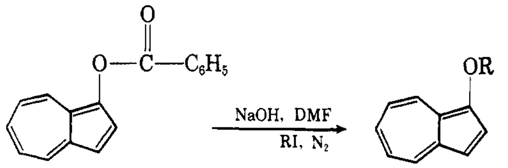
These ethers are conveniently prepared by the basic cleavage of 1-azulyl benzoate[4] (**3**) in N,N-dimethylformamide (DMF) in the presence of methyl or ethyl iodide (nitrogen atmosphere). 1-Methoxyazulene (**1**) was obtained in 81% yield as a green oil that crystallized when it was cooled and scratched, m.p. 26–28°.



3

1, R = CH_3
2, R = C_2H_5

A slightly lower yield (69%) of **1** was obtained when the reaction was carried out without a nitrogen atmosphere. The ethyl ether, **2**, was obtained in good yield (80%) as a green oil that would not crystallize. The spectra of **1** and **2** are nearly identical. As anticipated, their visible spectra show a strong bathochromic shift from that of azulene, with the principal maxima appearing at 684 and 686 mμ for **1** and **2** respectively.

The n.m.r. spectra of **1** and **2** show the characteristic patterns for a 1-substituted azulene[7] and for the particular alkoxy group. Thus the spectrum of **1** shows a sharp singlet (relative intensity of three) due to the methoxy group at τ 6.05, while the spectrum of **2** shows the characteristic splitting pattern for an ethyl group with the methylene quartet appearing at τ 5.80, and the methyl triplet at τ 8.53.[8]

The ester **3** is quite susceptible to basic cleavage as shown by the mild conditions, room temperature, and weakly alkaline (*ca.* 0.16 *N*) solution employed. Also an immediate color change was observed when the methanolic sodium hydroxide solution was added to the DMF solution of the ester and alkyl iodide. If methanol was used as the solvent in the preparation of **1**, only small amounts of the product could be isolated, and extensive decomposition occurred. Attempts to isolate the unknown 1-azulol were unsuccessful, and only resinous material was obtained.

The question of the identity of the products isolated by Treibs and Stein[2] still remains. One might postulate that a rearrangement occurred and they isolated the isomeric 2-methoxyazulene. However, this cannot be so since Nozoe, *et al.*[9] have prepared 2-methoxyazulene, and its properties do not correspond with those of the "methoxyazulene" reported by the German workers. It seems likely that Treibs and Stein did not have a methoxyazulene at all since the reported properties do not correspond with those of the known 1-methoxy, 2-methoxy, 4-methoxy,[6] or 5-methoxyazulene,[6] and a 6-methoxy group is reported[10] to cause a spectral shift of −43 mμ in the visible spectrum.

Experimental[11]

1-Methoxyazulene (**1**).—To a stirred solution containing 50 mg. (0.20 mmole) of 1-azulyl benzoate,[4] 10 ml. of N,N-dimethylformamide, and 1.0 ml. of methyl iodide was added 1.0 ml. of a 1.9 *N* methanolic sodium hydroxide solution (nitrogen atmosphere). Upon addition of the base, the solution changed from blue to bluish green in color. The reaction mixture was stirred at room temperature for 5 hr., and ether was added. The blue-green ethereal solution was washed with several portions of water, then with saturated salt solution, and dried over sodium sulfate. Removal of solvent left a green oil which was chromatographed over acid-washed alumina (Merck). The large, blue band was eluted with a 3:1 petroleum ether–dichloromethane mixture. Dichloromethane eluted a faint purple band, and ether eluted a small yellow band. Removal of solvent from the blue eluate left 25.5 mg. (81%) of a green oil that crystallized when cooled and scratched, m.p. 26–28°. A cyclohexane solution showed λ_{max} in mμ in the ultraviolet (log ε) at 236 (4.15), 285 (4.71), 341 (3.46), 350 (3.54), 358 (3.76), 367 (3.48), 376 (3.79), and in the visible (ε) with a shoulder at 632 (249), 661 (291), 684 (317), 725 (274), 815 (117), and 863 (104).

The n.m.r. spectrum of a carbon tetrachloride solution of **1** showed a pair of doublets ($J \simeq 9$ c.p.s.) of unit intensity at τ 1.89 and 2.12 which were assigned to the 4- and 8-protons. Two other doublets ($J \simeq 3.5$ c.p.s.) were observed at τ 2.76 and 2.99 and were assigned to the 2- and 3-protons, respectively. The methoxyl group resonance appeared as a sharp singlet of three times unit intensity at τ 6.05. The rest of the spectrum, including the integrated intensities, was consistent with a 1-substituted azulene.[7]

Anal. Calcd. for $C_{11}H_{10}O$: C, 83.51; H, 6.38. Found: C, 83.53; H, 6.32.

1-Ethoxyazulene (**2**).—A 1.9 *N* methanolic sodium hydroxide solution (1 ml.) was added dropwise, over a period of 20 min., to a stirred solution containing 50 mg. (0.20 mmole) of 1-azulyl benzoate,[4] 1.0 ml. of ethyl iodide, and 10 ml. of N,N-dimethylformamide (nitrogen atmosphere). The bluish green reaction mixture was stirred for another 50 min. and then poured into water. The aqueous mixture was extracted with petroleum ether, and the green organic phase was washed well with water and dried over sodium sulfate. Removal of solvent left a green oil which was chromatographed over acid-washed alumina (Merck). The large blue band was eluted with dichloromethane. The residue from the blue eluate was rechromatographed, and the single blue band eluted with a 3:1 petroleum ether–dichloromethane mixture. Removal of solvent from the blue eluate left 27.5 mg. (80%) of a green oil that would not crystallize when cooled and scratched. A cyclohexane solution showed λ_{max} in mμ in the ultraviolet (log ε) at 236 (4.16), 286 (4.72), 343 (3.47), 351 (3.55), 359 (3.75), 368 (3.49), and 378 (3.77), and in the visible (ε) with a shoulder at 637 (254), 662 (293), 686 (319), 725 (272), 765 (258), 814 (116), and 867 (97).

The n.m.r. spectrum of **2** showed the same aromatic proton spectrum as **1**, and the characteristic splitting pattern of an ethyl group with the quartet at τ 5.80 and a triplet at τ 8.53, due to the methylene protons and methyl protons, respectively.

Anal. Calcd. for $C_{12}H_{12}O$: C, 83.68; H, 7.03. Found: C, 83.97; H, 7.14.

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[7] A. G. Anderson, Jr., and L. L. Replogle, unpublished data.

[8] *Cf.* Experimental for a more complete analysis.

[9] T. Nozoe, S. Seto, and S. Matsumura, *Bull. Chem. Soc. Japan*, **35**, 1990 (1962).

[10] K. Hafner and H. Kaiser, *Ann.*, **618**, 140 (1958).

[11] The melting point was taken on a Fisher-Johns apparatus and is uncorrected. Ultraviolet and visible absorption spectra were taken on a Cary Model 14 spectrophotometer. N.m.r. spectra were determined on carbon tetrachloride solutions, containing internal tetramethylsilane as a marker, using a Varian A-60. Microanalyses were performed by Dr. A. Bernhardt, Max Planck Institute, Mulheim, Germany.

The Rate-Determining Step for the Reaction of Acridine N-Oxide with Acetic Anhydride[1a]

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Received April 23, 1964

In a recent paper from this laboratory, it was shown that the rearrangement of acridine N-oxide with excess acetic anhydride to form acridone proceeded *via* an

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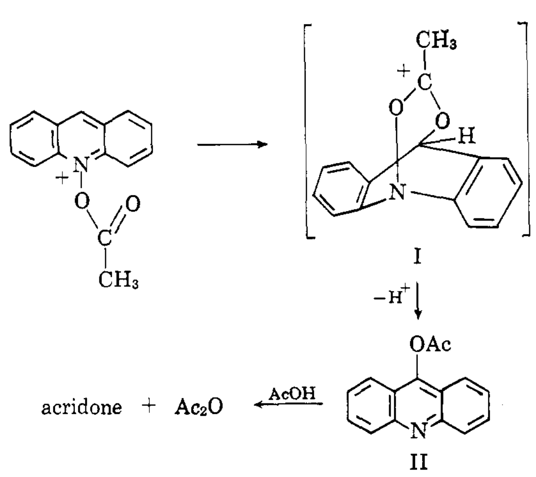
[1] (a) Rearrangement of Aromatic N-Oxides. III. (b) Based on the Honors Thesis of C. G. Carson, III, 1964.

external ion pair as the kinetically significant intermediate.[2] The following series of equilibria (where ANO represents acridine N-oxide) was invoked to account for pseudo-first-order kinetic behavior, conductance data, and effects of added salts.

$$\begin{tikzcd}
\mathrm{ANO} + \mathrm{Ac_2O} \arrow[d, shift left] \\
{[\mathrm{A\overset{+}{N}OAc\ AcO^-}]} \arrow[u, shift left] \arrow[d, shift left] \\
\mathrm{A\overset{+}{N}OAc \| AcO^-} \arrow[u, shift left] \arrow[d, shift left] \arrow[r, "k"] & \text{product} \\
\mathrm{A\overset{+}{N}OAc} + \mathrm{AcO^-} \arrow[u, shift left]
\end{tikzcd} \qquad (1)$$

It was further postulated that the N-acetoxyacridinium ion ($\mathrm{A\overset{+}{N}OAc}$) underwent an intramolecular rearrangement *via* a bicyclic intermediate (I), a process consistent with the reported activation parameters.



(2)

The present paper reports the identification of the rate-determining step for the rearrangement of $\mathrm{A\overset{+}{N}OAc}$ to 9-acetoxyacridine (II). A more convenient method for the oxidation of acridine and some anomolies in infrared absorption accompanying isotopic substitution are also noted.

For the above rearrangement (eq. 2) there are two possibilities for the rate-determining step.[3] In the

$$\mathrm{A\overset{+}{N}OAC} \xrightarrow{\text{slow}} [\mathrm{I}] \xrightarrow{\text{fast}} \mathrm{II} \qquad (3)$$

$$\mathrm{A\overset{+}{N}OAC} \rightleftarrows [\mathrm{I}] \xrightarrow{\text{slow}} \mathrm{II} \qquad (4)$$

first case (eq. 3), the formation of the bicyclic intermediate (I) is the slow step, followed by a rapid deprotonation. The second possibility (eq. 4) involves the reversible formation of I prior to the rate-determining departure of the hydrogen at C-9. Both mechanisms are consistent with the observed kinetics. A distinction can be made, however, on the basis of isotopic substitution. The results of such studies are presented in Table I. Each value is the average of two or more separate experiments. In all cases a good pseudo-first-order plot was obtained. The absence of an isotope effect in the rearrangement of acridine N-oxide with acetic anhydride indicates that proton elimination is not kinetically significant. The mechanism, therefore, involves the rate-determining formation of I (eq. 3).

TABLE I

RATES OF REARRANGEMENT OF ACRIDINE N-OXIDE IN ACETIC ANHYDRIDE AT 16.00°

N-Oxide	A_0,[a] M	$k \times 10^4$ sec.$^{-1}$	k_H/k_D
Acridine	0.01	3.53 ± 0.17[b]	1.00
Acridine-9-d_1	0.01	3.52 ± 0.03	

[a] Initial concentration of the N-oxide. [b] Previously reported[2] value for k over a threefold change in concentration was $3.51 \pm 0.06 \times 10^{-4}$ sec.$^{-1}$.

The commonly accepted method for the preparation of acridine N-oxide is the oxidation of acridine by perbenzoic acid.[4] This procedure, which has not always afforded satisfactory results,[5] requires the use of freshly prepared solutions of the peracid.[6] We have found that such an oxidation is effected conveniently by *m*-chloroperbenzoic acid, a stable, crystalline compound. Acridine N-oxide and acridine-9-d_1 N-oxide were prepared by this method in yields comparable to that obtained with perbenzoic acid.

The anomolous infrared spectrum of the latter compound is noteworthy. The aromatic C–D stretching band is usually observed at about 4.4 μ. Such peaks for pyridine-2-d_1[7] and acridine-9-d_1 occur at 4.42 and 4.39 μ, respectively. Acridine-9-d_1 N-oxide, however, exhibits no absorption between 4 and 6 μ except a single, sharp peak at 5.76 μ which is present at much lower intensity as one of several peaks (5.1, 5.5, and 5.8 μ) characteristic of aromatic absorption in acridine, acridine N-oxide, and acridine-9-d_1.[8] No such enhancement was observed in the absence of isotopic substitution: acridine and acridine N-oxide exhibited identical absorption at 5–6 μ. It was established that there was no loss in isotopic content during the oxidation and purification steps.

Experimental[9]

Materials.—Acridine N-oxide was prepared by the method followed previously,[2] except that *m*-chloroperbenzoic acid[10] was used. The crude product (45%) was recrystallized from 95% ethanol, triturated with 1 N NaOH and recrystallized again from 95% ethanol to afford acridine N-oxide (21%), m.p. 169.0–169.8°.

Acridine-9-d_1, obtained from Merck Sharp and Dohme of Canada, contained 96 atom % deuterium. The oxidation and purification

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[2] J. H. Markgraf and M.-K. Ahn, *J. Am. Chem. Soc.*, **86**, 2699 (1964).

[3] That formation of the ion pair is not rate determining was established by the following considerations. The specific conductance of the reaction solution increased to a maximum value immediately upon dissolution of the substrate in acetic anhydride. Also, rate data derived from conductance measurements were in agreement with those obtained by spectrophotometric procedures.[2]

[4] A. Kliegl and A. Brösamle, *Ber.*, **69**, 197 (1936).

[5] (a) K. Lehmstedt and H. Klee, *ibid.*, **69**, 1514 (1936); (b) R. M. Acheson, B. Adcock, G. M. Glover, and L. E. Sutton, *J. Chem. Soc.*, 3367 (1960).

[6] L. S. Silbert, E. Siegel, and D. Swern, *Org. Syn.*, **43**, 93 (1963).

[7] R. A. Abramovitch and C.-S. Giam, *Can. J. Chem.*, **41**, 3127 (1963).

[8] A similar shift was observed for pyridine-2,6-d_2 and its N-oxide. The C–D peak at 4.40 μ present in the spectrum of the former compound was absent in the spectrum of the corresponding N-oxide, while the sole peak between 4 and 6 μ in the latter spectrum was the enhanced absorption at 5.85 μ (unpublished results with G. G. Spence).

[9] Melting points are uncorrected. Ultraviolet absorptions were measured with a Cary spectrophotometer, Model 14. Infrared spectra were obtained as chloroform solutions with a Perkin-Elmer Infracord spectrophotometer, Model 137. Deuterium analyses were made by J. Nemeth, Urbana, Ill.

[10] We thank the FMC Corp. for a generous supply of this material.

steps, which were identical with those described above, yielded acridine-9-d_1 N-oxide (14%), m.p. 168.4–169.0°. The product contained 10.25 (corresponding to 92.3/9) atom % deuterium.

Acetic anhydride and the solvent system of acidified methanol were the same as those used previously.[2]

Rate Measurement.—The procedure followed was identical with that described earlier.[2] Aliquots (2 ml.) of the reaction solution (0.1 *M* acridine N-oxide in acetic anhydride) were quenched by delivery into 50-ml. portions of the methanol–perchloric acid solvent. The spectrophotometric method of analysis was used. All runs were followed to 60–70% completion.

An attempt was made to follow the rate of rearrangement conductometrically.[11] The apparatus was less sophisticated than that used previously[2] and, although k_H/k_D was 1.07 by these data, the absolute rate constants did not correspond well to those determined spectrophotometrically.

Acknowledgment.—We are grateful to the Research Corporation for a Frederick Gardner Cottrell grant which supported this work.

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[11] We are indebted to Dr. R. C. Petersen of the Sprague Electric Co. for assistance with these measurements.

Reaction of Benzyne with Nitrosobenzene. A New Route to the Carbazole Ring System

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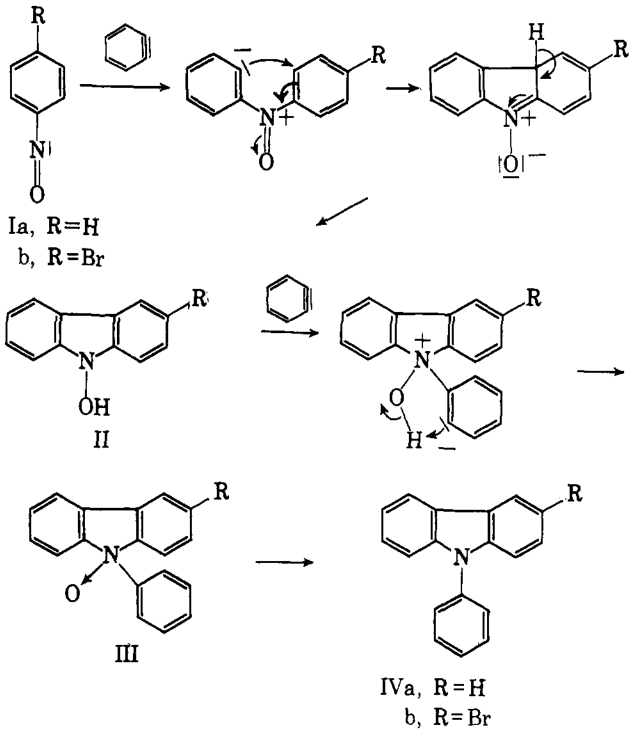
Received May 8, 1964

Nitrosobenzene has been reported to react as a dienophile.[1] It has also been noted to react with diphenylketene,[2] substituted ethylenes,[3] and azomethines[4] to form four-membered rings. We wish to report that the reaction of nitrosobenzene (Ia) with benzyne results in the formation of the carbazole ring system. Generation of benzyne by the decomposition of 4,5-benzothiadiazol 1,1-dioxide[5,6] in tetrahydrofuran in the presence of nitrosobenzene gave a 45% yield of N-phenylcarbazole (IVa).

It appears likely that, because of the electrophilic nature of benzyne,[7] the reaction path involves initial coordination of the nitrogen lone pair of electrons with benzyne. The second step is the formation of the hydroxylamine derivative II, which itself reacts with a second molecule of benzyne to yield the N-oxide III. The unstable N-oxide then loses oxygen to give IV (Chart I).

CHART I



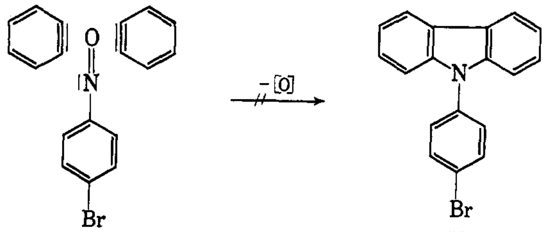
Ia, R=H
b, R=Br

II

III

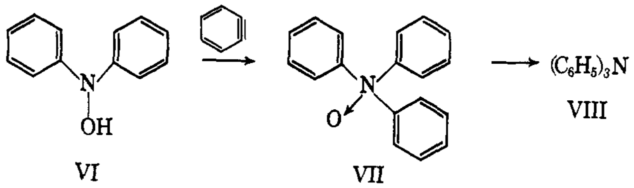
IVa, R=H
b, R=Br

An alternative but less likely route to the carbazole ring system would involve the direct reaction of the nitroso compound with two molecules of benzyne. This mechanism could be excluded when it was found that the product of the analogous reaction of benzyne with *p*-bromonitrosobenzene[8] (Ib) was 3-bromo-N-phenylcarbazole (IVb, 40% yield) instead of the N-(*p*-bromophenyl)carbazole[9] (V) which should have been formed from the direct reaction. As expected, N-phenylcarbazole and its 3-bromo derivative had very similar ultraviolet spectra.



V

Evidence that the postulated hydroxyamine derivative II is an intermediate in the reaction was provided by reacting the structurally similar diphenylhydroxyamine[10] (VI) with benzyne under the same experimental conditions. Triphenylamine (VIII) was formed in 40% yield, identical in all respects with an authentic sample.



VI VII VIII

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[1] S. B. Needleman and M. C. Chang Kuo, *Chem. Rev.*, **62**, 407 (1962).

[2] H. Staudinger and J. Jelagin, *Ber.*, **44**, 365 (1911).

[3] C. K. Ingold and S. D. Weaver, *J. Chem. Soc.*, 1456 (1924).

[4] C. K. Ingold, *ibid.*, 87 (1924).

[5] G. Wittig and R. W. Hoffman, *Angew. Chem.*, **73**, 435 (1961); *Chem. Ber.*, **95**, 2718 (1962).

[6] Other techniques for generating benzyne in nonalkaline media have been presented by (a) M. Stiles and R. G. Miller, *J. Am. Chem. Soc.*, **82**, 3802 (1960); M. Stiles, R. G. Miller, and U. Burckhardt, *ibid.*, **85**, 1792 (1963); (b) G. Wittig and H. F. Ebel, *Angew. Chem.*, **72**, 564 (1960); *Ann.*, **650**, 20 (1961); (c) E. LeGoff, *J. Am. Chem. Soc.*, **84**, 3786 (1962); F. M. Behringer and S. J. Huang, *J. Org. Chem.*, **29**, 445 (1964); (d) L. Friedmann and F. M. Logullo, *J. Am. Chem. Soc.*, **85**, 1549 (1963).

[7] R. Huisgen, "Organometallic Chemistry," H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, pp. 36–87.

[8] C. K. Ingold, *J. Chem. Soc.*, 94 (1924).

[9] C. Buchanan and S. H. Tucker, *ibid.*, 2750 (1958).

[10] H. Wieland and K. Roth, *Ber.*, **53**, 216 (1920).