1,8,8-Trimethyl-3-thiabicyclo[3,2,1]octane

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PLEŠEK *et al.*[1] have stated that reaction of 1,2,2-trimethyl-1,3-bis-(*p*-tolylsulphonyloxymethyl)cyclopentane (Ia) with sodium sulphide in ethanol yielded either 1,5,5-trimethyl-2-thiabicyclo[2,2,2]octane (III) or 5,8,8-trimethyl-6-thiabicyclo[3,2,1]octane (IV), and not the expected 1,8,8-trimethyl-3-thiabicyclo[3,2,1]octane (II). Since this casts doubt on the structures of the *exo-* and *endo-*1,8,8-timethyl-3-thiabicyclo[3,2,1]octane oxides,[2] which we have recently described, and on the validity of the spectral data (u.v. and o.r.d.) reported for them it is necessary for us to refute it.

Compound (II) [m.p. 185° (slight), 191° (start), 199—203° (most) (sealed tube)†; n.m.r.‡ ($CDCl_3$) 52, 55·5, and 59 (3s, 8·55H, Me), 100—134 (m centred at 111, 7·51H, $-CH_2-$, ⩾CH, >CH–S–CH<, and 168, 180, 185·5, and 197 (1·94H, >CH–S–CH<)] was prepared by the reaction of either (Ia) or (Ib) with sodium sulphide in ethanol or dimethylformamide. Comparison of the i.r. and n.m.r. spectra of our compound with those of a sample of (II) obtained from Plešek

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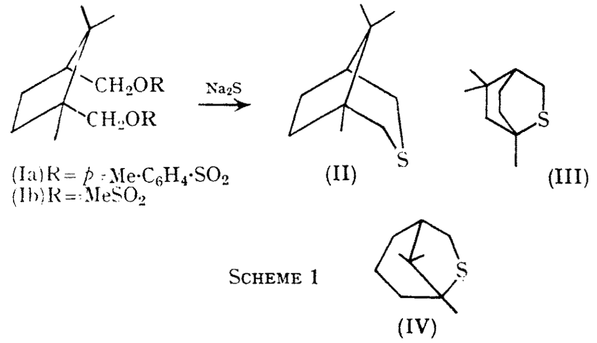
† While this m.p. can be duplicated (ref. 1), it probably does not represent the initial m.p. of the compound. A phase transition occurs at 69·5–71·5° (differential thermal analysis, calibrated) but this transition is difficult to detect in a sealed m.p. tube.

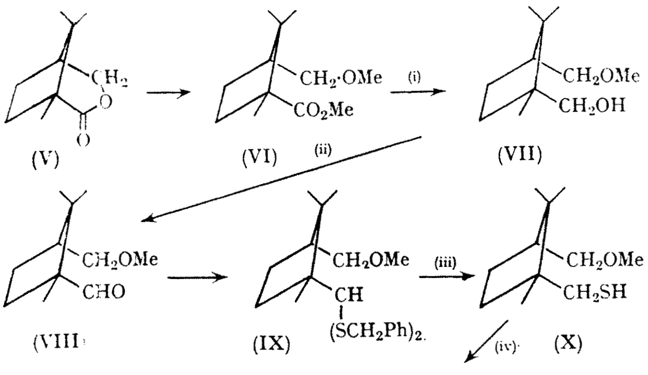
‡ Determined with a Varian Associates A-60 spectrometer (p.p.m. downfield from tetramethylsilane).

and Hermanek established the identity of the materials. The compounds did differ in purity. In our hands, the m.p.s of the compounds in this series have not been satisfactory criteria of purity or identity.



SCHEME 1

In order to eliminate the possibility of the rearrangements postulated by Plešek and his co-workers,[1] we had synthesised (II) previously from α-campholide (V),[3] m.p. 212—214° (sealed tube), $[\alpha]_D^{32^\circ}$ −20·0° (EtOH) [lit.,[4] m.p. 209—211·5°, $[\alpha]_D$ −20·2° (EtOH)], by the sequence of reactions shown in Scheme 2. The sulphide (II) so obtained was identical (i.r., n.m.r., and o.r.d. spectra) with the 1,8,8-trimethyl-3-thiabicyclo[3,2,1]octane (II) synthesized by the reaction shown in Scheme 1.

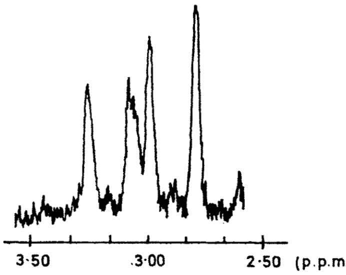


SCHEME 2

Reagents: (i) LiAlH₄, (ii) CrO₃–pyridine, (iii) Li–NH₃, (iv) p-Me·C₆H₄·SO₂·OH, toluene.

To provide further evidence for structure, compound (II) was desulphurized with Raney nickel, and the hydrocarbon so obtained was purified by gas chromatography. The n.m.r. spectrum of this hydrocarbon indicated the presence of five methyl groups; the resonance band for one of the methyl groups was split into a doublet, J ca. 6·3 c./sec. The ratio of methyl hydrogen atoms to methylene and methine hydrogen atoms was 3·1 : 1. The hydrocarbons that would be obtained from compounds of structures (III) or (IV) would have four methyl groups and the ratio of methyl hydrogen atoms to methylene and methine hydrogen atoms would be 1·5 : 1.

The assignment of structures (III) or (IV) by Plešek and his co-workers to the sulphide obtained from the reaction depicted in Scheme 1, was based on the fact that the four resonance bands found at low field in the n.m.r. spectrum integrated for only two protons. Their interpretation assigned these bands to an AB system ($-CH_2-S-$). Thus they eliminated structures with two methylene groups adjacent to sulphur. However, the intensities of these bands do not at all correspond to those of a typical AB system[5] (see Figure). Also, if this were an AB system, coupling to other protons would be relatively small. Irradiation[5] of the protons absorbing around 118 c./sec. markedly perturbed the downfield absorption bands. We have tentatively assigned these bands to the two axial protons on the carbon atoms α to sulphur in (II). It should also be noted that the n.m.r. spectra of (II) *exo*-monoxide and (II) dioxide integrate for four protons in the downfield multiplet.



FIGURE

We have been plagued by the broad m.p.s of this series of compounds. Since synthesis of 2-thiacholestane by the method (Scheme 1) leads to the formation of considerable quantities of dimer, compound (II) was purified by sublimation at 80° and atmospheric pressure. An osmotic molecular weight determination in benzene indicated a molecular weight of 173 ± 9 for (II) (theory 170). Thermal analysis§ of a sample of (II) dioxide, m.p. 225° (slight), 251° (start), 257—260° (most) (sealed tube), *M* 191 (freezing-point depression of benzene) (theory 202), using a transition point at 102·4°, indicated the (II) dioxide to be 99·9% pure.[6]

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§ The thermal analysis was run on a Perkin-Elmer Differential Scanning Calorimeter, Model DSC-1B, with indium metal as the primary standard. The transition temperature recorded (102·4°) was the instrument reading and was not independently calibrated.

[1] J. Plešek, S. Heřmánek and B. Štíbr, *Coll. Czech. Chem. Comm.*, 1968, **33**, 2336.
[2] R. Nagarajan, Brian H. Chollar, and R. M. Dodson, *Chem. Comm.*, 1967, 550.
[3] Brian H. Chollar, Ph.D. Thesis, University of Minnesota, March, 1967.
[4] R. R. Sauers, *J. Amer. Chem. Soc.*, 1959, **81**, 925; J. Véne, *Bull. Soc. chim. France*, 1942, **9**, 776.
[5] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, Oxford, 1965; p. 310, 455.
[6] F. D. Rossini, "Chemical Thermodynamics," Wiley, New York, 1950, p. 294, 454.