Acid-catalysed Rearrangement of the 5-Bromo-5-methanesulphinylbicyclo-[2,2,1]hept-2-enes[1]

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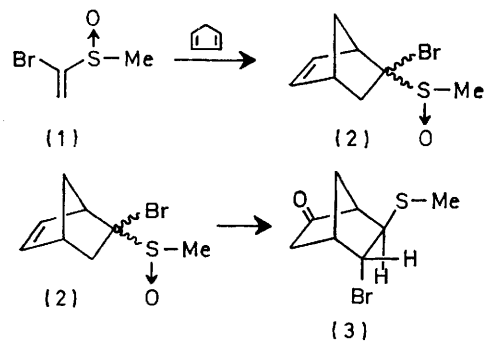
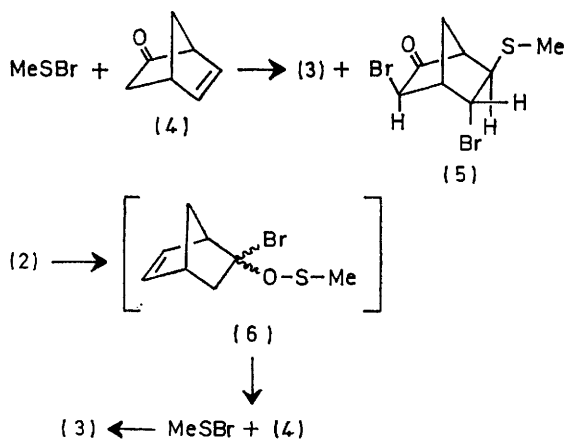
Summary The acid-catalysed rearrangement of the norbornenyl α-bromo sulphoxides (**2**) results in a cleavage–recombination sequence ultimately generating the regioselective addition product of dehydronorcamphor and methanesulphenyl bromide.

RECENT interest in the synthetic utility of sulphenate esters[2] and, in particular, the generation of an α-chlorosulphenate ester *via* a 2,3-sigmatropic rearrangement[3] prompts us to report our work on the applicability of α-halogenovinyl sulphoxides as keten synthons.



The Diels–Alder cycloaddition of methyl α-bromovinyl sulphoxide (**1**)†‡ with cyclopentadiene was investigated as a source of α-bromosulphoxides (**2**), in order to compare the chemistry of these compounds with that of the corresponding α-bromo sulphones.[4] All four possible diastereoisomers of (**2**) were obtained in the Diels–Alder reaction, although attempts at complete separation of these unstable



stereoisomers were only partially successful. Preparative t.l.c. of the mixture on silica gel afforded three fractions containing one of the *exo*-methanesulphinyl compounds, a mixture of both the *exo*-methanesulphinyl compounds, and

† The sulphoxide (**1**) was prepared by bromination–dehydrobromination of methyl vinyl sulphoxide.

‡ Satisfactory elemental analyses and spectra were obtained for all indicated new compounds.

a mixture of the two *endo*-methanesulphinyl isomers respectively. *m*-Chloroperbenzoic acid oxidation of each fraction afforded the expected sulphones.[4] Attempted column chromatography on silica gel also gave partial separation of (**2**) with an additional compound, the ketone (**3**), m.p. 93—94°, ‡ $\nu_{C=O}$ 1753 cm^{-1}, being isolated pure. Compound (**3**) could also be isolated in 30—40% yield upon treatment of a CH_2Cl_2 solution of (**2**) with anhydrous HBr. The structure of (**3**) was deduced from spectral data, chemical correlations with compounds of known stereochemistry,§ and independent synthesis (85% isolated yield) *via* the regioselective, *trans*-addition of MeSBr[5] to dehydronorcamphor (**4**).[6] The bromo-ketone (**5**)‡ was also observed in this reaction when > 1 equiv. of Br_2 and MeSSMe was used in the preparation of MeSBr.

We suggest the possibility that MeSBr and the ketone (**4**) are formed by decomposition of an intermediate α-bromo sulphenate ester (**6**) derived from rearrangement of (**2**), and that (**3**) is formed by the reaction of MeSBr with (**4**). The acid catalysis, which is apparently unnecessary for the decomposition of intermediates such as (**6**) and is to be avoided when α-halogeno-sulphenates are prepared by 2,3-sigmatropic rearrangements,[3] argues for initial protonation of (**2**) on oxygen[7] followed by heterolytic cleavage and recombination to give the α-bromo sulphenate ester (**6**). Alternatively, MeSBr and (**4**) could result directly from the decomposition of a sulphur dibromide (R_2SBr_2) intermediate[8] formed from the reaction of (**2**) with HBr.

We thank the Research Corporation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support.

(*Received*, 21*st May* 1974; *Com.* 590.)

§ The exact location and stereochemistry of the various functional groups in (**3**) and (**6**) follow from involved chemical structure proofs that we prefer to discuss in detail in the full paper.

[1] Abstracted in part from the MS Thesis, 1974, of M.P.
[2] See for example P. A. Grieco and R. S. Finkelhor, *J. Org. Chem.*, 1973, **38**, 2245; D. A. Evans, G. C. Andrews, T. J. Fugimoto, and D. Wells, *Tetrahedron Letters*, 1973, 1385, 1389 and references cited therein.
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[5] G. K. Helmkamp and D. J. Pettitt, *J. Org. Chem.*, 1964, **29**, 3258.
[6] S. J. Cristol and P. K. Freeman, *J. Amer. Chem. Soc.*, 1961, **83**, 4427.
[7] G. Gatti, A. Levi, V. Lucchini, G. Modena, and G. Scorrano, *J.C.S. Chem. Comm.*, 1973, 251.
[8] K. Mislow, T. Simmons, J. T. Melillo, and A. L. Ternay, Jr., *J. Amer. Chem. Soc.*, 1964, **86**, 1452.