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ORGANOGERMANIUM COMPOUNDS

XI*. THE THERMAL REARRANGEMENT OF OPTICALLY ACTIVE ETHYL(1-NAPHTHYL)PHENYLGERMANECARBOXYLIC ACID

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SUMMARY

The stereochemistry of the conversion of (–)-$R'_3GeCO_2H \rightarrow$ (–)-$R'_3GeO_2CGeR'_3$, where $R'_3Ge = Et(1\text{-}C_{10}H_7)PhGe$, is discussed.

INTRODUCTION

Germanecarboxylic acids, R_3GeCO_2H, are known to undergo loss of carbon monoxide on heating to give the esters $R_3GeCO_2GeR_3$, the process being thought to involve the consecutive reactions (1a) and (1b)[2]. We recently described the preparation

$$R_3GeCO_2H \rightarrow R_3GeOH + CO \quad (1a)$$

$$R_3GeOH + R_3GeCO_2H \rightarrow R_3GeO_2CGeR_3 \quad (1b)$$

of the optically active germanecarboxylic acid (–)-R'_3GeCO_2H, where $R'_3Ge = Et(1\text{-}C_{10}H_7)PhGe$ [which was made from the hydride (*R*)(+)-R'_3GeH, via the lithium derivative R'_3GeLi, with retention of configuration at germanium], and showed that it gave an optically active ester (–)-[$R'_3GeO_2CGeR'_3$] on heating[3]. We consider below the possible stereochemistry of this reaction.

RESULTS AND DISCUSSION

We first note that the decarbonylation process, (1a), can be confidently expected to involve retention at the germanium atom, since the very closely related reaction (2) is known to do so[3].

$$R'_3GeCO_2Me \rightarrow R'_3GeOMe + CO \quad (2)$$

It is not so easy to predict the stereochemistry of reaction of type (1b), however. We first note that, in view of the relative acidities of the reacting entities, bonds are more likely to be broken in the sense indicated in (3a) than in that indicated in (3b), and we shall assume that the sense indicated by (3a) is correct, and thus that the config-

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* For Part XII see ref. 1.

uration is retained at the germanium atom of the R_3GeCO_2H system. For the probable

$$\mathrm{R_3Ge}\boxed{\mathrm{{-}OH+H{-}}}\mathrm{OCOGeR_3} \tag{3a}$$

$$\mathrm{R_3GeO}\boxed{\mathrm{{-}H+OH{-}}}\mathrm{COGeR_3} \tag{3b}$$

stereochemistry at the germanium atom of the R_3GeOH system, we can look for guidance to results available for R_3SiX compounds, $[R_3Si = Me(1\text{-}C_{10}H_7)PhSi]$ since these closely resemble R'_3GeX compounds in their stereochemical behaviour[8], but unfortunately this does not provide an unambiguous answer. In reactions involving cleavage of the M–O bonds, the R'_3GeOH system should resemble the R_3SiOMe system, and most of the reactions of the latter occur with retention of configuration[4], but it is known that this can give way to inversion in polar protic media[5,6]; the melt which provides the medium for reaction (1b) will be of just such a type, so that inversion at the germanium atom of the hydroxide would be quite likely.

As previously noted[3], the acid $(-)\text{-}R'_3GeCO_2H$ is converted into the optically active ester (I) when heated at 200° for 10 min, as in eqn. (4). The problem of establishing

$$\underset{[\alpha]_D -9.1^\circ}{2\,(-)\text{-}\mathrm{R_3GeCO_2H}} \rightarrow \underset{\text{(I)},\ (\alpha]_D -10.0^\circ}{(-)\text{-}\mathrm{R'_3GeCO_2GeR'_3}} + \mathrm{CO} \tag{4}$$

$$\overset{(\alpha)}{\underset{\textcircled{R}}{\mathrm{R'_3Ge}}}\mathrm{O_2C}\overset{(\beta)}{\underset{\textcircled{R}}{\mathrm{GeR'_3}}} \qquad\qquad \overset{(\alpha)}{\underset{\textcircled{I}}{\mathrm{R'_3Ge}}}\mathrm{O_2C}\overset{(\beta)}{\underset{\textcircled{R}}{\mathrm{GeR'_3}}}$$

(Ia) (Ib)

the stereochemistry of reaction (4) is one of deciding whether the germanium centre in the ester (I) has the retained configuration [denoted $\textcircled{R}$] with respect to the hydride $(R)(+)\text{-}R'_3GeH$, as in (Ia), or the inverted configuration [denoted $\textcircled{I}$] as in (Ib).

That optical activity (but not necessarily configuration) has been retained at both germanium centres in (I) was shown by reduction with lithium aluminium hydride in ether, which gave the (–)-hydride, $(-)\text{-}R'_3GeH$, and the (+)-carbinol, $(+)\text{-}R'_3GeCH_2OH$, as in eqn. (5). The rotation of the carbinol is, as expected, in the direction associated with a configuration corresponding to that of the original (+)-hydride[3].

$$\underset{[\alpha]_D -10.0^\circ}{(-)\text{-}\mathrm{R'_3GeO_2CGeR'_3}} + \mathrm{LiAlH_4} \rightarrow \underset{[\alpha]_D -2.8}{(-)\text{-}\mathrm{R'_3GeH}} + \underset{[\alpha]_D +2.0^\circ}{(+)\text{-}\mathrm{R'_3GeCH_2OH}} \tag{5}$$

The rotation of the hydride formed in reaction (5), on the other hand, shows that it has the inverted configuration with respect to the original hydride, and the inversion must have occurred in either reaction (4) or reaction (5). We could decide between (Ia) and (Ib) if we could be sure of the stereochemistry of the formation of the hydride in reaction (5). Unfortunately, there is again ambiguity, for while the germanium esters of the type R'_3GeO_2CR where (*e.g.* R = Me or Ph), would be expected, by analogy with the behaviour of the analogous silicon compounds[7], to give the hydride R'_3GeH with inversion at germanium, it is not certain that the $R_3GeCO_2^-$ group would be as good a leaving group as RCO_2^-, and, moreover, there is the possibility, in the case of (I), that the initial reaction takes place preferentially at the carbonyl group.

A further set of observations is relevant, but again not conclusive. The ester $(\pm)$-$\mathrm{R'_3GeO_2CGeR'_3}$-$(-)$, (II), $[\alpha]_D$ $-5.9°$, was made from the racemic chloride as in eqn. (6)*. When this ester (II), was heated at 270° for 10 min, it gave a digermoxane,

$$\underset{[\alpha]_D\ +19.0°}{(+)\text{-}\mathrm{R'_3GeH}} \rightarrow \mathrm{R'_3GeCO_2H} \rightarrow \mathrm{R'_3GeCO_2Li} \xrightarrow{(\pm)\text{-}\mathrm{R_3GeCl}} \underset{\text{(II)},\ [\alpha]_D\ -5.9°}{(\pm)\text{-}\mathrm{R'_3GeO_2CGeR'_3}\text{-}(-)} \tag{6}$$

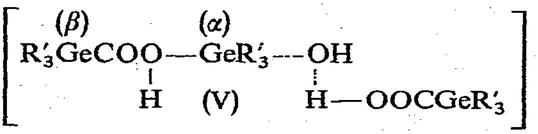
(III), of rotation $+1.7°$, as shown in eqn. (7), whereas when the ester (I), having $[\alpha]_D$ of $-9.1°$ was heated it gave digermoxane, (IV), having a rotation of only $+0.2°$, as in

$$\underset{\text{(II)},\ [\alpha]_D\ -5.9°}{(\pm)\text{-}\mathrm{R'_3GeO_2CGeR'_3}\text{-}(-)} \xrightarrow{270°} \underset{\text{(III)},\ [\alpha]_D\ +1.7°}{(+)\text{-}\mathrm{R'_3GeOGeR'_3}\text{-}(\pm)} \tag{7}$$

$$\underset{\text{(I)},\ [\alpha]_D\ -9.1°}{(-)\text{-}\mathrm{R'_3GeO_2CGeR_3}\text{-}(-)} \xrightarrow{270°} \underset{\text{(IV)},\ [\alpha]_D\ +0.2°}{(+)\text{-}[\mathrm{R'_3GeCOGeR'_3}]} \tag{8}$$

eqn. (8). Since this conversion seems most likely to occur with retention at both germanium centres, the very low rotation of the digermoxane (IV) implies opposing configurations at the two germanium centres of the ester (I).

In view of this last result we are inclined to favour the composition (Ib), with an inverted configuration at germanium atom (α), for ester (I). We note that on the simplest assumptions of additivity, the relative magnitudes of the rotations of esters (I) and (II) support this tentative assignment. This is because the substantially larger rotation of (I) is consistent with a negative contribution to the rotation from the germanium centre (α), reinforcing that from centre (β), and a negative rotation in a $\mathrm{R'_3GeOX}$ species is most readily associated with a configuration inverted with respect to that of the original $(+)$-$\mathrm{R'_3GeH}$. [Compare the negative rotations of $\mathrm{R'_3GeOMe}$ formed from the hydride via the chloride with inversion[8], and of several $(-)$-$\mathrm{R'_3SiO_2}$-$\mathrm{CR''}$ species having configurations inverted with respect to that of $(+)$-$\mathrm{R_3SiH}$[4].] The weakness in this reasoning is, of course, that conformational asymmetry effects could easily swamp out the effects expected for simple additivity. However, the balance of the evidence seems to us to be slightly in favour of structure (Ib), even though this involves the troublesome implication that $(-)$-$\mathrm{R'_3GeH}$ is formed by reduction of the ester (I) with inversion at germanium centre (α), and thus that the $\mathrm{R'_3GeCO_2^-}$ group behaves as a poor leaving group. Acceptance of structure (Ib) would imply inversion at the germanium atom of the germanol in reaction (Ib), and this would be consistent with a plausible transition state of type (V), involving nucleophilic, backside attack at this germanium atom, and prior or synchronous protonation of the separating hydroxyl group.



$$\left[\begin{array}{lll} (\beta) & (\alpha) & \\ \mathrm{R'_3GeCO\underset{\displaystyle \mathrm{H}}{\underset{|}{O}}} & \!\!\text{—}\mathrm{GeR'_3}\text{---} & \mathrm{\underset{\displaystyle \mathrm{H{—}OOCGeR'_3}}{\underset{\vdots}{O}H}} \\ & \text{(V)} & \end{array}\right]$$

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* Only inactive ester was obtained when the (−)-chloride, (−)-$\mathrm{R'_3GeCl}$, was treated with racemic (±)-$\mathrm{R'_3GeCO_2Li}$.

Additional information will be needed before the doubts described can be resolved, but unfortunately there is no prospect of our being able to study this system further in the foreseeable future.

A NOTE ON PART X OF THIS SERIES OF PAPERS

In a previous paper in this series we used the designations (*R*)- and (*S*)-R'_3GeX without stating explicitly that we intended by this simply to indicate that the configuration corresponded with that of (*R*)(+)-R'_3GeH or (*S*)(−)-R'_3GeH, respectively, though this would become apparent on careful reading of the discussion[8]. Thus, in that paper, an (*R*) designation applied to, say, (−)-R'_3GeCl was intended to denote that the configuration corresponds with that of (+)-R'_3GeH. [The absolute configuration of the (−)-R'_3GeCl, is, of course, by convention, described as (*S*), since although its actual configuration is the same as that of (*R*)(+)-R'_3GeH, the atom of lowest "priority" (lowest atomic number) in the latter has been replaced by one of higher priority than carbon.]

In Table 5 of Part X, for R'_3GeX and R_3SiX species having configurations corresponding to that of (*R*)(+)-R'_3GeH, the wrong signs for the rotations are shown for X = OMe, OH, SH, SPh, and N_4H_4, as is apparent from the discussion[8]. No conclusions were affected by this error.

EXPERIMENTAL

All rotations were measured at 25° in benzene.

Behaviour of (−)-R'_3GeCO_2H on heating (cf. ref. 3)

The acid (−)-R'_3GeCO_2H, $[\alpha]_D$ −9.1° (182 mg) was heated at 200° for 10 min, after which time evolution of gas had ceased. The viscous oil (170 mg, 95%), $[\alpha]_D$ −9.8° (*c*, 8.5). was identified as (−)-[ethyl(1-naphthyl)phenylgermyl ethyl(1-naphthyl)-phenylgermanecarboxylate], (I), by the identity of its IR spectrum and GLC retention time with those of the sample containing a racemic centre, described in the following experiment.

Preparation of (±)-$R'_3GeO_2CGeR'_3$-(−), (II)

(+)-R'_3GeH (0.6 mmol), $[\alpha]_D$ +19.0°, was metallated with n-butyllithium in ether and carbon dioxide was passed in, as described in ref. 3. The resulting solution of R_3GeCO_2Li was refluxed with (+)-R'_3GeCl (0.5 mmol) in n-pentane (30 ml) for 8h, during which a white precipitate formed slowly. A large volume of ether was added, and the ethereal solution was shaken several times with 0.2 *M* aqueous sodium hydroxide, separated, washed, and dried ($MgSO_4$). Removal of the solvent left, as a colourless viscous oil, (±)-ethyl(1-naphthyl)phenylgermyl (−)-ethyl(1-naphthyl)phenylgermanecarboxate (290 mg, 85%), $[\alpha]_D$ −5.9° (*c*, 14.4). (Found: C, 67.5; H, 5.7. $C_{37}H_{34}GeO_2$ calcd.: C, 67.9; H, 5.2%.) The IR spectrum showed, in addition to the usual R'_3Ge peaks, a strong sharp band at 1655 cm^{-1} attributable to ν(C=O) and strong band centred at 1170 cm^{-1} attributable to ν(C−O).

A similar experiment, but involving optically active chloride, (−)-R_3GeCl, gave an ester having $[\alpha]_D$ of −4.4°, while another involving the (−)-chloride and the racemic (±)-R'_3GeCO_2Li gave only inactive material.

Conversion of esters (I) and (II) into digermoxanes

The ester (II) (200 mg, 30 mmol), $[\alpha]_D$ −5.9°, was heated at 270° for 10 min, after which gas evolution had ceased. The viscous gum left was the digermoxane, (+)-$R'_3GeOGeR'_3$-(±) (190 mg, 98%), $[\alpha]_D$ +1.7° (*c*, 9.5) (Found: C, 68.4; H, 5.5. $C_{36}H_{34}Ge_2O$ calcd.: C, 68.9; H, 5.4%.) The IR spectrum revealed that the absorptions due to C=O and C–O, at 1655 and 1170 cm^{-1}, respectively, had been replaced by a new, intense absorption at 860 cm^{-1}, attributable to GeOGe.

The same procedure with ester (I) gave digermoxane with $[\alpha]_D$ +0.2° (*c*, 8.0), having an IR spectrum and GLC retention time identical with the sample derived from (II).

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REFERENCES

1 C. Eaborn, R. E. E. Hill, and P. Simpson, *J. Organometal. Chem.*, 37 (1972) 275.
2 A. G. Brook and H. Gilman, *J. Amer. Chem. Soc.*, 76 (1954) 77.
3 C. Eaborn, R. E. E. Hill, and P. Simpson, *J. Organometal. Chem.*, 37 (1972) 267.
4 L. H. Sommer, *Stereochemistry, Mechanism and Silicon*, McGraw Hill, New York, 1965, Chapter 3.
5 L. H. Sommer and H. Fujimoto, *J. Amer. Chem. Soc.*, 90 (1968) 982.
6 R. Baker, R. W. Bott, C. Eaborn and P. W. Jones, *J. Organometal. Chem.*, 6 (1963) 37.
7 L. H. Sommer, G. A. Parker, and C. L. Frye, *J. Amer. Chem. Soc.*, 86 (1964) 3280.
8 C. Eaborn, R. E. E. Hill, and P. Simpson, *J. Organometal. Chem.*, 37 (1972) 251.