

## The Stereochemistry of Substitutions at Germanium

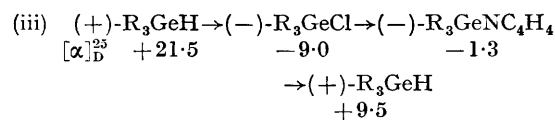
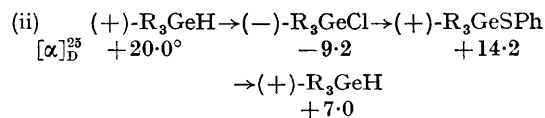
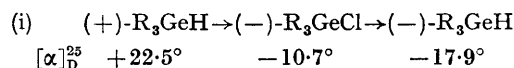
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OPTICALLY ACTIVE germanium compounds, first prepared some five years ago,<sup>1,2</sup> were shown to undergo some reactions with a fair degree of stereospecificity.<sup>1-4</sup> We have now examined a range of reactions of optically active ethyl-(1-naphthyl)-phenylgermanium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

Loss of optical activity seems generally to be greater than in comparable reactions of methyl-(1-naphthyl)phenylsilicon compounds.<sup>8</sup> However, the Walden cycle (i) occurs with 90%, the cycle

(ii) with 68%, and the cycle (iii) with 72% overall stereospecificity:



Some loss of optical activity is not surprising, since the chloride  $(-)-R_3GeCl$  is known to racemize fairly readily in solution,<sup>9</sup> as is the closely related chloride  $Me-(1-C_{10}H_7)PhGeCl$ ,<sup>10</sup> and the hydride

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,

*Reactions of optically active  $Et-(1-C_{10}H_7)PhGeX$  Compounds<sup>a</sup>*

Reaction No.	$R_3GeX$	$[\alpha]_D^{250}$	Reagents, etc.	Product(s)	$[\alpha]_D^{250}$	Predominant stereochemistry
(1)	$R_3GeCl$	-8.2	$MeOH, Pr^1_2NH$	$R_3GeOMe$	-4.9	Inv.
(2)	$R_3GeCl$	-9.0	$PhSH, Pr^1_2NH$	$R_3GeSPh$	+21.5	Inv.
(3)	$R_3GeCl$	-7.0	$H_2S, Et_3N$	$R_3GeSGeR_3$	+29.9	Inv. <sup>b</sup>
(4)	$R_3GeCl$	-10.7	$LiAlH_4, Et_2O$	$R_3GeH$	-17.2	Inv. <sup>c</sup>
(5)	$R_3GeCl$	-9.0	$Bu^aLi, Et_2O$	$R_3GeBu^a$	+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	$Bu^aLi, Et_2O$	$R_3GeBu^a$	-2.7	Ret.
(10)	$R_3GeOMen^d$	-63.8	$LiAlH_4, Et_2O$	$R_3GeH$	+22.6	Ret.
(11)	$R_3GeOMen^d$	-63.8	$Bu^aLi, Et_2O$	$R_3GeBu^a$	-5.6	Ret.
(12)	$R_4GeSPh$	+14.2	$LiAlH_4, Et_2O$	$R_3GeH$	+7.0	Inv.
(13)	$R_3GeSGeR_3$	+21.5	$Bu^aLi, Et_2O$ (2 hr.)	$R_3GeBu^a$ , $R_3GeSGeR_3$	-2.2 +	Inv. <sup>e</sup>
(14)	$R_3GeSGeR_3$	+21.5	$Bu^aLi, Et_2O$ (24 hr.)	$R_3GeBu^a$	0.0	
(15)	$R_3GeNC_4H_4$	-1.3	$LiAlH_4, Et_2O$	$R_3GeH$	+9.5	Inv.
(16)	$R_3GeNC_4H_4$ (1) (2)	-1.3	$Bu^aLi, Et_2O$	$R_3GeBu^a$	-3.5	Inv.
(17)	$R_3GeO_2CGeR_3$	-10.0	$LiAlH_4, Et_2O$	$R_3GeH$ , $R_3GeCH_2OH$	-2.8 +2.0	Inv. (Ge-1) Ret. (Ge-2)
(18)	$R_3Ge[OGeR_3-(\pm)]$	+1.7	$LiAlH_4, Et_2O$	$R_3GeH$ , $R_3GeOGeR_3$	+1.6	Ret. (Ge-1)

<sup>a</sup> Rotations were measured in benzene. <sup>b</sup> Inversion occurs at both germanium centres. <sup>c</sup> Cf. ref. 4. <sup>d</sup> Refers to the  $(-)$ -menthoxide. <sup>e</sup> Not isolated. <sup>f</sup> Inversion occurs at one germanium centre and retention at the other.

$(+)-R_3GeH$  racemizes readily (without significant decomposition) when heated at  $100^\circ$ .<sup>9</sup>

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  $O_2CGeR_3$ ,

*viz.*, reactions (1), (3)—(6), (8)—(11), and (18),<sup>8,11</sup> the predominant stereochemical consequences are the same as for the germanium compounds.

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