Racemization Mechanism of Asymmetric Chlorogermanes

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IN a former paper, we undertook to reassess the racemization mechanism of methylphenyl-α-naphthylchlorosilane. We have shown[1] that this mechanism proceeds *via* an extension of the silicon atom co-ordination, rather than by an intermediate siliconium ion, as suggested by Sommer and his co-workers.[2,3] We have extended our studies to organogermanes, as the cleavage of Ge–Cl[4] is more difficult than that of Si–Cl bond.[5]

Methylphenyl-α-naphthylchlorogermane[6,7] is optically stable in hydrocarbons, as well as in chloroform and carbon tetrachloride. Racemization is not observed in ether, dioxan, or anisole, but is fast in tetrahydrofuran (THF) (complete within 8 min.).

Racemization is brought about by solvents with a nucleophilic atom, as in the case of the analogous chlorosilane. The same order for racemization rates applies (glycodimethyl ether GDME) $>$ THF $>>$ Et_2O, dioxan; also $PhCO_2Et$ $>$ $MeCO_2Et$. It should be emphasized that the racemization of chlorogermane is far easier (*e.g.* no racemization for chlorosilane in THF).

When lithium perchlorate is added to ether or to THF, the racemization rate increases (ether + $LiClO_4$, racemization within 16 hr., THF + $LiClO_4$ racemization within 5 min.). These results are analogous to those for the chlorosilane, and may be interpreted as an electrophilic catalysis through Li^+, allowing the Ge–Cl bond to be stretched.

Alcohols and water in solution in benzene, dioxan, and ether racemize chlorogermane without substitution. Moreover, we noticed that the substitution reaction (alcoholysis or hydrolysis) was always lower than 0·1% even after complete racemization, and was always lower than 1%, even with equimolecular amounts of solvent and alcohol.

From those results it is possible to suggest a mechanism of racemization identical for chlorogermane and chlorosilane. However, chlorogermane racemization is far easier, though substitution of the halogen atom is more difficult. For instance, both racemization and chlorosilane substitution occur[8]† with all the alcohols studied, whereas chlorogermane racemization occurs without substitution. The mechanism of racemization probably involves the co-ordination of two molecules of solvent round the central atom.[1] This co-ordination is easier, for Ge is more bulky than Si, which could account for the greater ease of the racemization of chlorogermanes. On the other hand, substitution involves the cleavage of Ge–Cl bond, which is more difficult than that of Si–Cl.

When it is carried out with alcohols, the racemization is dependent upon two factors: the nucleophilic power of the oxygen atom and the possible Ge–Cl bond stretching by hydrogen bonding. This second factor accounts for the far higher rate of racemization in benzene than in ether or dioxan, those two latter solvents being able to effect hydrogen bondings with alcohols. The -OH groups are then less able to increase the electrophilic power of the germanium atom.

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† It should be noted that substitution with alcohols is stereospecific only in the presence of an amine.

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