Synthesis of 3-Aminocycloheptatrienylidenamines

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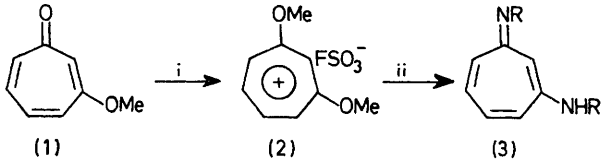
Summary Methylation of 3-methoxytropone with methyl fluorosulphonate to give 1,3-dimethoxytropenylium ion, followed by reaction with primary amines in the presence of strong base gives 3-aminocycloheptatrienylidenamines which are more stable for arylamino than alkylamino substituents; a similar reaction with 1-methoxy-3-dimethylaminotropenylium ion failed.

UNLIKE tropolones where the synthesis of the β-isomer was reported shortly after that of the α-isomer,[1] there has been no report on 3-aminocycloheptatrienylidenamines, whereas the corresponding 2-amino-isomers[2] have been known for some time.

We report the synthesis of 3-aminocycloheptatrienylidenamines from 3-methoxytropone (**1**) (Scheme). Methylation of (**1**) with an excess of methyl fluorosulphonate in benzene gives 1,3-dimethoxytropenylium fluorosulphonate (**2**),† m.p. 104—106 °C, δ (CD_3CN, rel. to Me_4Si) 8·00 (4H, m), 7·43 (1H, t, *J* 3 Hz), and 4·27 (6H, s). Addition of (**2**) (0·33 mmol in 2 ml dried methanol) to 2·5 ml of a methanolic solution containing 0·66 mmol of *p*-toluidine and 0·33 mmol of KOMe at room temperature, with stirring under N_2, immediately produced a yellow colour. A sticky red material separated when crushed ice was added to the reaction mixture but it was difficult to isolate. The mixture was rapidly decanted and the sticky residue was dissolved in light petroleum which produced yellow crystals at −80 °C. The solvent was first removed by decantation and then under reduced pressure to give (**3**, R = C_6H_4Me-*p*) as a red oil (0·040 g).



SCHEME. i: $MeSO_3F$, C_6H_6, room temperature; ii: RNH_2 (2 mol. equiv., R = C_6H_4Me-*p* or Bu^n), KOMe (1 mol. equiv.), MeOH, room temperature.

The structure (**3**, R = C_6H_4Me-*p*) is supported by its ^1H n.m.r. spectrum [δ(CCl_4 rel. to Me_4Si) 6·80 (8H, A_2X_2, ArH), 6·20 (4H, m, H-4–H-7), 5·82 (1H, t, *J* 2·5 Hz; H-2), and 2·15 (1H, sbr, exchangeable with D_2O, NH)] and by satisfactory analysis of its picrate derivative, m.p. 174—175 °C (recrystallised from ethanol, with $3H_2O$). Clearly the two aryl groups in (**3**, R = C_6H_4Me-*p*) are equivalent. It shows absorptions at λ_{max} (MeOH) 322 (with a long tail, perhaps including other small maxima, into the visible), 306, and (the most intense) 255 nm.

† Satisfactory analytical data were obtained for this compound.

Compound (**3**, R = C_6H_4Me-*p*) is stable for days in dilute solution in the cold, but polymerises in concentrated solution; polymerisation occurs more rapidly in the absence of solvent. A hygroscopic hydrochloride is obtained with dry HCl in light petroleum.

Reaction of (**2**) with n-butylamine similarly led to (**3**, R = Bu^n) which was characterised by its ^1H n.m.r. spectrum and picrate derivative. This compound was much less stable than (**3**, R = C_6H_4Me-*p*).

In contrast, attempts to prepare unsymmetrically substituted 3-aminocycloheptatrienylidenamines by reaction of 1-methoxy-3-dimethylaminotropenylium fluorosulphonate with primary amines were unsuccessful both under the conditions specified for (**2**) and in the absence of methoxide indicating that a fine balance of factors is responsible for the success of reactions shown in the Scheme.

It is worth noting that the ring protons in (**3**) resonate at higher fields than those in β-tropolone derivatives.[1,4] Therefore, rationalization of the analogous phenomenon for 2-aminocycloheptatrienylidenamine–α-tropolone couples in terms of concentration of negative charge on the 7-membered ring in the imine compounds[2] is perhaps not warranted. Unlike the 1,2-isomers, the NH proton in (**3**) cannot bridge the two nitrogen atoms intramolecularly.

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[1] F. Pietra, *Chem. Rev.*, 1973, **73**, 293.
[2] W. R. Brasen, H. E. Holmquist, and R. E. Benson, *J. Amer. Chem. Soc.*, 1960, **82**, 995; *ibid.*, 1961, **83**, 3125.
[3] M. Cavazza, C. A. Veracini, and F. Pietra, *J.C.S. Perkin I*, in the press.
[4] B. Ricciarelli, thesis, Pisa, 1974.