

63.1 mg (93%); mp 73–74 °C (lit.¹⁸ mp 75–76 °C); $[\alpha]^{25}_D +18.2^\circ$ (c 0.98, CHCl₃) (lit.¹⁸ $[\alpha]^{18}_D +18.8^\circ$); R_f 0.25 (Et₂O); NMR (CDCl₃, partial) δ 7.25 (s, 10 H), 4.56 (m, 4 H), 3.31 (s, 3 H); IR (CHCl₃) 3400, 1220, 750, 680 cm⁻¹; mass spectrum, m/e (relative abundance) 374 (1, M⁺), 283 (7), 253 (4), 121 (5), 92 (7), 91 (100); mol wt calcd for C₂₁H₂₆O₆ 374.1729, found 374.1716.

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during work by B.H.L. on the total synthesis of (–)-*N*-methylmaysenine in the laboratories of Professor E. J. Corey at Harvard University. We also thank Dr. H. Webb for recording the mass spectral data.

Registry No. **1**, 100-06-1; **2**, 27150-99-8; **7**, 51440-56-3; **8** (isomer 1), 77397-48-9; **8** (isomer 2), 77397-50-3; **9**, 77397-49-0; **10** (isomer 1), 77270-37-2; **10** (isomer 2), 77270-42-9; **11**, 77270-38-3; **12** (isomer 1), 77270-39-4; **12** (isomer 2), 77270-43-0; **13** (isomer 1), 77270-40-7; **13** (isomer 2), 77270-44-1; **14** (isomer 1), 77341-11-8; **14** (isomer 2), 77270-45-2; **14** (isomer 3), 77340-67-1; **14** (isomer 4), 77340-68-2; **15**, 2612-30-8; *cis*-**16**, 77270-41-8; *trans*-**16**, 77270-46-3.

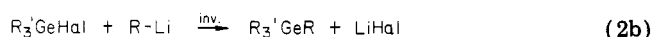
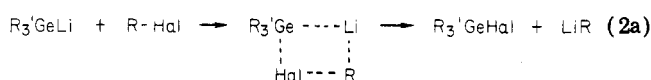
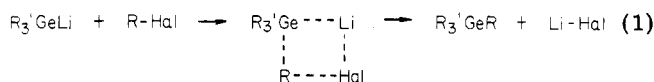
Communications

Organogermyl Anion Chemistry: Free-Radical Involvement in Reactions with Alkyl Bromides

Summary: The importance of free-radical pathways in substitution reactions of secondary bromides with R₃GeLi (R = CH₃, C₆H₅) reagents is indicated strongly by determinations of product stereochemistry in cyclohexyl systems and cyclization of the 6-hepten-2-yl moiety to yield [(2-methylcyclopentyl)methyl]germanes, with the appropriate *cis*/*trans* ratio. Appropriate comparisons are made with the corresponding organotinlithium reagents.

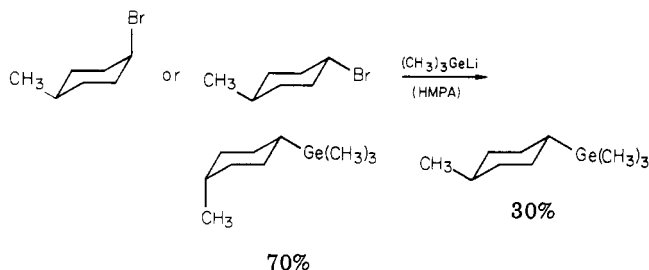
Sir: Although considerable information has accumulated regarding the reactions of organostannyl alkalis (R₃SnM) with alkyl halides,^{1–11} the mechanistic picture for the corresponding organogermyl derivatives is unclear.⁷ Some years ago, Eaborn, Hill, and Simpson¹² examined some reactions of optically active [ethyl(1-naphthyl)phenylgermyl]lithium with simple alkyl, allyl, and benzyl halides and identified systems proceeding with predominant retention at germanium (alkyl bromides and chlorides) or predominant inversion (alkyl iodides and benzyl bromide). No stereochemical information at carbon was available but the following sequences were suggested for the predominant retentive (eq 1) and invertive processes (eq 2).

In view of the potential importance of these reactions for forming C–Ge bonds, we have conducted further examination of some (R₃GeLi; alkyl bromide) systems which permit mechanistic conclusions and provide interesting



comparisons with the corresponding organostannyl systems.

Reaction of either *cis*-⁷ or *trans*-4-methylcyclohexyl bromide with (CH₃)₃GeLi⁷ provided the same 70:30 mixture of *cis* and *trans* germanes. This apparently complete stereoequilibration indicates that a single-step four-center process (eq 1) is unimportant but could be consistent with electron-transfer and free-radical processes.¹³ To investigate this possibility further, certain reactions were conducted with the primary 6-bromo-1-hexene and the secondary 6-bromo-1-heptene, the free radicals from which (loss of Br•) are known to cyclize rapidly to yield cyclo-



pentylmethyl and (2-methylcyclopentyl)methyl products, respectively.^{14,15}

With the above primary bromide, none of the reagents (CH₃)₃SnLi, (CH₃)₂(C₆H₅)SnLi, CH₃(C₆H₅)₂SnLi, (C₆H₅)₃SnLi, (CH₃)₃GeLi, and (C₆H₅)₃GeLi provided rearranged cyclopentylmethyl product, and the S_N2 pathway is presumably the important one.^{3,10,16} However, with the secondary bromide (lowered "S_N2" reactivity at the more

(1) H. G. Kuivila, *Ann. N.Y. Acad. Sci.*, **239**, 315 (1974); *Adv. Chem. Ser.*, No. 157, 43 (1976); H. G. Kuivila, J. L. Considine, and J. D. Kennedy, *J. Am. Chem. Soc.*, **94**, 7206, (1972); H. G. Kuivila and K. R. Wursthorn, *Tetrahedron Lett.*, 4357 (1975); K. R. Wursthorn, H. G. Kuivila, and G. F. Smith, *J. Am. Chem. Soc.*, **100**, 2779 (1978).

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(3) P. L. Bock and G. M. Whitesides, *J. Am. Chem. Soc.*, **96**, 2826 (1974).

(4) F. R. Jensen and D. D. Davis, *J. Am. Chem. Soc.*, **93**, 4047 (1971).

(5) A. Rahm and M. Pereyre, *Tetrahedron Lett.*, 1333 (1967).

(6) K. Sisido, S. Kozima, and K. Takizawa, *Tetrahedron Lett.*, 33 (1967).

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(8) J. San Filippo, J. Silbermann, and P. J. Fagan, *J. Am. Chem. Soc.*, **100**, 4834 (1978).

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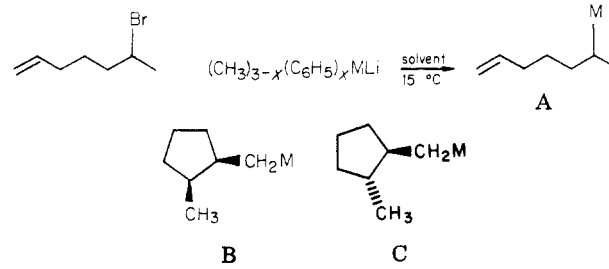
(11) H. G. Kuivila and G. F. Smith, *J. Org. Chem.*, **45**, 2919 (1980).

(12) C. Eaborn, R. E. E. Hill, and P. Simpson, *J. Organomet. Chem.*, **37**, 275 (1972).

(13) It is interesting to note that whereas (CH₃)₃GeLi (HMPA) provides a 70:30 *cis*/*trans* mixture of germanes from either 4-methylcyclohexylbromide, (CH₃)₃SnLi (either THF or HMPA) leads to an ca. 30:70 *cis*/*trans* mixture of stannanes. This reversal in distribution indicates important differences in the transition states for abstraction of (CH₃)₃Ge and (CH₃)₃Sn by the 4-methylcyclohexyl radical. For a general discussion see F. R. Jensen, L. H. Gale, and J. E. Rodgers, *J. Am. Chem. Soc.*, **90**, 5793 (1968).

(14) D. Lal, D. Griller, S. Husband, and K. V. Ingold, *J. Am. Chem. Soc.*, **96**, 6355 (1974).

Table I



entry ^a	M	x	solvent	product ratio			% yield
				A	B	C	
1	Sn	0	THF	21	58	21	60
2	Sn	0	HMPA	82	13	5	16
3	Sn	1	THF	15	61	24	86
4	Sn	2	THF	86	10	4	93
5	Sn	3	THF	100			83
6 ^b	Ge	0	HMPA	83	13	4.4	52
7	Ge	3	THF	68	22.4	9.6	27

^a Product ratios established by ¹H and ¹³C NMR examination. ^b The (83%) noncyclized product germane consisted of 35% *cis*-6-germyl-1-heptene, 40% *cis*-6-germyl-2-heptene, and 8% *trans*-6-germyl-2-heptene. We have encountered post-substitution alkene isomerization in other reactions of metalloidal anions in HMPA. Structures of products are based on analyses and ¹H and ¹³C NMR spectra. Yields refer to isolated yields of distilled or recrystallized products. Isomeric ratios are derived from examination of (total) crude product. Elimination (and coupling) can accompany some reactions.

congested secondary center) each of the above reagents, excepting (C₆H₅)₃SnLi, provides significant and sometimes predominant amounts of rearranged (2-methylcyclopentyl)methyl derivatives. The *cis/trans* ratios (of ca. 2.7) observed in these products are extremely similar to those established for authentic free-radical reactions.^{15,17} The cyclized product from the (CH₃)₃SnLi reactions is in agreement with other evidence that electron-transfer processes are very important in its reactions with secondary bromides.^{1,7-9,11} The results are in Table I.

The change from methyl to phenyl in the tinlithium reagents apparently has a drastic effect on the oxidation potential, as electron-transfer processes are not in evidence for (C₆H₅)₃SnLi, which provides no rearrangement products with suitable bromides and reacts strictly with inversion at carbon with various methylcyclohexyl bromides.^{18,19} In contrast, (C₆H₅)₃GeLi⁷ does yield rearranged [(2-methylcyclopentyl)methyl]germanes (Table I) and substantial stereoleakage with cyclohexyl bromides as shown below.

The variations in the product *cis/trans* ratios (with starting bromide configuration) indicate some S_N2 contribution,²⁰ particularly with the *cis*-bromide.²¹

(15) A. L. J. Beckwith, I. Blair, and G. Phillipou, *J. Am. Chem. Soc.*, **96**, 1613 (1974), and references therein.

(16) Geminate combination of primary radicals would be included.

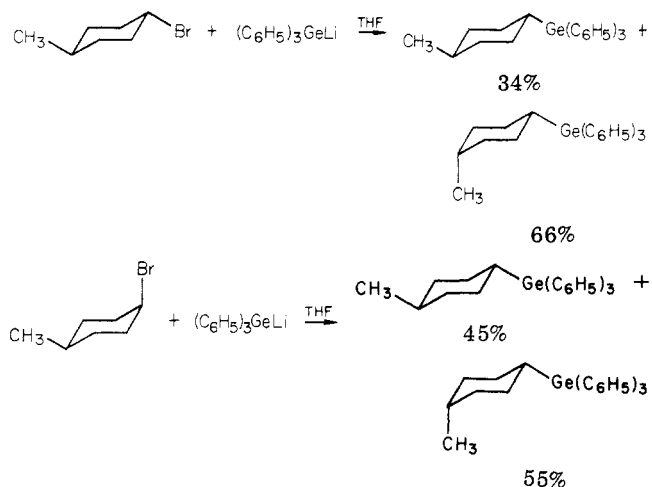
(17) Tributylstannane-*d*/AIBN reduction of 6-bromo-1-heptene and ²H NMR examination of the deuterio-1,2-dimethylcyclopentanes yielded a *cis/trans* ratio of ~2.7.

(18) H. Olszowy and K. Harvey, unpublished results. Even cyclopropylcarbinyl bromide, regarded^{8,9} as sensitive toward free-radical involvement, does not afford ring-opened product with (C₆H₅)₃SnLi.

(19) Jensen and Davis⁴ have reported that reaction of (C₆H₅)₃SnNa (DME solvent) with (*S*)-(+)-*sec*-butyl chloride proceeds with 90% inversion, the bromide with 88%, and the iodide with 71%.

(20) Jensen and Davis⁴ report that 67% inversion accompanies the reaction of (C₆H₅)₃GeNa (NH₃ solvent) with (*S*)-(+)-*sec*-butyl bromide. The S_N2 component would compete more efficiently with electron-transfer processes in the acyclic than in cyclohexyl bromides.

(21) See E. L. Eliel and R. G. Haber, *J. Am. Chem. Soc.*, **81**, 1249 (1959).



The present results confirm that free-radical pathways are important in the substitution reactions of secondary bromides with (CH₃)₃GeLi (HMPA) and (C₆H₅)₃GeLi (THF). This result is consistent with the generalization that electron transfer appears more facile with the higher members of the group 4B derived metalloidal alkali reagents. The connection between these results and those reported¹² for the [ethyl(1-naphthyl)phenylgermyl]lithium reactions is not direct, but it would be surprising if electron transfer was completely suppressed in its reactions with secondary bromides. Some knowledge of stereochemistry at carbon in these reactions would be particularly informative.

A full discussion of this chemistry will be presented at a later date.

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Registry No. *cis*-4-Methylcyclohexyl bromide, 28046-90-4; *trans*-4-methylcyclohexyl bromide, 28046-91-5; *cis*-1-methyl-4-(trimethylgermyl)cyclohexane, 64871-32-5; *trans*-1-methyl-4-(trimethylgermyl)cyclohexane, 64871-31-4; 6-bromo-1-hexene, 2695-47-8; 6-bromo-1-heptene, 38334-98-4; 6-(trimethylgermyl)-1-heptene, 76879-49-7; *cis*-6-(trimethylgermyl)-2-heptene, 76879-50-0; *trans*-6-(trimethylgermyl)-2-heptene, 76879-51-1; 6-(trimethylstannyl)-1-heptene, 76879-52-2; 6-[dimethyl(phenyl)stannyl]-1-heptene, 76879-53-3; 6-[diphenyl(methyl)stannyl]-1-heptene, 76879-54-4; 6-(triphenylstannyl)-1-heptene, 76879-55-5; 6-(triphenylgermyl)-1-heptene, 76879-56-6; *cis*-1-methyl-2-(trimethylstannyl)methylcyclopentane, 76879-57-7; *trans*-1-methyl-2-(trimethylstannyl)methylcyclopentane, 76879-58-8; *cis*-1-methyl-2-[dimethyl(phenyl)stannyl]methylcyclopentane, 76879-59-9; *trans*-1-methyl-2-[dimethyl(phenyl)stannyl]methylcyclopentane, 76879-60-2; *cis*-1-methyl-2-[diphenyl(methyl)stannyl]methylcyclopentane, 76879-61-3; *trans*-1-methyl-2-[diphenyl(methyl)stannyl]methylcyclopentane, 76879-62-4; *cis*-1-methyl-2-(trimethylgermyl)methylcyclopentane, 76879-63-5; *trans*-methyl-2-(trimethylgermyl)methylcyclopentane, 76879-64-6; *cis*-methyl-2-(triphenylgermyl)methylcyclopentane, 76900-25-9; *trans*-methyl-2-(triphenylgermyl)methylcyclopentane, 76900-26-0; *cis*-1-methyl-4-(triphenylgermyl)cyclohexane, 76879-65-7; *trans*-1-methyl-4-(triphenylgermyl)cyclohexane, 76879-66-8; (CH₃)₃SnLi, 17946-71-3; (CH₃)₂(C₆H₅)SnLi, 76879-67-9; CH₃(C₆H₅)₂SnLi, 4167-85-5; (C₆H₅)₃SnLi, 4167-90-2; (C₆H₅)₃GeLi, 3839-32-5; (CH₃)₃GeLi, 18489-76-4.

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