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# STABILISATION OF SIGMA - ADDUCTS FROM TROPONOIDS BY BIVALENT SULPHUR SUBSTITUENTS AT C(3) OR C(4)

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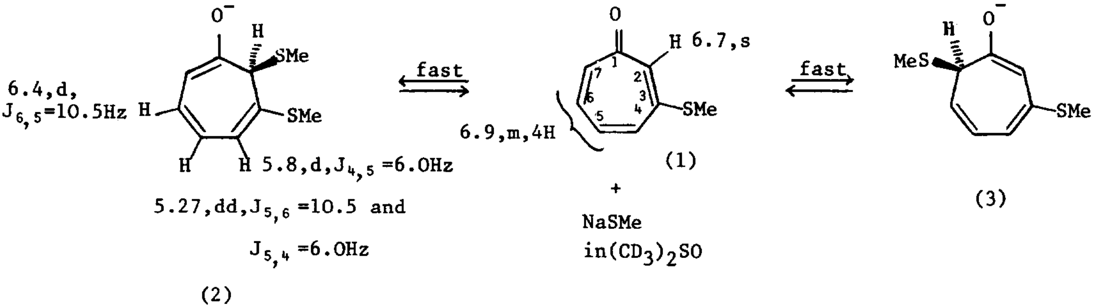
Interaction of either 3-methoxy-[1] or 4-methoxytropone[2] with methoxide anion in $(CH_3)_2SO$ leads to the formation of sigma adducts, as indicated by u.v. spectra, although detailed structures remained unclarified because all $^1H$ nmr signals were swamped out by the radical anions of the starting troponoid.

We report here that the sulphur analogues of the above troponoids in $(CD_3)_2SO$ gave good nmr signals leading to the identification of sigma adducts of thiolate attack at C(2) or C(7) in the case of 3-thiomethyl- or 4-thiomethyltropone, respectively.

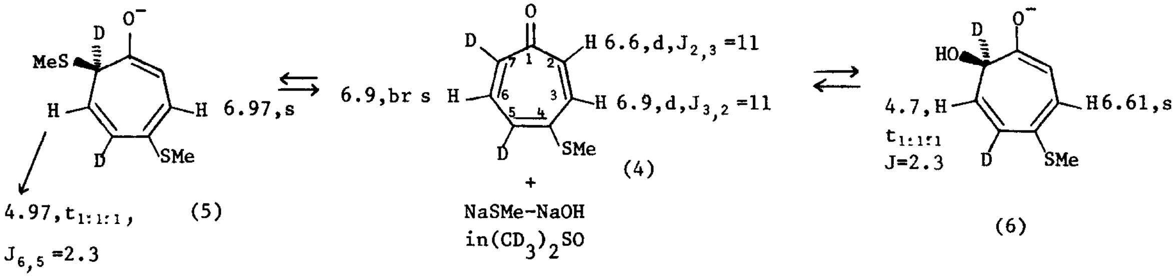
Thus, 3-thiomethyltropone[3] (1), 0.022 g, and sodium methylmercaptide, 0.010 g, in ca. 0.4 ml of $(CD_3)_2SO$ under $N_2$ at ca. 27°, gave the $^1H$ nmr signals indicated for species (2) in Scheme 1. Rapid equilibration via (1) with (3), which is required to be present in only trace amounts, accounts for the absence of both the H(2) and the H(7) signals. Assignment of signals in the spectrum of (2) is self evident when it is recognized that the doublet at 6.4 ppm is more reasonably assigned to H(6) than to H(4) because of the expected[4] larger coupling between protons connected to carbon-carbon double bond rather than single bond moieties.



*Chem. shifts for (1) refer to (1) in the absence of thiolate whereas chem. shifts for (2) refer to the actual signals from the reaction mixture with thiolate. Under the latter conditions the signals for (1) disappeared completely. (Chem. shifts in ppm with respect to internal TMS).*
*SCHEME 1*

In the case of 4-thiomethyltropone,[3] 0.025 g, and equimolar sodium methylmercaptide in ca. 0.4 ml of dried $(CD_3)_2SO$ under $N_2$ at ca. 27°, the situation was more complex, two sets of signals being observed. The first one predominated under our best "dry" conditions, whilst the other one prevailed when less care was taken to avoid atmospheric moisture. Therefore, attack by the thiolate in the first case, or by hydroxide in the second case, was assumed. The situation is best appreciated by examination of the case of the dideuteriated substrate,[5] for which all signals can be assigned (Scheme 2). The absence of the H(2) signal in the adducts (5) and (6) can be accounted for in terms of rapid equilibria of attack at C(2)(rapid equilibria of attack at C(7) account for the absence of the H(7) signal in the analogous case of the non deuteriated substrate). The triple signals of 1:1:1 intensity for the H(6) protons (which appear as multiplets in the non deuteriated case) are unequivocally indicative of adjacency to a deuterium.

Unfortunately, rates of exchange of H(2) and H(7) could not be altered substantially because heating of the mixture led both to interference with the many other $^1$H nmr signals which underwent a shift, and to rapid decomposition of the sample. The raising of thiolate concentration also led to interference among various signals. Cooling was prevented by the nature of the solvent.



*Chem. shifts for (4) refer to (4) in the absence of thiolate whereas chem . shifts for (5) and (6) refer to the actual signals from the reaction mixture with thiolate. Under the latter conditions the signals for (4) disappeared completely. NaOH is thought to arise from moisture.*

*SCHEME 2*

Both (2) and (5) are supported by uv spectra typical of sigma anionic complexes from troponoids (absorption band at $\lambda_{max}$ 364 and 370 nm in (CH$_3$)$_2$SO for (2) and (5), respectively).

The above results clearly show that the position of preferential attack on the cycloheptatrienone nucleus is primarily dictated by both the proximity of the carbonyl group and the negative charge acceptance by the thiomethyl substituent at the ring. Exploitation of these findings to synthesis in this field will be reported later.

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