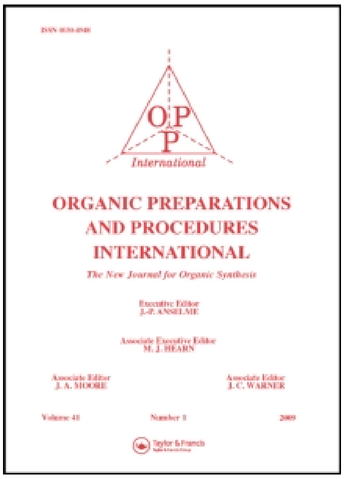

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A CONVENIENT PREPARATION OF 9-DIMETHYLAMINO-10-CARBOMETHOXYANTHRACENE

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A CONVENIENT PREPARATION OF 9-DIMETHYLAMINO-10-CARBOMETHOXYANTHRACENE

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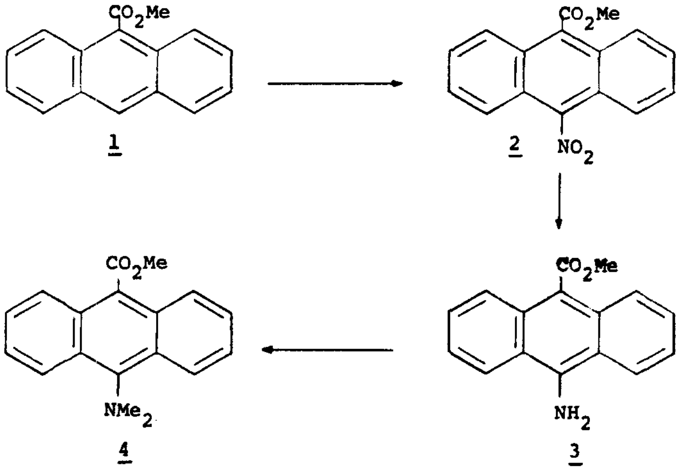
The novel title compound 4 was required in connection with a study of extended conjugation in triarylmethane dyes;[1] the immediate precursor, 9-

amino-10-carbomethoxyanthracene (3), is potentially a synthetically useful intermediate. A suitable route to ester 4 appeared to be the nitration of 9-carbomethoxyanthracene (1) followed by reduction and methylation. The problems caused by undesired side-reactions prompted us to develop an improved synthesis of 4.



Esterification of 9-anthroic acid is readily achieved by the method of Parish and Stock,[2] using trifluoroacetic anhydride and methanol. Nitration of the ester (1), dissolved in acetic acid and acetic anhydride, with a mixture of nitric and sulphuric acids[3] gave a moderate yield (50%) of 9-carbomethoxy-10-nitroanthracene (2); material of adequate purity was obtained by recrystallization from acetic acid. Although tin(II) chloride and hydrochloric acid in acetic acid have been used to convert 9-nitroanthracene into the corresponding amine,[4] this reagent afforded mainly anthraquinone with the nitro ester 2. It is known[5] that 9-aminoanthracene and its 10-substituted derivatives are susceptible to aerial oxidation, leading to iminohydroperoxide formation whose hydrolytic decomposition would then give the parent quinone. Successful selective reduction of the nitro derivative 2 was achieved with hydrazine hydrate and Raney nickel;[6] this reagent has been used recently for the partial reduction of nitro compounds.[7] Only a trace of anthraquinone could be detected in the reaction mixture which however was found to contain an appreciable amount of 9-carbomethoxyanthracene (1) as well as the desired amino compound (3); it is noteworthy that the parent ester (1) and the nitro derivative have very similar R_f values, but the former compound exhibits an intense blue fluorescence in ultraviolet light. Prolonged reaction times and an excess of reagent led to the formation of larger quantities of the ester (1), presumably by displacement (deamination) of the amino group from compound 3. Thus it is known that 9-aminoanthracene with sodium amalgam in ethanol forms the 9,10-dihydro derivative[8] which eliminates ammonia on heating to give anthracene.[9] Treatment of the amine (3) with an excess of methyl iodide in methanol[10] resulted in a high yield (87%) of the desired tertiary amine (4); formation of the quaternary iodide is conveniently suppressed by *peri*-hindrance.

EXPERIMENTAL SECTION

9-Amino-10-carbomethoxyanthracene (3).- Hydrazine hydrate (99%, 2.1 ml) was added together with a small amount of freshly prepared W-2 Raney nickel[11] to a warm solution of 9-carbomethoxy-10-nitroanthracene (2) (4.0 g, 16 mmol) in methanol (450 ml). After 20 min, the reaction mixture was heated under reflux for 30 min and a further small quantity of Raney nickel was added. The mixture was filtered and the yellow solution was concentrated to half its volume before pouring into water. The dried crude product was dissolved in cold dichloromethane (100 ml) and chromatographed on alumina. Removal of solvent from the eluted pale yellow first band gave 2.0 g (56%) of 1, mp. 110-112°, lit.[2] mp. 115°. An equal volume of light petroleum (bp. 60-80°) was added to the eluted bright orange second band and the solution was evaporated to half its volume. The cooled solution afforded 1.4 g (40%) of 3 as bright orange rhombic crystals, mp. 173° (DTA). IR(KBr): 3440, 3350, 1690, 1640, 1425, 1290, 1215 cm^{-1}; NMR (CD_2Cl_2): δ

4.12 (s, 3, CO_2CH_3), 5.35 (s, 2, NH_2), 7.50 (m, 6, aromatic) and 8.06 (m, 2, 4- and 5-H).

Anal. Calcd for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57

Found: C, 76.68; H, 5.32; N, 5.77

9-Dimethylamino-10-carbomethoxyanthracene (4).- A mixture of 9-amino-10-carbomethoxyanthracene (3.4 g, 13.5 mmol), sodium carbonate (5.6 g), methyl iodide (22.4 g, 160 mmol) and methanol (60 ml) was stirred and heated under reflux for 48 hrs, a further equal portion of methyl iodide being added after 24 hrs. The oil obtained upon removal of the excess of methyl iodide (by distillation) and pouring the methanolic solution into water, was extracted into dichloromethane (200 ml). Removal of solvent afforded a viscous orange oil which was dissolved in light petroleum (bp. 60-80°) and chromatographed on alumina, using a gradient elution technique with light petroleum and benzene as the eluent mixture. The eluted bright yellow first fraction was evaporated to a small volume to give, on cooling, 3.3 g (87%) of 4 as bright yellow rhombic crystals, mp. 127° (DTA).

IR(KBr): 2950, 2840, 2790, 1730, 1220 cm^{-1}; NMR ($CDCl_3$): δ 3.28 (s, 6, $N(CH_3)_2$), 4.18 (s, 3, CO_2CH_3), 7.51 (m, 4, aromatic), 8.04 (m, 2, 4- and 5-H) and 8.36 (m, 2, 1- and 8-H).

Anal. Calcd for $C_{18}H_{17}NO_2$: C, 77.40; H, 6.13; N, 5.01

Found: C, 77.14; H, 6.22; N, 5.03

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MILD SELECTIVE OXIDATION OF SULFIDES TO SULFONES

Submitted by (12/27/84)

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Oxidation of sulfides to sulfones can be accomplished by a variety of techniques including hydrogen peroxide,[1] peracid,[2] or chromic acid.[3] One report describes the selective oxidation of sulfides containing amine and alkene functionality with peroxytrifluoroacetic acid;[2] however, caution must be exercized to ensure complete decomposition of the peracid. This caution and interference from functional groups such as carbon-carbon double bonds[4] has prompted us to develop a procedure employing periodate and permanganate under neutral conditions. Unlike the Lemieux-von Rudolff reagent[5] which uses a catalytic amount of permanganate in the presence of sodium periodate, the method herein described requires one equivalent each of periodate, permanganate and sulfide. The periodate oxidizes the sulfide