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Thio-analogues of Meisenheimer Complexes

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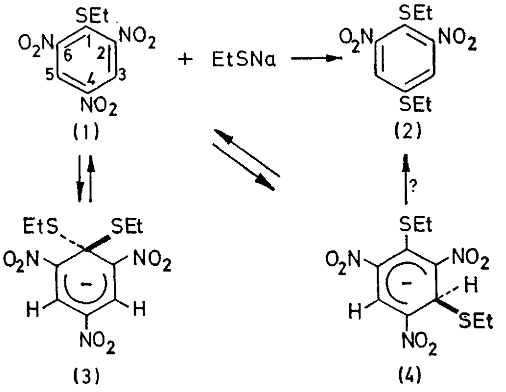
Summary The first gem-di(alkylthio)-analogue of Meisenheimer complexes is obtained in equilibrium with, and is appreciably less stable than, the addition complex at an unsubstituted aromatic ring carbon when ethyl thiopicrate is mixed with sodium ethanethiolate in Me_2SO; both complexes are transient species because of specific rapid replacement of the *p*-nitro-group by ethanethiolate.

IT is implied[1a,2] that gem-di(alkylthio)-analogues of Meisenheimer complexes[3] should not be obtainable because sulphur nucleophiles are known[1,2] to add selectively to unsubstituted ring positions of the aromatic substrate.

We report evidence for the first such gem-compound which differs from the corresponding Meisenheimer complexes[3] in important chemical properties. Thus, when ethyl thiopicrate (**1**; Scheme) (10^{-5}M) in Me_2SO is mixed under N_2 with a solution of EtSNa (1·1—10-fold excess) in Me_2SO at 24°, a deep-red colour immediately developed and then rapidly faded. Extrapolation to zero time indicated two u.v. absorptions [λ_{max} (logϵ) 464 (*ca.* 4·0) and 545 nm (*ca.* 4·2)], which are typical of 1 : 1 Meisenheimer complexes.[1a] In contrast, with a 200-fold excess of EtSNa, stable coloured solutions were obtained, the u.v. spectrum of which showed a single absorption (λ_{max} 525 nm, logϵ *ca.* 4·1) which is typical of 2 : 1 Meisenheimer complexes.[1a]

A fast-scan ^{1}H n.m.r. spectroscopic study (60 or 100 MHz; Me_4Si internal standard) of the reaction, with 0·3M reagents in Me_2SO under N_2, immediately after mixing of the reagents showed singlets at δ 8·48, 8·43, 8·23, and 6·17, as well as complex absorptions at δ 3·4—2·4 and 1·6—0·8 while signals for (**1**) [δ 9·15 (2H, s), 3·0 (2H, q, *J* 7.5 Hz), and 1·2 (3H, t, *J* 7·5 Hz] were absent. The signals at δ 8·48, 8·43, and 6·17 p.p.m. decreased in intensity with time while that at δ 8·23 showed a corresponding increase. The above spectrum still persisted 3 min after mixing, whereas after 3 h that of (**2**) [δ 8·23 (2H, s), 3·22 (2H, q, *J* 7·5 Hz), 3·11 (2H, q, *J* 7·5 Hz), 1·28 (3H, t, *J* 7·5 Hz), and 1·08 (3H, t, *J* 7·5 Hz)] was observed. Throughout, the ratio of the peak areas was 1 : 3 for the sum of the signals at δ 8·48, 8·43, 8·23, and 6·17 relative to that at δ 1·6—0·8 and 1 : 1 for the δ 8·48 signal relative to that at δ 6·17. Compound (**2**), m.p. 90—91°, was isolated (90%) from 0·3M solutions of (**1**) and EtSNa.



SCHEME

The last two signals can be attributed to (**4**) and the δ 8·43 signal to (**3**), in agreement with chemical-shift data for Meisenheimer complexes;[1a] the lack of spin–spin coupling between the cyclohexadienide protons in both (**3**) and (**4**) conforms with the case of the complex between trinitrobenzene and EtSNa.[2b] A singlet at δ 8·43 is also consistent with a Meisenheimer complex derived from (**1**) by addition of EtSNa at C(4). However, owing to the high mobility of the nitro-group in nucleophilic aromatic substitution,[4] we can exclude this possibility. The signal at δ 8·23 is clearly attributable to (**2**), whilst the aliphatic region in the spectrum of the mixture after 3 min is complicated.

The relative areas of the signals for (**3**) and (**4**) (which are observed at their equilibrium ratio because they are formed at rates which are too high to be observed with standard stopped-flow techniques and then decay in a parallel fashion) show that (**4**) is appreciably more stable than (**3**), which is the reverse of the situation encountered with the corresponding Meisenheimer complexes.[5] We attribute this to the tendency of bivalent sulphur in (**4**) to accept electrons by *d*-orbital participation. Clearly, this cannot operate with (**3**).

Since disappearance of (**3**) and (**4**), or formation of (**2**), follow rigorously first-order kinetics over a wide range of reagent concentrations, if the unimolecular transformation of (**4**) into (**2**) can be ruled out, (**2**) must originate entirely from free (**1**) and thiolate. The specific rate of this process must be extremely high since so little (**1**) was present that equilibria could not be measured. The method[2b] of adding alcohol to measure equilibria could not be used because in ethanol, in contrast with the Meisenheimer case where the fully oxygenated analogue of (**3**) was precipitated,[3] we isolated, instead of (**2**), a compound, m.p. 305—306°, which probably arises from reductive dimerization of (**1**).

Specific replacement of the *para*-nitro-group in (**1**) is also to be attributed to electron acceptance by the *para*-sulphur atom owing to *d*-orbital participation. We ascribe the remarkable activation of C(4) to a dipole effect operating maximally in the C(4)–C(1) direction for molecular symmetry reasons.

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[1] (a) M. J. Strauss, *Chem. Rev.*, 1970, **70**, 667; (b) M. R. Crampton, *Adv. Phys. Org. Chem.*, 1969, **7**, 211; P. Buck, *Angew. Chem.*, 1969, **81**, 136; E. Buncel, A. R. Norris, and K. E. Russell, *Quart. Rev.*, 1968, **22**, 123; R. Foster and C. A. Fyfe, *Pure Appl. Chem.*, 1966, **16**, 61; F. Pietra, *Quart. Rev.*, 1969, **23**, 504.

[2] (a) M. R. Crampton, *J. Chem. Soc.* (*B*), 1967, 1341; A. R. Norris, *Canad. J. Chem.*, 1967, **45**, 175; M. R. Crampton and M. El-Ghariani, *J. Chem. Soc.* (*B*), 1969, 330; (b) M. R. Crampton, *ibid.*, 1968, 1208.

[3] J. Meisenheimer, *Annalen*, 1902, **323**, 205.

[4] F. Pietra and D. Vitali, *J.C.S. Perkin II*, 1972, 385.