Direct Observation of an Adduct of 2-Chlorotropone and Potassium Methoxide: Attack at an Unsubstituted Cycloheptatrienone Ring Carbon

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Summary It is shown by ^1H Fourier transform n.m.r. spectroscopy that potassium methoxide in dimethyl sulphoxide adds at C-7 of an *activated* cycloheptatrienone like 2-chlorotropone; this adduct rapidly disappears owing to competitive direct replacement of chlorine by methoxide from 2-chlorotropone present at equilibrium to give 2-methoxytropone which, finally, is trapped by methoxide as a *gem*-dimethoxy-adduct.

Adducts of cycloheptatrienones and bases have been recently suggested as intermediates in reactions of cycloheptatrienones in basic systems,[1] direct structural evidence having been produced for *gem*-dimethoxy-adducts between methoxide and either 2-methoxytropone[2] or 2-methoxy-5-nitrotropone.[3]

In contrast, evidence for adducts resulting from base attack at unsubstituted cycloheptatrienone ring carbons, though postulated as being common,[1] merely rests on kinetic[1a,b] and product studies.[1c]

A major obstacle to structural proof of adducts of the latter type has been their lability. This has now been overcome by ^1H Fourier transform (FT) n.m.r. spectroscopy, with the structural elucidation of the first adduct of base addition at an unsubstituted cycloheptatrienone ring carbon. Thus, on adding 0·4M-methanolic KOMe (0·003 ml) to 2-chlorotropone (0·007 g) in carefully dried $(CD_3)_2SO$ (0·3 ml), and recording the ^1H FT n.m.r. spectrum after 20 s, signals attributable to species (**2**) (Scheme) were observed: δ 5·65 (d, J 10·7 Hz, 3-H), 5·56, 4·59, and 4·12 (all dd, $w_{\frac{1}{2}}$ 20 Hz, 5-, 6-, and 4-H, respectively[‡]), and 2·82 (d, J 0·8 Hz, 7-H), together with a signal at 6·42 (m) from unchanged 2-chloro-tropone. These assignments were based on results using 2-chloro[3,5,7-$^2H_3$]tropone[4] in place of 2-chlorotropone, whereby only two broad singlets were observed at δ 4·59 and 4·12 on addition of methoxide.

On adding 4M-methoxide (0·005 ml) to 2-chlorotropone (0·004 g) in $(CD_3)_2SO$ (0·3 ml), signals for (**1**) were not detectable, as expected for the equilibrium (**1**) + $MeO^- \rightleftharpoons$ (**2**).

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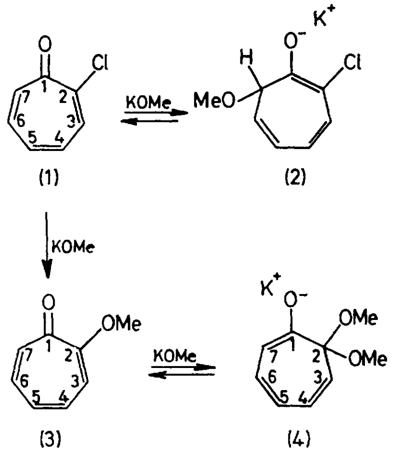
[‡] The upfield shift for 6- and 4-H is attributable to delocalization of the negative charge in species (**2**) at C-6 and C-4. This is supported by the occurrence of the u.v. absorption of (**2**) at much longer wavelength, 377 nm, than in tropone ethylene acetal, 258 nm (H. E. Simmons and T. Fukunaga, *J. Amer. Chem. Soc.*, 1967, **89**, 5208) pointing to a flattened conformation for **2**. However, on the basis of the present data, we cannot rule out the alternative assignment of the δ 4·59 and 4·12 signals to 4- and 6-H, although this is immaterial in the present report.

In the above experiments the intensity of the signals attributed to species (**2**) rapidly decreased with time while signals for (**4**)[2] began to appear. After *ca.* 10 min only the signals due to (**4**)[2] were detectable and neutralization of the mixture led, in the case of deuteriated materials, to 2-methoxy[3,5,7-$^{2}H_{3}$]tropone in high yield.



(1) (2)

(3) (4)

All these observations can be rationalized in terms of the reactions in the Scheme which is self explanatory. Direct observation of species (**2**) supports our suggestion[1b,c] that with activated cycloheptatrienones (by chlorine here) attack by bases occurs most readily at unsubstituted ring carbon atoms. In the light of these results, previous ideas[5] that 2-halogenotropones are only capable of rearrangement into benzenoid compounds in basic media need to be changed.

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