Bicyclo[4.3.0]nonene was prepared according to the method of Christol and Solladié.[15]

Bicyclo[4.3.0]nonene oxide was prepared by the same method as the decene oxide; since the alkene was impure, the oxide was also, bp 60–68° (15 mm) (lit.[15] bp 70–76° (20 mm)). No attempt was made at further purification.

trans-**8-Hydrindanol (2).** This alcohol was prepared by the lithium aluminum hydride reduction of the epoxide, as above. The yield was 85% of product, bp 82–85° (11 mm).

cis-**8-Hydrindanol (5).** This alcohol was prepared by the same hydroboration–oxidation sequence used for **4**. It had bp 85–88° (4.5 mm). Since gas chromatography indicated that it was only about 75% pure (contamination with secondary alcohols), it was further purified by column chromatography on alumina.

trans-**8-Hydrindanyl** *p*-**nitrobenzoate (11),** prepared as above, had mp 138.5–139.5°. The yield was 65%.

Anal. Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62. Found: C, 66.56; H, 6.56.

cis-**8-Hydrindanyl** *p*-**nitrobenzoate (8),** obtained in 62% yield, had mp 100.5–101.5°.

Anal. Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62. Found: C, 66.58; H, 6.70.

Bicyclo[3.3.0]octene. The method of Corey[20] and Paquette[21] was employed. In our hands the yield was 65% of a substance having ir and pmr spectra identical with those reported.

Bicyclo[3.3.0]octene Oxide. This epoxide was prepared as described above. The yield was 78% of epoxide, bp 55–60° (20 mm) (lit.[55] bp 92° (74 mm)).

trans-**Bicyclo[3.3.0]octan-1-ol (8).** This preparation followed that of **1**. There was obtained 61% product, bp 75–78° (20 mm), solidifying to a waxy solid in the receiver.

cis-**Bicyclo[3.3.0]octan-1-ol (6).** This alcohol was prepared by the hydroboration–oxidation method. Yield was 65% of material with bp 85–87° (16 mm) which solidified in the receiver. The ir was identical with that reported by Cope.[55]

trans-**1-Bicyclo[3.3.0]octyl** *p*-**nitrobenzoate (12)** was obtained in only 25% yield. It had a pseudo melting point at 135–136° and decomposed at 235°.

Anal. Calcd for $C_{15}H_{17}NO_4$: C, 65.44; H, 6.22; Found: C, 65.48; H, 6.17.

cis-**1-Bicyclo[3.3.0]octyl** *p*-**nitrobenzoate (9)** was obtained in 65% yield and had mp 124.0–124.8°.

Anal. Calcd for $C_{15}H_{17}NO_4$: C, 65.44; H, 6.22. Found: C, 65.59; H, 6.21.

Test for Ion Pair Formation. A 100-mg portion of ester was refluxed in 15 ml of 60% acetone for one half-life. The resulting solution was poured into water and extracted four times with small portions of ether. The combined extracts were washed with 10% sodium carbonate to remove *p*-nitrobenzoic acid, with water, and with brine, and dried over sodium sulfate. After removal of solvent, the entire residue was dissolved in deuteriochloroform and its pmr spectrum obtained. Spectra of authentic mixtures were employed for comparison, and it was shown that as little as 5% of one isomer in the other could be detected.

Resonances important for characterization were the *p*-nitrobenzoate absorption which differed by about 4 Hz between isomers and an absorption at 2.2 ppm in the cis isomers which was entirely lacking in the trans isomers.

Acknowledgments. We wish to thank the Petroleum Research Fund for support of this research in its early stages through Type G Grant No. 530. R. C. F. expresses his appreciation to Kent State University for a Faculty Research Fellowship.

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(55) A. C. Cope, J. M. Grisar, and P. E. Peterson, *J. Amer. Chem. Soc.*, 82, 4299 (1960).

Ether Cleavage and 1,3-Hydride Shifts in Reactions Involving Unsaturated Carbonium Ions[1a]

Melvin S. Newman[1b] and Charles D. Beard

Contribution from the Evans Chemistry Laboratory, The Ohio State University, Columbus, Ohio 43210. Received April 23, 1970

Abstract: High yields of anisole and 2-methoxyethyl 2-methyl-1-propenyl ether (III) are obtained when a solution of 5,5-dimethyl-*N*-nitrosooxazolidone (I) and phenol in 1,2-dimethoxyethane is treated with sodium phenoxide. A mechanism involving formation of an oxonium salt from solvent and an unsaturated carbonium ion is proposed to account for the results. Treatment of I with sodium phenoxide in benzene containing phenol yields a mixture of 2-methyl-1-propenyl phenyl ether (IV) and 2-methallyl phenyl ether (V) which are not interconverted under the experimental conditions. Mechanisms involving a 1,3-hydride shift are proposed to account for the results. An isotope effect is apparent in the 1,3-hydride shift.

The reaction of 5,5-dialkyl-*N*-nitrosooxazolidones with alkoxides in alcohols leads to the formation of a variety of vinyl ethers in good to high yields.[2] The present work was undertaken to see if aryl vinyl ethers could be prepared by a similar route.

When a solution of 5,5-dimethyl-*N*-nitrosooxazolidone (I) in glyme (1,2-dimethoxyethane) was added to a solution of sodium phenoxide and phenol in glyme an exothermic reaction took place and approximately the theoretical yield of nitrogen was evolved. By suitable work-up and glpc analysis of the products 79% anisole (II), 74% 2-methoxyethyl 2-methyl-1-propenyl ether (III), and only 11% of the expected 2-methyl-1-propenyl phenyl ether (IV) were shown to be present. The unexpected cleavage of the solvent in this reaction can be explained by postulating that an unsaturated carbonium ion (A) is formed from I and complexes with an ether linkage of glyme to yield the oxonium salt (B) which is attacked by phenoxide ion to yield anisole (II) and the vinyl ether III as shown in Scheme I.[3]

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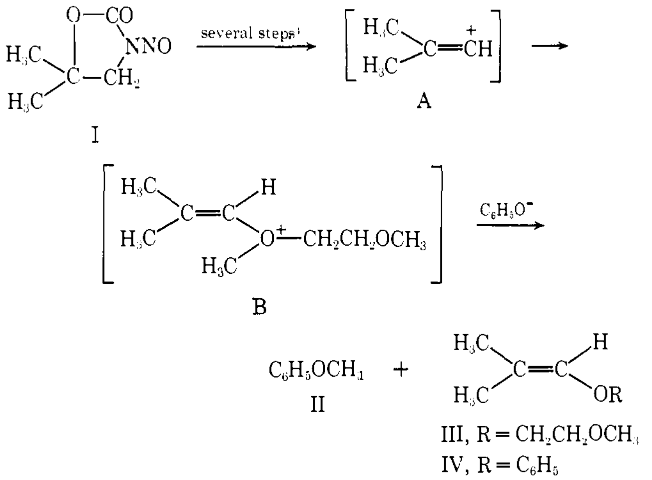
(1) (a) This research was supported by Grant 5552 of the National Science Foundation and Research Fund 178107 of The Ohio State University; (b) to whom correspondence should be addressed.

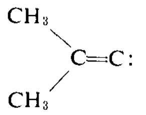
(2) M. S. Newman and A. O. M. Okorodudu, *J. Org. Chem.*, 34, 1220 (1969).

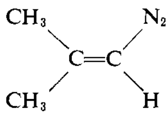
(3) When tetrahydrofuran was used as solvent in place of glyme no comparable ether cleavage was noted. For a similar cleavage of glyme during aprotic diazotization reactions, see A. T. Jurewicz, J. H. Boyless, and L. Friedman, *J. Amer. Chem. Soc.*, 87, 5789 (1965).

Scheme I



The above reactions represent an unusual cleavage of an ether linkage under alkaline conditions and indicate strongly that the unsaturated carbonium ion (A) is involved and not the corresponding unsaturated carbene (C).[2,5] As there was not even a transient color produced in the reactions with sodium phenoxide, the postulated unsaturated diazonium ion[4] (D) evidently reacts before it can couple to produce an azophenol.


C

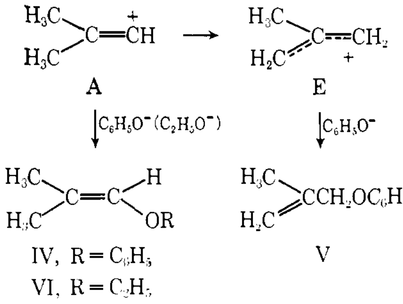

D

The structure of III was supported by elemental analyses, nmr spectral data, and the fact that the same compound was produced in high yield by treatment of I in 2-methoxyethanol with base as described for the general case.[2]

On attempting to prepare pure IV by treatment of a solution of I and phenol in benzene with sodium phenoxide, a mixture (7:3) of IV and 2-methallyl phenyl ether (V) was obtained in 65% yield. Both IV and V were shown to be stable under the reaction conditions. Under similar conditions treatment of I and ethanol in benzene with sodium ethoxide yielded only ethyl 2-methyl-1-propenyl ether (VI).

These results were tentatively explained (see Scheme II) by postulating that the unsaturated carbonium ion (A) is involved in each case. In the latter case, ethoxide ion, being a powerful nucleophile, reacts rapidly with A to form 2-methyl-1-propenyl ethyl ether (VI). However, when the weaker nucleophile, phenoxide ion, is involved, two reactions occur: one in which A reacts with phenoxide ion to form 2-methyl-1-propenyl phenyl ether (IV), and the second in which a 1,3-hydride shift occurs to form the allylic cation E which yields V on reaction with phenol or phenoxide ion (Scheme II).

Scheme II

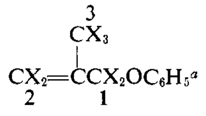


In an attempt to illucidate the mechanism the hexadeuterionitroso compound (I) was prepared from hexadeuterioacetone and treated as in Scheme II with sodium phenoxide in phenol and benzene. The deuterated compounds IV and V were isolated by preparative glcp and analyzed by nmr. The deuterated phenyl ether (IV) was shown to have one vinyl hydrogen and no methyl hydrogens, a result compatible with the reaction of either A (with two CD_3 groups) or C (two CD_3 groups) with phenol.

The 2-methallyl phenyl ether (V) obtained had more than one aliphatic hydrogen unequally distributed between positions 1 and 2 as recorded in Table I (experiments A and B). Hence the mechanism outlined in Scheme II is inadequate to account completely for the number of hydrogens found in V and in their uneven distribution between positions 1 and 2 because if E were the only intermediate involved, the distribution of hydrogen should be the same.

In a similar experiment except that undeuterated I was treated with sodium phenoxide and excess phenol-*O-D* in benzene, the results shown in experiment C, Table I, were obtained. This experiment also shows that deuterium exchange must have taken place prior to the final formation of compounds IV and V because more than one (1.39) deuterium atom appears in the products (which are stable to sodium phenoxide in benzene at reflux). Interestingly, the ratio of IV:V formed varies appreciably depending upon whether I or I-d_6 is used, indicating a kinetic isotope effect. When I is involved the ratio of IV:V is about 7:3 but with I-d_6 the ratio is 9:1.

Table I. Deuterated 2-Methallyl Phenyl Ether (V)



$$\overset{\overset{3}{CX_3}}{\underset{2}{CX_2}=\underset{1}{C}CX_2OC_6H_5}{}^{a}$$

Expt	Position	H	%	D	%
A[b]	1	1.51	76	0.49	24
	2	0.38	19	1.62	81
	3	0	0	3.00	100
B[b]	1	1.55	78	0.45	22
	2	0.24	12	1.76	88
	3	0.0	0	3.0	100
C	1	1.00	50	1.00	50
	2	1.61	81	0.39	19
	3	3.00	100	0.00	0

[a] X refers to H or D. [b] Since the reactions are heterogeneous at the start (see Experimental Section) exact reproducibility is difficult. Experiment C involved treatment of undeuterated I with sodium phenoxide and C_6H_5OD. This experiment was done only once after experience with experiments similar to A and B had been gained.

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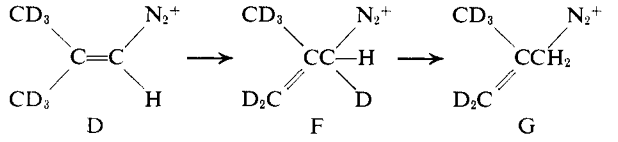
(4) See M. S. Newman and A. Kutner, *J. Amer. Chem. Soc.*, 73, 4199 (1951), for the hypothetical mechanism leading to A.

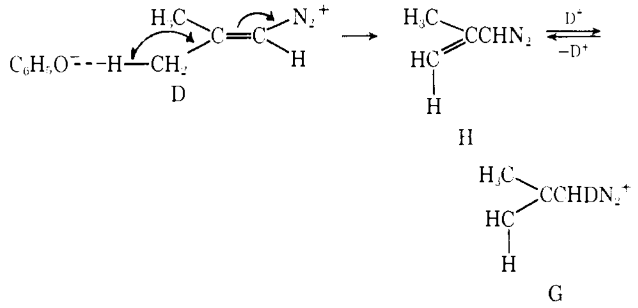
(5) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, pp 36–37, 64, 107–108, contains references of cleavage reactions of ethers by carbenes; however, these take place under pyrolytic conditions. For ether cleavage by photochemically generated methylene, see V. Franzen and L. Fikentscher, *Justus Liebigs Ann. Chem.*, 617, 1 (1958).

The results can be explained by assuming that one or more of the following mechanisms is involved: (1) a 1,3-hydride shift in the vinyl cation A (Scheme II);[6] (2) a 1,3-hydride shift in the postulated vinyl diazonium ion D (Scheme III); and (3) proton abstraction from a methyl group of D (Scheme IV).

Scheme III



Scheme IV



Mechanism 1 cannot be involved entirely because this pathway does not adequately account for the loss of deuterium in experiment A (Table I). The labeling data do not allow distinction between mechanism 2 and 3; however, both ultimately lead to the same intermediate F which can then undergo base-catalyzed hydrogen exchange[7,8] on the carbon attached to the diazonium group (Scheme III). This exchange is apparently not complete under the experimental conditions, but accounts for the excess of hydrogen in phenol solvent (experiments A and B, Table I) and deuterium in phenol-*O-D* (experiment C).

The fact that the excess hydrogen (deuterium) was found at position 1 (Table I) demands that paths 2 and/or 3 are involved. This conclusion is not unreasonable in view of studies[9] on alkaline treatment of nitrosocarbamates which show that the optically active 2-octyl and 2-butyl systems give considerable net inversion. In addition the fact that the ether corresponding to the original allylic nitrosocarbamate predominates on treatment of such carbamates with sodium methoxide lends support for mechanisms 2 and 3.[9,10]

Experimental Section[11]

2-Methoxyethyl 2-Methyl-1-propenyl Ether (III). A 20% solution of sodium 2-methoxyethoxide (0.039 mol) in 2-methoxyethanol was added dropwise to a solution of 5.0 g (0.035 mol) of I in 100 ml of 2-methoxyethanol at room temperature.[2] After the nitrogen evolution was complete the mixture was diluted with water and worked up as usual to yield 3.29 g (71%) of III, bp 151–155° (750 mm). The analytical sample [nmr bands at δ 5.75 (m, 1 H, $=CH$), 3.83–3.33 (A_2B_2 m, 4 H, OCH_2CH_2O), 3.32 (s, 3 H, OCH_3), 1.53 (m, 6 H, $(CH_3)_2C=$)] was obtained by preparative glpc near 145° with a helium flow of 120–140 cc/min.

Anal. Calcd for $C_7H_{14}O_2$: C, 64.6; H, 10.8. Found: C, 64.3; H, 10.8.

2-Methyl-1-propenyl Phenyl Ether (IV) and 2-Methallyl Phenyl Ether (V). To a dry stirred mixture at room temperature of 17 g of phenol and 5.6 g (0.048 mol) of sodium phenoxide in 100 ml of benzene was added dropwise a solution of 5.0 g (0.035 mol) of I[4] in 20 ml of benzene. The reaction was exothermic and was held at 40–50° for 2 hr when the theoretical amount of nitrogen had been collected. The initially heterogeneous reaction mixture became homogeneous after most of I had been added. The mixture was poured on water and, after the usual work-up which included three washes with 5% KOH, distillation afforded 3.1 g of a liquid, bp 45–60° (0.2 mm), shown to be a mixture of IV and V in the ratio 7:3 by glpc. The analytical sample of IV [nmr bands at δ 7.03 (m, 5 H, aromatic H), 6.17 (m, 1 H, $=CH$), 1.70 (s, 3 H, CH_3C-), 1.65 (s, 3 H, $CH_3C=$)] afforded a 2,4-DNPH derivative, mp and mmp with authentic 2,4-DNPH of isobutyraldehyde, 182–183°.

Anal. Calcd for $C_{10}H_{12}O$: C, 81.0; H, 8.2. Found: C, 81.0; H, 8.0.

The pure sample of V proved identical with an authentic sample prepared from 2-methallyl chloride and phenol as described.[12] No trace of IV was present in the synthetic sample of V[10] as shown by glpc analysis. In separate experiments pure IV and V were recovered unchanged after being held in refluxing benzene containing phenol and sodium phenoxide for 4 hr.

Ethyl 2-Methyl-1-propenyl Ether (VI). A suspension of 4.3 g of I in 30 ml of ethanol at 3–10° was treated with 3.2 g of lithium ethoxide ethanolate in portions during 30 min. After the nitrogen evolution ceased the mixture was poured on 50 ml of ice-water. The ethereal extract of the mixture was concentrated by distillation and the residue (1.93 g) was separated by preparative glpc on a 5 ft × 0.25 in. 20% FFAP (free fatty acid phase) column at 50° with a flow rate of 90 ml/min of helium. The analytical sample had nmr bands (CCl_4, TMS) at δ 1.20 (t, 3 H, OCH_2CH_3), 1.56 (m, small splitting, 6 H, $CH_3)_2C=C$), 3.70 (q 2, H. OCH_2CH_3), 5.76 (m, 1 H, $=CH$); ir absorption at 5.93 μ.

Anal. Calcd for $C_6H_{12}O$: C, 71.9; H, 12.1. Found: C, 71.8; H, 12.1.

Decomposition of I in Phenol–Glyme. A solution of 5.0 g of I in 15 ml of glyme was added dropwise to a solution of 5.6 g of sodium phenoxide and 17.5 g of phenol in 150 ml of glyme. The exothermic reaction was controlled at 40–50° for 2 hr. The mixture was poured on ice and worked up as usual to yield on distillation 6.89 g of liquid, bp 152–158° (755 mm), which by glpc analysis was shown to consist (mole ratios) of 48% anisole (II), 45% III, and 7% IV.[13] Calculations show that II, III, and IV were formed in 79, 74, and 11% yields, respectively.

Deuterium Experiments. A mixture of 6.4 g (0.1 mol) of acetone-d_6,[14] 16.7 g (0.1 mol) of ethyl bromoacetate, 6.6 g of activated zinc, and 100 ml of pure dry tetrahydrofuran was stirred for 4 hr at room temperature. A voluminous white solid appeared. Hydrolysis was effected with 30 ml of 1:1 glycerol–ammonium hydroxide.[15] After the usual work-up 10.1 g (72%) of ethyl 3-hydroxy-3-methylbutyrate-d_6 [bp 66–68° (15 mm); nmr (CCl_4) δ 4.17 (q, 2 H, OCH_2), 3.33 (s, 1 H, OH). 2.40 (s, 2 H, CH_2CO). 1.27 (t, 3 H, OCH_2CH_3)] was obtained. This ester was converted *via* the hy-

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(6) The 1,3-hydride shift and loss of nitrogen could be concerted and thus bypass the vinyl cation, A, *e.g.*, $D \rightarrow E + N_2$.

(7) See M. S. Newman and T. B. Patrick, *J. Amer. Chem. Soc.*, **91**, 6461 (1969), and references therein for a discussion of the formation of the postulated vinyl diazonium ion (D).

(8) A discussion of acidity of similar hydrogens in other cases is given in E. H. White, *ibid.*, **77**, 6014 (1955), and J. H. Bayless, A. T. Jurewicz, and L. Friedman, *ibid.*, **90**, 4465 (1968). See ref 2 also.

(9) (a) R. A. Moss and G. H. Temme, *Tetrahedron Lett.*, 3219 (1968); (b) R. A. Moss and S. M. Lane, *J. Amer. Chem. Soc.*, **89**, 5655 (1967).

(10) H. Hart and J. L. Brewbaker, *ibid.*, **91**, 716 (1969).

(11) Temperature readings are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. The term "worked up as usual" means that an ether–benzene solution of the products was washed with dilute acid and/or alkali as required, then with saturated salt solution, and dried by filtration through anhydrous magnesium sulfate. Nmr measurements were taken in CCl_4 with TMS as internal standard (δ, 0) on a Varian-A60 instrument. Analytical glpc were done in an Aerograph Hi-Fi Model 600 equipped with a flame ionization detector. A 6 ft × 1/8 in. aluminum column packed with 7% Carbowax 20M on 60–80 mesh Chromosorb W was used. Preparative glpc was performed in an Aerograph Model A-700 with a thermal conductivity detector. An aluminum column, 8 ft × 3/8 in., packed with 12% Carbowax 20M on 40–60 mesh Chromosorb W, was used.

(12) Q. R. Bartz, R. F. Miller, and R. Adams, *J. Amer. Chem. Soc.*, **57**, 371 (1935).

(13) When this and similar experiments were done, no examination of IV for the presence of small amounts of V was made.

(14) Used as obtained from the Strohler Isotope Inc. Nmr analysis showed no hydrogen within the sensitivity of the instrument.

(15) This improved method for running the Reformatsky reaction, in which the temperature is controlled and only molar amounts of zinc and bromo ester are used, was communicated to us by Dr. Michael W. Rathke of Michigan State University.

drazide, azide, and oxazolidone to I-d_6 as described for the undeuterated compounds.[4,6] The reactions with sodium phenoxide[16] and phenol (and work-up) were carried out exactly as described above for I. The results are listed in Table I. The result of a similar experiment involving I and C_6H_5OD[17] is also listed in Table I.

Acknowledgment. We thank Professors Jack Hine and Paul Gassman for interesting discussions concerning mechanisms of these reactions, and Mr. Wei Liang for the preparation and characterization of VI.

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(16) W. R. Boehme, "Organic Syntheses," Coll. Vol. IV, Wiley, New York, N. Y., 1963, p 592. The sodium phenoxide, further dried by distilling benzene from it, did not liberate gas when treated with sodium hydride.

(17) M. Charpentier-Morize, M. Mayes, and B. Tchoubar, *Bull. Soc. Chim. Fr.*, 529 (1965).

Optically Active Silyl- and Germylmethyllithium Reagents and the Stereochemistry of Carbene Insertions into the Silicon–Hydrogen and Germanium–Hydrogen Bonds

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Contribution from the Department of Chemistry,
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Abstract: The preparations of three optically active metalloidal-methyllithium reagents 1-NpPhMeMCHR′Li (M = Si, R′ = H or Ph; M = Ge, R′ = H) of known absolute configuration are described. These reagents have been used to determine the stereochemistry of the following reactions: the insertion of dibromocarbene into the SiH and GeH bonds; the insertion of carbethoxycarbene into the SiH bond; the thermal rearrangement of $R_3Si^*CH_2CO_2H$ and $R_3Si^*CHPhCO_2H$; and the base-catalyzed rearrangement of $R_3Si^*CHPhCO_2H$. In addition, the establishment of the absolute configuration and maximum specific rotation of R_3Ge^*Et now makes possible the unambiguous assignment of the stereochemistries of a number of reactions at asymmetric germanium.

In a recent publication several methods of preparing silyl- and germylmethyllithium reagents were reported and it was shown that use of the halogen–metal exchange reaction between n-butyllithium and α-bromosilanes and -germanes was a generally applicable route of considerable synthetic value.[1] This work has now been extended to some related optically active organolithium compounds and this paper describes the preparation and some applications of three such 1-naphthylphenylmethylmetalloidal reagents to stereochemical problems.

$$R_3M^*CH_2Br \xrightarrow{n\text{-BuLi}} R_3M^*CH_2Li,\quad M = Si, Ge$$

$$R_3Si^*CH_2Ph \xrightarrow{n\text{-BuLi–TMEDA}} R_3Si^*CHPhLi$$

Interest in this work arose from a desire to study the rearrangements of silylacetic acids (for which $R_3Si^*CHR'Li$ were obvious precursors) to their related acetoxysilanes.[2] However, since the reagents have known absolute configurations at the metalloid atom and can be prepared in high yield with nearly 100% optical purity, it is apparent that they will prove to be valuable intermediates for stereochemical studies in general, since their achiral analogs undergo a variety of reactions with different types of substrates (*e.g.*, carbon dioxide, alkyl iodides, cyanogen, ethyl chloroformate, and carbonyl compounds[1,3]) yielding β-functional organometalloids.

The 1-naphthylphenylmethylsilyl- and -germylmethyllithium reagents were prepared, as described previously for achiral substrates,[1] by insertion of dibromocarbene into the optically active silane, R_3Si^*H, or germane, R_3Ge^*H. While the dibromo compounds

$$R_3M^*H \xrightarrow{PhHgCBr_3} R_3M^*CHBr_2 \xrightarrow[2.\ HBr]{1.\ n\text{-BuLi}} R_3M^*CH_2Br \xrightarrow{n\text{-BuLi}} R_3M^*CH_2Li$$

R_3M^* = 1-NpPhMeSi or 1-NpPhMeGe

were in each case liquids, the monobromomethylsilane and -germane, the immediate precursors to the organolithium reagents, were crystalline solids. This was important because it was then possible to crystallize these to optical purity as judged by constant specific rotation. At the time this work was initiated it had been shown by Ritter and Sommer[4] that insertion of dibromocarbene into the SiH bond of R_3Si^*H gave an optically active product and it appeared possible from these studies to establish the stereochemistry of this insertion reaction using the reactions shown above as part of a Walden cycle. More recently, Sommer, *et al.*,[5] have shown that the insertion involves retention of configuration with high stereospecificity by correlating the configurations of 1-naphthylphenylmethyldibromo-

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* To whom correspondence should be addressed.

(1) A. G. Brook, J. M. Duff, and D. G. Anderson, *Can. J. Chem.*, **48**, 561 (1970). For a recently described alternative route to the monohalomethyl precursors see D. Seyferth and S. P. Hopper, *J. Organometal. Chem.*, **23**, 99 (1970).

(2) A. G. Brook, D. G. Anderson, and J. M. Duff, *J. Amer. Chem. Soc.*, **90**, 3876 (1968).

(3) C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960, p 394.

(4) A. Ritter and L. H. Sommer, Abstracts of First International Symposium on Organosilicon Chemistry, Prague, Czechoslovakia, Aug 1965, p 279.

(5) L. H. Sommer, L. A. Ulland, and A. Ritter, *J. Amer. Chem. Soc.*, **90**, 4486 (1968).