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ORGANOGERMANIUM COMPOUNDS
XII*. THE STEREOCHEMISTRY OF THE REACTIONS BETWEEN OPTICALLY ACTIVE ETHYL(1-NAPHTHYL)PHENYLGERMYLLITHIUM AND ALKYL HALIDES

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SUMMARY

The interaction of optically active ethyl(1-naphthyl)phenylgermyllithium, R'_3-Ge*Li, with alkyl halides, RX, to give optically active R'_3Ge*R compounds, occurs with predominant retention of configuration at germanium in the case of MeBr, i-PrCl, i-PrBr, n-BuCl, n-BuBr, t-BuCl, t-BuBr, CH_2=$CHCH_2Cl$, CH_2=$CHCH_2Br$ and $PhCH_2Cl$, but with predominant inversion in the case of MeI, i-PrI, CH_2=$CHCH_2I$, $PhCH_2I$, and $PhCH_2Br$. It is suggested that the retention reactions involve direct coupling between R'_3Ge*Li and RX, in a four-centre process, while the inversion reactions involve halogen–lithium exchange, to give R'_3GeX and RLi, also in a four-centre retentive process, followed by coupling between R'_3GeX and RLi in an invertive process.

INTRODUCTION

We previously described the reactions with carbonyl compounds of the optically active (*R*)-Et(1-$C_{10}H_7$)PhGeLi obtained as an ethereal solution by treating the hydride (*R*)(+)-Et(1-$C_{10}H_7$)PhGeH with n-butyllithium[1]. We discuss below the reactions of the germyllithium reagent (referred to as R'_3Ge*Li, or, where more appropriate, as (*R*)-R'_3Ge*Li) with alkyl halides, in which an interesting stereochemical crossover appears. A preliminary account has been published previously[2] and the reaction with the methyl iodide has also been reported earlier[3].

RESULTS AND DISCUSSION

The results of the reactions of R'_3Ge*Li with some organic halides RX are shown in Table 1, which also reveals that the rate of reaction usually falls markedly in the sequence $X = I > Br > Cl$. We have previously shown that (+)-R'_3GeH and (+)-R'_3GeBu-n have opposite configurations[4], and it follows that the reaction of n-butyl chloride or bromide with R_3Ge*Li involves predominant retention of

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* For Part XI see ref. 1.

TABLE 1

REACTIONS OF R'_3Ge^*Li WITH THE ORGANIC HALIDES RX

$[\alpha]_D^{25}$ (°) of (*R*)-R'_3GeH[a]	RX	Reaction time(s)[b]	$[\alpha]_D^{25}$ (°) of R'_3GeR[a]	Predominant stereochemistry
+13.0	MeBr	5 min[c]	−0.2	Ret.
+22.0	MeI	1 min[c]	+1.9	Inv.
+13.0	i-PrCl	16 h, 20 h	−0.6	Ret.
+13.0	i-PrBr	15 min, 1 h	−4.7	Ret.
+13.0	i-PrI	1 min[c]	+2.9	Inv.
+13.0	n-BuCl	5 h, 7 h	−2.7	Ret.
+13.0	n-BuBr	30 min, 4 h	−2.7	Ret.
+13.0	n-BuI	1 min[c]	+2.7	Inv.
+22.0	t-BuCl	18 h, 20 h	−6.3	Ret.
+22.0	t-BuBr	1 h, 2 h	−6.2	Ret.
+22.0	$CH_2{=}CHCH_2Cl$	4 h, 6 h	−1.6	Ret.
+22.0	$CH_2{=}CHCH_2Br$	1 min[c]	−1.6	Ret.
+22.0	$CH_2{=}CHCH_2I$	1 min[c]	+1.2	Inv.
+22.0	$PhCH_2Cl$	5 min[c], 1 h	−1.3	Ret.
+22.0	$PhCH_2Br$	4 h, 8 h	+5.2	Inv.
+22.0	$PhCH_2I$	1 min[c]	+6.1	Inv.

[a] All rotations were measured in benzene. [b] Where two times are given, the first denotes the time taken for disappearance of the red colour of the R'_3Ge^*Li, and the second the complete time for which reaction was allowed to continue. Reactions were under reflux, except as noted in footnote (*c*). [c] No external heating.

configuration at germanium while that of n-butyl iodide involves predominant inversion.

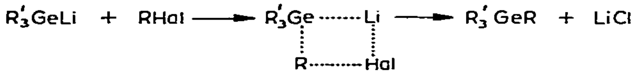
It is known that the (+)-R'_3GeH reacts with chlorine to give (−)-R'_3GeCl with retention of configuration, and that the chloride reacts with methyllithium, in what can be assumed with confidence to be an invertive process[4], to give (+)-R'_3GeMe. It thus follows, from a comparison of sequences (1) and (2), that the reaction of methyl iodide with R'_3Ge^*Li involves inversion (*cf.* ref. 5).

$$(+)\text{-}R'_3GeH \xrightarrow[\text{Ret.}]{Cl_2} (-)\text{-}R'_3GeCl \xrightarrow[\text{Inv.}]{\text{MeLi}} (+)\text{-}R'_3GeMe \qquad (1)$$

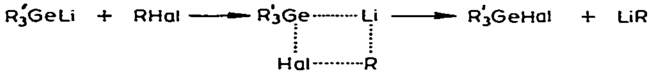
$$(+)\text{-}R'_3GeH \xrightarrow[\text{Ret.}]{n\text{-BuLi}} R'_3Ge^*Li \xrightarrow[\text{Inv.}]{\text{MeI}} (+)\text{-}R'_3GeMe \qquad (2)$$

By analogy, we conclude that the reactions with RCl and RBr involve predominant retention of configuration when R = i-Pr, t-Bu and $CH_2{=}CHCH_2$, and that the reactions with the corresponding iodides involve inversion (except possibly for tert-butyl iodide, which was not studied). With benzyl halides, both the bromide and the iodide react with predominant inversion, and even with the chloride much racemization accompanies the predominant retention. The considerable racemization which accompanies the predominant retention in the reaction involving isopropyl chloride appears somewhat anomalous, since in this case the bromide clearly reacts with retention.

In explanation of the results, we suggest that retentive reactions, as given by most chlorides and bromides, involve direct formation of the R'_3GeR product in a single-step, four-centre process (3), while the invertive reactions, mainly involving iodides, proceed through lithium–halogen exchange in a two-step sequence (4). In such a sequence the initial halogen–lithium exchange would be expected to involve a four-centre, retentive process, (4a) while coupling of the R'_3GeHal with RLi, (4b) would almost certainly involve inversion[4], so that overall inversion would occur, as observed.



$$R'_3GeLi + RHal \longrightarrow \begin{array}{c} R'_3Ge\cdots\cdots Li \\ \vdots \qquad \vdots \\ R\cdots\cdots Hal \end{array} \longrightarrow R'_3GeR + LiCl \quad (3)$$



$$R'_3GeLi + RHal \longrightarrow \begin{array}{c} R'_3Ge\cdots\cdots Li \\ \vdots \qquad \vdots \\ Hal\cdots\cdots R \end{array} \longrightarrow R'_3GeHal + LiR \quad (4a)$$

$$R'_3GeHal + RLi \xrightarrow{Inv.} R'_3GeR + LiHal \quad (4b)$$

In agreement with the explanation, we found that when racemic R'_3GeLi [from (±)-R'_3GeH] was treated with methyl iodide in the presence of n-butyllithium, a substantial amount of the compound R'_3GeBu-n was formed along with R'_3GeMe, whereas with methyl bromide only a trace of the n-butyl compound was produced under the same conditions. It was shown separately that no significant metal halogen exchange occurs between methyl iodide and n-butyllithium under these conditions, and thus the formation of R'_3GeBu-n in the methyl iodide reaction can reasonably be attributed to sequence (5).

$$R'_3GeLi + MeI \rightarrow R'_3GeI + MeLi \quad (5a)$$

$$R'_3GeI + n\text{-}BuLi \rightarrow R'_3GeBu\text{-}n + LiI \quad (5b)$$

Further confirmation of our proposals came from examination of the reaction of a mixture of R'_3Ge^*Li and n-butyllithium with ethyl chloride or ethyl iodide. With the chloride the crude product was optically inactive, as expected for exclusive formation of $Et_2(1\text{-}C_{10}H_7)PhGe$, while with the iodide the crude product had a specific rotation of +2.1°, which is consistent with a mixture of $Et_2Ge(1\text{-}C_{10}H_7)PhGe$ and (+)-R'_3GeBu-n.

Our explanation is also consistent with the behaviour of triphenylsilyllithium with ethyl halides[6]. With ethyl chloride the simple coupling product Ph_3SiEt is obtained in 80% yield. With ethyl bromide and iodide this product is formed in only 46 and 28% yield, respectively, while the disilane $(Ph_3Si)_2$ is formed in 30 and 40% yield, apparently via metal–halogen interchange as in sequence (6).

$$Ph_3SiI + EtLi \rightarrow Ph_3SiLi + EtI \quad (6a)$$

$$Ph_3SiLi + Ph_3SiI \rightarrow Ph_3SiSiPh_3 + LiI \quad (6b)$$

With benzyl halides the cross-over in mechanism and stereochemistry occurs between the chloride and the bromide, the germyl bromide (−)-R'_3GeBr presumably being formed as an intermediate. Substantial loss of optical activity occurs with benzyl chloride, suggesting that lithium–halogen exchange plays a substantial part in this case also. An additional, somewhat anomalous, feature is that the reaction of the benzyl chloride was much faster than that of the bromide, as judged by the rate of disappearance of the red colour of the R'_3Ge^*Li (see Table 1).

We cannot at present conclude that the extensive racemization accompanying the reaction of isopropyl chloride is the result of lithium–chlorine exchange. An additional feature of the isopropyl system is that the (positive) rotation of product from the iodide is significantly lower than the (negative) rotation of that from the bromide, suggesting that the exchange sequence (4) does not operate with isopropyl iodide as cleanly as it does with n-butyl iodide.

If our proposals are correct, it follows that every reaction of $R'Ge^*Li$ so far examined proceeds with retention of configuration at germanium. It also follows that the bromide and iodide R'_3GeBr and R'_3GeI are fairly optically stable in inert non-polar solvents; in the case of the bromide there is other evidence for this[4].

EXPERIMENTAL

General

Solvents were dried as previously described[4]. Rotations were measured in benzene.

Interaction of R'_3Ge^*Li and organic halides

A solution of R'_3Ge^*Li in ether was prepared from (+)-R'_3GeH and n-butyllithium[1], and a small excess of the halide RX was added from a pipette. After the reaction time shown in Table 1, the ether was removed and the residue extracted with pentane. The extract was filtered, the pentane was evaporated off, and the residual oil was kept at 80°/0.2 mm for a few minutes to remove any volatile material. The oil was then eluted in chloroform through chromatographic silica gel (1 m × 0.5 cm). Any unreacted R'_3GeH (which could be recognised by the brilliant fluorescence which a spot of it on filter paper shows under UV light) came through as the first fraction and was discarded. The presence of the required product in the later fractions was detected by the dull fluorescence given by its spots, and removal of chloroform left an oil. The rotation and refractive index of the oil were measured, and its IR spectrum

TABLE 2

PROPERTIES OF R'_3GeR COMPOUNDS FROM R'_3Ge^*Li AND RX

R	n_D^{25}	Analysis found (calcd.) (%)	
		C	H
i-Pr	1.6080	72.4 (72.3)	7.0 (6.9)
n-Bu	1.6031	72.9 (72.8)	7.5 (7.2)
t-Bu	1.6000	72.5 (72.8)	7.5 (7.2)
$CH_2CH{=}CH_2$	1.6228	72.3 (72.7)	6.3 (6.4)
CH_2Ph	1.6413	75.6 (75.4)	6.2 (6.3)

was shown to be identical with that of an authentic sample of (+)-R'_3GeR where this was a known compound. Small samples were then distilled, but in no case did this cause a significant change in the values of $[\alpha]_D$ or n_D^{25}. In the case of new compounds, the distilled samples were analysed for carbon and hydrogen, with the results shown in Table 2.

Reaction of R'_3GeLi and MeI or MeBr in presence of n-BuLi

A solution of (±)-R'_3GeLi (0.50 mmole) in ether was treated with methyl iodide (0.80 mmole) in presence of n-butyllithium (0.50 mmole). The mixture was worked up as above until the crude oil was obtained, and this was analysed by GLC (SE 30 on 100–120 mesh silanized Chromosorb G), and shown to contain R'_3GeMe and R'_3GeBu-n in comparable quantities.

When the reaction was repeated with methyl bromide, the sole major product was R'_3GeMe, and only a trace of R'_3GeBu-n was present.

Reaction of R'_3Ge^*Li with ethyl chloride or iodide

The preceding experiment was repeated with ethyl iodide or chloride and optically active R'_3Ge^*Li prepared from (+)-R'_3GeH, $[\alpha]_D +22.5°$. The product from ethyl iodide had $[\alpha]_D +2.1°$ (*c*, 10.0), while that from ethyl bromide was optically inactive.

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