lower frequency than is that for the dihydrolactone (1742 cm.$^{-1}$), whereas it would be at a higher frequency than in the dihydrolactone, if the double bond were β,γ.[9]

The present evidence for the structure of Ia and Ib coupled with the striking similarity in infrared spectra[7] and chemical behavior[2-4] as well as methods of synthesis,[7] for all previously reported and otherwise unsubstituted 1,5-diaryl-2,3-pyrrolidinediones constitutes a reasonable basis for assigning to all such compounds the 5-aryl-3-arylamino-2(5H)-furanone (V) structure.[10] Thus there is no available evidence for the existence of the otherwise unsubstituted 1,5-diaryl-2,3-pyrrolidinedione system,[11] and the previously reported reaction, I ⇄ II, becomes a special case of lacto-enoic tautomerism:[12] V ⇄ II.

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(2) W. R. Vaughan and L. R. Peters, *J. Org. Chem.*, **18**, 393 (1953).

(3) W. R. Vaughan and L. R. Peters, *J. Org. Chem.*, **18**, 405 (1953).

(4) W. R. Vaughan and D. I. McCane, *J. Org. Chem.*, **20**, 143 (1955).

(5) W. R. Vaughan, *J. Org. Chem.*, **20**, 1613 (1955).

(6) W. R. Vaughan, *J. Org. Chem.*, **20**, 1619 (1955).

(7) W. R. Vaughan and L. R. Peters, *J. Org. Chem.*, **18**, 382 (1953).

(8) Spang Microanalytical Laboratories, Ann Arbor, Michigan.

(9) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 160.

(10) This structure is the enamine form of the α-iminolactone proposed by K. Garzarolli-Thurnlackh [*Monatsh.*, **20**, 480 (1899); *Ber.*, **32**, 2274 (1899)] and was suggested to one of us (W.R.V.), along with a similar interpretation of our published infrared data[7] and the present type of structure proof, in 1953 by Dr. J. A. King in a private communication.

(11) It should be emphasized that this disproof of structure does not in any way apply to 2,3-pyrrolidinediones with 4-substituents or to the simpler 1-substituted compounds, for which conclusive structural evidence is available.

(12) R. P. Linstead and H. N. Rydon, *J. Chem. Soc.*, 580 (1933).

(13) National Science Foundation Predoctoral Fellow, 1954–1957.

Steroids. LXXXIV.[1] Synthesis of 6-Methyl Hormone Analogs

Sir:

The recent communication[2] describing the preparation of 6α-methyl cortical hormone analogs prompts us to announce at this time the synthesis of a number of 6-methyltestosterone and progesterone derivatives some of which possess potentiated biological activity. Perbenzoic acid oxidation of Δ^5-androstene-3β,17β-diol diacetate and reaction of the resulting 5α,6α-oxide (m.p. 165–166°, $[\alpha]_D$ −71°. Found: C, 70.65; H, 9.08[3]) with methylmagnesium bromide in ether-benzene gave 6β-methylandrostane-3β,5α,17β-triol (I)[4] (m.p. 137–138°, $[\alpha]_D$

(1) Paper LXXXIII, H. J. Ringold and G. Rosenkranz, *J. Org. Chem.*, in press.

(2) Spero, Thompson, Magerlein, Hanze, Murray, Sebek, and Hogg, *J. Am. Chem. Soc.*, **78**, 6213 (1956).

(3) All melting points are uncorrected. Rotations were determined at 20° in chloroform and ultraviolet absorption spectra in 95% ethanol.

(4) Ushakov and Madaeva, *J. Gen. Chem.* (U.S.S.R.), **9**, 436 (1939), first observed the opening of cholesterol α-oxide with methylmagnesium iodide. Turner, *J. Am. Chem. Soc.*, **74**, 5363 (1952) investigated this reaction further and prepared 6α- and 6β-methylcholestone from the Grignard reaction product.