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Stereochemistry of the Reactions of Trimethylgermyl Anions with 4-*t*-Butylcyclohexyl Derivatives

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Synopsis. The stereochemistry of trimethylgermyllithium, -sodium, and -potassium with *cis*- and *trans*-4-*t*-butylcyclohexyl bromides and trimethylstannanes was investigated by ^{1}H NMR spectroscopy. With the 4-*t*-butylcyclohexyl derivatives trimethylgermyl anions gave mixtures of *cis*- and *trans*-4-*t*-butylcyclohexyltrimethylgermanes. These results confirmed that free-radical pathways are important in such reactions.

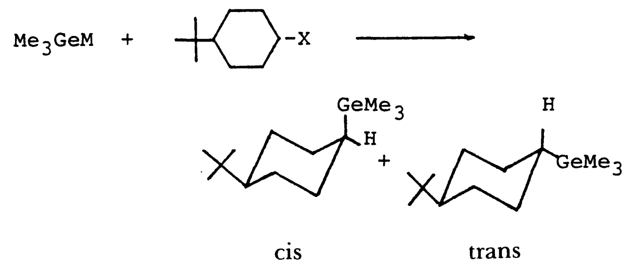
In earlier reports we described the reactions of trialkylgermyl anions with aryl halides[1] and aryltrialkylstannanes.[2] These results revealed that free-radical pathways are important on the basis of the formation of products and radical trapping experiments.

Stereochemical studies also provide valuable mechanistic information concerning substitution reactions of trialkylgermyl anion with cyclohexyl derivatives. Recently, Kitching et al. reported that the reactions of trimethylgermyllithium with 4-methylcyclohexyl bromides gave mixtures of *cis*- and *trans*-4-methylcyclohexyltrimethylgermanes.[3,4] Since 4-methylcyclohexyl bromides exist as an equilibrium mixture of conformations, two steric courses of the reaction, i.e. axial and equatorial approaches of trimethylgermyl groups to cyclohexyl derivatives, cannot be distinguished. The introduction of a *t*-butyl group on the ring prevents a ring inversion. Then, a distinction of such two steric courses of the reaction may be possible.

In this paper, the stereochemical courses of the substitution reactions of trimethylgermyl anions with conformationally stable 4-*t*-butylcyclohexyl derivatives are described.

Results and Discussion

The stereochemistry of the substitution reactions of trimethylgermyllithium, -sodium, and -potassium with *cis*- and *trans*-4-*t*-butylcyclohexyl bromides and trimethylstannanes was examined by ^{1}H NMR spectroscopy.



M=Li, Na, K; X=Br, SnMe$_3$

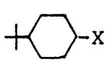
^{1}H NMR spectroscopy has been widely employed to determine the stereochemistry of 4-*t*-butylcyclohexyl derivatives, particularly, when electronegative groups, such as bromine atom, significantly deshield the methine proton ($>$C(H)X; X=Br) from the general cyclohexyl absorption and axial protons give rise to a resonance upfield from their counter parts.[5] In germanium and tin compounds, the methine proton ($>$C(H)Ge$\lessgtr$ and $>$C(H)Sn$\lessgtr$) would be of rather limited use. However, studies of the ^{13}C and ^{1}H NMR spectra of cyclohexyl and related organogermanes and -stannanes have shown that equatorial trimethylgermyl and trimethylstannyl groups give rise to a resonance upfield from their counterparts.[6]

trans-4-*t*-Butylcyclohexyl bromide (100%), prepared by the triphenylphosphine-bromine procedure for transforming an alcohol, reacted with trimethylgermyllithium to give *cis*- and *trans*-4-*t*-butylcyclohexyltrimethylgermanes in the ratio of 86 : 14. With *cis*-4-*t*-butylcyclohexyl bromide (100%), trimethylgermyllithium gave the corresponding trimethylgermanes (cis/trans=76 : 24).

trans-4-*t*-Butylcyclohexyltrimethylstannane (100%), prepared by a reaction of *cis*-4-*t*-butylcyclohexylmagnesium bromide with trimethylchlorostannane, reacted with trimethylgermyllithium to give *cis*- and *trans*-4-*t*-butylcyclohexyltrimethylgermanes in the ratio of 80 : 20. With *cis*-4-*t*-butylcyclohexyltrimethylstannane (100%), prepared by a treatment of *trans*-4-*t*-butylcyclohexyl tosylate with lithium trimethylstannate, reacted with trimethylgermyllithium to give the corresponding trimethylgermanes (cis/trans=81 : 19).

Reactions of trimethylgermylsodium and -potassium with *cis*- and *trans*-4-*t*-butylcyclohexyl bromides and trimethylstannanes were also examined. These results

Table 1. Reactions of Trimethylgermyl Anions with 4-*t*-Butylcyclohexyl Derivatives

No.	Reactants		Product
	Me$_3$GeM	-X (isomeric purity/%)	cis : trans
	M=	X=	
1	Li	*cis*-Br (100)	76 : 24
2		*trans*-Br (100)	86 : 14
3		*cis*-SnMe$_3$ (100)	81 : 19
4		*trans*-SnMe$_3$ (100)	80 : 20
5	Na	*cis*-Br	75 : 25
6		*trans*-Br	85 : 15
7		*cis*-SnMe$_3$	81 : 19
8		*trans*-SnMe$_3$	82 : 18
9	K	*cis*-Br	77 : 23
10		*trans*-Br	82 : 18
11		*cis*-SnMe$_3$	81 : 19
12		*trans*-SnMe$_3$	81 : 19

are summarized in Table 1.

The *cis*- and *trans*-4-*t*-butylcyclohexyltrimethylgermanes were conformationally stable with trimethylgermyl anions under these reaction conditions.

The counterions and leaving groups have little influence on the ratio of cis and trans products shown in Table 1.

Either cyclohexyl derivatives provided a mixture of the germanes, with the cis isomer being predominant. The present results are consistent with the electron-transfer and free-radical processes previously proposed by Kitching and co-workers, as well as us. Thus, an electron-transfer from trimethylgermyl anions to 4-*t*-butylcyclohexyl derivatives leads to a trimethylgermyl radical and anion radicals of 4-*t*-butylcyclohexyl derivatives. A subsequent dissociation of the 4-*t*-butylcyclohexyl radical from unstable radical anions of 4-*t*-butylcyclohexyl derivatives was followed by a combination with the trimethylgermyl radical. The trimethylgermyl radical approaches the 4-*t*-butylcyclohexyl radical from an axial direction.

Steric effects clearly do not explain the product distributions shown in Table 1. These reaction preferences may be explained by torsional effects.[7,8] A 4-*t*-butylcyclohexyl radical has a chair conformation with a dihedral angle between C–H_{2ax} and the axis of the p orbital of about 20°. For an axial attack of the trimethylgermyl radical (the cis germane), no torsional interactions occur since the hydrogen on the C_1 atom does not eclipse the equatorial hydrogens on the C_2 and C_6 atoms, On the other hand, the reaction of the 4-*t*-butylcyclohexyl radical from an equatorial attack of the germyl radical (the trans germane) results in the development of torsional interactions. Therefore, the cis germane is formed predominantly.

However, S_N2 displacement and four-center processes are not always excluded.

Experimental

NMR Spectra. ^1H NMR spectra were recorded on a JEOL GX-270 at 270 MHz for $CDCl_3$ solutions, and chemical shifts are with reference to internal Me_4Si.

Materials. Me_3GeCl[9] and Me_3SnCl[10] were prepared by established methods. *cis*-[11] and *trans*-4-*t*-Butylcyclohexyl bromides,[7] *cis*- and *trans*-4-*t*-butylcyclohexyltrimethylstannanes,[6] and *cis*- and *trans*-4-*t*-butylcyclohexyltrimethylgermanes[6] were prepared according to methods cited in the literature.

Preparation of Trimethylgermyl Anions. Trimethylgermyllithium, -sodium, and -potassium were prepared from reactions of trimethylchlorogermane with alkali metals in HMPA–ether in the manner described by Bulten and Noltes.[12]

Reactions of 4-*t*-Butylcyclohexyl Derivatives with Trimethylgermyl Anions. In a typical reaction, 10 cm^3 (ca. 0.4 mmol) of trimethylgermyllithium, prepared from a reaction of trimethylchlorogermane and lithium metal in HMPA–ether, was added by syringe to 100 mg (0.4 mmol) of 4-*t*-butylcyclohexyl bromide. Reactions were carried out under an atmosphere of argon at 15 °C for 30 min; then, the system was quenched with water. The ethereal layer was separated and the aqueous layer was extracted with ether. The combined organic layers were dried over sodium sulfate. The germane was obtained by a Varian 920 preparative GLC (6 mm×2 m column, 20% SE30 on celite 545).

Stability of 4-*t*-Butylcyclohexyltrimethylgermane. 4 cm^3 (ca. 1.6 mmol) of trimethylgermyllithium was added by syringe to 50 mg (0.20 mmol) of *trans*-4-*t*-butylcyclohexyltrimethylgermane (98% pure). Reactions were carried out under an atmosphere of argon at 15 °C for 1 h. After hydrolysis of the reaction mixture with water, the ethereal layers were dried over sodium sulfate. The germane product was recovered by a preparative GLC, which was unchanged to have a trans/cis ratio of 98:2.

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