

PRELIMINARY COMMUNICATION

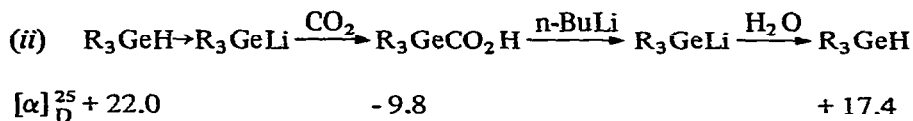
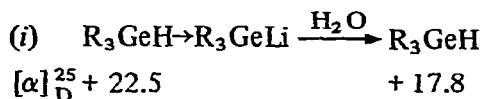
THE STEREOCHEMISTRY OF REACTIONS OF OPTICALLY-ACTIVE ETHYL-PHENYL(1-NAPHTHYL)GERMYLLITHIUM. A NOVEL STEREOCHEMICAL CROSSOVER

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We recently reported the stereochemistry of a range of nucleophilic reactions of optically-active ethylphenyl(1-naphthyl)germanium compounds, R_3GeX , with nucleophilic reagents¹, and we now summarize (see Tables) the results of a study of reactions of the optically-active R_3GeLi compound. This was made by treatment of the hydride (+)- R_3GeH with n-buthyllithium in ether, a process believed to involve retention of configuration at germanium (*cf.* refs. 2 and 3). Stereochemical assignments are based on application of Brewster's rules, and on the assignments in ref.1., and lead to internal consistency. (Reactions 1–3 in Table 1 have been studied for the closely-related reagent $MePh(1-C_{10}H_7)GeLi$ ², and in all cases the stereochemistries in the two systems agree.) In all the reactions of Table 1 there is predominant retention of configuration at germanium. The stereospecificities are fairly high in some of these reactions; for example, the overall stereospecificity is 90% in both the Walden cycles (i) and (ii).



Reactions with alkyl and benzyl chlorides also involve predominant retention, but in every case the corresponding iodides react with predominant inversion at germanium (Table 2). With alkyl and allyl bromides retention predominates, but with benzyl bromide inversion clearly predominates. The relatively low rotation of the (-)- R_3GeCH_2Ph obtained from benzyl chloride suggests that a substantial proportion of the reaction involves inversion in this case also.

The probable explanation of this new type of stereochemical crossover is that direct coupling wholly or mainly takes place with organic chlorides and most bromides in a retentive

TABLE 1

REACTIONS OF R_3GeLi WITH WATER AND CARBONYL COMPOUNDS

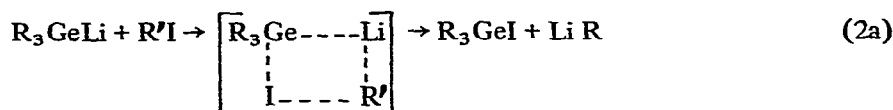
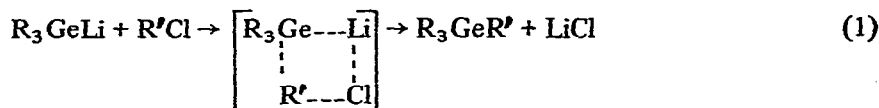
No.	$[\alpha]_D^{25}$ for R_3GeH	Reagent	Product, with $[\alpha]_D^{25}$	Predominant stereochemistry
1	+ 22.5	H_2O	$(+)-R_3GeH$, + 17.8	Ret.
2	+ 22.0	$(f) CO_2$, $(th) H_2O$	$(-)-R_3GeCO_2H$, - 9.8	Ret.
3	+ 13.0	$Ph_2C=O$	$(-)-R_3Ge(OH)Ph_2$, - 15.2	Ret.
4	+ 13.0	2-methylcyclohexanone	$(-)-R_3GeC(OH)CHMe(CH_2)_3CH_2$, - 7.2	Ret.
5	+ 13.0	$(para) HCHO$	$(+)-R_3GeCH_2OH$, + 1.0	Ret.

TABLE 2

REACTIONS OF R_3GeLi WITH ORGANIC HALIDES, R^*X

$[\alpha]_D^{25}$ for R_3GeH	R^*X	$[\alpha]_D^{25}$ for R_3GeR	Predominant stereochemistry
+ 13.0	MeI	+ 0.9	Inv.
+ 13.0	i-PrCl	- 0.6	Ret. (+ much rac.)
+ 13.0	i-PrBr	- 4.7	Ret.
+ 13.0	i-PrI	+ 2.9	Inv.
+ 13.0	n-BuCl	- 2.7	Ret.
+ 13.0	n-BuBr	- 2.7	Ret.
+ 13.0	n-BuI	+ 2.7	Inv.
+ 22.0	t-BuCl	- 6.3	Ret.
+ 22.0	t-BuBr	- 6.3	Ret.
+ 22.0	$CH_2=CHCH_2Cl$	- 1.6	Ret.
+ 22.0	$CH_2=CHCH_2Br$	- 1.6	Ret.
+ 22.0	$CH_2=CHCH_2I$	+ 1.2	Inv.
+ 22.0	$PhCH_2Cl$	- 1.3	Ret.
+ 22.0	$PhCH_2Br$	+ 5.2	Inv.
+ 22.0	$PhCH_2I$	+ 6.1	Inv.

process, possibly that shown in reaction (1), whereas metal-halogen interchanges occurs with the iodides and benzyl bromide, also in a retentive process (2a), and this is followed by reaction 2b, which would be expected to involve inversion at germanium (*cf.* ref. 1). In agreement with this proposal, when the (racemic) reagent R_3GeLi is treated with methyl



iodide in presence of n-butyllithium, substantial amounts of the compound R_3GeBu -n are formed along with the expected product R_3GeMe , whereas with methyl bromide under the same conditions only a trace of the butyl compound is produced. (It was shown that no metal-halogen interchange occurs between methyl iodide and butyllithium under the reaction conditions.) If the explanation offered for the crossover is correct, then every reaction of the reagent R_3GeLi so far studied proceeds with retention of configuration at germanium.

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