One-step synthesis of 2-aminobenz[*kl*]acridines by reaction of 1-nitroacridones with malononitrile

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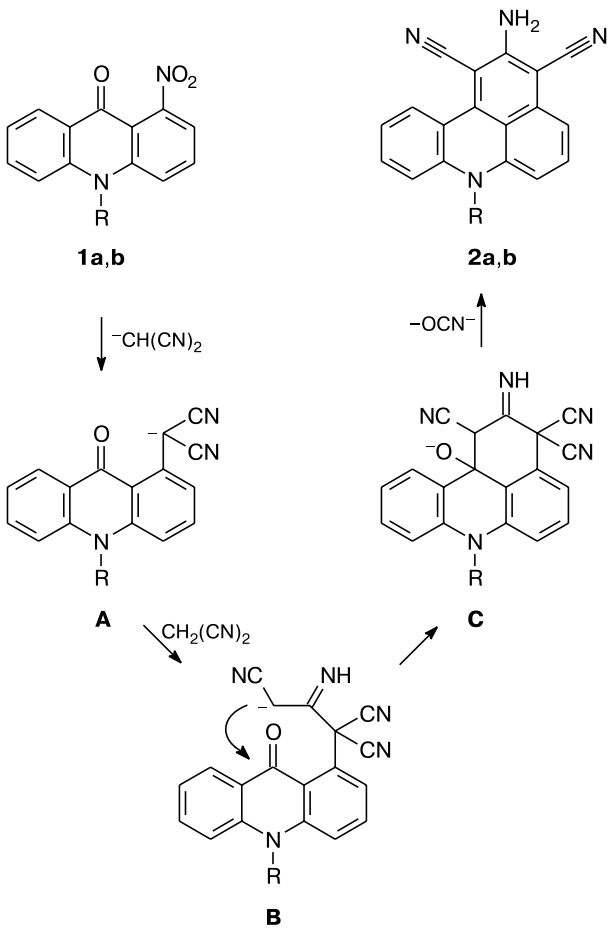
Reaction of 1-nitro- and 10-methyl-1-nitro-9-acridone with malononitrile leads directly to the corresponding 2-amino-1,3-dicyanobenz[*kl*]acridines.

Key words: acridones, benz[*kl*]acridines, malononitrile, heterocyclization.

Benz[*kl*]acridines belong to the scarcely accessible group of compounds. 7*H*-Benz[*kl*]acridine itself and its 8,10-dinitro derivative were synthesized by the thermolysis of naphtho[1,8-*de*]triazines, formed by the action of diazotizating agent on *N*-phenyl- and *N*-(2,4-dinitrophenyl)-1,8-diaminonaphthalenes.[1,2] In the present paper we report on the *peri*-annelation of a benzene ring to an acridine core, which results in the formation of earlier unknown 2-aminobenz[*kl*]acridines.

Scheme 1



The sufficient fugacity of the nitro group in position 1 of acridone in the amination reactions[3] prompted us to investigate a possible reaction of 1-nitro-9-acridones (**1a,b**) with C-nucleophile. It turned out that the heating of 1-nitro-9-acridone (**1a**) or 10-methyl-1-nitro-9-acridone (**1b**) with excess of malononitrile salt in DMF led to the tetracyclic compounds, *viz.*, 2-amino-1,3-dicyanobenz[*kl*]acridine (**2a**) and 2-amino-1,3-dicyano-7-methylbenz[*kl*]acridine (**2b**), respectively (Scheme 1). The methylation converts benzacridine **2a** to 7-methyl derivative **2b**.

This reaction is similar to the transformation of 1-nitroanthraquinone to 1,3-disubstituted 2-aminobenzanthrone under treatment with the same reagent.[4] It can be conceived as the addition of carbanion **A**, arising during the nucleophilic substitution in 1-nitroacridone **1**, to the C≡N bond of the second malononitrile molecule. The subsequent attack of the carbanionic center (**B**) at the carbonyl group of acridone and the elimination of the cyanate-ion from *peri*-cyclic intermediate **C** does finalize the transformation to 2-aminobenz[*kl*]acridines **2** (see Scheme 1).

In conclusion, reaction of 1-nitroacridone with anion of malononitrile provides a straightforward one-step transformation to benz[*kl*]acridine derivatives.

Experimental

IR spectra were recorded on a FSM 1201 Fourier spectrometer in KBr pellets. Mass spectrum was registered on a Kratos MS 30 instrument (EI, 70 eV) with direct injection of samples, the temperature of ionizing chamber was 250°C. ^{1}H NMR spec-

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tra were recorded on a Bruker AM-400, ^{13}C NMR spectra were recorded on a Bruker AV-300, signals of CH and C atoms were distinguished using *J*-modulation, DMSO-d_6 was used as the solvent, Me_4Si, as the internal standard. 1-Nitro-9-acridone (**1a**)[5] and 10-methyl-1-nitro-9-acridone (**1b**)[6] were synthesized according to the described procedures.

2-Amino-1,3-dicyanobenz[*kl*]acridine (2a). A solution of 1-nitroacridone **1a** (1.20 g, 5 mmol) in DMF (50 mL) was added to a solution of malononitrile sodium salt, obtained by the reaction of malononitrile (2.0 g, 30 mmol) and sodium hydride (0.73 g, 30 mmol) in DMF (60 mL). This was stirred for 2 h at 100—105 °C, cooled, diluted with water (20 mL), the precipitate was separated, washed with DMF and water and dried. The yield was 0.61 g (43%), m.p. >350 °C (from aq. DMF). IR, ν/cm^{-1}: 2198 (CN); 3295 (NH); 3348, 3465 (NH_2). Found (%): C, 69.67; H, 3.90; N, 18.65. $C_{18}H_{10}N_4$. Calculated (%): C, 69.76; H, 3.68; N, 18.59. ^1H NMR, δ: 6.14 (s, 2 H, NH_2); 6.75 (d, 1 H, H(6), J = 8.5 Hz); 6.96 (d, 1 H, H(4), J = 8.0 Hz); 7.15 (t, 1 H, H(10), J = 7.8 Hz); 7.28 (d, 1 H, H (8), J = 8.1 Hz); 7.55 (t, 1 H, H(9), J = 7.8 Hz); 7.51 (t, 1 H, H(5), J = 8.1 Hz); 8.97 (d, 1 H, H(11), J = 8.4 Hz); 11.26 (s, 1H, NH) (*cf.* ^1H NMR spectrum of 7-phenylbenz[*kl*]acridine[7]). ^{13}C NMR, δ: 81.35, 83.13 (both CN); 104.30 (C(6)H); 110.15 (C(8)H); 115.56, 115.62, 116.96 (C(11a), C(11b), (C(11c)); 117.02 (C(4)H); 118.97 (C(3a)); 121.08 (C(10)H); 125.25 (C(11)H); 132.96, 133.03 (C(5)H, C(9)H); 136.09, 138.48, 139.73, 141.52 (C(1), C(3), C(6a), C(7a)); 153.20 (C(2)).

2-Amino-1,3-dicyano-7-methylbenz[*kl*]acridine (2b). ***A.*** A mixture of 10-methyl-1-nitroacridone **1b** (0.51 g, 2 mmol) and DMF (30 mL) was heated to 60 °C, a solution of malononitrile sodium salt, obtained from malononitrile (1.32 g, 20 mmol) and sodium hydride (0.48 g, 20 mmol) in DMF (20 mL), was added and this was stirred for 1 h at 100 °C, cooled, the precipitate was separated, washed with DMF and water and dried. The yield was 0.34 g (67%), m.p. >350 °C (from chlorobenzene). IR, ν/cm^{-1}: 2197 (CN); 3422, 3343 (NH_2). MS, m/z (I_{rel} (%)): 296 $[M]^+$ (100); 281 $[M - Me]^+$ (79). Found (%): C, 77.18; H, 4.40; N, 18.98. $C_{19}H_{12}N_4$. Calculated (%): C, 77.01; H, 4.08; N, 18.91. ^1H NMR, δ: 3.68 (s, 3 H, NMe); 6.45 (s, 2 H, NH_2); 6.92 (d, 1 H, H(6), J = 7.8 Hz); 7.15 (d, 1 H, H(4), J = 8.7 Hz); 7.28 (t, 1 H, H(5)); 7.40—7.75 (m, 3 H, H (8), H(9), H(10)); 8.85 (1 H, H(11), J = 8.0 Hz).

B. Iodomethane (0.5 mL, 8 mmol) was added to a blue-reddish in color mixture of benzacridine **2a** (0.28 g, 1 mmol), DMF (20 mL), and finely powdered KOH (0.40 g), this was stirred for 1 h at 30 °C, poured in water (50 mL), the precipitate was filtered off, washed with water and dried. The yield was 0.18 g (60%). According to TLC and IR data, the product obtained was identical to the sample prepared as above.

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