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THE CONFIGURATION OF THE SELENOXIDES

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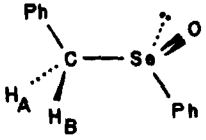
In 1926 4-aminophenyl 4'-methylphenyl sulfoxide and m-methylsulfinylbenzoic acid were resolved for the first time into the respective optical enantiomers (1). Since then ample examples of the optically active sulfoxides have been reported, and it has been well recognised that the sulfur atom in the sulfoxide is an asymmetric center, the two adjacent carbon atoms, the oxygen atom and the lone pair of electrons occupying the each apex of the tetrahedron.

As a natural extension with reference to the periodical table, the asymmetric selenoxides had been subjected to the optical resolution (2, 3). In striking contrast with the sulfoxides, all the attempts which worked well for the resolution of the sulfoxides turned out to be ineffective, and there has been no example of the optically active selenoxide. Thus it seems interesting to know whether the failure of the resolution is due to the intrinsic nature of the configuration of the selenoxide moiety or is due to merely technical reasons of the optical resolution.

To this end, the n.m.r. and i.r. spectra of benzyl phenyl selenoxide were examined in various solvents. The selenoxide was obtained in a 85 % yield by passing the excess of ozone to a solution of benzyl phenyl selenide (4) in carbon tetrachloride and recrystallized from acetone to give colorless prisms, m.p., 135~136°C. Anal. Found: C, 59.31 ; H, 4.70. Calcd. for $C_{13}H_{12}OSe$: C, 59.32 ; H, 4.60 % .

The n.m.r. spectra* of the selenoxide in $CDCl_3$ are composed of signals (from internal TMS standard) at 7.5 (singlet for the aromatic protons of the benzyl group), 7.4~7.0 (multiplet for the protons of C_6H_5SeO-), and 4.09 p.p.m. (AB-quartet, $\delta_{AB}=13.1$, $J_{AB}=11.3$ c.p.s., of the methylene protons). Since the methylene protons constitute an AB-quartet signal, it is firmly concluded that the selenium atom in the selenoxide is an asymmetric center as is the sulfur atom in the sulfoxides and shown in I, and that the life-time of the enantiomer is expected to be longer than several seconds at room temperature. The benzylic methylene protons give an AB-quartet signal even at 100°C in o-dichlorobenzene.



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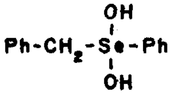

$$\mathrm{Ph{-}CH_2{-}\overset{OH}{\underset{OH}{Se}}{-}Ph}$$

II

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* The spectra were measured on a Varian A-60 n.m.r. spectrometer operating at 60 Mc/sec.

The chemical shift between the unequivalent methylene protons, H_A and H_B, depends uniquely on the solvent used for the n.m.r. measurement; thus δ_{AB}'s are 7.3 in C_6D_6, 7.9 in $o\text{-}Cl_2C_6H_4$, 8.6 in DMSO-d_6, and 0 c.p.s. in D_2O. Since the plot of the solvent dielectric constant vs. δ_{AB} between the geminal protons does not fit the smooth curve*(5), the solvent effect can not be explained in terms of the contribution of the conformers in equilibrium which may be established by rotation around the Se-CH_2 bond. Rather, the singlet in aqueous solution indicates the apparent loss of asymmetry of the selenium atom in this medium. The hydrate of type II often quoted in the literature (2,3) may be expected, but its formation was denied by observing $\nu_{Se=O}$ at 800 cm^{-1} in deuterium oxide solution**. In DMSO-d_6 containing 10 % D_2O, the AB-quartet observed at room temperature approaches each other as the temperature rises, and coalesces to a singlet at 110°C. The phenomenon is reminiscent of the existence of some kind of racemization process in which II is supposed to be an intermediate. The life-time of an enantiomer is estimated to be 4 sec. at

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* δ_{AB} bears an approximate inverse relation to the dielectric constant in benzyl α-phenethyl ether (5).

** The i.r. spectra were measured on DS-402 G spectrometer (Japan Spectroscopic Co. Ltd.). $\nu_{Se=O}$ in nujol mull is at 820 cm^{-1}, and the shift to the lower frequency in D_2O can be satisfactorily explained by formation of the hydrogen bonding.

room temperature.

It is concluded that the failure in resolution of the selenoxides so far is due to the mere technical defect, and that the presence of water in the ordinary resolution process seems to accompany the racemization. It is hoped that some selenoxides may be resolved into optically active forms under anhydrous conditions.

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