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ORGANOGERMANIUM COMPOUNDS

X*. THE STEREOCHEMISTRY OF SUBSTITUTION AT GERMANIUM IN SOME REACTIONS WITH NUCLEOPHILIC REAGENTS

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SUMMARY

The preparation of a range of derivatives from the compound (*R*)(+)-Et(1-$C_{10}H_7$)PhGeH has led to the establishment of the stereochemistries of some nucleophilic substitutions at the germanium atom. For the reactions studied in both silicon and germanium systems, the stereochemistries are identical to those previously established for the Me(1-$C_{10}H_7$)PhSiX compounds.

Contrary to results with the Me(1-$C_{10}H_7$)PhSiX compounds, the signs of the plain optical rotatory dispersion curves of Et(1-$C_{10}H_7$)PhGeX compounds above 320 nm do not show a simple correlation with the structures assigned on chemical grounds and by application of Brewster's Rules.

INTRODUCTION

We previously described the preparation of the optically-active germanium compound (+)-ethyl(1-naphthyl)phenylgermane, (+)-R'_3GeH**, and demonstrated the occurrence of the Walden cycle shown in eqn. (1)[5,6]. (The occurrence of the same

$$(+)\text{-}R'_3GeH + Cl_2 \rightarrow (-)\text{-}R'_3GeCl \rightarrow (-)\text{-}R'_3GeH \qquad (1)$$

cycle with the closely related methyl(1-naphthyl)phenylgermanium system, R_3GeX, was independently demonstrated by Brook and Peddle[4].) We now describe a study of the stereochemistry of a range of reactions of optically-active R'_3GeX compounds with nucleophilic reagents, the results of which have been briefly reported previously[7].

RESULTS AND DISCUSSION

The chemical and optical consequences of the reactions studied are shown in

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* For Part IX see ref. 1.

** The hydride was not necessarily optically pure, as discussed below. We use R'_3, rather than R_3, in order to indicate that the organic groups are not identical with those in Sommer's Me(1-$C_{10}H_7$)-PhSiX series (denoted R_3SiX)[2] or Brook and Peddle's Me(1-$C_{10}H_7$)PhGeX series, (denoted R_3GeX)[3,4].

TABLE 1

REACTIONS OF OPTICALLY ACTIVE $Et(1\text{-}C_{10}H_7)PhGeX$ COMPOUNDS

R'_3GeX	$[\alpha]_D^{25}$ [a] (°)	*Reagents, etc.*	*Product*	$[\alpha]_D^{25}$ [a] (°)	*Predominant stereochemistry*
R'_3GeCl	−8.2	MeOH, $i\text{-}Pr_2NH$	R'_3GeOMe	−4.9	Inv.
R'_3GeCl	−9.0	PhSH, $i\text{-}Pr_2NH$	R'_3GeSPh	+21.5	Inv.
R'_3GeCl	−7.0	H_2S, Et_3N	$R'_3GeSGeR_3$	+29.9	Inv.[b]
R'_3GeCl	−10.7	$LiAlH_4$, Et_2O	R'_3GeH	−17.2	Inv.[c]
R'_3GeCl	−9.0	n-BuLi, Et_2O	$R'_3GeBu\text{-}n$	+6.3	Inv.
R'_3GeCl	−9.0	MeLi, Et_2O	R'_3GeMe	+1.6	Inv.
R'_3GeCl	−9.0	*N*-lithiopyrrole, Et_2O	$R'_3GeNC_4H_4$	−1.3	Inv.
R'_3GeOMe	−4.9	$LiAlH_4$, Et_2O	R'_3GeH	−6.0	Ret.
R'_3GeOMe	+3.6	n-BuLi, Et_2O	$R'_3GeBu\text{-}n$	−2.7	Ret.
$R'_3GeOMen$[d]	−63.8	$LiAlH_4$, Et_2O	R'_3GeH	+22.6	Ret.
$R'_3GeOMen$[d]	−63.8	n-BuLi, Et_2O	$R'_3GeBu\text{-}n$	−5.6	Ret.
R'_3GeSPh	+14.2	$LiAlH_4$, Et_2O	R'_3GeH	+7.0	Inv.
$(R'_3Ge)_2S$	+17.6	n-BuLi, Et_2O (0.5 h)	$R'_3GeBu\text{-}n$	−2.2	Inv.
$(R'_3Ge)_2S$	+21.1	n-BuLi, Et_2O (24 h)	$R'GeBu\text{-}n$	0.0	Rac.
$R'_3GeNC_4H_4$	−1.3	$LiAlH_4$, Et_2O	R'_3GeH	+9.5	Inv.
$R'_3GeNC_4H_4$	−1.3	n-BuLi, Et_2O	$R'_3GeBu\text{-}n$	−3.5	Inv.

[a] Rotations were measured in benzene.

[b] Inversion occurs at both germanium centres.

[c] *Cf.* ref. 5.

[d] Refers to the (−)-menthoxide.

TABLE 2

OPTICAL CYCLES AND PSEUDO-CYCLES FROM $(R)(+)\text{-}Et(1-C_{10}H_7)PhGeH$

Optical cycle	*Overall stereochemical result and stereospecificity (%)*	
$(+)\text{-}R'_3GeH \rightarrow (-)\text{-}R'_3GeCl \rightarrow (-)\text{-}R'_3GeH$	Inv.	93[a,b]
$(+)\text{-}R'_3GeH \rightarrow (-)\text{-}R'_3GeCl \rightarrow (-)\text{-}R'_3GeOMe \rightarrow (-)\text{-}R'_3GeH$	Inv.	67
$(+)\text{-}R'_3GeH \rightarrow (-)\text{-}R'_3GeCl \rightarrow (+)\text{-}R'_3GeSGeR'_3 \rightarrow (+)\text{-}R'_3GeH$	Ret.	71[c]
$(+)\text{-}R'_3GeH \rightarrow (-)\text{-}R'_3GeCl \rightarrow (+)\text{-}R'_3GeSPh \rightarrow (+)\text{-}R'_3GeH$	Ret.	68
$(+)\text{-}R'_3GeH \rightarrow (-)\text{-}R'_3GeCl \rightarrow (-)\text{-}R'_3GeNC_4H_4 \rightarrow (+)\text{-}R'_3GeH$	Ret.	72
$(+)\text{-}R'_3GeH \rightarrow (-)\text{-}R'_3GeCl \rightarrow (+)\text{-}R'_3GeBu\text{-}n$	Inv.	80[d]
$(+)\text{-}R'_3GeH \rightarrow (-)\text{-}R'_3GeCl \rightarrow (+)\text{-}R'_3GeSPh \rightarrow (-)\text{-}R'_3GeBu\text{-}n$	Ret.	71[d]
$(+)\text{-}R'_3GeH \rightarrow (-)\text{-}R'_3GeCl \rightarrow (+)\text{-}R'_3GeSGeR'_3 \rightarrow (-)\text{-}R'_3GeBu\text{-}n$	Ret.	71[d]
$(+)\text{-}R'_3GeH \rightarrow (-)\text{-}R'_3GeCl \rightarrow (-)\text{-}R'_3GeNC_4H_4 \rightarrow (-)\text{-}R'_3GeBu\text{-}n$	Ret.	84[d]

[a] Previously reported[4,5].

[b] Overall stereospecificities of 100 and 98% were reported for $(+)\text{-}Me(1\text{-}C_{10}H_7)PhMH$ where M = Ge and Si, respectively[2,3].

[c] An overall specificity of 96% was reported for $(+)\text{-}Me(1\text{-}C_{10}H_7)PhSiH$[11].

[d] In these pseudo-cycles, overall specificities are based on the approximate assumption that optically pure $(+)\text{-}R'_3GeH$ and $(+)\text{-}R'_3GeBu\text{-}n$ are obtained from the menthoxide on treatment with lithium aluminium hydride or n-butyllithium.

Table 1, along with the conclusions about the predominant stereochemistries. In Table 2 are shown the several optical cycles established, along with their overall stereospecificities. The (+)-R'_3GeH is known to have the *R*-configuration[8].

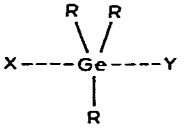
It will be appreciated that much effort had to go into the assignment of the stereochemistries of the reactions as they were studied, but in the light of the overall picture now developed it seems unnecessary to consider the assignment for each reaction individually. Instead we note the following features which we believe justify these assignments:

(1). They are internally consistent within the cycles observed.

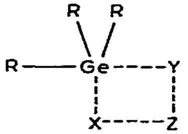
(2). They are consistent with signs of rotation deduced by application of Brewster's Rules (see below).

(3). Where the corresponding reactions are known for the R_3SiX compounds the assigned stereochemistries for the reactions of the germanium and silicon compounds are in agreement. For these cases, and for the few reactions not studied in the silicon system, the assignments are consistent with Sommer's observation that good leaving groups (*e.g.* Cl, SR) depart with inversion and poor leaving groups (*e.g.* H, OR) with retention of configuration at the metalloid atom[9–11].

It was somewhat surprising (and rather disappointing) that no example of contrasting stereochemical behaviour was found for the R'_3GeX and R_3SiX systems, since it is known that changes either in the groups attached to silicon[12,19] or in the reaction medium[12,13,14,19] can cause marked changes in stereochemistry for silicon compounds. It seems likely that other reactions will be found in which the R'_3GeX and R_3SiX compounds behave differently, but in the meantime, in view of the close correspondence there is little point in discussing either the individual reactions or the possible reaction mechanisms in detail, since this has been done so thoroughly for silicon compounds[2]. Thus for the present we make the simple assumptions that of the reactions we have observed, those proceeding with inversion at germanium involve a 180° angle between the bonds to entering group, Y, and the leaving group, X, in a transition state approximating to a trigonal bipyramid as in (I), while those proceeding with retention involve an angle of approximately 90° between the bonds to X and Y, in a four centre transition state such as (II)[15], though we also envisage the possibility that inversion could result from a 120° angle between the bonds to X and Y, as in (III) (*cf.* ref. 13). There is nothing in our results to indicate whether or not 5-coordinate germanium species are real intermediates in the reactions.



(I)



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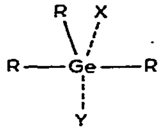

(III)

Some features of our results merit brief comment, as follows:

(*a*). The stereospecificities of the reactions are generally lower for R'_3GeX than for R_3SiX compounds. It is not surprising that this is so, since, for example, the chlorides R'_3GeCl and R_3GeCl are known to undergo racemization rapidly in solution, especially in polar media[16,17], and even the hydride R'_3GeH undergoes racemization moderately quickly in polar solvents such as ether, ethanol and tetrahydrofuran, and more rapidly on being heated alone, especially above 100° [16]. Indeed, the stereospecificities observed in some of the cycles in Table 2 are rather better than might have been expected in view of the ease of such racemizations.

(*b*). The reactions of the chloride $(-)$-R'_3GeCl with methanol or thiophenol in the presence of a base, and with n-butyllithium, methyllithium, and lithium aluminium hydride all involve predominant inversion at germanium*. It follows from the optical results that reduction of the compound $(+)$-R'_3GeSPh with lithium aluminium hydride also involves predominant inversion.

(*c*). In the reaction of the chloride $(-)$-R'_3GeCl with hydrogen sulphide in the presence of triethylamine, it can be assumed that the compound R'_3GeSH is formed with inversion, and that this then reacts with unchanged $(-)$-R'_3GeCl with inversion at the germanium atom of the chloride to give the final product, $(+)$-$(R'_3Ge)_2S$, in which inversion has occurred at both germanium atoms; the high rotation of the product is consistent with this. Inverted product, $(+)$-R'_3GeBu-n, is obtained, but with marked loss of activity, when $(+)$-$(R'_3Ge)_2S$ is allowed to react incompletely with n-butyllithium, but if reaction is prolonged to give complete coupling only racemic product is obtained. In the light of results in some related reactions with $(+)$-$(R_3Si^*)_2S$[11], it seems likely that the first Ge–S bond breaks fairly rapidly with inversion, and the second relatively slowly with retention, so that at complete reaction only racemic product is obtained. A separate experiment showed that $(-)$-R'_3GeBu-n does not lose any activity under the reaction conditions.

(*d*). The Walden cycle $(+)\text{-}R'_3GeH \rightarrow (-)\text{-}R'_3GeCl \rightarrow (-)\text{-}R'_3GeNC_4H_4 \rightarrow (+)\text{-}R'_3GeH$ involves an overall retention of 72% (see Table 2). In a somewhat analogous cycle in the R_3SiX system, but involving the *N*-pyrrolidine derivative, $R_3SiNHC_4H_8$, rather than the pyrrole derivative, predominant inversion was observed[10]. It follows that the stereochemistries for the germanium and silicon systems must differ either for the reaction of the chlorides with the $LiNC_4H_4$ and $LiNHC_4H_8$, respectively, or for the reaction of the germylpyrrole or silylpyrrolidine with lithium aluminium hydride in ether. In the light of the general inversion stereochemistry so far observed for chlorides in all the silicon and the germanium systems studied, it seems very likely that the reaction of $(-)$-R'_3GeCl with *N*-lithiopyrrole involves inversion, which means that the reduction of $(-)$-$R'_3GeNC_4H_4$ to the hydride $(+)$-R'_3GeH involves inversion, whereas the corresponding reduction of $(+)$-$R_3SiNHC_4H_8$ involves retention[10]. This difference is not at all surprising, and cannot be taken to imply a departure from the generalization about the agreement of the stereochemistries with silicon and germanium systems, since it is known for the silicon derivatives that relatively small changes in the structure of the amino group can result in changes of stereochemistry[10].

Reasoning similar to that in the preceding paragraph leads to the conclusion that the reaction of $(-)$-$R'_3GeNC_4H_4$ with n-butyllithium in ether, to give $(-)$-R'_3GeBu-n (see Table 2), also involves inversion.

(*e*). With the R'_3GeOR compounds, the examined reactions of the menthoxide and methoxide all appear to involve retention, as do the corresponding reactions of

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* The reactions of the chloride $(-)$-i-Pr$(1\text{-}C_{10}H_7)$PhGeCl with Grignard reagents and organolithium compounds also involve inversion[31].

the silicon alkoxides[18], although it is known that under some conditions cleavage of Si–OR bonds can involve inversion[13,14,19].

The optical purity of the hydride (+)-R'_3GeH

Except for the compound (−)-R'_3GeBu-n, which was also obtained by treatment of the menthoxide with n-butyllithium, all the optically active R'_3GeX compounds were derived from the hydride (+)-R'_3GeH, and it is thus important to note that even our best sample of the hydride, having $[\alpha]^{25}_D$ of +23.6° (benzene), was probably not optically pure. Samples of the hydride (+)-R'_3GeH obtained by lithium aluminium hydride reduction of apparently identical samples of the menthoxide, m.p. 80.0±0.5°, $[\alpha]_D$ 64±1° (benzene), gave specific rotations varying between +18 and +23.6° (in benzene). It is known that the racemization of (+)-R'_3GeH and (+)-R_3GeH in ether is catalyzed by presence of lithium aluminium hydride[16,20] and it seems likely that the variability of the rotation of the samples of the hydride (+)-R'_3GeH arises from racemization following the reduction of the menthoxide. By reducing the time taken for the reduction, we were able to obtain hydride samples with rotations consistently in the range 22.0–23.6° (benzene), but it seems unlikely that we avoided racemization entirely even in the case of the best sample.

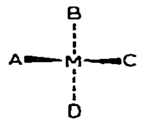
Application of Brewster's Rules

Brook and Limburg[21] showed that Brewster's Atomic Asymmetry Rules correctly predict the configurations of a range of (+)-R_3SiX compounds, and Brook and Peddle[4] found that these rules also predict correctly the configurations of the (+)-R_3GeX compounds with X = OMe, H, Cl, and COOMe, and found excellent agreement between these predictions and the configurations established by the Fredga method[3,20]. Their work represented the first application of Brewster's Rules to an asymmetric centre other than carbon, but later Sokolov and Reutov showed that the rotation calculated for (+)-ethylmethylphenylphosphine oxide by application of the Rules was in excellent agreement with the observed value[23]. We have applied Brewster's Rules with some success to our germanium systems, and so we give details of our calculations.

We use the expression (2) derived by Brewster for the molecular rotation of a molecule for which the rotation is determined by atomic asymmetry[22]. In this expression, $[M]_D$ is the molecular rotation for the sodium-D line and A, B, C and D

$$[M]_D = -k\cdot(A+B+C+D)\cdot\frac{(A-B)(A-C)(A-D)(B-C)(B-D)(C-D)}{(A+B)(A+C)(A+D)(B+C)(B+D)(C+D)} \quad (2)$$

are the atomic refraction values, R_D, of the groups A, B, C, and D which are tetrahedrally disposed about the asymmetric centre M in the configuration represented by the projection (I). By the use of the R_D values listed in Table 3, values of k can be calculated for the hydrides (R)(+)-Me(1-$C_{10}H_7$)PhMH, where M = Ge or Si, and



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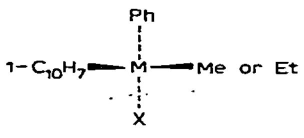

(II)

TABLE 3

R_D VALUES FOR SUBSTITUENTS X IN R_3MX[a]

X	R_D	*X*	R_D	*X*	R_D
H	1.00	SH	7.29	Ph	3.38
Cl	5.84	SPh	9.20	$1\text{-}C_{10}H_7$	4.00
Br	8.74	OH	1.59	CO_2H	3.38
F	0.81	OMe	1.49	CO_2R	3.10
NC_4H_4	2.36				

[a] Mainly from ref. 22.

TABLE 4

CALCULATED VALUES OF CONSTANT *k* IN EQN. 2

System	$[\alpha]$[a] (°)	*k*[a]
(*R*)(+)-Me(1-$C_{10}H_7$)PhGeH	+26.5°	-2.054×10^4
(*R*)(+)-Et(1-$C_{10}H_7$)PhGeH	+23.6[b]	-2.066×10^4
(*R*)(+)-Me(1-$C_{10}H_7$)PhSiH	+36.4	-2.371×10^4
(*R*)(+)-Me(1-$C_{10}H_7$)PhCH	+7.5	-4.708×10^3

[a] The values for the (+)-Et(1-$C_{10}H_7$)PhGeH system refer to rotations in benzene. The others refer to the rotations in cyclohexane.

[b] This is based on the highest rotation observed, but the sample may not have been optically pure (see text).

the results are shown in Table 4 along with the corresponding value for the compound with M=C. Use of the highest observed value of $[\alpha]_D$ for our hydride (*R*)(+)-Et(1-$C_{10}H_7$)PhGeH in benzene, *viz.* 23.6°, gives a value of *k* for the (*R*)R'_3GeX system*. Use of the values of *k* along with the appropriate R_D values then allows values of $[\alpha]_D$ to be calculated for the several series of compounds, and it will be seen from Table 5 that there is good numerical agreement between the observed and calculated values for the R_3SiX series, and moderately good agreement for the R_3GeX series. For the R'_3GeX series the numerical agreement is somewhat less satisfactory in a few cases, which is not surprising since replacement of a methyl by an ethyl group leads to conformational effects not present in the other systems, but in all cases the sign of rotation is clearly predicted to be in the direction agreeing with our assignments, which themselves lead to internal consistency within our results, and which are in complete agreement with the stereochemistries established for the R_3Si^*X compounds by Sommer. The calculations indicate that compound (*R*)-$R'_3GeNC_4H_4$ should have a small negative rotation in benzene, which is consistent with our assignments, but it should be noted that the same sample has a small positive rotation in cyclohexane.

Application of Brewster's Rules in their simplest form, as above, must fail

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* We emphasise that our best sample of the hydride (+)-R'_3GeH may not have been optically pure, as discussed above, and so the true values of *k* and of the calculated and actual rotations for this system may be higher than those we list. It will be appreciated that if Brewster's Rules apply strictly, then for rotations in the same solvent the value of *k* should be the same for R_3GeX and R'_3GeX systems.

TABLE 5

ROTATIONS CALCULATED BY USE OF BREWSTER'S RULES

	X	$[\alpha]_D$ (°)
		Observed (*calcd.*)
(*R*)-Me(1-$C_{10}H_7$)PhSiX	Cl	−6.3 (−5.9)
	Br	−28.6 (−28.8)
	F	−47.0 (−48.8)
	SH	+26.0 (+22.1)
	OH	−16.0 (−12.5)
(*R*)-Me(1-$C_{10}H_7$)PhGeX	OMe	−9.8 (−8.0)
	Cl	−6.7 (−4.5)
	CO_2H	−5.2 (−9.0)
(*R*)-Et(1-$C_{10}H_7$)PhGeX	Cl	−10.5 (−4.0)
	Br	−15.6[a] (−19.7)
	SPh	+22.0 (+23.6)
	OMe	−6.8 (−7.3)
	CO_2H	−9.8 (−10.0)
	NC_4H_4	−1.3 (−0.4)

[a] Probable approximate value in carbon tetrachloride, see text.

when serious conformational effects are present. It is presumably such effects which account for the anomalous variations in the rotations of the least soluble of the R_3SiOMen-(−), R_3GeOMen-(−), R'_3GeOMen-(−), and (1-$C_{10}H_7$)(Ph)(CH_2=CH)-Si*OMen-(−) diastereoisomers (OMen = menthoxide). In each case the least soluble diasteroisomer gives the corresponding (+)-hydride on reduction with lithium aluminium hydride[2,3,5,24] and so it is practically certain that in all cases the configuration at the atom M in the least soluble menthoxide is the same in each case, yet for the R_3SiOMen-(−) and R'_3GeOMen-(−) pairs it is the least soluble diastereoisomer which has the more negative rotation[2,5], while in the case of the R_3GeOMen-(−) and (1-$C_{10}H_7$)(Ph)(CH_2=CH)SiOMen-(−) pairs the least soluble diastereoisomer has the less negative rotation[3,24]. The behaviour of the R_3GeOMen-(−) and (1-$C_{10}H_7$)-(Ph)(CH_2=CH)SiOMen-(−) systems is in accord with predictions for menthoxides by Brewster's Rules, while that of the other two systems is not. Peddle has suggested that conformational effects render the rule inapplicable for the R_3SiOMen-(−) system, but are smaller in the R_3GeOMen-(−) system because of the slightly larger size of the central atom[20]. If this is so, it follows that in these very delicately balanced systems the introduction of a vinyl group in place of a methyl group in the silicon systems reduces the conformational effects and restores the applicability of Brewster's Rules, while replacement of a methyl by an ethyl group in the germanium systems increases the conformational effect and destroys the applicability of the Rules.

Possible formation of (−)-R'_3*GeBr*

When the hydride (+)-R'_3GeH was treated with a 1.2 molar proportion of bromine in carbon tetrachloride at room temperature the rotation changed rapidly to a negative value, reached a maximum negative value after 2 min, and then decreased, falling to half the maximum negative value in about 0.5 h. The maximum rotation corresponded to a value of $[\alpha]_D$ for (−)-R'_3GeBr of −15.6° in carbon tetrachloride, compared with a value of −19.7° predicted for benzene solutions by application of Brewster's Rules (Table 4). Analysis of the products after the rotation had fallen almost to zero indicated that hydrogen bromide cleavage of Ge–$C_{10}H_7$ bonds had occurred, and it may be this reaction which mainly causes the loss of activity in the carbon tetrachloride solution. However, attempts to isolate optically active (−)-R'_3GeBr by rapid work-up immediately after the mixing of the (+)-R_3GeH and bromine in carbon tetrachloride were unsuccessful, racemic material being obtained. It seems that the bromide readily undergoes racemization during work-up, which is not surprising in view of the tendency even of the chloride to undergo self-racemization[16] (*cf.* ref. 17).

It is noteworthy that Brook and Peddle obtained only the racemic bromide from the reaction between the hydride (+)-R_3GeH and bromine in carbon tetrachloride, and Peddle suggested that the mechanism of the bromination might be very different from that of chlorination, possibly involving free radical processes[20]. Our results suggest that the optically active bromide is indeed formed, with retention of configuration as is the chloride but that it undergoes racemization readily during work-up.

USE OF PLAIN DISPERSION CURVES, AND A NOTE ON SOLVENT EFFECTS ON ROTATIONS

Sommer and his colleagues showed that analysis of the shapes of plain optical rotatory dispersion curves leads to correlations of relative configurations of Me(1-$C_{10}H_7$)PhSiX compounds which are in complete agreement with assignments based on other methods[25]. Thus the compounds (+)-R_3SiX, where X=H, OH, F, OMe, and OCOMe, and (−)-R_3SiCl, which have the same (*R*) configurations, give positive plain curves above 340 nm*. We find that there is no such consistency with R'_3GeX compounds.

In Table 6 are listed the specific rotations $[\alpha]_\lambda$ of various R'_3GeX compounds, at various wave lengths, λ, down to 320 nm, and the signs of the plain curves associated with these rotations. In Table 7 are shown the absolute configurations (based on assignment of the *R*-configuration to (+)-R'_3GeH[8]) which would be implied if compounds of the same sign of plain curve had the same configurations, as is the case with the silicon compounds, and it will be seen that the results are seriously at variance with the assignments made on chemical grounds and by application of Brewster's Rules. A convincing example of the breakdown of the use of the plain curves is that (−)-R'_3GeCOOMe gives a plain curve of opposite sign to that of (−)-R'_3GeCOOH, even though the ester is obtained from the acid, by treatment with diazomethane, without involvement of the germanium centre. Furthermore, whereas the signs of the optical rotation of R'_3GeX agree completely with those of the analogous R_3SiX compounds of the same configuration, opposite signs of the plain curves are found for several of the R'_3GeX/R_3SiX pairs.

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* Sommer and McLick have more recently studied the ORD and CD behaviour of these compounds below 340 nm[26], which is a more significant region of the spectrum.

TABLE 6

MOLECULAR ROTATIONS FOR R'_3GeX COMPOUNDS IN CYCLOHEXANE AT VARIOUS WAVE LENGTHS

Compound	$[M]_\lambda$					*Sign of plain curve*
λ (*nm*)	589	500	400	350	320	
(+)-R'_3GeH	12	41	75	122	171	Positive
(−)-R'_3GeCl	−9	−10	−23	−28	−27	Negative
(+)-R'_3GeBu-n	3	3	5	9	16	Positive
(−)-R'_3GeOMe	0	−1	−1	−3	−18	Negative
(+)-R'_3GeSPh	22	16	40	84	140	Positive
(+)-$R'_3GeNC_4H_4$[a]	4	8	15	27	51	Positive
(−)-R'_3GeCO_2H	−4	−15	−10	+8	+45	Positive
(−)-$R'_3GeCOOMe$	−3	−3	−9	−12	−18	Negative
(−)-$R'_3GeCH(OH)CHMe(CH_2)_3CH_2$	−7	−9	−14	−19	−31	Negative

[a] The compound had a negative rotation at 589 nm in benzene.

TABLE 7

COMPARISON OF ASSIGNED CONFIGURATIONS WITH THOSE IMPLIED BY THE PLAIN OPTICAL ROTATORY DISPERSION CURVES

Compound	*Sign of plain curve*	*Confign. implied by ORD*	*Actual confign. assigned on other grounds*
(*R*)(+)-R'_3GeH	+	*R*[a]	*R*
(−)-R'_3GeCl	−	*S*	*R*
(+)-R'_3GeBu-n	+	*R*	*S*
(−)-R'_3GeOMe	−	*S*	*S*
(+)-R'_3GeSPh	+	*R*	*S*
(−)-$R'_3GeNC_4H_4$	+	*R*	*S*
(−)-R'_3GeCO_2H	+	*R*	*R*
(−)-$R'_3GeCOOMe$	−	*S*	*R*
(−)-$R'_3GeCH(OH)CHMe(CH_2)_3CH_2$	−	*S*	*R*

[a] Assumed.

While we have not carried out any systematic study of the influence of solvents on the specific rotation of the R'_3GeX compounds, we have incidentally noticed some quite large effects on values of $[\alpha]_D$ simply on changing from benzene to cyclohexane. This can be seen from the data in Table 8, which refers to measurements in the two solvents on the same sample of an R'_3GeX compound at fairly similar concentrations. The most marked effects are the change in the sign of rotation found for $R'_3GeNC_4H_4$ and the fall of the rotation of the (−)-R'_3GeOMe compound almost to zero in cyclohexane. We have not, on the other hand, observed any significant dependence of rotations on concentration.

TABLE 8

SOLVENT EFFECTS ON SPECIFIC ROTATIONS OF R'_3GeX COMPOUNDS

Compound	$[\alpha]_D$, *benzene* (°)	$[\alpha]_D$, *cyclohexane* (°)
(+)-R'_3GeH	+19.0	+12.0
(−)-R'_3GeOMe	−4.9	−0.3
(−)-R'_3GeCl	−8.7	−9.2
(−)-$R'_3GeNC_4H_4$	−0.9	+3.5
(+)-R'_3GeMe	+1.9	+4.8
(−)-R'_3GeBu-n	−2.7	−0.8
(−)-R'_3GeCO_2H	−9.6	−4.4

CRYSTAL CHARACTER AND CELL DIMENSIONS OF (+)-R'_3GeH (In association with Dr. A. T. McPhail).

An attempt to determine the complete crystal structure of (+)-R'_3GeH was abandoned because the only satisfactory single crystal obtained deteriorated during the study, in which X-ray reflection intensities were recorded on multiple-film equi-inclination Weissenberg photographs of *hk*0-2 layers, a total of 730 independent structure amplitudes being evaluated.

The unit cell dimensions were determined from precession photographs taken with Mo-$K\alpha$ radiation. The crystal was orthorhombic, with $a = 8.94$, $b = 19.32$, and $c = 8.80$ Å. Density (calcd.), 1.306 g/cm^3; $Z = 4$; space group $P2_12_12_1(D_2^4)$; absorption coefficient for X-rays ($\lambda = 1.542$ Å), $\mu = 27.7$ cm^{-1}. A comparison of the cell dimensions for (+)-R'_3GeH, (+)-R_3SiH[27] and (+)-R_3GeH[28], all of which have space group $P2_12_12_1$, is shown in Table 9. It can be concluded with confidence that the structures of all three are very similar, although it is known that the distortion from planarity of the naphthyl group is smaller in (+)-R_3GeH than in (+)-R_3SiH[28].

TABLE 9

UNIT CELL DIMENSIONS (Å)

	(+)-Et(1-$C_{10}H_7$)PhGeH	(+)-Me(1-$C_{10}H_7$)PhGeH	(+)-Me(1-$C_{10}H_7$)PhSiH
a	8.94	8.82	8.72
b	19.32	20.09	19.89
c	8.80	7.93	7.88

EXPERIMENTAL

General

Solvents were carefully dried. Ether and n-pentane were distilled from lithium aluminium hydride under dry nitrogen into the reaction vessel. Chloroform and carbon tetrachloride were dried over phosphorus pentoxide and distilled from it, and amines, including pyrrole, were dried over barium oxide for at least 24 h and distilled from it as required. Methanol was dried with aluminium tert-butoxide.

GLC analyses were carried out on columns of 5% S.E. 30 on 100–120 mesh silanized Chromosorb G.

Optical rotations. These were measured at 25° in benzene unless otherwise stated.

ORD studies. Measurements were made with a Bendix Ericson Spectropolarimeter Model 62.

Preparation of (+)-R'_3GeH

A mixture of (−)-ethyl(1-naphthyl)phenylgermyl (−)-menthoxide[5−7] (4 g, 8.7 mmole), m.p. 80.0°, $[\alpha]_D$ −63.8° (benzene), and lithium aluminium hydride (1.3 g, 33 mmole) in ether (200 ml) was refluxed for 2 h. Work up as previously described[5−7] gave (+)-ethyl(1-naphthyl)phenylgermane (2.4 g, 95%), m.p. 32–33°, $[\alpha]_D$ +23.6° (*c*, 8.1).

Preparation of (−)-R'_3GeBu-*n*

A mixture of (−)-ethyl(1-naphthyl)phenylgermyl (−)-menthoxide, (400 mg, 0.9 mmole), $[\alpha]_D$ −63.8°, and n-butyllithium (1.5 mmole of a 1.6 *M* solution in hexane) in pentane (25 ml) was refluxed for 30 min. The mixture was cooled and shaken vigorously with a little water (2 mmole). Lithium hydroxide was filtered off, and the filtrate was evaporated to leave an oil. This was heated at 160° at 0.2 mm until the specific rotation remained constant, and the residue was (−)-butylethyl(1-naphthyl)phenylgermane (280 mg, 85%), n_D^{25} 1.6031, $[\alpha]_D$ −5.6 (*c*, 6.8). The IR spectrum was identical with that of an authentic sample of (±)-R'_3GeBu-n.

Reactions of (−)-R'_3GeCl

(*i*). A solution of (−)-R'_3GeCl, (100 mg, 0.3 mmole), $[\alpha]_D$ −9.0°, in carbon tetrachloride was added to an ice-cooled mixture of thiophenol (0.030 ml, 0.3 mmole) and anhydrous diisopropylamine (0.05 ml, 0.35 mmole) in a Schlenk tube. The precipitate was filtered off and volatile materials were removed under reduced pressure at 60° to leave (+)-ethyl(1-naphthyl)phenylgermyl thiophenoxide (nc) (105 mg, 97%), $[\alpha]_D$ +21.5° (*c*, 5.25), n_D^{25} 1.6703 as an oil. The IR spectrum was identical with that of (±)-ethyl(1-naphthyl)phenylgermyl thiophenoxide, n_D^{25} 1.6703, prepared by the same method but on a larger scale, and culminating in distillation (b.p. 210–214°/ca. 0.3 mm). (Found: C, 69.0; H, 5.3. $C_{24}H_{22}GeS$ calcd.: C, 69.5; H, 5.3%.)

Strong bands in the IR spectrum at 408 and 375 cm^{-1} can be attributed to the Ge–S bond (*cf.* ref. 29).

(*ii*). A solution of (−)-R'_3GeCl (230 mg, 0.70 mmole), $[\alpha]_D$ −7.0°, in pentane (10 ml) was added to an ice-cooled solution of anhydrous triethylamine (0.15 ml, 1.5 mmole) in pentane through which a rapid stream of anhydrous hydrogen sulphide was bubbling. After 5 min the precipitate was filtered off in a Schlenk tube and volatile materials were removed under reduced pressure. The glass remaining was recrystallized twice from pentane to give (+)-1,3-diethyl-1,3-di-1-naphthyl-1,3-diphenyldigermthiane (nc) (170 mg, 70%), m.p. 48–50°, $[\alpha]_D$ +29.9° (*c*, 8.5). (Found: C, 67.5; H, 5.2. $C_{36}H_{34}GeS$ calcd.: C, 67.4; H, 5.5%.) An intense band at 415 cm^{-1} in the IR spectrum can be attributed to the Ge–S–Ge linkage (*cf.* ref. 29).

(*iii*). A solution of (−)-R'_3GeCl (400 mg, 1.1 mmole), $[\alpha]_D$ −9.1°, in ether

(20 ml) was added to a suspension of *N*-lithiopyrrole obtained by slow addition of n-butyllithium (14 mmole) of a 1.6 *M* solution in hexane) to a stirred ice-cooled solution of pyrrole (0.97 g, 15 mmole) in pentane (20 ml). The mixture was refluxed for 24 h, then added to 0.1 *M* hydrochloric acid. Extraction with ether, followed by washing, drying ($MgSO_4$) and evaporation of the extract gave a solid, which was recrystallized three times from ethanol to give (−)-*N*-[ethyl(1-naphthyl)phenylgermyl]pyrrole (nc) (260 mg, 60%), m.p. 68–69°, $[\alpha]_D$ −1.3° (*c*, 13.0). (Found: C, 71.2; H, 5.4; N, 3.7. $C_{22}H_{22}GeN$ calcd.: C, 71.2; H, 5.1; N, 3.8%.) The IR spectrum showed, in addition to the bands associated with the R'_3Ge group, strong bands at 1037, 1077, 1177, and 1260 cm^{-1}.

Optically inactive, but otherwise identical (±)-$R'_3GeNC_4H_4$ was similarly obtained in 80% yield from (±)-R'_3GeCl.

(*iv*). A solution of (−)-R'_3GeCl (100 mg, 0.30 mmole), $[\alpha]_D$ −9.0°, in pentane (15 ml) was added quickly to a mixture of anhydrous methanol (0.015 ml, 0.3 mmole) and diisopropylamine (0.05 ml, 0.35 mmole) in pentane (20 ml) at −70° in a Schlenk tube. The precipitate was filtered off, and solvent removed under reduced pressure from the filtrate to leave an oil, which crystallized to give solid (−)-ethyl(methoxy)-(1-naphthyl)phenylgermane (90 mg, 90%), m.p. 65–66°, $[\alpha]_D$ −4.9° (*c*, 4.5). (Found: C, 67.5; H, 6.1. $C_{19}H_{20}GeO$ calcd.: C, 68.2; H, 6.0%.)

(*v*). A mixture of (−)-R'_3GeCl (310 mg, 0.9 mmole), $[\alpha]_D$ −8.1° and an excess of n-butyllithium in pentane (25 ml) was refluxed for 30 min. The precipitate was filtered off, and the solvent was removed from the filtrate under reduced pressure. The residual oil was distilled to give (+)-n-butylethyl(1-naphthyl)phenylgermane (200 mg, 65%) n_D^{25} 1.6041, $[\alpha]_D$ +6.3 (*c*, 8.0), as an oil. (Found: C, 72.9; H, 7.0. $C_{22}H_{26}Ge$. calcd.: C, 73.0; H, 7.2%.)

(*vi*). Methyllithium was prepared from methyl iodide (2.13 g, 15 mmole) and lithium (231 mg, 30 mmole) in ether (20 ml). The excess of lithium was filtered off, the solution was cooled to −80°, and (−)-R'_3GeCl (490 mg, 1.5 mmole) $[\alpha]_D$ −9.0°, in ether (15 ml) was added rapidly with stirring. After a few minutes at −80° the mixture was allowed to warm to room temperature during 3 h. Ethanol was carefully added to destroy any unchanged methyllithium, and the mixture was added to 0.1 *M* hydrochloric acid. Extraction with ether followed by washing, drying ($MgSO_4$), and evaporation of the extract left a gum (436 mg, 88%), which was distilled (bath temperature 160°/ca. 0.05 mm) to give (+)-ethylmethyl(1-naphthyl)phenylgermane as a colourless oil, n_D^{25} 1.6244 $[\alpha]_D$ +1.6° (*c*, 22). (Found: C, 70.7; H, 6.3. $C_{19}H_{20}Ge$ calcd.:.C, 71.0; H, 6.3%.) The IR spectrum of the product was identical with that of the materials obtained by treatment of R'_3Ge^*Li with methyl halides[30].

(*vii*). Reduction of (−)-R'_3GeCl, $[\alpha]_D$ −10.7°, with lithium aluminium hydride, as previously described[6], gave (+)-R'_3GeH, $[\alpha]_D$ −17.9° (*c*, 5.5).

Reactions of (−)- *and* (+)-R'_3GeOMe

(*i*). A mixture of (+)-R'_3GeOMe (140 mg, 0.4 mmole), $[\alpha]_D$ +3.6°, and n-butyllithium (1 mmole) in hexane (25 ml) was refluxed for 15 min. Solid was filtered off, and volatile material was removed under reduced pressure at 40° to give, as an oil, (−)-n-butylethyl(1-naphthyl)phenylgermane (150 mg, 100%), n_D^{25} 1.6038, $[\alpha]_D$ −2.7° (*c*, 7.5), having an IR spectrum identical with that of an authentic sample.

(*ii*). A mixture of (−)-R'_3GeOMe (83 mg, 0.29 mmole) $[\alpha]_D$ −4.9°, and lithium aluminium hydride (300 mg, 0.8 mmole) in ether (30 ml) was refluxed for 30 min. After cautious addition of acetone the mixture was added to 0.1 *M* hydrochloric acid, and ether extraction, followed by washing and drying ($MgSO_4$) of the extract and removal of volatile material gave (−)-R'_3GeH (87 mg, 96%), $[\alpha]_D$ −6.0° (*c*, 4.4), having an IR spectrum identical with that of an authentic sample. Similarly from (+)-R'_3GeOMe was obtained (+)-R'_3GeH (98%), $[\alpha]_D$ +8.3° (*c*, 5.7).

Reactions of (−)-$R'_3GeNC_4H_4$

(*i*). A mixture of (−)-$R'_3GeNC_4H_4$ (99 mg, 0.3 mmole) $[\alpha]_D$ −1.3°, and n-butyllithium (10 mmole of a 1.6 *M* solution in hexane) in pentane (30 ml) was refluxed for 30 min. A little water was cautiously added to the cooled solution and solids were removed by filtration. Removal of solvent left, as an oil, (−)-n-butylethyl(1-naphthyl)-phenylgermane (93 mg, 90%), n_D^{25} 1.6025, $[\alpha]_D$ −3.5° (*c*, 4.7), having an IR spectrum identical with that of an authentic sample.

(*ii*). A mixture of (−)-$R'_3GeNC_4H_4$, (100 mg, 0.30 mmole), $[\alpha]_D$ −1.3°, and lithium aluminium hydride (400 mg, 1.0 mmole) in ether (25 ml) was refluxed for 6 h, this being found to be the minimum time for complete reduction. After cautious addition of acetone, the mixture was added to 0.1 *M* hydrochloric acid, and the ethereal layer was separated, washed, and dried ($MgSO_4$), and the ether was removed. The residual oil was eluted in chloroform through a 1 m × 0.5 mm column of chromatographic silica gel, to give (+)-R'_3GeH (70 mg, 90%), $[\alpha]_D$ +9.8° (*c*, 3.5), having an IR spectrum identical with that of an authentic sample.

Reduction of R'_3GeSPh

A mixture of (+)-R'_3GeSPh (134 mg, 0.30 mmole), $[\alpha]_D$ +14.3°, and lithium aluminium hydride (400 mg, 1.0 mmole) was refluxed for 1 h. The mixture was cooled, and after addition of acetone was added to 0.1 *M* hydrochloric acid. Ether extraction, followed by washing and drying ($MgSO_4$) of the extract, and removal of volatile material at 50° under reduced pressure left (+)-R'_3GeH (77 mg, 90%), $[\alpha]_D$ +7.0° (*c*, 3.9), having an IR spectrum identical with that of an authentic sample.

Reaction of (+)-$(R'_3Ge)_2S$ *with n-butyllithium*

(*i*). A mixture of (+)-$(R'_3Ge)_2S$ (300 mg, 0.5 mmole), $[\alpha]_D$ +17.6°, and n-butyllithium (1.0 mmole of a 1.6 *M* solution in hexane) in ether (30 ml) was refluxed for 30 min then cooled and added to 0.1 *M* hydrochloric acid. Ether extraction, followed by washing and drying ($MgSO_4$) of the extract and removal of solvent left a viscous oil, $[\alpha]_D$ +7.9° (*c*, 13.0). This was dissolved in ether and treated with mercuric chloride (70 mg, 0.3 mmole), and the yellow precipitate which formed was filtered off to leave a clear oil, $[\alpha]_D$ −0.6° (*c*, 12.5). This was eluted in chloroform through a 1 m × 8 mm column of B.D.H. chromatographic silica gel. The first (and only) fraction recovered was (−)-R'_3GeBu-n (115 mg, 40%), n_D^{25} 1.6050, $[\alpha]_D$ −2.2° (*c*, 5.7), having an IR spectrum identical with that of an authentic sample.

(*ii*). A mixture of (+)-$(R'_3Ge)_2S$ (230 mg, 0.30 mmole), $[\alpha]_D$ +21.1°, and n-butyllithium (0.7 mmole) in ether (25 ml) was refluxed for 24 h. The cooled solution was added to 0.1 *M* hydrochloric acid, and ether extraction, followed by washing, drying ($MgSO_4$), and evaporation of the extract left (±)-R'_3GeBu-n (240 mg, 95%), n_D^{25} 1.6057, having an IR spectrum identical with that of an authentic sample. Treatment with mercuric chloride in ether gave no precipitate, showing that no unchanged $(R'_3Ge)_2S$ was present.

(*iii*). When (−)-R'_3GeBu-n (150 mg, 0.40 mmole), $[\alpha]_D$ −5.6°, was refluxed with n-butyllithium (1 mmole) in ether (25 ml) for 24 h it was recovered with unchanged rotation. Distillation of the same sample (200°/ca. 0.2 mm) also caused no change in the rotation.

Bromination of (+)-R'_3GeH

A solution of (+)-R'_3GeH (151 mg, 0.50 mmole), $[\alpha]_D$ +22.0° (+17.3° in CCl_4), in carbon tetrachloride (2 ml) was treated at 0° with bromine (0.60 mmole of a solution of 100 g Br_2 in 100 ml CCl_4). The mixture was shaken vigorously for 5 s and transferred quickly to a polarimeter tube at room temperature. The rotation changed rapidly from the initial positive value to reach after 2 min a maximum negative rotation corresponding to a value of $[\alpha]_D$ of 15.6° (*c*, 9.5 in CCl_4) if all the rotation was due to (−)-R'_3GeBr, then fell to half this value in approximately 18 min. In 100 min the rotation fell to ca. 15% of its peak value in one experiment and to 5% in a second similar experiment. Solvent and unchanged bromine were removed after this time, to leave an oil, which was shown by GLC to contain substantial amounts of naphthalene and dibromo(ethyl)phenylgermane and only a small amount of R'_3GeBr.

In several experiments the R'_3GeBr was isolated quickly after mixing of the reactants in carbon tetrachloride, sometimes with a deficiency of bromine, and sometimes in presence of triethylamine, but in all cases the product obtained was racemic.

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