Preparation of the First *gem*-Dialkylthio-analogues of Meisenheimer Complexes from Troponoids

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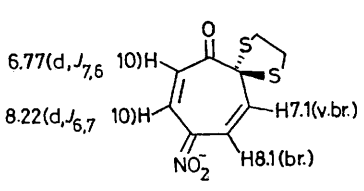
Summary Both the labile *gem*-dialkylthio-adduct (**2**) of attack of methanethiolate at C(2) of 2-methylthio-5-nitrotropone and its spiro analogue (**1**), which is in equilibrium with the prevailing non-cyclized form, have been obtained; the absence of the 5-nitro-group leads either to non-*gem*-adducts or to no adduct at all.

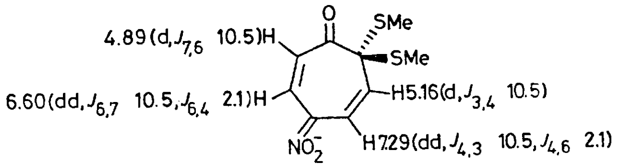
In contrast to *gem*-dialkoxy Meisenheimer complexes, which are well known for both six-[1] and seven-membered ring systems,[2] their *gem*-dialkylthio-analogues have been difficult to obtain; they have been obtained only for six-membered ring systems, where the *gem*-adducts, although thermodynamically disfavoured with respect to the non-*gem*-adducts,[3] were forced to be formed *via* a spiroannelation route.[4] With seven-membered ring systems only non-*gem*-adducts have been observed, as, for example, in the attack of EtS^- at C(7) of 2-ethylthiotropone.[5]

We report now that the driving force alone which could be provided by an intramolecular cyclization route failed to lead to a *gem*-dialkylthio-adduct with seven-membered ring systems. In fact, 2-(2-mercaptoethylthio)tropone† gave no evidence for σ-anionic complex formation on treatment with CD_3O^- in $(CD_3)_2SO$. Nevertheless, formation of *gem*-dialkylthio-adducts could be achieved with 5-nitro-tropone derivatives. Thus, addition of a concentrated solution of disodium dithioglycolate in CD_3OD to an equimolar amount of 2-chloro-5-nitrotropone in $(CD_3)_2SO$ led to the species (**1**), the structure of which is supported by its ^1H n.m.r. spectrum. In fact, whilst the two doublets can be assigned as shown in (**1**) owing to the combined effects of deshielding of 6-H by the nitro-group and shielding by the negative charge which is delocalizable at C(7),[2] the broadest signal can be attributed to 3-H because this proton is closest to the exchange centre (opening and reclosure of the dithian ring). This exchange phenomenon is reflected in coupling with 4-H, which also appears as a broad signal.

However, the extremely modest upfield shift of the seven-membered ring protons of (**1**) is in contrast with the pronounced upfield shifts for ring protons of typical anionic σ-adducts (see later), indicating that (**1**) is in fast equilibrium with the non-cyclized form. Therefore chemical shifts given for (**1**) must be the average for the cyclized and the non-cyclized form, with the latter prevailing.



(**1**)



(**2**)

δ values with respect to internal Me_4Si for (**1**) and (**2**) [averaged value for (**1**) for the cyclized and the non-cyclized form which is prevalent]; *J* values in Hz; assignments for 4- and 6-H for (**2**) are tentative and can be reversed.

That the driving force for formation of such a *gem*-dialkylthio-species stems primarily from the nitro-group at C(5) is shown by the formation of (**2**) from 2-methylthio-5-nitrotropone† and sodium methanethiolate in $(CD_3)_2SO$. Although (**2**) was labile, thus preventing accurate decoupling experiments, its structure is supported by its ^1H n.m.r. spectrum which, in contrast with that of (**1**) does not show rapid exchange phenomena. In fact, all the signals were shifted towards higher field compared with the starting tropone by as much as *ca.* 2 p.p.m., as usual for formation of typical anionic σ-adducts, [2–4] on addition of the thiolate; the two double doublets can be assigned to 4-H and 6-H protons (we do not know which is which) because of a *meta* coupling of 2·1 Hz. The two doublets at higher field can be assigned to 3-H and 7-H in accordance with the shielding effect of the negative charge delocalized at both C(3) and C(7).[2] We tentatively assign the doublet at lowest field to 3-H by analogy with the assignment for (**1**). The above structural assignments are further supported by u.v. spectroscopy; generation of either (**1**) or (**2**), as described above, is accompanied by the appearance of an absorption band at 462 nm. This absorption also arises when disodium glycolate is added to 2-chloro-5-nitrotropone in dimethyl sulphoxide, consistent with the formation of the oxygen analogue of (**1**).‡ Therefore the 460 nm absorption band is characteristic of the conjugated system present in both (**1**) and (**2**).

It is interesting that the recognized[4c] tendency of dithian rings in σ-anionic adducts to break at the spiro carbon–sulphur bond is at an extreme in the case of (**1**), spiroannelation thus being an unfavourable factor here.

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† New compounds gave satisfactory elemental and spectral analyses.

‡ Unfortunately, excess of glycol, which proved difficult to remove, prevented the ^1H n.m.r. spectrum from being obtained in this case.

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