SYNTHESIS OF 3,4,5,6-TETRAHYDROBENZO[c]PHENANTHRIDIN-3-ONES

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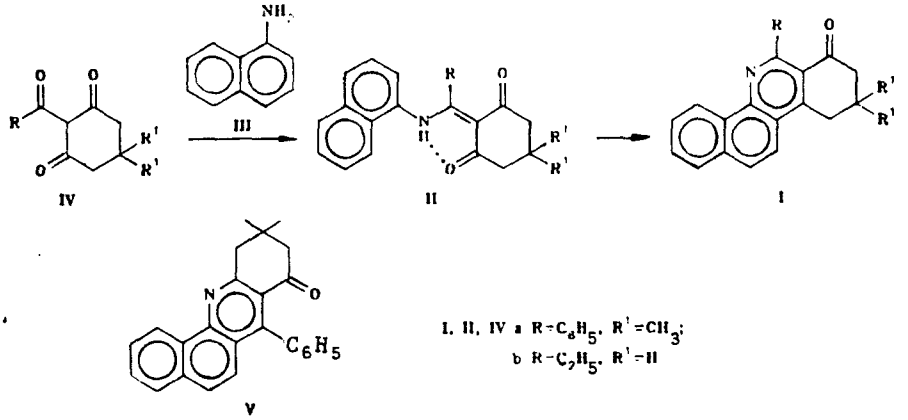
In 1971, the synthesis was reported of the tetrahydrobenzacridine (V), which was originally assigned the tetrahydrobenzo[c]phenanthridine structure (Ia). The erroneous nature of the structure assigned was shown by Cortes et al. [2] on the basis of x-ray diffraction data.

We have synthesized compounds (Ia, b) by intramolecular cyclization of the enaminoketones (IIa, b), obtained from α-naphthylamine (III) and the β-triketones (IVa, b).

5,5-Dimethyl-2-[α-(2-naphthylaminobenzylidene]cyclohexane-1,3-dione (IIa). A mixture of 2.44 g (10 mmoles) of benzoyldimedone and 1.43 g (10 mmoles) of α-naphthylamine in 60 ml of toluene was boiled for 2 h with a Dean and Stark attachment. The toluene was evaporated, and the residue crystallized from 20 ml of ethyl acetate to give 3.33 g (90%) of the enaminodiketone (IIa), mp 202-202°C. IR spectrum (KBr): 1536 (C=C); 1580, 1658 (C=O); 3440 cm^{-1} (NH). PMR spectrum ($CDCl_3$): 15.05 (1H, s, NH); 8.10 (1H, d, J = 7.5 Hz, 8"-H); 7.70-6.90 (9H, m, arom.); 6.74 (1H, d, J = 7.3 Hz, 2"-H); 2.64 and 2.38 (2H each, s, CH_2); 1.16 ppm (6H, s, $2CH_3$). M^+ 369.



5,5-Dimethyl-2-phenyl-3,4,5,6-tetrahydrobenzo[c]phenanthridin-3-one (Ia). The enaminodiketone (IIa) (1.84 g, 5 mmoles) was heated at 170°C with stirring in 40 g of polyphosphoric acid (134 g of P_2O_5 + 65 ml H_3PO_4) for 1.5 h. The mixture was then cooled, carefully diluted with 50 ml of ice water, and neutralized with solid KOH to pH ~6.0. The solid was filtered off, washed with water, and dried in air to give 1.54 g (88%) of (Ia), mp 246-247°C (from ethyl acetate). IR spectrum (KBr): 1500, 1552, 1570 (C=N, C=C), 1678 cm^{-1} (C=O). PMR spectrum ($CDCl_3$): 9.36 (1H, m, 12-H); 8.00-7.40 (10H, m, arom.); 3.34 (2H, s, 6-H); 2.62 (2H, s, 4-H); 1.22 ppm (6H, s, $2CH_3$), M^+ 351.

Obtained similarly were **2-[1-(2-naphthylamino)propylidene]cyclohexane-1,3-dione (IIb)** [mp 172-174°C (from ethyl acetate)]. IR spectrum (KBr): 1552 (C=C), 1570 (C=O), 1650 (C=O), 3440 cm^{-1} (NH). PMR spectrum ($CDCl_3$): 15.29 (1H, s, NH); 7.90-7.30 (7H, m, arom.); 2.86 (2H, q, J = 7.3 Hz, 2-H); 2.62 (4H, m, $2CH_2$); 2.00 (2H, q, J = 6.3 Hz, 5-H); 1.04 ppm (3H, t, J = 7.3 Hz, CH_3). Yield 91%, M^+ 293, and **2-ethyl-3,4,5,6-tetrahydrobenzo[c]phenanthridin-3-one (Ib)** [mp 170-172°C (from ethyl acetate). IR spectrum (KBr): 1509, 1562 (C=C, C=N); 1680 cm^{-1} (C=O). PMR spectrum ($CDCl_3$): 9.39 (1H, m, 12H); 7.76 (6H, m, atom.); 3.44 (2H, q, J = 7.3 Hz, CH_2); 3.34 (2H, t, J = 6.3 Hz, 6-H); 2.72 (2H, t, J = 6.3 Hz, 5-H); 1.46 ppm (3H, t, J = 7.3 Hz, CH_3). Yield 89%, M^+ 275].

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SYNTHESIS OF 1-(3-METHYLPYRAZOLYL-1)ANTHRAQUINONE

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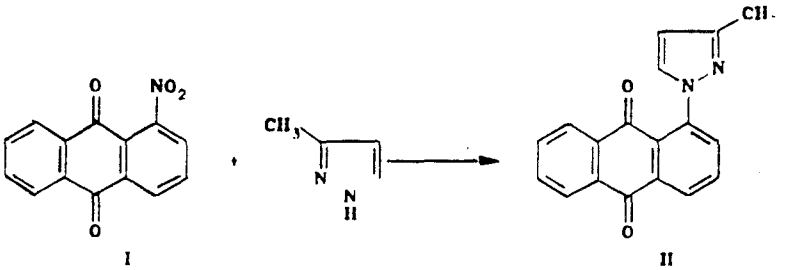
Nucleophilic replacement of the nitro group in 1-nitroanthraquinone (I) by amino takes place under quite drastic conditions.

We have found that 3(5)-methylpyrazole, a weak N-nucleophile (pK_a 3.32 [2]), reacts with 1-nitroanthraquinone under prolonged heating at 150°C to form one of two possible isomers, viz., 1-(3-methylpyrazolyl-1)anthraquinone (II). In the ^{13}C NMR spectrum (DMSO-D_6) of (II) the methyl signal at 13.25 ppm corresponds to the particular isomer, because the chemical shifts of the methyl carbons at positions 3 and 5 of the heterocycle are quite different from one another [3]. As is known, in going from $CDCl_3$ to DMSO-D_6 the PMR spectra of 1-substituted pyrazoles show a characteristic shift of the 5-H proton signal to the weak field [4]. Analogous changes in the spectrum of (II) also confirm its structure.



I II

1-(3-Methylpyrazolyl-1)anthraquinone (II). A mixture of 1.27 g of (I) and 5 ml of 3(5)-methylpyrazole was held at 150°C for 30 min. Methylpyrazole was distilled off in vacuum, and the residue was chromatographed on a column of 100/400 μm silica gel (benzene eluent). There was obtained 1.1 g (76%) of (II), mp 189-190°C, R_f 0.44. PMR spectrum ($CDCl_3$): 2.43 (3H, s, 3'-CH_3), 6.33 (1H, d, 4'-H), 7.59 (1H, d, 5'-H), 7.75-8.45 ppm (7H, m, $C_{14}H_7$). PMR spectrum (DMSO-D_6): 2.28 (3H, s, 3'-CH_3), 6.28 (1H, d, 4'-H), 7.90 (1H, d, 5'-H), 7.85-8.33 ppm (7H, m, $C_{14}H_7$). M^+ 288.

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