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SYNTHESIS OF DIBENZO[c,g]-2,5-DIAZA-1,6-OXIDO[10]ANNULENE AND 12-METHYLDIBENZ[c,g]-2-AZA-1,6-OXIDO[10]ANNULENE[1)]

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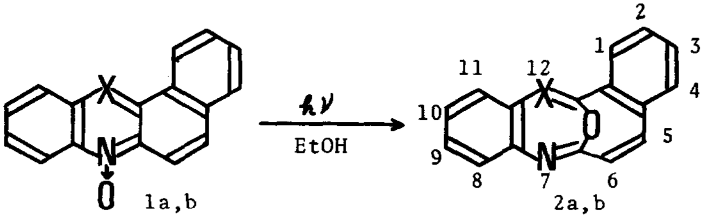
We have found that irradiation of 7-oxide[2)] (1a or 1b) of benzo[a]phenazine and benz[a]acridine in ethanol gives rise to the title compound (2a or 2b) in a very high yield. This synthesis resembles the formation of the corresponding annulenes (11) from acridine 10-oxides reported in our previous communication[3)] but differs in the fact that any other rearrangement product has not been obtained from the present reaction mixture.

	X
a	N
b	C-CH_3



1a,b

2a,b

Photolysis of 1a with a high pressure mercury lamp (450W, Hanovia, Pyrex filter) resulted in the formation of a crystalline compound (2a) in 75-85% yield, having an elemental composition identical with the starting N-oxide, together with benzo[a]phenazine (10, 2-5%).

Dibenzo[c,g]-2,5-diaza-1,6-oxido[10]annulene (2a), $C_{16}H_{10}ON_2$*, formed light yellow crystals, m.p. 117-119°; ir band at 1615 cm^{-1}; uv spectrum: λ_{max} 261 and 365 mμ (logε 4.61 and 3.97). The nmr spectrum showed an AB quartet (2 protons) centered at 2.7 and 3.0 τ with J=12 Hz, a multiplet (1 proton) at 1.5 τ and complex signals (7 protons) between 1.9 and 2.5 τ. The nmr band positions in a low field demonstrated the existence of a ring current in the ten-membered ring as found in

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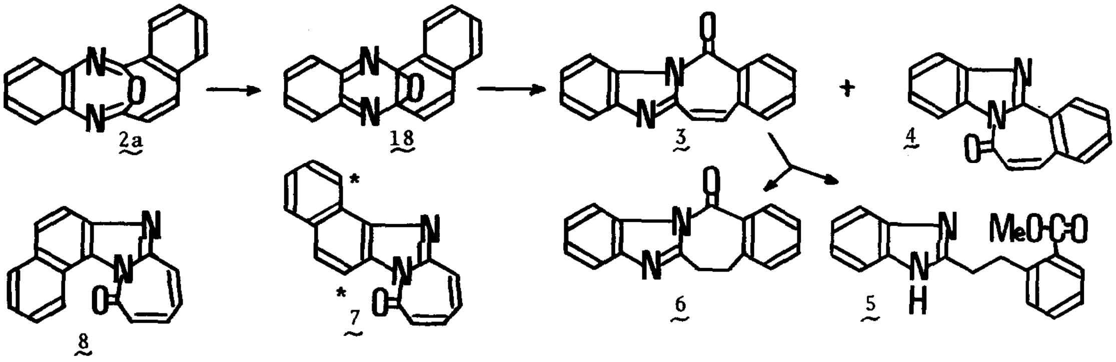
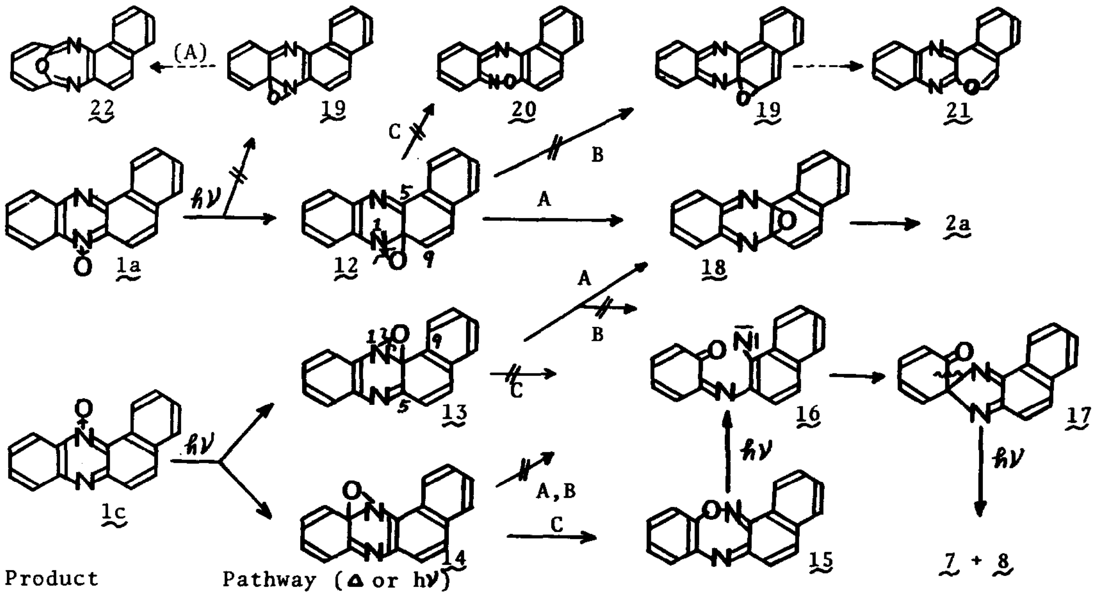
* All compounds described showed satisfactory elemental analyses and the structures were supported by spectral data (mass, nmr, uv and ir). The spectra were determined in $CDCl_3$(nmr), in 95% EtOH (uv), and as KBr pellet (ir).

a related aza-annulene3) (**11**) and its carbocyclic analog, such as 1,6-oxido[10]-annulene4). Several reactions described below further confirmed the correctness of the assigned structure (**2a**).

The compound (**2a**) undergoes an intramolecular rearrangement reaction via its valence bond tautomer (**18**) by the action of an acid, reminiscent of its related compounds, such as benz[*d*]-1,3-oxazepines5) and **11**3). Thus, in trifluoroacetic acid, **2a** undergoes rearrangement to two isomeric amides, **3**, m.p. 158-160° (1665 cm^{-1}), and **4**, m.p. 142-147° (1670 cm^{-1}), in the respective yield of 80 and 5%. These structures have been firmly established from their nmr spectra in which two ethylenic protons appeared as an AB quartet [centered at 2.7 and 2.9 τ (J=11 Hz) for **3** and 2.7 and 3.4 τ (J=12 Hz) for **4**] in the higher field region than those of other proton signals. The structure of the major product was further confirmed by the catalytic hydrogenation over palladium-charcoal. In methanol, a methyl ester (**5**), m.p. 163-165° (1720 cm^{-1}), was obtained in 80% yield. Its uv spectrum [λ_{max} 235, 276 and 282 mμ (log ε 4.17, 4.05 and 4.10)] resembles that of benzimidazole6) and its nmr spectrum showed the presence of four aliphatic protons as a multiplet centered at 6.62 τ. Reduction of **3** in ethanol gave the expected dihydro compound (**6**), m.p. 146-147° (1680 cm^{-1}), in 80% yield. Such a rearrangement seems to occur during the reduction of **2a** in ethanol, since **6** was obtained in 40% yield together with the expected phenazine (**10**, ca. 35%). The structures of these rearrangement products (**3**, **4** and **6**) exclude an alternative annulene structure (**22**) for **2a**.



The photolysis of benzo[*a*]phenazine 12-oxide (**1c**) under the same condition gave rise to **2a** and two isomeric amides, **7**, m.p. 179-181° (1665 and 1630 cm^{-1}), and 8, m.p. 148-149° (1675 cm^{-1}), in the respective yield of 30, 25 and 20%. The nmr spectra of 7 and 8 were similar, except that the former showed in the low field region a doublet at 1.2 τ(J=10 Hz) and a multiplet at 1.25 τ due to the protons on the asterisked carbon atoms. The catalytic reduction of 7 in ethanol gave a tetrahydro compound (9), m.p. 123-127° (1720 cm^{-1}), whose uv spectrum (λ_{max} 240, 304 and 327 mμ) resembles that of naphthalene. The nmr spectrum of 9 showed the presence of eight aliphatic protons between 8.0 and 6.6 τ.



Product		Pathway (Δ or hν)
2a	←	A: 1,5-oxygen rearrangement process (Δ)
(21 etc.)	←	B: 1,9-oxygen rearrangement process (Δ)
7, 8	←	C: 1,2-oxazepine rearrangement process (Δ and hν)

Scheme 1.

A tentative mechanism of these photochemical reactions is presented in Scheme 1. Among the three oxaziridine species[7,8] (12-14), only 14 is expected to be less stable than the corresponding 1,2-oxazepine (15) and thus should form the products via its valence-bond tautomer[9], possibly by the sequence of reactions (15→16→17). Differing from the photolysis of acridine 10-oxide derivatives[3], none of the corresponding oxepines was obtained from 1a and 1c and this fact indicates the preferential 1,5- to 1,9-oxygen rearrangement reaction from each of the other two oxaziridines (12 and 13). Considering the thermal nature of a 1,4n+1 oxygen rearrangement process[10], this fact can be reasonably explained from the estimation of the relative stability of the oxirane intermediates. For example, in two 1,4n+1 oxygen rearrangement paths from **17**, **18** is expected to be more stable than **19**, since the former oxirane alone still retains a benzene ring$^{11)}$.

As in accordance with the proposed scheme, irradiation of **1b** in ethanol gave the corresponding annulene (**2b**) as a sole rearrangement product (ca. 80%), m.p. 200-205° (1625 cm^{-1}). The similarity of the nmr spectrum [an AB quartet centered at 2.8 and 3.1 τ(H_5 and H_6, J=11 Hz), complex signals between 2.0 and 2.7 τ (H_{2-4} and H_{8-11}) and a singlet at 7.6 τ(CH_3)] and uv spectrum [λ_{max} 270 and 340 mμ (log ε 4.71 and 4.07)] with those of **2a** confirmed its structure unequivocally.

REFERENCES AND FOOTNOTES

1) This paper forms Part XVII of "Studies on the N-Oxides of π-Deficient N-Heteroaromatics". Preceding paper, Part XVI, see reference 5. This paper also forms Part 6 of "Photochemistry of Heterocyclic Compounds" by M. Ishikawa and C. Kaneko. Preceding paper, Part 5, see reference 3.

2) **1a** and **1c** were prepared according to the procedure described by I.J. Patcher and M.C. Kloetzel (*J. Am. Chem. Soc.*, **73**, 4958(1951)). **1b** (m.p. 170-171°) was obtained from the parent amine with perbenzoic acid in benzene.

3) C. Kaneko, Sa. Yamada and M. Ishikawa, *Chem. Pharm. Bull.(Tokyo)*, **17**, 1294 (1969).

4) A. Shani and F. Sondheimer, *J. Am. Chem. Soc.*, **89**, 6310(1967).

5) Sa. Yamada and C. Kaneko, *Rept. Res. Inst. Med. Eng., Tokyo Med. Dent. Univ.*, **3**, 75(1969).

6) *"UV Atlas"*, Vol. **2**, H11/1. Butterworth, London(1966).

7) The wealth of information on the photochemical rearrangement reaction of aromatic amine oxides which appeared in the literature in the past has been interpreted in terms of oxaziridine species as intermediates. For a survey, see C. Kaneko, *J. Synth. Org. Chem. Japan*, **26**, 758(1968).

8) Using MO theory, we have found the method predicting the structure of an oxaziridine of a given N-oxide from which the formation of two oxaziridines can be formally expected. The method satisfied the results of the present reactions. See C. Kaneko, Sa. Yamada, I. Yokoe and T. Kubota, to be published as Part XVIII of the present series.

9) The products via 1,2-oxazepine rearrangement process were obtained from the N-oxides, whose oxaziridine is expected to have less (or at least same) stabilization energy than (or to) the corresponding 1,2-oxazepine. Pyridine and pyrazine 1-oxides fall in this category. See (a) M. Ishikawa, C. Kaneko, I. Yokoe and Sa. Yamada, *Tetrahedron*, **25**, 295(1969). (b) N. Ikekawa and Y. Homma, *Tetrahedron Letters*, 1197(1967).

10) R.B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 2511(1965).

11) Essentially the same argument was first applied to explain the thermal intramolecular rearrangement reactions of 8,16-oxido[2,2]methacyclophane-1,9-diene by Boekelheide *et al*. See B.A. Hess, Jr., A.S. Bailey, B. Bartusek and V. Boekelheide, *J. Am. Chem. Soc.*, **91**, 1665(1969).

12) A part of this work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan.