The Stereochemistry of Substitutions at Germanium

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OPTICALLY ACTIVE germanium compounds, first prepared some five years ago,[1,2] were shown to undergo some reactions with a fair degree of stereospecificity.[1-4] We have now examined a range of reactions of optically active ethyl-(1-naphthyl)-phenylgermanium compounds, R_3GeX, with nucleophilic reagents, and the results are summarized in the Table. The stereochemical assignments are based on Brewster's rules[5] (which seem to apply well to germanium and silicon compounds[3,6,7]) and lead to internal consistency.

Loss of optical activity seems generally to be greater than in comparable reactions of methyl-(1-naphthyl)phenylsilicon compounds.[8] However, the Walden cycle (i) occurs with 90%, the cycle (ii) with 68%, and the cycle (iii) with 72% overall stereospecificity:

$$\text{(i)}\quad \begin{array}{lccc} & (+)\text{-}R_3GeH \rightarrow & (-)\text{-}R_3GeCl \rightarrow & (-)\text{-}R_3GeH \\ [\alpha]_D^{25} & +22{\cdot}5^\circ & -10{\cdot}7^\circ & -17{\cdot}9^\circ \end{array}$$

$$\text{(ii)}\quad \begin{array}{lccc} & (+)\text{-}R_3GeH \rightarrow & (-)\text{-}R_3GeCl \rightarrow & (+)\text{-}R_3GeSPh \\ [\alpha]_D^{25} & +20{\cdot}0^\circ & -9{\cdot}2 & +14{\cdot}2 \\ & & \rightarrow (+)\text{-}R_3GeH & \\ & & +7{\cdot}0 & \end{array}$$

$$\text{(iii)}\quad \begin{array}{lccc} & (+)\text{-}R_3GeH \rightarrow & (-)\text{-}R_3GeCl \rightarrow & (-)\text{-}R_3GeNC_4H_4 \\ [\alpha]_D^{25} & +21{\cdot}5 & -9{\cdot}0 & -1{\cdot}3 \\ & & \rightarrow (+)\text{-}R_3GeH & \\ & & +9{\cdot}5 & \end{array}$$

Some loss of optical activity is not surprising, since the chloride (−)-R_3GeCl is known to racemize fairly readily in solution,[9] as is the closely related chloride Me-(1-$C_{10}H_7$)PhGeCl,[10] and the hydride (+)-R_3GeH racemizes readily (without significant decomposition) when heated at 100°.[9]

Reactions of optically active Et-(1-$C_{10}H_7$)PhGeX *Compounds*[a]

Reaction No.	R_3GeX	$[\alpha]_D^{25^\circ}$	Reagents, *etc.*	Product(s)	$[\alpha]_D^{25^\circ}$	Predominant stereochemistry
(1)	R_3GeCl	−8·2	MeOH,Pr^i_2NH	R_3GeOMe	−4·9	Inv.
(2)	R_3GeCl	−9·0	PhSH,Pr^i_2NH	R_3GeSPh	+21·5	Inv.
(3)	R_3GeCl	−7·0	H_2S,Et_3N	$R_3GeSGeR_3$	+29·9	Inv.[b]
(4)	R_3GeCl	−10·7	$LiAlH_4$,Et_2O	R_3GeH	−17·2	Inv.[c]
(5)	R_3GeCl	−9·0	Bu^nLi,Et_2O	R_3GeBu^n	+6·3	Inv.
(6)	R_3GeCl	−9·0	MeLi,Et_2O	R_3GeMe	+1·6	Inv.
(7)	R_3GeCl	−9·0	*N*-lithiopyrrole, Et_2O	$R_4GeNC_4H_4$	−1·3	Inv.
(8)	R_3GeOMe	−4·9	$LiAlH_4$,Et_2O	R_3GeH	−6·0	Ret.
(9)	R_4GeOMe	+3·6	Bu^nLi,Et_2O	R_3GeBu^n	−2·7	Ret.
(10)	$R_3GeOMen$[d]	−63·8	$LiAlH_4$,Et_2O	R_3GeH	+22·6	Ret.
(11)	$R_3GeOMen$[d]	−63·8	Bu^nLi,Et_2O	R_3GeBu^n	−5·6	Ret.
(12)	R_3GeSPh	+14·2	$LiAlH_4$,Et_2O	R_3GeH	+7·0	Inv.
(13)	$R_3GeSGeR_3$	+21·5	Bu^nLi,Et_2O (2 hr.)	R_3GeBu^n, $R_3GeSGeR_3$	−2·2 + [e]	Inv.
(14)	$R_3GeSGeR_3$	+21·5	Bu^nLi,Et_3O (24 hr.)	R_3GeBu^n	0·0	
(15)	$R_3GeNC_4H_4$	−1·3	$LiAlH_4$,Et_2O	R_3GeH	+9·5	Inv.
(16)	$R_3GeNC_4H_4$	−1·3	Bu^nLi,Et_2O	R_3GeBu^n	−3·5	Inv.
(17)	$\overset{(1)}{R_3Ge}O_2C\overset{(2)}{GeR_3}$	−10·0	$LiAlH_4$,Et_2O	R_3GeH R_3GeCH_2OH	−2·8 +2·0	Inv. (Ge-1) Ret. (Ge-2)
(18)	$\overset{(1)}{R_3Ge}[O\overset{(2)}{GeR_3}\text{-}(\pm)]$	+1·7	$LiAlH_4$,Et_2O	R_3GeH $R_3GeOGeR_3$	+1·6	Ret. (Ge-1)

[a] Rotations were measured in benzene. [b] Inversion occurs at both germanium centres. [c] *Cf.* ref. 4. [d] Refers to the (−)-menthoxide. [e] Not isolated. [f] Inversion occurs at one germanium centre and retention at the other.

It will be seen from the Table that in the reactions so far studied inversion apparently occurs with the relatively good leaving groups (*cf.* ref. 8) Cl, SPh, $SGeR_3$, NC_4H_4, and O_2CGeR_3, while retention occurs with the poorer leaving groups OMe, menthoxide, and $OGeR_3$. In cases in which the corresponding reactions for Me-(1-$C_{10}H_7$)PhSiX compounds have also been studied, *viz.*, reactions (1), (3)—(6), (8)—(11), and (18),[8,11] the predominant stereochemical consequences are the same as for the germanium compounds.

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