

A Neutral Thiolate–Cycloheptatrienone Adduct: the First Direct Evidence of Base Addition at Two Different, Unsubstituted Cycloheptatrienone Carbon Atoms

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Summary 2-(Dimethylthio)troponone tetrafluoroborate gives a *ca.* 1:1 equilibrium mixture of two neutral adducts after methanethiolate attack at C(3) and C(7), which slowly change into the adduct of methanethiolate attack on 2(methylthio)troponone.

In spite of much attention to σ -adducts of bases and cycloheptatrienones,¹ evidence for base addition at more than one unsubstituted cycloheptatrienone carbon atom, to give a mixture of σ -adducts, merely rests on either kinetic and product studies,² or indirect n.m.r.³ evidence. As this inter-relation between σ -adducts has been suggested to determine the outcome of several transformations with troponoids,² we report here the first direct evidence of such a case.

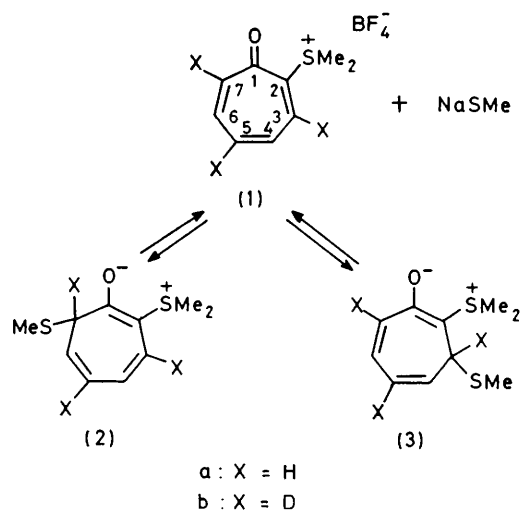
On the addition of sodium methanethiolate (2–3 molar excess) to the sulphonium salt (**1a**)⁴ in dried (CD₃)₂SO at room temperature under nitrogen, both the n.m.r. signals

at δ 8.16 (dd, 3-H) and at 7.2–7.8 (m, 4-H–7-H) (Me₄Si as internal standard) of (**1**) disappeared. A new signal appeared at δ 6.9–7.5 (m, 3H), together with two very broad signals, at δ 6.2 and 5.2 (each 1H). We attribute the latter two signals to 7-H and 3-H (which is which is uncertain) of the adducts (**2a**) and (**3a**) in a *ca.* 1:1 ratio. The broadness of the signals is indicative of rapid exchange of the methylthio group. The multiplet can be attributed to 3-H–6-H of (**2a**) and 4-H–7-H of (**3a**).†

This assignment is supported by similar experiments with (**1b**)⁴ when the two broad singlets at δ 7.53 and 7.72 for 4-H and 6-H disappeared, while two new broad singlets at 7.40 and 7.30 appeared. These can be attributed to 4-H and 6-H of (**2b**) and (**3b**) (which is which is uncertain).†

This rapid exchange phenomenon with sulphur nucleophiles is in line with previous findings.¹ In particular, such exchanges receive further support here by the finding that the signals at δ 7.40 and 7.30 for (**2b**) and (**3b**) broadened with increased temperature. When the sample was cooled to

† The multiplet can also be partially attributed to the corresponding CH and CD positions of (**1**).



room temperature it gave the original signals again. Such behaviour is indicative of rapid exchange phenomena at adjacent centres.

On increasing the thiolate concentration further, after a few hours the above situation for the (2)–(3) mixture changed into a very similar situation to that already

observed for the interaction of sodium methanethiolate with 2-(ethylthio)tropone.⁵ Clearly, demethylation of (1) must have occurred, followed by thiolate attack at C(7) and, perhaps, also at C(2) of 2-methylthiotropone.⁵

It is interesting that both C(7)H and C(3)H of (1a) undergo an unusually small¹ upfield shield on sp^3 carbon rehybridization. This must be a consequence of the exchange phenomena. Also, both C(4)H and C(6)H of (1b) experience a small upfield shift on adduct formation. This is indicative of little negative charge dispersal on the seven-membered ring (suggesting a sulfonium ylide without charge separation⁴) which adds to the contribution by exchange phenomena.

Finally, in contrast to multiple attack by the thiolate, selective attack at C(7) of (1) by piperidine⁴ may be a consequence of assistance by the hydrogen bond formed between the developing ammonium proton and the negatively charged oxygen atom.² In this case the C(5) position is less activated than both the C(7) and C(3) positions presumably because C(5) is farthest from both the carbonyl and sulfonium activating groups.

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⁵ C. A. Veracini and F. Pietra, *J.C.S. Chem. Comm.*, 1974, 623.