

Reaction of (Triphenylmethyl)-, (Triphenylsilyl)-, (Triphenylgermyl)-, and (Triphenylstannyl)lithium with Optically Active 2-Octyl Tosylate, Chloride, and Bromide¹

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The reaction of (triphenylmethyl)-, (triphenylsilyl)-, (triphenylgermyl)-, and (triphenylstannyl)lithium with optically active 2-octyl bromide, chloride, and tosylate has been examined. Alkylation of all four anions in THF proceeds stereospecifically with 2-C₈H₁₇OTs. By comparison, the corresponding reactions between 2-octyl chloride and bromide and Ph₃CLi, Ph₃GeLi, and Ph₃SnLi also proceed with high stereoselectivity, whereas the corresponding alkylation of Ph₃SiLi is notably less stereospecific: 70-75% net inversion observed with 2-octyl chloride and 25-55% net inversion occurred with 2-octyl bromide. The parallels and contrasts between the reactivity and stereoselectivity of (CH₃)₃SnLi, -Na, -K and Ph₃MLi are examined.

In previous studies we examined the reaction of (trimethylstannyl)lithium, -sodium, and -potassium with selected alkyl halides and tosylates.^{2a,b} The investigation we report here extends these studies to the aryl homologues of the group 4 family, viz., triphenylmethyl, -silyl, -germyl, and -stannyl anions, Ph₃Me⁻ (M = C, Si, Ge, Sn).

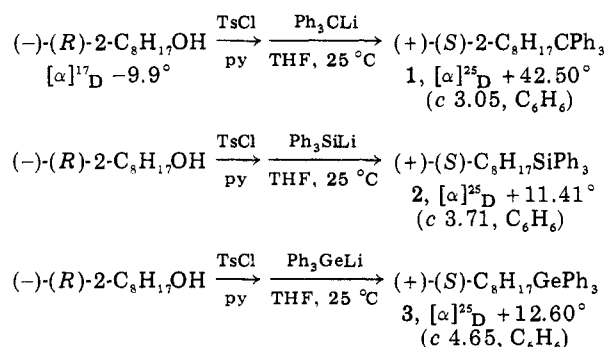
Results

Although other studies^{2c,d} have sought to compare chemical reactivity within a homologous series of group 4 anions, these early efforts failed to appreciate the very substantial influence that even minor variations in reaction conditions can impart to the reactivity of such reagents.^{2a,b} For this reason we briefly examined the general and relative reactivity of Ph₃CLi, Ph₃SiLi, Ph₃GeLi, and Ph₃SnLi under uniform experimental conditions. The results, summarized in Table I, reveal the following profile. First, product distribution is unaffected by the order of reagent addition. Second, olefin production is the dominant reaction observed when either 2-octyl tosylate, chloride, or bromide is treated with Ph₃CLi. With one exception, the corresponding reactions of Ph₃SiLi, Ph₃GeLi, and Ph₃SnLi are dominated by the production of the substitution product 2-C₈H₁₇MPh₃. The reaction of 2-octyl bromide with Ph₃SiLi is the sole exception to this general pattern of reactivity; the principal product in this instance is the hydrocarbon *n*-octane. In an attempt to identify the origin of this product, the usual aqueous workup was replaced by deuterium oxide. No deuterium incorporation was observed.

Finally, the influence of the leaving group, X, on the yield of the substitution product, 2-C₈H₁₇MPh₃, is summarized as follows: C, Cl > OTs > Br; Si, Cl > OTs > Br; Ge, Br > OTs > Cl; Sn, Br > OTs > Cl while the *general* reactivity as judged by the consumption of 2-octyl chloride obeys the order Ph₃CLi ≈ Ph₃SiLi > Ph₃GeLi > Ph₃SnLi.

Absolute Rotation of 2-Octyltriphenylmethane, -silane, -germane, and -stannane. Stereochemical studies employing optically active substrates require knowledge of the absolute rotation of reactants and

Scheme I



products. The absolute rotations of optically pure 2-octyl alcohol, chloride, and bromide are known with reasonable accuracy;^{2a} however, the corresponding rotations of 2-octyltriphenylmethane, -silane, and -germane are unknown. To circumvent the problems associated with the resolution of such substances, we developed a stereospecific synthesis of compounds 1-3, relying on an extension of the previously reported procedure for the preparation of optically pure 2-octyltriphenyltin, 4.^{2a}

Our results, which are summarized in Scheme I, offer the additional opportunity to examine the empirical procedure developed by Davis and Jensen^{3a} for calculating the absolute rotation of a number of 2-butyl, 2-pentyl, and 2-octyl compounds, including 1-4. The values calculated by these authors are based on an empirical correlation between optical rotation and bond refraction. Their results lead to the linear relationship illustrated for compounds 1-4 in Figure 1. For comparison, the absolute rotations suggested by Scheme I are also shown. It is apparent that although a linear relationship does appear to exist between bond refraction and the experimentally determined value of the molecular rotation for the compounds 2-4, the agreement between the observed and calculated values of rotation is very poor.

The absolute rotation of 2-octyltriphenylmethane presents an anomaly for it exhibits a substantial displacement from the linear relationship exhibited by compounds 2-4. In an effort to understand this behavior, we examined the NMR spectra of compounds 1-4 for possible

(1) Supported by the National Science Foundation, Grant 80-17405, and DOE, Contract DE-AS05-80ER-1062.

(2) (a) San Filippo, J., Jr.; Silberman, J. *J. Am. Chem. Soc.* **1982**, *104*, 2831 and references therein. (b) San Filippo, J., Jr.; Silberman, J. *Ibid.* **1981**, *103*, 5588. (c) Jensen, F. R.; Davis, D. D. *Ibid.* **1971**, *93*, 4047. (d) Koerner, G. S.; Hall, M. L.; Traylor, T. G. *Ibid.* **1972**, *94*, 7205. Smith, G. F.; Kuivila, H. F.; Simon, R.; Sultan, L. *Ibid.* **1981**, *103*, 833 and references therein.

(3) (a) Davis, D. D.; Jensen, F. R. *J. Org. Chem.* **1970**, *35*, 3410. (b) Poh, B.-L. *Aust. J. Chem.* **1980**, *33*, 1409. (c) A similar conclusion has been reported by Pereyre and co-workers for Ph₃Sn(sec-C₄H₉) (cf. ref. 11).

Table I. Distribution of Products from the Reaction of Ph_3MLi with 2-Octyl Tosylate, Chloride, and Bromide

Ph_3MLi , $M =$	$2-C_8H_{17}X$, $X =$	reactn temp, °C	reactn time, h	mode of additn	products, %			recovered $2-C_8H_{17}X^g$
					octane [#]	octene(s) ^g	$2-C_8H_{17}MPh_3^h$	
C^a	OTs	25	5	normal ^e	<1	62	21	<i>i</i>
Si^b				inverse ^f	<1	58	21	<i>i</i>
Ge^c				normal	<1	<1	15	<i>i</i>
				inverse	<1	<1	20	<i>i</i>
				normal	<1	<1	90	<i>i</i>
Sn^d				inverse	<1	<1	91	<i>i</i>
				normal	<1	<1	90	<i>i</i>
C	Cl	25	5	inverse	<1	58	26	<i>i</i>
Si				normal	<1	62	27	17
Ge				inverse	9	3	68	16
				normal	8	2	72	17
Sn				inverse	4	<1	50	18
				normal	3	<1	40	44
C	Br	25	2.5	inverse	<1	<1	35	54
Si				normal	<1	<1	30	64
Ge				inverse	<1	66	16	66
				normal	<1	66	19	18
Sn				inverse	51	12	13	16
				normal	45	17	8	<1
C		0	0.25	inverse	3	<1	94	<1
Si			0.25	normal	2	<1	94	<1
Ge			0.25	inverse	4	<1	91	<1
Sn			0.25	normal	4	<1	92	<1
				inverse	<1	65	16	<1
				normal	42	15	14	8
				inverse	2	<1	96	<1
				normal	9	<1	59	<1

^a Prepared by the reaction of lithium dispersion with triphenylmethyl chloride. ^b Prepared by the reaction of lithium dispersion with hexaphenyldisilane. ^c Prepared by the reaction of lithium dispersion with hexaphenyldigermane. ^d Prepared by the reaction of triphenyltin chloride with lithium dispersion. ^e Indicates that a solution of $2-C_8H_{17}X$ was added to a stirred solution of Ph_3MLi . ^f Indicates that a solution of Ph_3MLi was added to a stirred solution of $2-C_8H_{17}X$. ^g Determined by GLPC. ^h Determined by HPLC. ⁱ Undetermined. ^j R = $2-C_8H_{17}$.

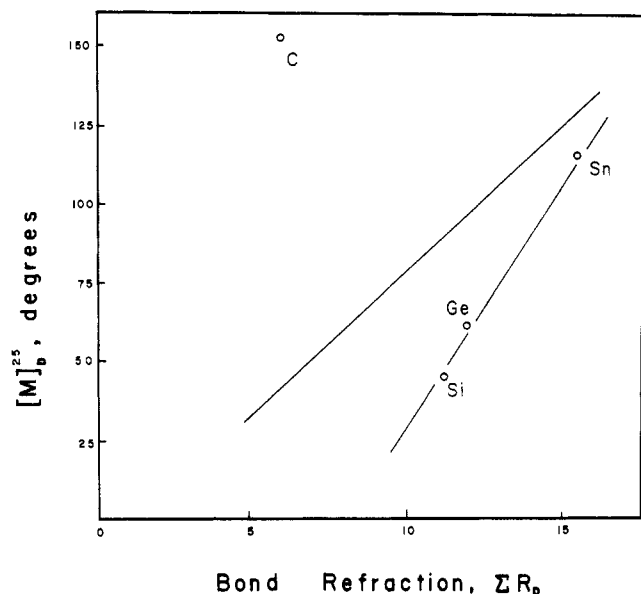


Figure 1. A plot of the experimentally observed (O) molecular rotation vs. bond refraction for (S)-2-C₈H₁₇MPh₃ (M = C, Si, Ge, Sn). All rotations were recorded on solutions in benzene. The solid line represents predicted values.^{3a}

conformational differences. In fact, the ¹³C spectrum of 1 shows significant ambient-temperature differences from the corresponding spectra displayed by compounds 2-4. At elevated temperatures (≥80 °C), these differences are removed and the ¹³C spectrum of 1 approaches those of compounds 2-4. In view of the substantial conformational dependence of optical activity,⁴ we reasoned that the absolute rotation of 1 would cease to behave anomalously under conditions which permitted its apparent conformational equity with compounds 2-4, i.e., at temperatures ≥80°. However, as Figure 2 reveals, the absolute rotation of compound 1 exhibits no unusual dependence on temperature and we remain unable to explain the origin(s) of the anomalously high value for the absolute rotation of this compound.

Stereochemistry of the Reaction with 2-Octyl Chloride and Bromide.⁵ Since stereochemistry provides the single most informative piece of information about the nature of a substitution process at a tetrahedral carbon, we investigated the reaction of (triphenylmethyl)-, (triphenylsilyl)-, (triphenylgermyl)-, and (triphenylstannyl)-lithium with optically active 2-octyl chloride and bromide. These results, which are summarized in Table II, reveal several points. First, alkylation of Ph₃MLi (M=C, Si, Ge, Sn) with 2-octyl chloride and bromide proceeds with predominant inversion of configuration at carbon. Indeed, in only two instances does alkylation proceed with a stereoselectivity notably <90%. The principal exceptions to this behavior are the alkylation of (triphenylsilyl)lithium which takes place with ~70-75% net inversion, and the corresponding reaction with 2-octyl bromide, which ex-

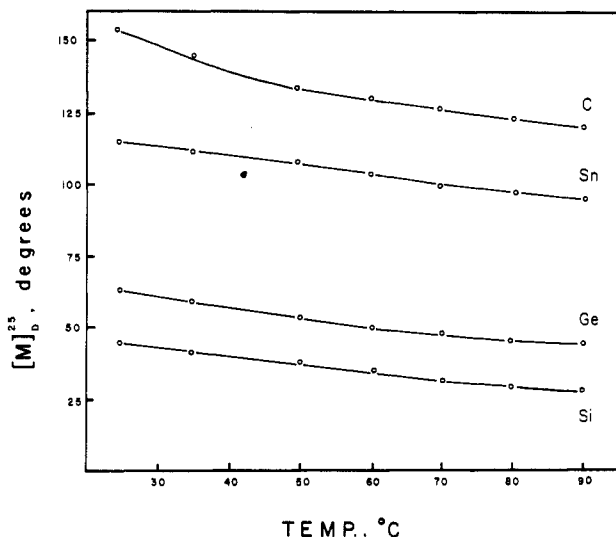


Figure 2. The influence of temperature on the molecular rotation of (S)-2-C₈H₁₇MPh₃. All rotations were recorded on xylene solutions.

hibits even less stereoselectivity (~25-55% net inversion). Second, the stereochemistry of this last reaction as well as the equivalent reactions of Ph₃GeLi (but not Ph₃SnLi or Ph₃CLi) shows appreciable dependence on the mode of reagent addition. Specifically, a significant enhancement in stereoselectivity obtains when these reactions are carried out with inverse addition. A similar effect has also been noted in the reaction of (CH₃)₃SnLi and -Na with 2-octyl bromide.^{2a} Third, the leaving group exhibits an influence on the stereoselectivity of alkylation that depends on the anion. Thus, for Ph₃CLi, the order is OTs ≈ Cl ≈ Br, while for Ph₃SiLi the order becomes OTs > Cl > Br, but for Ph₃GeLi and Ph₃SnLi the observed order is OTs > Br > Cl.

Finally, the influence of temperature on reaction stereoselectivity deserves brief mention. It is apparent from Table II that temperature has little effect on the stereoselectivity of the reaction of Ph₃MLi (M = C, Si, Sn) with either 2-octyl chloride or bromide. However, the parallel reactions of Ph₃GeLi are clearly *more* stereoselective at elevated temperatures. By comparison, the corresponding reactions of (CH₃)₃SnLi, -Na and -K all exhibited an *inverse* relationship between reaction temperature and stereoselectivity.^{2a}

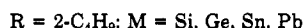
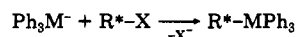
Discussion

Taken together, the data reported here support the proposal that the alkylation of Ph₃CLi, Ph₃GeLi, and Ph₃SnLi by 2-octyl chloride or bromide proceed by what are formally S_N2 processes. This behavior stands in contrast to the corresponding reaction of (CH₃)₃SnLi and -Na with 2-haloocanes, the stereoselectivity of which varies considerably with reaction conditions and, most specifically, with the mode of reagent addition and with temperature.^{2a,b}

The fact that the principal product from the reaction of Ph₃SiLi with 2-octyl bromide is *n*-octane suggests that this reaction proceeds by a notably different pathway than do the corresponding reactions of Ph₃CLi, Ph₃GeLi, and Ph₃SnLi. The apparent origin of this hydrocarbon and the significantly diminished stereoselectivity which characterizes the alkylation of Ph₃SiLi by 2-octyl bromide (and to a lesser extent 2-octyl chloride) suggest that in this instance at least two distinctly different reaction pathways are operating—one a stereospecific and therefore presumably an S_N2 process, the other being one or more nonst-

(4) Brewster, J. H. *Tetrahedron* 1974, 30, 1807. Kauzmann, W.; Clough, F. B.; Tobias, I. *Ibid.* 1961, 13, 57 and references therein.

(5) In a pioneering investigation, Jensen and Davis^{2c} reported the first preparation of a homologous series of compounds in which a chiral carbon is directly bonded to a group 4 atom.



However, the reaction stereoselectivities they reported are subject to question in light of the apparent failure of the empirical relationship which they used to determine the absolute rotation of 2-butyltriphenylsilane, -germane, -stannane, and -plumbane (see text).

Table II. Reaction of Ph_3MLi with Optically Active 2-Octyl Tosylate, Chloride, and Bromide
$$Ph_3MLi (0.3 M) + R^*-X (0.4 M) \xrightarrow{THF} R^*-MPh_3$$

1

Ph_3MLi , M =	R^*LX^a , X =	$[\alpha]^{25}_D$, deg	temp, °C	% yield ^b of R^*-MPh_3	$[\alpha]^{25}_D$, deg		ee, ^d %
					obsd ^c	corrected ^a	
Normal Addition ^f							
C	OTs	-9.40 ^e	25	20.5	+39.21	+41.30	97.2
	Cl	+31.6	25	25.8	-35.20	-41.55	97.8
	Br	+30.3	0	16.3	-27.48	-39.36	92.6
		+30.3	25	15.8	-27.73	-39.72	93.5
Inverse Addition ^f							
C	OTs	-9.40 ^e	25	20.5	+40.35	+42.50	100
	Cl	+31.6	25	27.0	-36.00	-42.49	99.9
	Br	+30.3	0	22.1	-28.92	-41.42	97.5
		+30.3	25	18.6	-28.71	-41.12	96.8
Normal Addition ^f							
Si	OTs	-9.34 ^e	25	14.9	+10.09	+10.69	93.7
	Cl	+33.9	0	37.7	-7.34	-8.08	70.8
		+33.9	25	68.1	-7.38	-8.12	71.2
		+31.6	50	90.0	-6.89	-8.13	71.3
	Br	+29.2	0	14.1	-1.98	-2.94	25.8
		+30.5	25	13.0	-2.75	-2.75	24.1
Inverse Addition ^f							
Si	OTs	-9.34 ^e	25	20.1	+10.76	+11.41	100
	Cl	+33.9	0	37.7	-7.53	-8.29	72.7
		+33.9	25	72.0	-7.81	-8.59	75.3
		+31.6	50	92.5	-7.37	-8.70	76.2
	Br	+29.2	0	7.7	-4.25	-6.32	55.4
		+30.5	25	7.8	-4.00	-5.69	49.9
Normal Addition ^f							
Ge	OTs	-9.61 ^e	0	85.5	+11.57	+11.96	94.9
		-9.61 ^e	25	90.0	+11.65	+12.04	95.6
	Cl	+31.6	0	10.7	-6.70	-7.91	62.8
		+31.6	25	50.1	-8.74	-10.32	81.9
		+31.6	50	87.7	-8.71	-10.28	81.6
	Br	+30.3	0	92.3	-7.27	-10.41	82.6
		+30.5	25	94.0	-7.55	-10.74	85.2
		Inverse Addition ^f					
Ge	OTs	-9.61 ^e	0	86.0	+12.14	+12.51	99.3
	Cl	-9.70 ^e	25	90.5	+12.35	+12.60	100
		+31.6	0	13.4	-8.02	-9.47	75.2
		+31.6	25	40.0	-8.83	-10.42	82.7
	Br	+31.6	50	91.2	-10.04	-11.85	94.0
		+30.3	0	91.8	-8.16	-11.69	92.8
+30.5	25	93.7	-8.79	-12.51	99.3		
Normal Addition ^f							
Sn	OTs	-9.61 ^e	25	90.1	+22.62	+23.30	100
	Cl	+31.6	25	35.0	-17.40	-20.54	88.2
		+31.6	50	75.4	-17.90	-21.13	90.7
		+30.3	0	88.5	-15.87	-22.73	97.6
	Br	+30.3	25	91.3	-16.00	-22.92	97.8
Inverse Addition ^f							
Sn	OTs	-9.61 ^e	25	91.5	+22.62	+23.30	100
	Cl	+31.6	25	30.0	-18.61	-21.97	94.3
		+31.6	50	71.1	-18.72	-22.10	94.8
		+30.3	0	90.0	-15.91	-22.79	97.8
	Br	+30.3	25	92.5	-16.12	-23.09	99.1

^a The (absolute) rotation of optically pure (*S*)-2-chloro- and (*S*)-2-bromooctane is respectively $[\alpha]^{20}_D +37.3^\circ$ and $[\alpha]^{20}_D +43.4^\circ$ (see ref 2a). ^b Yields were determined by HPLC. ^c Determined as solutions in benzene. ^d Based on a value of $[\alpha]^{25}_D$ 42.50, 11.41, 12.60, and 23.30°, respectively, for the absolute rotation of 1, 2, 3, and 4 (see text for discussion).

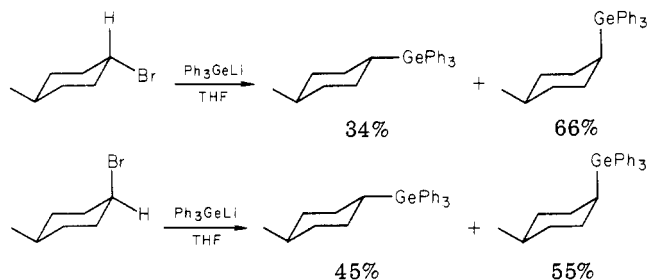
^e This value represents the specific rotation of the precursor (*R*)-2-octanol (the absolute rotation of this latter substance is taken as $[\alpha]^{17}_D +9.90^\circ$ (see ref 2a)). ^f See Table I for explanation.

ereospecific process(es)¹² which the collective evidence cannot distinguish between.

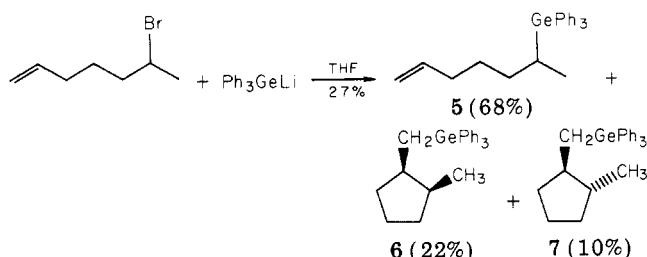
Finally, previous studies of the reaction of $(CH_3)_3SnLi$, -Na, and -K with alkyl halides revealed that the nature of the carbon center undergoing substitution strongly influ-

ences the mechanisms of these processes.^{2a} This fact suggests that the generalized extension of the present findings to all related substitution processes involving (triphenylmethyl)-, (triphenylsilyl)-, (triphenylgermyl)-, and (triphenylstannyl)lithium may be unwise. In this

regard the recent observations of Kitching and co-workers⁶ are noteworthy. These workers report that the reaction off (triphenylgermyl)lithium with *cis*- and *trans*-4-methylcyclohexyl bromide proceeds with substantial but not complete loss of stereochemical integrity.



They also observed that the reaction of Ph₃GeLi with 2-bromohept-6-ene yields a product mixture, compounds 5-7, which suggest that a minimum of 32% of Ge-C sub-



stitution product is formed by a pathway involving kinetically free 6-hepten-2-yl radicals. By comparison, the stereochemical results reported in Table II suggests only 17% of the substitution product formed during the alkylation of Ph₃GeLi by 2-bromooctane is formed by a free radical pathway. This difference may be a reflection of different reaction conditions.¹⁰

Experimental Section

General Methods. All reactions involving organometallic compounds were performed under an atmosphere of prepurified nitrogen. Tetrahydrofuran (THF) was distilled under nitrogen from lithium aluminum hydride immediately prior to use. Optically active 2-octanol (Aldrich Chemical Co.), triphenylmethyl chloride, and triphenylmethane (Aldrich Chemical Co.), triphenyltin chloride (Alfa Inorganics), hexaphenyldisilane (Silar Labs.), triphenylgermanium chloride (Alfa Inorganics), and hexaphenyldigermane (Orgmet, Inc.) were all employed without further purification. Lithium metal (200- μ m dispersion, 50% by weight in mineral oil) was purchased from Lithium Corp. of America.

Melting points and boiling points are uncorrected. Infrared spectra were determined in sodium chloride cell on a Perkin-Elmer Model 727B grating spectrometer. ¹H and ¹³C NMR spectra were recorded on a Varian FT-80 spectrometer; chemical shifts are reported in parts per million from tetramethylsilane (Me₄Si). Optical rotations were recorded at 589 nm on solutions employing a 1-dm cell and a Perkin-Elmer Model 141 spectropolarimeter.

GLPC and HPLC analyses were performed, respectively, on a Hewlett-Packard 5750 and Waters Associates Model 6000A chromatographs equipped with a Hewlett-Packard Model 3380-A electronic integrator. Reported yields are estimated to have an error range of $\pm 2\%$. Quantitation was achieved by using internal standard techniques with response factors obtained from authentic samples. Mass spectra were recorded on a Hewlett-Packard 5985 GC/MS. A Vacuum Atmospheres inert-atmosphere glovebox was used to transfer all air- and moisture-sensitive solids.

(+)-(*S*)-2-Octyl bromide and chloride were prepared from (-)-(*R*)-2-octanol as previously described.^{7,8}

(-)-2-Octyl tosylate was prepared from (-)-(*R*)-2-octanol according to the procedure of Streitwieser et al.⁹

Normal-Addition Reaction of (+)-(*S*)-2-Octyl Chloride with (Triphenylsilyl)lithium (Prepared from Hexaphenyldisilane) and (Triphenylgermyl)lithium (Prepared from Hexaphenyldigermane) (Typical Procedure). In a glovebox, lithium dispersion was rinsed three times with dry pentane to remove its mineral oil coatings. Hexaphenyldisilane (1.142 g, 2.20 mmol) and lithium (0.208 g, 30.0 mmol) were placed in a flame-dried, 40-mL centrifuge tube equipped with a Teflon-coated magnetic stirrer bar. The vessel was capped with a rubber septum and removed from the glovebox. THF (15 mL) was added by syringe and the mixture stirred for 3 h at room temperature. The resulting dark brown solution was transferred by cannula through a 70–100- μ m fritted-glass filter into a 100-mL, three-necked, flame-dried, nitrogen-flushed flask equipped with a Teflon-coated magnetic stirrer bar and a 30-mL Kontes slow-addition funnel stoppered with a rubber septum and charged with a solution of (+)-(*S*)-2-octyl chloride ($[\alpha]_D^{25} + 33.9^\circ$, optical purity 91%; 0.595 g, 4.00 mmol) in THF (10 mL) at 25 °C. Addition was accompanied by efficient stirring and was carried out over a 2-h period after which the resulting solution was stirred an additional 3 h at 25 °C before adding water (10–20 mL) and dodecane (1.511 g; internal standard). This mixture was extracted with pentane and the organic layer dried (MgSO₄) and filtered. The yield of (-)-(*R*)-2-octyltriphenylsilane was determined by analytical HPLC. A suitable sample was subsequently isolated from a 2-ft, ¹/₈-in. column of 10% SE-30 on Chromosorb W. The colorless oil exhibited the following properties: $[\alpha]_D^{25} - 7.38^\circ$ (c 3.62, benzene); ¹H NMR (CCl₄) δ 0.63–2.0 (m, 17 H), 7.1–7.7 (m, 15 H); mass spectrum (70 eV), *m/e* (relative intensity) 373 (0.1), 372 (0.2), 260 (26), 259 (100), 181 (12), 105 (7.7).

Repetition of this procedure using hexaphenyldigermane (1.276 g, 2.10 mmol) yielded (-)-(*R*)-2-octyltriphenylgermane as a colorless oil: $[\alpha]_D^{25} - 8.74^\circ$ (c 3.77, benzene); ¹H NMR (CL₄) δ 0.6–2.3 (m, 17 H), 7.2–7.7 (m, 15 H); mass spectrum (70 eV), *m/e* (relative intensity) 417 (0.2), 415 (0.9), 305 (100), 303 (74.6), 301 (57.6), 227 (22), 225 (20), 223 (13), 151 (41), 149 (32), 147 (20).

Inverse-Addition Reaction of (+)-(*S*)-2-Octyl Bromide with (Triphenylsilyl)lithium (Prepared from Hexaphenyldisilane) and (Triphenylgermyl)lithium (Prepared from Hexaphenyldigermane) (Typical Procedure). A solution of (+)-(*S*)-2-octyl bromide ($[\alpha]_D^{25} + 30.3^\circ$, optical purity 70%; 0.773 g, 4.00 mmol) in THF (10 mL) was added by syringe into a 100-mL, three-necked, flame-dried, nitrogen-flushed flask equipped with a Teflon-coated magnetic stirrer bar and a 30-mL Kontes slow-addition funnel. The solution of (triphenylsilyl)lithium (prepared as described above) was transferred by cannula through 70–100- μ m fritted-glass filter into a Kontes slow-addition funnel. Addition was carried out over a 2-h period and the resulting mixture stirred an additional 3 h at room temperature and then quenched with water (10–20 mL). Dodecane (1.535 g) was added as internal standard. The mixture was extracted with pentane and the organic layer dried (MgSO₄) and subjected to analysis. An isolated sample of (-)-(*R*)-2-octyltriphenylsilane showed a specific rotation $[\alpha]_D^{25} - 4.00^\circ$ (c 2.57, benzene).

The equivalent reaction carried out with (triphenylgermyl)lithium yielded (-)-(*R*)-2-octyltriphenylgermane with a specific

(7) San Filippo, J., Jr.; Romano, L. J. *J. Org. Chem.* 1975, 40, 1514.

(8) Hudson, H. R. *Synthesis* 1969, 1, 112.

(9) Streitwieser, A., Jr.; Walsh, T. D.; Wolfe, J. R., Jr. *J. Am. Chem. Soc.* 1965, 87, 3682.

(10) In this regard it is perhaps cogent to note that these authors report a combined yield of 27% for compounds 5–7, while we observe the corresponding reaction between Ph₃GeLi and 2-bromooctane results in a 94% yield of compound 3.

(11) Pereyre, M.; Quintard, J.-P. *Pure Appl. Chem.* 1981, 53, 2401 and references therein.

(12) One such process can be viewed as originating in a one-electron transfer leading to the production of 2-octyl radicals which can be expected to produce *n*-octane and octenes by radical-radical disproportionation and hydrogen atom abstraction from the solvent (THF). Another process potentially capable of a similar product distribution is that arising from the reactions of 2-octyllithium (formed as a result of metal-halogen exchange) with solvent and alkyl halide.

(6) Kitching, W.; Olszowy, H.; Harvey, K. *J. Org. Chem.* 1981, 46, 2423; 1982, 47, 1893.

rotation $[\alpha]_D^{25} -8.79^\circ$ (*c* 3.73, benzene).

Normal- and Inverse-Addition Reactions of (+)-(S)-2-Octyl Bromide with (Triphenylstannyl)lithium (Prepared from Triphenyltin Chloride) were carried out as previously described.^{2a}

Normal-Addition Reaction of (+)-(S)-2-Octyl Chloride with (Triphenylmethyl)lithium (Prepared from Triphenylmethyl Chloride) (Typical Procedure). After several rinses with dry pentane in a glovebox to remove its mineral oil coatings, lithium (0.140 g, 20.2 mmol) was placed in a flame-dried, 40-mL centrifuge tube containing a Teflon-coated magnetic stirrer bar and capped with a rubber septum. THF (5 mL) was added by syringe. The centrifuge tube was placed in a water bath (25 °C) and a solution of triphenylmethyl chloride (1.210 g, 4.34 mmol) in THF (10 mL) was added through a cannula. The resulting dark red solution was allowed to stir for 2 h and then passed through a 70–100- μ m fritted glass filter into a 100-mL, three-necked, flame-dried flask equipped with a Teflon-coated magnetic stirrer bar and a 30-mL Kontes slow-addition funnel stoppered with a rubber septum and charged with a solution of (+)-(S)-2-octyl chloride ($[\alpha]_D^{25} +31.6^\circ$, optical purity 85%; 0.595 g, 4.00 mmol) in THF (10 mL). Addition was accompanied by efficient mixing and was completed in 2 h; the resulting reaction mixture was allowed to stir for an additional 3 h before quenching with water (10–20 mL). After being extracted with pentane, the organic layer was dried (MgSO₄). 2-Octyltriphenylmethane was isolated from GC by injection of the crude product which had been previously collected from HPLC. This material exhibited the following: $[\alpha]_D^{25} -35.20^\circ$ (*c* 3.17, benzene); ¹H NMR (CCl₄) δ 0.6–1.7 (m, 16 H), 3.3 (m, 1 H), 7.0–7.5 (m, 15 H); mass spectrum *m/e* (relative intensity) 357 (0.1), 356 (0.2), 244 (21.7), 243 (100.0), 166 (3.5), 165 (19.5).

Inverse-Addition Reaction of (+)-(S)-2-Octyl Bromide with (Triphenylmethyl)lithium (Prepared from Triphenylmethane) (Typical Procedure). Into a flame-dried, nitrogen-flushed 40-mL centrifuge tube equipped with a Teflon-coated magnetic stirrer bar were added *n*-butyllithium (1.6 M in pentane, 2.5 mL, 4.0 mmol) and THF (5 mL) by syringe, and the solution was chilled to –78 °C. Triphenylmethane (1.231 g, 5.04 mmol) in THF (10 mL) was slowly added by syringe. The temperature was slowly increased to 25 °C. A solution of (+)-(S)-2-octyl bromide ($[\alpha]_D^{25} + 30.3^\circ$, optical purity 70%; 0.773 g, 4.00 mmol) was placed in a 100-mL, three-necked, flame-dried, nitrogen-flushed flask equipped with a Teflon-coated magnetic stirrer bar and a 30-mL Kontes slow-addition funnel. The solution of (triphenylmethyl)lithium was filtered through 70–100- μ m fritted-glass filter into a Kontes slow-addition funnel. Addition was carried out over a 2-h period; this mixture was then stirred an additional 0.5 h at 25 °C and finally quenched with water. The resulting mixture was extracted with pentane and the organic layer dried (MgSO₄) and filtered. The optical rotation of (–)-(R)-2-octyltriphenylmethane was $[\alpha]_D^{25} -28.80^\circ$ (*c* 3.41, benzene).

Normal-Addition Reaction of (+)-(S)-2-Octyl Chloride with Triphenylsilyllithium (Prepared from Triphenylsilyl Chloride) (Typical Procedure). After several rinses with dry pentane in a glovebox to remove its mineral oil coatings, lithium (0.140 g, 20.2 mmol) was placed in a flame-dried, 40-mL centrifuge tube equipped with a Teflon-coated magnetic stirrer bar and capped with a rubber septum. THF (5 mL) was added by syringe. The centrifuge tube was placed in a water bath (25 °C), and a solution of triphenylsilyl chloride (1.240 g, 4.20 mmol) in THF (10 mL) was added through a cannula. The resulting dark brown solution was allowed to stir for 2 h and then transferred by cannula into a 70–100- μ m fritted-glass filter and whence into a 100-mL, three-necked, flame-dried, nitrogen-flushed flask equipped with a Teflon-coated magnetic stirrer bar and a 30-mL Kontes slow-addition funnel stoppered with a rubber septum containing a solution of (+)-(S)-2-octyl chloride ($[\alpha]_D^{25} +31.6^\circ$, optical purity 85%; 0.595 g, 4.00 mmol) in THF (10 mL). Addition was carried out over a 2-h period, and the resulting mixture was allowed to stir for an additional 3 h before quenching with water (10 mL). After being extracted with pentane, the organic layer was dried (MgSO₄). Analyses by HPLC showed 70% 2-octyltriphenylsilane ($[\alpha]_D^{25} -6.47^\circ$ (*c* 4.39, benzene)).

Reaction of the Tosylate of (–)-(R)-2-Octanol with Ph₃MLi (M = C, Si, Ge, Sn) (Typical Procedure). The solution Ph₃MLi in THF (15 mL) (prepared as described above) was filtered through a 70–100- μ m fritted-glass filter into a 30-mL Kontes slow-addition funnel equipped with a 100-mL, three-necked, flame-dried flask containing a solution of the tosylate of (–)-(R)-2-octanol ($[\alpha]_D^{25} -9.61^\circ$, optical purity 97%; 1.074 g, 4.00 mmol) in THF (10 mL). Addition was complete after 2 h and the resulting reaction mixture allowed to stir at 25 °C for additional 3 h before quenching with water (10–20 mL). The organic layer was dried (MgSO₄), filtered, and concentrated. Pure 2-C₈H₁₇MPH₃ was collected from GC by injection of the concentrated crude 2-C₈H₁₇MPH₃ collected from HPLC.

Relative Reactivity Profile. The relative reactivity of Ph₃MLi was determined by injecting a solution of the appropriate reagent into a 40-mL centrifuge tube equipped with a Teflon-coated stirrer bar, capped with a rubber septum and containing a solution of 2-octyl chloride or bromide in THF. After a predetermined period of time, the mixture was quenched with water and the yield of unreacted 2-octyl chloride or bromide determined.

Registry No. (–)-(R)-1, 82838-62-8; (+)-(S)-1, 82823-90-3; (–)-(R)-2, 82823-87-8; (+)-(S)-2, 82823-91-4; (–)-(R)-3, 82823-88-9; (+)-(S)-3, 82823-92-5; (+)-(S)-2-C₈H₁₇Br, 1191-24-8; (+)-(S)-2-C₈H₁₇Cl, 16844-08-9; (–)-(R)-2-C₈H₁₇OTs, 27770-99-6; (–)-(R)-2-C₈H₁₇SnPh₃, 82823-89-0; (+)-(S)-2-C₈H₁₇SnPh₃, 79055-00-8; Ph₃CH, 519-73-3; (–)-(R)-2-C₈H₁₇OH, 5978-70-1; Ph₃SiLi, 791-30-0; Ph₃GeLi, 3839-32-5; Ph₃SnLi, 4167-90-2; Ph₃CLi, 733-90-4; Ph₃CCl, 76-83-5; Ph₃SiCl, 76-86-8; TsCl, 98-59-9; hexaphenyldisilane, 1450-23-3; hexaphenyldigermane, 2816-39-9.

Secondary α -Deuterium Isotope Effects on Reactions of the Grignard Reagent from 1-Bromopentane-1,1-*d*₂

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Secondary α -deuterium isotope effects have been determined for reactions of the Grignard reagent from 1-bromopentane-1,1-*d*₂ with phenylacetylene and with benzonitrile. Isotope effects were found to be $0.99_3 \pm 0.03$ and $1.00_3 \pm 0.02_2$, respectively. The small isotope effects may be consistent with a variety of mechanisms, including electron transfer and cyclic or open polar electrophilic attacks on the carbon-magnesium bond.

Secondary deuterium isotope effects have assumed a very significant role in identifying mechanisms of nu-

cleophilic substitution at saturated carbon and in refining our understanding of the details of these mechanisms.¹