

Nuclear Magnetic Resonance Experiments on Acetals.¹ Barrier for Inversion of 1,3-Diselenan

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Summary The free enthalpy of activation of 1,3-diselenan has been found by low-temperature n.m.r. to be 8.2 ± 0.1 kcal./mole.

DURING conformational studies of 1,3-dioxans and 1,3-dithians, 1,3-diselenan was synthesised for comparative purposes. It was obtained from propane-1,3-diselenol by reaction of 1,3-dibromopropane and disodium selenosulphite² in aqueous ethanol to afford the disodium salt of propane-1,3-diselenosulphonic acid which was oxidised with hydrogen peroxide to give a polymeric trimethylene diselenide³ (50%, based on 1,3-dibromopropane). Treatment of the polymer with potassium in liquid NH₃ gave the dipotassium salt of propane-1,3-diselenol which upon cyclisation afforded 1,3-diselenan. The cyclisation was performed either by heating the potassium diselenolate for 5 hr. under reflux with strong acidic aqueous formaldehyde (yield of 1,3-diselenan, separating as a light brown mass, 50% based on the polymer; b.p. 250°/760 mm., m.p. 66°) or

by stirring the potassium 1,3-diselenolate at room temperature for 12 hr. in dimethylformamide and dichloromethane (30% yield with some polymeric product). The 1,3-diselenan was purified by preparative g.l.c.

The n.m.r., i.r., u.v., and mass spectra are consistent with the structure. Characteristic i.r. bands are: 2810m (ν_{sym} Se-CH₂-Se) and 890s cm.⁻¹ (C-Se-C-Se-C). The n.m.r. spectrum (Varian HA-100) (100 Mc./sec., CS₂ solution) of 1,3-diselenan consists of a multiplet at δ 2.08 (two protons at C-5), an asymmetric triplet at δ 2.79 (two protons at C-4; two at C-6) and a singlet at δ 3.64 (two protons at C-2) accompanied by a doublet [for ⁷⁷Se, $I = \frac{1}{2}$ (ref. 4); ³J(H-2-⁷⁷Se) = 14.4 c./sec.] The spectrum of 1,3-diselenan in CS₂-CHCl₃-pyridine (4:1:1) coalesces at $178 \pm 0.5^\circ$ K, giving an AB system for the C-2 protons ($\delta_{2e \rightarrow 2a}$ ca. 85 c./sec). At this temperature ΔG^\ddagger is 8.2 ± 0.1 kcal./mole.

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¹ Previous paper, G. Swaelens and M. Anteunis, *Bull. Soc. chim. belges*, in the press. See also e.g. J. Gelan and M. Anteunis, *ibid.*, 1968, 77, 423.

² Houben Weyl, Vol. 9, p. 1090.

³ Houben Weyl, Vol. 9, p. 1091.

⁴ J. W. Emsley, J. Feeney, and L. A. Sutcliffe, "High Resolution NMR Spectroscopy," Pergamon, Oxford, 1965.