

Sulphide Extrusion from Methyl Sulphonium Salts of the Sulphur-bridged Sesquiterpenes, Mintsulphide and Isomintsulphide by Alkyl-lithium

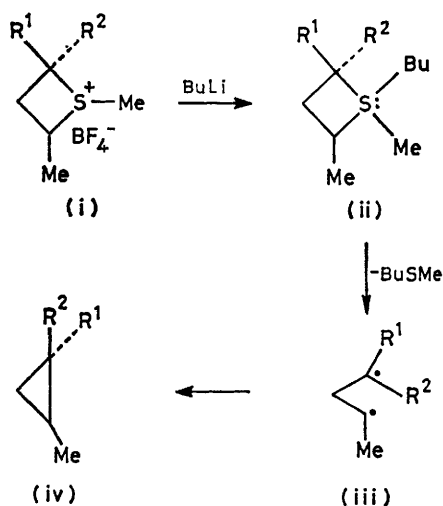
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Summary Reaction of the methylsulphonium salts of mintsulphide (**1**) and isomintsulphide (**2**) with methyl-lithium gives the desulphurization products, *via* the biradical intermediates, and the [2,3]sigmatropic rearrangement products.

Of particular interest in organosulphur chemistry are desulphurization reactions giving the biradical species. Desulphurization at low temperatures only has precedent in the sulphide extrusion of thietanium salts with butyl-lithium [(i) → (iv) in Scheme 1; R¹ = H, R² = Me],

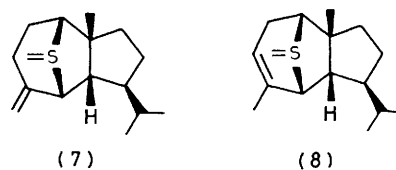
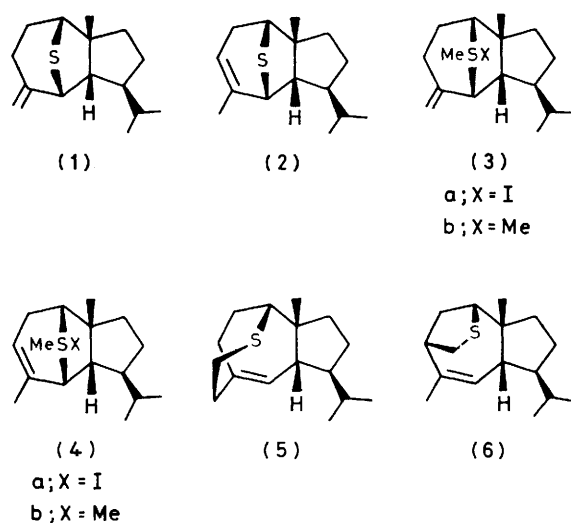
(**4a**), m.p. 142–144 °C (decomp.) by refluxing with methyl iodide for 8 h. The reaction of the sulphonium salts (**3a**) and (**4a**) with lithium di-isopropylamide (LDA) resulted in the exclusive formation of the respective homologous sulphides (**5**) and (**6**) in *ca.* 97% yield.† These sulphides may be derived by [2,3] sigmatropic rearrangements of the corresponding sulphonium methylides (**7**) and (**8**). Assuming that the ylide formation step proceeds with retention of configuration,² the S-methyl group of (**3a**) and (**4a**) should be located *syn* with respect to the three-carbon bridge.



SCHEME 1.

where the cyclopropane ring has been reported to form stereospecifically.¹ To assess the use of this desulphurization reaction for carbon-carbon bond formation, we have examined the reactions of the methylsulphonium salts of mintsulphide (**1**) and isomintsulphide (**2**). These seem to be suitable models since both are available in multigram quantities, in the optically active form.†

Mintsulphide (**1**) and its isomer (**2**) were easily converted in high yields (91–94%) into the corresponding methylsulphonium iodides (**3a**), m.p. 160–162 °C (decomp.) and

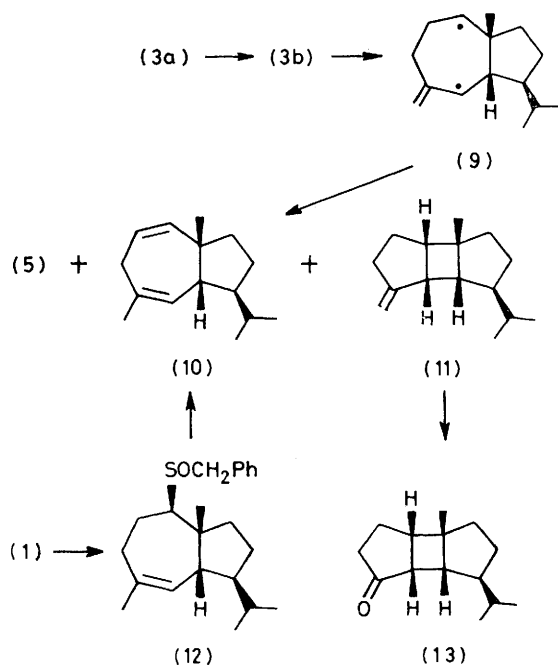


When (**3a**) was treated with methyl-lithium, the hydrocarbons (**10**) and (**11**) were formed in 43 and 29% yields, respectively, as well as the homologous sulphide (**5**) (22%).

† Isomintsulphide (**2**) is prepared from mintsulphide (**1**) quantitatively when treated with *p*-MeC₆H₄SO₃H in refluxing benzene. Mintsulphide (**1**) is a component of peppermint oil (*Mentha peperita*) (Y. Yoshida, S. Muraki, K. Takahashi, T. Kato, C. Kabuto, T. Suzuki, T. Ueyehara, and T. Ohnuma, *J. Chem. Soc., Chem. Commun.*, 1979, 512) and easily synthesized in *ca.* 50% yield by the photoinduced reaction of powdered sulphur with (–)-germacrene D in a hydrocarbon solvent (K. Takahashi, S. Muraki, and T. Yoshida, *Agric. Biol. Chem.*, in the press; T. Ueyehara, T. Ohnuma, T. Suzuki, T. Kato, T. Yoshida, and K. Takahashi, 22nd Symposium on the Chemistry of Natural Products, Symposium paper No. 235, 1979).

‡ Satisfactory elemental analyses have been obtained as well as satisfactory i.r. and ¹H and ¹³C n.m.r. spectra, which are in accord with the proposed structures; the details will be described in a full paper.

The same reaction with (4a) furnished a mixture of the isomeric homologous sulphide (6) and the hydrocarbon (15) in 8.5 and 79% yield, respectively. The ratio of these products depends largely on the reaction conditions.§

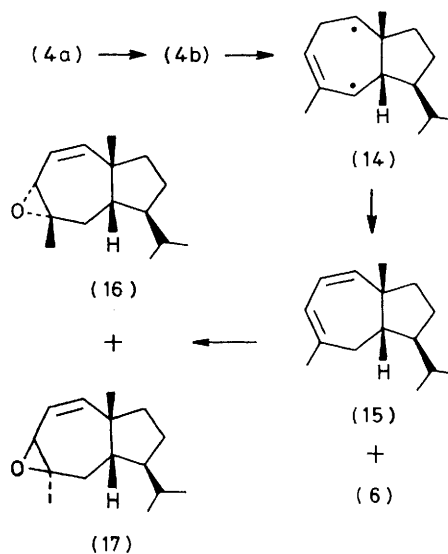


SCHEME 2.

In addition to satisfactory physical data, the following evidence supports the structure of the hydrocarbons. Oxidation of (15) with *m*-chloroperbenzoic acid gave a separable mixture of the epoxides (16) and (17). ¹H N.m.r. spectra demonstrate the presence of the R₃C-CH=CH-CH-O-CMe (R ≠ H) grouping in each compound [¹H n.m.r. (CCl₄) (16) δ 5.59 (dd, *J* 5.6 and 0.8 Hz, 1 H), 5.43 (d, *J* 5.6 Hz, 1 H), 2.88 (br s, *W*_{1/2} 1.5 Hz, 1 H), and 1.33 (s, 3 H); (17) 5.62 (dd, *J* 5.6 and 0.8 Hz, 1 H), 5.41 (dd, *J* 5.6 and 2.3 Hz, 1 H), 2.83 (dd, *J* 2.3 and 0.8 Hz, 1 H), and 1.30 (s, 3 H)]. Treatment with Li in NH₃ and then with PhCH₂Br-NaH, followed by oxidation with SeO₂-H₂O₂, converted the mintsulphide (1) into the sulphoxide (12), which was transformed into the hydrocarbon (10) in 26% overall yield. Oxidation of (11) with KMnO₄-NaIO₄ furnished the corresponding cyclopentanone derivative (13), i.r. ν 1730 cm⁻¹.¶

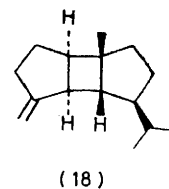
§ When butyl-lithium was applied at -78 °C, (3a) afforded (10) (7.2%), (11) (3.1%), and (5) (83%) while (4a) gave (9) (24%) and (6) (64%), respectively.

¶ The positive c.d. Cotton effect of (13) in cyclohexane (312.5 nm, Δε +1.93) strongly supports the assigned stereostructure of (11).



SCHEME 3.

Formation of the hydrocarbons (15), (10), and (11) suggests that the sulphide extrusion proceeds *via* the transient species (3b) and (4b), which are transformed into the respective biradical intermediates (9) and (14) by the fragmentation of MeSMe. The intramolecular hydrogen-shift then takes place, resulting in the formation of the dienes (10) and (15) (Schemes 2 and 3). The tricyclic product (11), a stereoisomer of (-)-β-bourbonene (18),³



would result from ring closure of the biradical intermediate (9) (Scheme 2). The stereoselective formation of the *cis-syn-cis* skeleton may reflect that the ring closure proceeds faster than the rotation of the radicals.

(Received, 17th October 1980; Com. 1125.)

¹ B. M. Trost, W. L. Schinski, I. B. Mants, and F. Chen, *J. Am. Chem. Soc.*, 1971, **93**, 676.

² B. M. Trost and R. F. Hammen, *J. Am. Chem. Soc.*, 1973, **95**, 962.

³ J. Krepinsky, Z. Samek, F. Sorm, D. Lamparsky, P. Ochsner, and Y. R. Naves, *Tetrahedron*, Supp. 8, Part 1, 1966, 53.