A Synthetic Approach to 4-Amino-1-imino-2,4,6-cycloheptatrienes

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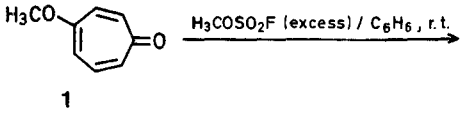
We report here on the preparation of some 4-amino-1-imino-2,4,6-cycloheptatrienes (**3**, 4-aminocycloheptatrienylidenamines), a previously unknown class of compounds. This is surprising because the oxygen analogue, 4-hydroxy-1-oxo-2,4,6-cycloheptatriene (γ-tropolone) was reported some time ago[1] and the synthesis of the α-isomer, 2-hydroxy-1-oxo-2,4,6-cycloheptatriene (α-tropolone) was soon followed by the synthesis of 2-amino-1-imino-2,4,6-cycloheptatrienes[2].



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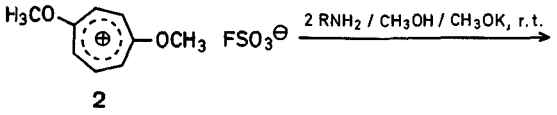

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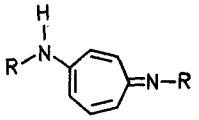

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The synthetic route is shown above. Thus, excess methyl fluorosulphonate was added to a benzene solution of 4-methoxytropone[1b] (**1**) to give 1,4-dimethoxytropylium fluorosulphonate (**2**). The latter compound, dissolved in methanol, gave, on addition of 2 equivalents of *n*-butylamine and 1 equivalent of potassium methoxide, 4-(*n*-butylamino)-1-(*n*-butylimino)-2,4,6-cycloheptatriene (**3**, R = *n*-C_4H_9) as an oil which tends to polymerise in the absence of solvent.

The 4-methylphenylamino derivative was prepared similarly and obtained as oily crystals. It is clear from the ^{1}H-N.M.R. data (see below) for compounds **3** that the two R groups are equivalent. Studies on the chemistry of **3** are in progress.

Preparation of 1,4-Dimethoxytropylium Fluorosulphonate (2):
To a solution of 4-methoxytropone[1b] (0.16 g) in dry benzene (30 ml) is added with stirring at room temperature under nitrogen methyl fluorosulphonate (0.5 ml). The dark solid which precipitates immediately is recrystallised from acetonitrile by addition of tetrahydrofuran until the first appearance of turbidity to give colourless, hygroscopic crystals of **2**; yield: 0.23 g (80%).

$C_9H_{11}FO_5S$	calc.	C 43.2	H 4.4	
(250.2)	found	43.1	4.5	

^{1}H-N.M.R. (CD_3CN/TMS): $\delta = 8.57$ (t, 1H, $J = 10$ Hz, H-6), 8.12 (br s, 2H, H-2 and H-3), 7.85 (d, 2H, $J = 10$ Hz, H-5 and H-7), 4.22 ppm (s, 6H, 2 CH_3).

Preparation of 4-(4-methylphenylamino)-1-(4-methylphenylimino)-2,4,6-cycloheptatriene (3, R = 4-H_3C—C_6H_4—):

To a solution of salt **2** (0.1 g, 0.4 mmol) in dry methanol (2 ml) is added with stirring at room temperature under nitrogen *p*-toluidine (0.8 mmol) dissolved in methanol (3 ml) containing potassium methoxide (0.4 mmol). The mixture becomes yellow-orange immediately and, after 20 min, it is added to crushed ice and extracted with tetrachloromethane. The organic layer is dried ($MgSO_4$) and rapidly evaporated under vacuum to give yellow-orange crystals of the product which tend to polymerise in the absence of solvent; yield: 0.074 g (63%). The analysis is thus carried out on the stable picrate which crystallises with two molecules of water; m.p. 110–113° (from ethanol).

$C_{27}H_{23}N_5O_7 \cdot 2H_2O$	calc.	C 57.3	H 4.8	N 12.4	O 25.5
(565.2)	found	57.1	4.9	12.2	25.1

U.V. (CH_3OH): $\lambda_{max} = 420$, 323 nm.

^{1}H-N.M.R. ($CDCl_3$/TMS): $\delta = 7.2$–6.4 (m, 13H), 2.2 (s, 6H, 2 CH_3), the position of the broad signal of the proton on nitrogen changed with the conditions.

Preparation of 4-(*n*-Butylamino)-1-(*n*-butylimino)-2,4,6-cycloheptatriene (3; R = *n*-C_4H_9):

Using the procedure described above with *n*-butylamine in place of *p*-toluidine, the product is isolated as a yellow-orange oil which tends to polymerise in the absence of solvent; yield: 72%. Analysis is therefore carried out on the stable picrate which crystallises with two molecules of water; m.p. 138–140° (from ethanol).

$C_{21}H_{27}N_5O_7 \cdot 2H_2O$	calc.	C 50.7	H 6.3	N 14.1	O 28.9
(497.5)	found	50.5	6.4	14.0	29.0

U.V. (CH_3OH): $\lambda_{max} = 400$, 330 nm.

^{1}H-N.M.R. ($CDCl_3$/TMS): $\delta = 7.0$–6.0 (m, 5H, *ring protons*), 3.6 (br s, 1H, NH, exchangeable with D_2O). 3.2 (t, 4H, N—CH_2), 1.5 (m, 8H, —CH_2—CH_2—CH_2—CH_3), 0.9 ppm (t, 6H, CH_3).

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