

Regiospecific C(2)-Addition of Thiolates to Methoxytropylium Ion. The First Practical Entry to the Monocyclic 1,7-Difunctionalized Cycloheptatriene Series

By MARINO CAVAZZA and GIOIA MORGANTI
(Istituto di Chimica Generale, Università di Pisa, 56100 Pisa, Italy)

and FRANCESCO PIETRA*
(Facoltà di Scienze, Libera Università di Trento, 38050 Pova-Trento, Italy)

Summary Thiolates were found to add to methoxytropylium fluorosulphonate in dichloromethane at -50°C to give exclusively the stable 1-methoxy-7-(alkyl- or arylthio)cycloheptatrienes in what constitutes the first regiospecific base addition to the tropylium system.

n-butanethiolate, toluene-*p*-thiolate, and ethane-1,2-dithiolate to give (2b), (2c), and (3),^{‡¶} respectively, as oils (Scheme). Although the yields were lower than with (2a), even here no trace of isomeric cycloheptatrienes was detectable.

ADDITION of bases to monosubstituted tropylium ions¹ such as, typically, methoxytropylium,² in spite of much investigation, has so far proven synthetically uninteresting because a mixture of 1,7-, 2,7-, and 3,7- disubstituted isomeric cycloheptatrienes was obtained.[†]

We report the first one-pot regiospecific addition of a base to a monosubstituted tropylium ion. Thus, to methoxytropylium fluorosulphonate (1) [m.p. 65°C (decomp.); δ (CD_3CN ; rel. Me_4Si) 4.23 (s, 3H) and 8.22 (m, 6H)] (0.486 g) in freshly distilled dichloromethane (25 ml) at -50°C , was added an equimolar amount of sodium methanethiolate as a 0.45 M solution in freshly distilled methanol. The mixture was set aside overnight at room temperature and then worked up by adding saturated aqueous sodium chloride, followed by extraction with chloroform and layer chromatography on silica gel to produce (2a) as an oil (R_F 0.8 with n-pentane-ether, 7:3, as eluant) in 60% yield (Scheme). No attempt has been made to optimize the yield, while isomeric cycloheptatrienes were not detectable.

Structure (2a)[‡] was supported by ^1H n.m.r. spectroscopy [δ (CDCl_3 ; rel. Me_4Si) 2.00 (s, 3H, SMe), 3.62 (s, 3H, OMe), 4.11 (dd, 1H, J 9.0, 2.0 Hz, 7-H), 5.56 (m, 2H, 2- and 6-H), and 6.22 (m, 3H, 3-, 4-, and 5-H); irradiation at δ 4.11 affects only the multiplet at δ 5.56, whilst on irradiation at δ 5.56 the double doublet at δ 4.11 becomes a singlet; also, on irradiation at δ 3.62 there is a nuclear Overhauser effect on the δ 4.11 and 5.56 signals].

The generality of the above process for (1) was proven by its similar behaviour towards a variety of thiolates, such as

† Addition of methoxide to methoxytropylium ion at low temperature is an exception because tropone dimethylacetal was obtained.

‡ Satisfactory elemental analysis and i.r. and u.v. spectra according to expectations were obtained (cf. ref. 1b).

§ The alternative structure 1-methylthio-7-methoxycycloheptatriene (2a') can be ruled out for two reasons. Thus, the δ 3.62 signal is typical of a methoxy group bound to an unsaturated carbon atom, whilst for the same group bound to C(7) a singlet between δ 3.0 and 3.3 would be expected (T. Nozoe and K. Takahashi, *Bull. Chem. Soc. Japan*, 1965, **38**, 665). Moreover, the δ 2.00 signal is typical of a methylthio group bound to a saturated carbon (R. M. Silverstein and G. C. Bassler, 'Spectrophotometric Identification of Organic Compounds,' 2nd edn., Wiley, New York) whilst for the same group bound to C(1) a singlet would be expected at δ 2.4, according to results of a recent unpublished preparation of 1,7-methylthiocycloheptatriene in these laboratories. The second reason is more cogent; the hypothetical change of (2a) into (2a') at room temperature is highly unlikely because the required shift of either the methoxy group or of hydrogen is known to require temperatures $\geq 115^\circ\text{C}$ for similarly substituted cycloheptatrienes (ref. 3; see also M. Cavazza, G. Morganti, and F. Pietra, *Tetrahedron Letters*, in the press).

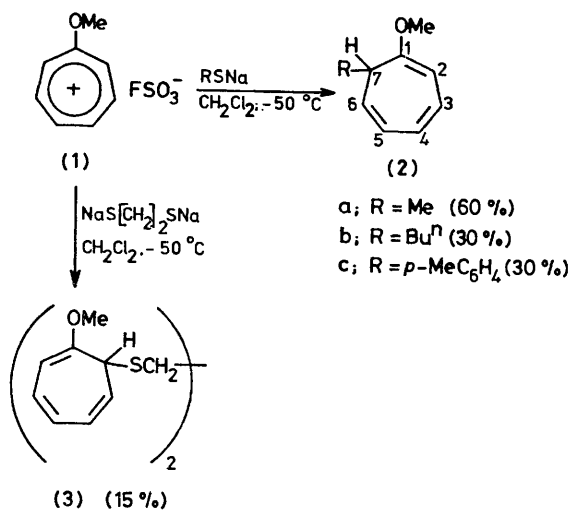
¶ These structures are supported by similar data to those given for (2a). In particular, the ^1H n.m.r. signals for the cycloheptatriene unit are practically identical to those for (2a).

** Although the yields of (2) and (3) are not high, and in some cases are rather low, these reactions can be defined as regiospecific, not only because isomeric cycloheptatrienes could not be detected, but also because t.l.c. revealed only intractable tars besides (2) and (3). Most important, products of types (2) and (3) always produced such tars on repeated t.l.c., even after previous purification, (2) and (3) being thermally unstable at room temperature. Thus there is no reason to suspect that other cycloheptatriene isomers of (2) and (3) should be much more unstable than (2) and (3) themselves, and thus be the cause of what is a seemingly regiospecific reaction. It is also clear that the best criterion of purity for (2) and (3) is their n.m.r. spectra.

¹ (a) F. Pietra, *Chem. Rev.*, 1973, **73**, 293; (b) H. Kessler, in 'Methoden der organische Chemie,' Houben-Weyl, 5/1d, G. Thieme, Stuttgart, 1972.

² B. Föhlich, C. Fisher, and W. Rogler, *Chem. Ber.*, 1978, **111**, 213.

³ R. W. Hoffmann, K. R. Eicken, H. J. Luthard, and B. Dittrich, *Chem. Ber.*, 1970, **103**, 1547.



SCHEME

Whether the regiospecificity of these processes** is due to cation bridging, in the low polarity solvent used, between oxygen and sulphur, or, alternatively, to a rapid 1,7-sigmatropic shift of sulphur from a hypothetical *gem*-intermediate of thiolate addition at C(1) on (1) is under examination.

We thank C.N.R., Roma, for financial support.

(Received, 20th March 1978; Com. 300.)