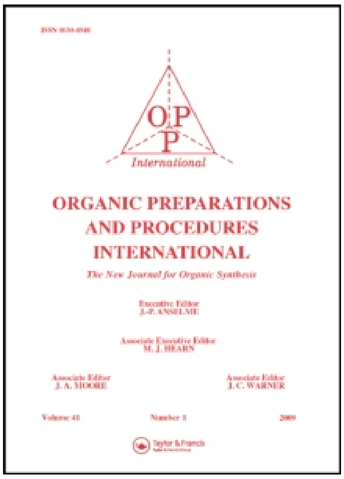

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AN IMPROVED SYNTHESIS OF 1,4-BIS(2'-METHYL-6'-ETHYLANILINO)ANTHRAQUINONE

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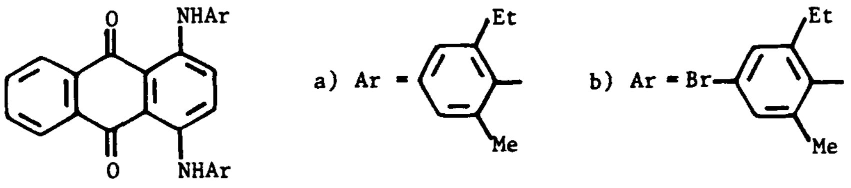
Efficient methods for the preparation of 1,4-bis(2'-methyl-6'-ethylanilino)anthraquinone 1a, an important dye used as a visual leak indicator in refrigerants[1] and in the production of polypropylene carpets,[2] are of interest. 1,4-Bis(alkylanilino)anthraquinones are commonly synthesized by the reaction of 1,4-dihydroxyanthraquinone (quinizarin) with the appropriate aniline in the presence of a reducing agent such as sodium dithionite or stannous chloride.[3] The reducing agent converts the quinizarin to leucoquinizarin (1,4,9,10-tetrahydroxyanthracene) which reacts much faster than quinizarin with the anilines. The condensation reaction is also greatly facilitated by the presence of boric acid. While this procedure works well with most anilines, other procedures are required for sterically hindered o,o'-disubstituted anilines.[3] The reported synthesis of 1a involves the condensation of 2-ethyl-6-methylaniline with preformed



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leucoquinizarin to give a reduced form of 1a which is then oxidized in a second step to 1a.[2]

We have found that 1a can be obtained directly from quinizarin in a one vessel operation if suitable reaction conditions are used. The condensation of quinizarin with ten equivalents of 2-ethyl-6-methylaniline containing both boric and propionic acids at 160° and using three-quarters of an equivalent of zinc metals as the reducing agent gave a good yield of pure 1a. The use of a lower reaction temperature, fewer equivalents of 2-ethyl-6-methylaniline, more equivalents of zinc dust or the use of acetic acid in place of propionic acid gave a lower yield of 1a. If neither propionic nor acetic acid were used, none of the product was formed. The use of sodium dithionite, aluminum metal or stannous chloride in place of zinc metal gave a reaction mixture which contained very little if any of 1a.

The structure and purity of 1a was determined by direct comparison of its visible and ^1H NMR spectra to a sample of 1a prepared by the reported procedure.[2] The observance of two sets of resonances for the methyl and methylene proton of the ethyl groups and two singlets for the other methyl groups in the ^1H NMR spectrum indicates steric hindrance to rotation in 1a. The chemical shift (6.54 ppm) of the C-2 and C-3 protons of 1a appears at unusually high field due to shielding by the 2'-methyl and 6'-ethyl groups. Bromination of 1a using bromine in acetic acid gave the expected dibromo derivative 1b. Except for the absence of the resonance for the 4'-protons, the ^1H NMR spectrum of 1b was similar to that of 1a.

In summary, an improved synthesis of 1a has been developed which uses less expensive quinizarin as starting material, can be carried out in one operation and provides a material of equal or better quality than the reported procedure.[2]

EXPERIMENTAL SECTION

Melting points were determined on a Koffler hot stage and are uncorrected. Visible spectra were recorded on a Cary Model 14 spectrophotometer. Proton NMR spectra were recorded on a Bruker WM-250 spectrometer.

1,4-Bis(2'-methyl-6'-ethylanilino)anthraquinone (1a).- A mixture of 5.0 g (0.02 mol) of quinizarin, 28 g (0.20 mol) of 2-methyl-6-ethylaniline, 6.9 g (0.09 mol) of propionic acid, 1.0 g boric acid and 1.0 g (0.015 g-atom) of zinc dust was heated at 160° for 6 hrs. During this period 2 mL of distillate was collected. The reaction mixture was poured into 500 mL of crushed ice containing 50 mL of concentrated hydrochloric acid. The residue remaining in the reaction flask was transferred to the ice-acid mixture using 40 ml of propionic acid. The stirred mixture was heated to 55° and filtered to give a mixture of 1a and 2-methyl-6-ethylaniline hydrochloride. This mixture was washed with 2 x 500 mL of hot (60-70°) 5% hydrochloric acid, 2 x 500 mL of water, 500 mL of 5% sodium hydroxide and 2 x 500 mL of water. The remaining fine blue crystals were recrystallized from methyl cellosolve to give 8.91 g (94%) of 1a, mp. 162-163°. The analytical sample was prepared by recrystallization from methyl cellosolve, mp. 168.5-169°. UV (toluene): λ_{max} 627 nm (ε 17,016), 582 (ε 15,384), 544) (ε 7,808); NMR ($CDCl_3$): δ 1.13 and 1.14 (2t, 6H, J = 7.7 Hz, $C\underline{H}_3CH_2$), 2.16 and 2.17 (2s, 6H, CH_3), 2.5-2.6 (m, 4H, $CH_3C\underline{H}_2$), 6.54 (s, C_2H and C_3H), 7.08-7.24 (m, 6H, C_3H, C_4H, C_5H), 7.75-7.78 (m, 2H, C_6H and C_7H), 8.39-8.44 (m, 2H, C_2H and C_8H) and 11.34 (s, 1H, NH).

Anal. Calcd for $C_{32}H_{30}N_2O_2$: C, 80.98; H, 6.37; N, 5.90

Found: C, 80.80; H, 6.40; N, 5.90

A sample of 1a was prepared by the reported procedure,[2] mp. 166-168°; UV (toluene): λ_{max} 627 nm (ε 16,750), 582 (ε 15,000), 544 (ε 7,680).

Compound 1a prepared by both procedures showed a faint spot at the origin in addition to the spot for the compound on thin layer chromatographic analysis (SiO_2, toluene). A sample of 1a purified by column chromatography (SiO_2, toluene) gave product which showed no origin spot, mp. 169.5-170°; UV (toluene): λ_{max} 627 nm (ε 17,550), 582 (ε 15,590) and 544 (ε 7,870).

1,4-Bis(2'-methyl-4'-bromo-6'-ethylanilino)anthraquinone (1b).- To a solution of 2.5 g (0.005 mol) of 1a in 25 mL of acetic acid at 25° was added 0.6 ml of bromine. After 2 hrs, the reaction mixture was diluted with 100 ml of 10% sodium acetate solution. The resulting solid was separated by filtration, washed with water, dried and recrystallized from a methylene chloride and ethanol mixture to give 2.4 g (76%) of 1b, mp. 204.5-205°.

UV (toluene): λ_{max} 632 nm (ε 17,362), 580 (ε 15,942) and 547 (ε 8,695); NMR ($CDCl_3$): δ 1.13 and 1.14 (2t, 6H, $C\underline{H}_3CH_2$), 2.13 and 2.14 (2s, 6H, CH_3), 2.44-2.62 (m, 4H, $CH_3C\underline{H}_2$), 6.53 (s, 2H, C_2H and C_3H), 7.29 (brs, 4H, C_3H and C_4H), 7.75-7.81 (m, 2H, C_6H and C_7H), 8.39-8.45 (m, 2H, C_5H and C_8H) and 11.69 (s, 1H, NH).

Anal. Calcd for $C_{32}H_{28}Br_2N_2O_2$: C, 60.77; H, 4.46; N, 4.43

Found: C, 60.68; H, 4.48; N, 4.44

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