

A Stable Adduct of Sodium Ethanethiolate Attack at the C-7 Ring Carbon of 2-Ethylthiotropone: Stabilisation of a Base Adduct to an Unsubstituted Cycloheptatrienone Ring Carbon by Bivalent Sulphur

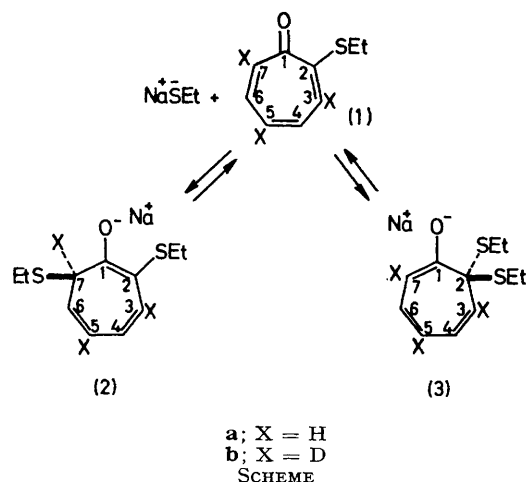
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Summary A stable base adduct to an unsubstituted cycloheptatrienone ring carbon (C-7) is unexpectedly obtained on the mixing of 2-thioethoxytropone with sodium ethanethiolate whilst the *gem*-di(ethylthio) adduct cannot be present in more than trace amounts.

ALTHOUGH stable *gem*-dialkoxy-adducts from cycloheptatrienones are well characterized,¹ direct evidence for adducts generated by base attack on unsubstituted cycloheptatrienone ring carbon atoms in spite of their suggested role in this area,² is scanty.^{1,2}

Available evidence indicates that base attack at unsubstituted ring carbon atoms only occurs for cycloheptatrienones carrying good electron attracting groups at C-2, giving very labile adducts.^{1,2} Therefore, it was surprising to observe that, on mixing 2-ethyl thiotropone (**1a**) (0.1M) with sodium ethanethiolate (0.4M) in dried (CD₃)₂SO, a spectrum attributable to species (**2a**) is obtained which persists indefinitely: δ (Me₄Si) 6.62 (d, *J* 10.0 Hz, 3-H), 6.12br (t, *J* 7.5 Hz, 5-H), 5.62br (4-H), 5.18br (6-H), 3.95vbr (7-H), 2.30 (q), and 1.06 (t).



The spectral assignment rests on the observations that (i) on neutralisation the above spectrum immediately

reverts to that of starting (**1a**) and ethanethiol; (ii) using (**1b**)† in place of (**1a**) the absorptions at δ 6.62, 6.12, and 3.95 are absent; (iii) on irradiation at δ 5.62 the doublet at δ 6.62 changes into a singlet. Moreover, appearance of the signal for 7-H at very high field is consistent with tetrahedral hybridisation at C-7, whilst the fact that the signals for 6-H and 4-H are at higher field than those for 5-H and 3-H is in accordance with higher electron density at C-6 and C-4 than at C-5 and C-3, as judged from the canonical forms which are possible for (**2**).^{1a}‡ Also, appearance of only one quartet and only one triplet in the above spectrum is consistent with fast exchange at both C-7 and C-2, which demands that a trace of (**3**) is in equilibrium with (**2**) and (**1**) (Scheme).

The strong activation to base attack on (**1**) at C-7 and great stability of (**2**) must be attributed to electron accept-

† Structure fully supported by elemental and ¹H n.m.r. data.

‡ Should (**3**) be the prevalent species, no signal for ring protons at such high field as δ 3.95 would be expected and, moreover, the ring proton resonances which disappear using (**1b**) in the place of (**1a**) in the reaction with sodium ethanethiolate should have been those three at highest field, contrary to what was observed. In fact, in the case of (**3**) the highest charge densities are expected at C-3, C-5, and C-7.^{1a}

¹ (a) G. Biggi, C. A. Veracini, and F. Pietra, *J.C.S. Chem. Comm.*, 1973, 523; (b) T. Abe and T. Asao, *Tetrahedron Letters*, 1973, 1327.

² (a) G. Biggi, F. Del Cima, and F. Pietra, *J. Amer. Chem. Soc.*, 1972, **94**, 4700; 1973, **95**, 7101; G. Biggi, A. J. de Hoog, F. Del Cima, and F. Pietra, *ibid.*, 1973, **95**, 7108.

³ J. Miller, 'Aromatic Nucleophilic Substitution,' Elsevier, Amsterdam, 1968, p. 87.

ance by bivalent sulphur, which, quantitatively, was unexpected in view of the very slight activation of nucleophilic aromatic substitution by such a group.³

Finally, clean reversion of (**2b**) to (**1b**) on neutralization probably implies that protonation of (**2**) at C-2 does not occur during neutralization, otherwise a symmetrical species would be obtained which, accounting for deuterium isotope effects, should give a mixture of (**1b**) and 2-ethylthio[4,6-²N₂]tropone. This was also unexpected in view of the generality of protonation at C-2 implied by previous results for all adducts of base attack at C-7 we have met before.²

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