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Rearrangement and Cleavage of [(Aryloxy)methyl]silanes by Organolithium Reagents: Conversion of Phenols into Benzylic Alcohols[1]

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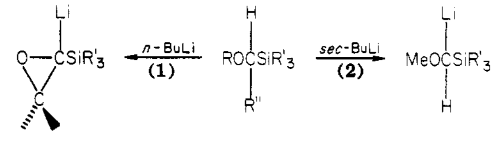
The feasibility of converting phenols into their corresponding benzylic alcohols by means of a novel Wittig rearrangement has been investigated. The method consists of (a) treating the phenol with (chloromethyl)trimethylsilane and base to produce the aryl (trimethylsilyl)methyl ether, (b) using *sec*- or *n*-BuLi in THF to transform this ether into the α-(trimethylsilyl)benzylic alcohol, and (c) removing the silyl group with alcoholic KOH to yield the benzylic alcohol. With phenols, such as phenol itself, 2-naphthol, and 9-phenanthrol, benzylic alcohols were obtained in 50–80% yields. Ring substituents of a nitro or methoxy type tend to favor α elimination in step b, at the expense of the Wittig rearrangement. The competitive nature of these latter two processes was examined as a function of substituents on the aryloxy groups or on the silicon, as well as a function of the lithium reagent and solvent employed. The independent synthesis and the thermal study of (phenoxymethyl)lithium demonstrated that in THF it undergoes an α elimination almost to the complete exclusion of any Wittig rearrangement. The relative importance of these two processes is discussed in terms of the locoselectivity of lithiation and an electron-transfer view of the Wittig aryl ether rearrangement.

The combined acidifying effect of an ether oxygen and an organosilyl group permits the smooth and selective lithiation of adjacent CH centers in silyl epoxides (1)[3] and in (alkoxymethyl)silanes (2);[4] (eq 1). The lithiations depicted in eq 1 are highly dependent upon the nature of the lithium reagent and the experimental conditions chosen. For example, epoxide 1 reacts with phenyllithium by attack at silicon to yield R'_3SiPh; similarly, ether 2 reacts with *n*-butyllithium to produce R'_3Si-*n*-Bu. In the present study we sought to apply these observations to effecting a novel type of a silyl Wittig rearrangement.[5] By selective lithiation of [(aryloxy)methyl]silanes (3) we hoped to induce an aryl migration to yield alcohol 4. Since 4 undergoes a facile desilylation with alcoholic KOH, the corresponding arylmethanol (5) could be readily produced. Finally, the starting ether 3 is accessible from the corresponding phenol 6. Were the rearrangement to succeed, the overall transformation would be the unusual homologization of a phenol (6) into its corresponding benzylic alcohol (5; Scheme I).

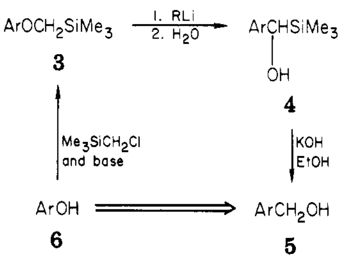


(1)

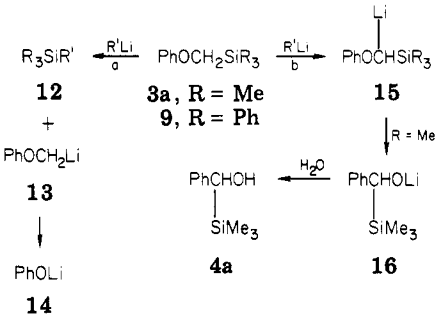
1, R with R'' as bridging C
2, R = Me; R'' = H

As will be seen in the following, this homologization procedure is realizable in a number of useful situations. Even with those ethers of type 3 where the reaction fails, some valuable insight has been gained concerning nucleophilic attack on silicon and the stability of [(aryloxy)alkyl]lithium reagents.

Scheme I



Scheme II



Results

Synthesis of [(Aryloxy)methyl]silanes. The [(aryloxy)methyl]trimethylsilanes (3) were prepared from the corresponding phenols (6) in high yields by two different procedures: (a) the preparation of the sodium phenoxide from sodium hydride in dimethyl sulfoxide and subsequent heating with (chloromethyl)trimethylsilane (7) [or with (chloromethyl)triphenylsilane (8)] or (b) the concerted interaction of the phenol 6, 7, and anhydrous K_2CO_3 in warm Me_2SO. The latter procedure proved superior for preparing the monocyclic aryl ethers with 7 (eq 2). Although the bulky Ph_3SiCH_2Cl reacted smoothly with sodium phenoxide by procedure a to yield the ether Ph_3SiCH_2OPh (9), a similar attempt with $(Me_3Si)_2CHCl$ (10) did not produce the corresponding ether

$$\underset{\textbf{6a–e}}{\mathrm{ArOH}} \xrightarrow[\text{2. } R_3SiCH_2Cl]{\text{1. base}} \underset{\textbf{3a–e}}{\mathrm{ArOCH_2SiMe_3}} \quad (2)$$

6a, Ar = Ph; **6b**, Ar = p-$MeOC_6H_4$; **6c**, Ar = p-$NO_2C_6H_4$; **6d**, Ar = 2-$C_{10}H_7$; **6e**, Ar = 9-$C_{14}H_9$

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[1] Part 16 of the series, "Organosilicon Compounds with Functional Groups Proximate to Silicon" (previous part: *J. Organometal. Chem.* **1982**, *225*, 5), as well as part 19 of the series, "Rearrangements of Organometallic Compounds".

[2] Visiting scholar from the Warsaw Technical University (Warszawa Politechnika).

[3] Eisch, J. J.; Galle, J. E. *J. Org. Chem.* **1976**, *41*, 2615; *J. Am. Chem. Soc.* **1976**, *98*, 4646; *J. Organometal. Chem.* **1976**, *121*, C10.

[4] Magnus, P. D.; Roy, G., *Chem. Commun.* **1979**, 822; full article: *Organometallics* **1982**, *1*, 553.

[5] (a) Schöllkopf, U. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 763. (b) West, R. In "Advances in Organometallic Chemistry"; Stone, F. G. A., West, R., Ed.; Academic Press: New York, 1977; Vol. 1b, p 1. (c) Eisch, J. J.; Kovacs, C. A.; Rhee, S.-G. *J. Organometal. Chem.* **1974**, *65*, 289.

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Table I. Hydrolysis Products from the Reaction of (Phenoxymethyl)silanes with Lithium Reagents

					composition of prod, %		
ether	lithium reagent	solvent	temp, °C	time, h	3a or 9 or SM[f]	ArOH	ArCHOHSiR$_3$
PhOCH$_2$SiMe$_3$ (3a)	*n*-BuLi	TMEDA	25	40		~100	*b*
	n-BuLi	THF	25	16	2	57	41[b]
	n-BuLi[c]	THF	25	24	30	40	30[b]
	n-BuLi[d]	hexane	70	6		~100	*b*
	n-BuLi	THF·Et$_2$O	25	20	3	81	16[b]
	n-BuLi	(MeOCH$_2$)$_2$	25	21	64	36	*b*
	n-BuLi	Et$_2$O	25	48	65	35	*b*
	sec-BuLi	THF	25	28	5	15	80[b]
	PhLi	THF	25	96	25	60	*e*
	PhLi	THF	70	20	10	85	*e*
PhOCH$_2$SiPH$_3$ (9)	MeLi	THF	25	16		~100	*e*
	n-BuLi	THF	25	16	12	88	*e*
2-C$_{10}$H$_7$OCH$_2$SiMe$_3$	*sec*-BuLi	THF	25	12	15	5	80
9-C$_{14}$H$_9$OCH$_2$SiMe$_3$	*sec*-BuLi	THF	25	12	25	10	55

[a] Unless otherwise noted, 2.0–2.5 equiv of RLi per 1 equiv of ROCH$_2$SiR'$_3$ were used. [b] Unless indicated, R$_n$SiR'$_{4-n}$ products were not analyzed. [c] One equivalent of RLi was used. [d] Three equivalents of RLi were used. [e] A mixture of R$_3$SiR' and R$_2$SiR$_2$' was formed (cf. Experimental Section and ref 6). [f] Starting material.

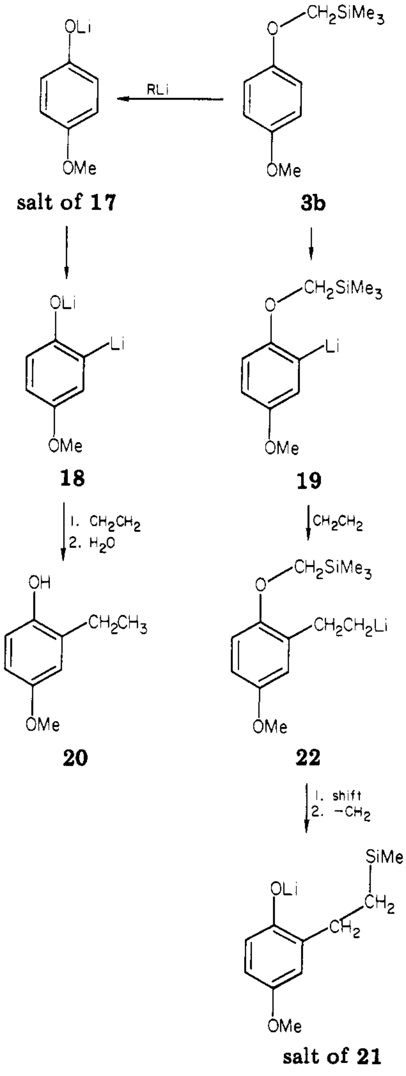
(Me$_3$Si)$_2$CHOPh (**11**) but only **3a**. Apparently **11** undergoes rapid further nucleophilic attack by phenoxide ion under the conditions of its formation (eq 3).

$$\underset{\textbf{10}}{(\mathrm{Me_3Si})_2\mathrm{CHCl}} \xrightarrow{\mathrm{NaOPh}} \underset{\textbf{11}}{(\mathrm{Me_3Si})_2\mathrm{CHOPh}} \xrightarrow[+\mathrm{H}^+]{\mathrm{NaOPh}} \underset{\textbf{3a}}{\mathrm{PhOCH_2SiMe_3}} \quad (3)$$

Lithiation of (Phenoxymethyl)silanes 3a and 9. In their lithiations, these ethers clearly illustrate how the nature of the lithium reagent determines the course of reaction (Table I). Two principal courses of reaction were competitive: nucleophilic attack on silicon (path a) and proton abstraction from the CH$_2$ group (path b; Scheme II). *n*-Butyllithium and especially *sec*-butyllithium in tetrahydrofuran solution favor the formation of **15** from **3a**. High yields of rearrangement product **4a** can be achieved in this manner. On the other hand, the use of *n*-butyllithium, either in ethyl ether or in *N,N,N′,N′*-tetramethylethylenediamine, gave no **4a** but only phenol, a sign of the generation and decomposition of **13** (cf. below). Likewise, phenyllithium in THF converted **3a** into a mixture of phenol, trimethylphenylsilane (**12**, R = Me, R′ = Ph), and dimethyldiphenylsilane[6] but gave no rearranged product **4a**. With the (triphenylsilyl)methyl ether **9**, neither *n*-butyllithium nor methyllithium in THF gave more than a trace of rearrangement. The predominant products were those resulting from nucleophilic attack at silicon (path a), namely, R$_3$SiR′ and phenol.

Lithiation of Other [(Aryloxy)methyl]trimethylsilanes 3b–3e. The (trimethylsilyl)methyl ethers of both 2-naphthol (**3d**) and of 9-phenanthrol (**3e**) underwent the desired rearrangement with *sec*-butyllithium in THF in good yields to give the corresponding arylmethanols (**5d** and **5e**). However, the *p*-nitrophenyl and *p*-methoxyphenyl ethers **3c** and **3b** did not react with lithiation of the OCH$_2$ grouping. Ever at −100 °C, **3c** underwent extensive decomposition, at least in part by path a in Scheme I, since some *p*-nitrophenol was formed. The reaction of the *p*-methoxy derivative **3b** with either *n*- or *sec*-butyllithium in THF took a more clear-cut course: the predominant formation of *p*-methoxyphenol (**17**) points to nucleophilic attack on silicon (path a, Scheme I) rather than lithiation of the OCH$_2$Si group. In the reaction with *n*-butyllithium, the considerable amounts of two ethylated products, **20** and **21**, suggest that lithio intermediates **18** and **19** are generated. These incorporate ethylene arising either from the α elimination of ArOCH$_2$Li[7] or from the lithiation of THF.[8] Intermediate product **22** probably undergoes a 1,6 silyl shift (for which rearrangement there

Scheme III



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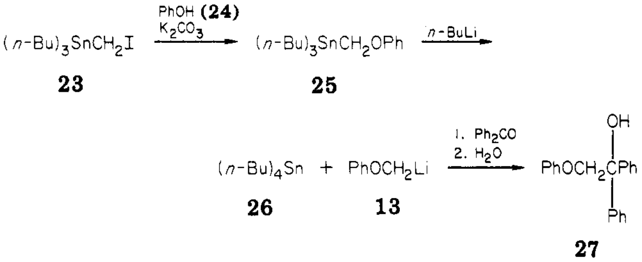
[6] In unpublished studies J. J Eisch and M.-R. Tsai have shown that arylsilanes of the types, Ar$_4$Si, Ar$_3$SiR, Ar$_2$SiR$_2$, and Ar$_3$SiSiR$_3$ tend to undergo redistribution of groups with RLi reagents, especially in THF or TMEDA media. In the present case, the Me$_3$SiPh initially formed from **3a** reacts further with PhLi to yield Me$_2$SiPh$_2$ as well.

Scheme IV

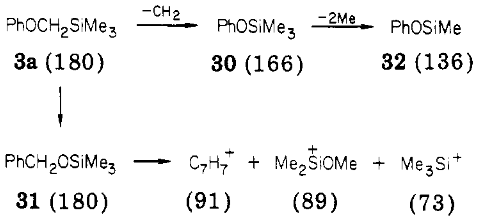


is precedent[9]) and an α elimination to yield the salt of product **21** (Scheme III).

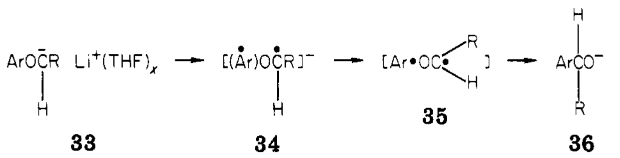
Generation and Behavior of (Phenoxymethyl)lithium (13) and Other Alkali Metal Derivatives. In order to produce lithium reagent **13** in an unambiguous fashion and study its chemical stability, we prepared the corresponding tin compound, tri-*n*-butyl(phenoxymethyl)tin (**25**).[10] Thus, the known tri-*n*-butyl(iodomethyl)tin (**23**) was treated in warm Me_2SO solution with phenol (**24**) and anhydrous K_2CO_3 to form **25** in 72% yield. Treatment of **25** with *n*-butyllithium in THF at −78 °C gave efficient tin–lithium exchange, as evidenced by the quantitative formation of tetra-*n*-butyltin (**26**). The other product, (phenoxymethyl)lithium (**13**), could be captured at low temperatures with benzophenone to give, upon hydrolysis, a good yield of 2-phenoxy-1,1-diphenylethanol (**27**; Scheme IV).

When lithium reagent **13** was generated at −78 °C in THF and the solution allowed to attain room temperature, no anisole or benzyl alcohol could be detected in the hydrolyzed product. Only phenol (85%) and tin derivative **26** were identified. This finding is in agreement with the behavior of $PhOCH_2SiMe_3$ (**3a**) and $PhOCH_2SiPh_3$ (**9**) toward phenyllithium in THF or *n*-butyllithium in TMEDA. In undergoing nucleophilic attack at silicon (path a in Scheme II) **3a** and **9** produce (phenoxymethyl)lithium (**13**), which appears to undergo α elimination to yield PhOLi faster than it undergoes a Wittig rearrangement.

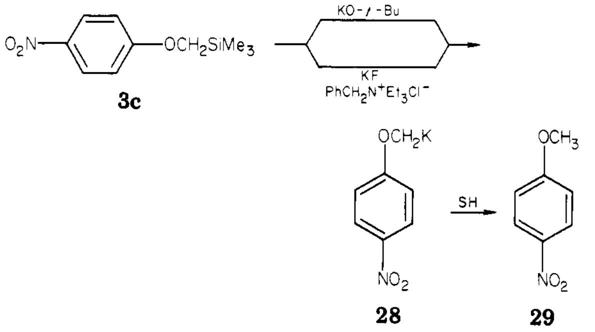
Scheme V



Scheme VI



In contrast, when the corresponding [(aryloxy)methyl]potassium reagent (**28**) was generated from *p*-nitrophenyl (trimethylsilyl)methyl ether (**3c**) in warm THF or acetonitrile, proton abstraction from the solvent was much faster than either α elimination or a Wittig rearrangement. As a result, *p*-nitroanisole (**29**) was formed (eq 4). A similar situation seems to obtain for the sodium salt, $PhOCHNaSiMe_3$, which is formed from $(Me_3Si)_2CHOPh$ and PhONa (eq 3). Here again, proton abstraction to yield $PhOCH_2SiMe_3$ is faster than a Wittig rearrangement.



(4)

α Elimination with (Phenoxymethyl)silanes upon Electron Impact. Although $PhOCH_2SiMe_3$ (**3a**) exhibits great thermal stability, showing no decomposition when kept at 200 °C for long periods, its mass spectrum at 70 eV shows interesting features. The principal peaks (intensity relative to the Me_3Si at 73 as 100) are at 180 (P, 29), 166 (30), 136 (30), 91 (41), 89 (10), 77 (12), and 73 (100). The strong peak at 166 is ascribed to $PhOSiMe_3$ (**30**), arising by α elimination of methylene. The presence of the 91, 89, and 73 peaks is consistent with a rearrangment to $PhCH_2OSiMe_3$ (**31**) and fragmentation to the tropylium ion, Me_3Si^+ and Me_2SiOMe^+. Finally, the peak at 136 can arise from **30** by α elimination to form silene **32** (Scheme V).

Discussion

Preparative Aspects. The attempted Wittig rearrangements of [(aryloxy)methyl]silanes succeeded in a sufficient number of cases to make it potentially useful in synthesizing arylmethanols from the corresponding phenols. At the same time, it is evident that electron-withdrawing, unsaturated substituents (NO_2) and electron-donating groups (MeO) can prevent the desired rearrangement. Despite its limitations, however, this homologizing procedure represents a unique way of utilizing a phenolic hydroxyl to build a carbon side chain on polycyclic aromatics.

Mechanism of Rearrangement. [(Aryloxy)methyl]lithium reagents bearing an α-trimethylsilyl group (**15a**) were found to undergo a smooth Wittig rearrangement, but the parent lithium reagent (**13**) gave essentially only α elimination. This dependence of the reaction path upon the structure of the lithium reagent can be rationalized in terms of a previously suggested mechanism for the Wittig rearrangement of aryl ethers.[5c] In this view, the solvent-separated ion pair **33** undergoes electron transfer (**34**), followed by homolysis (**35**). Collapse of the caged radicals yields the product (**36**; Scheme VI). The ease of rearrangement would then be determined by the electron affinity of the aryl group (step **33** → **34**) and the electron affinity of the carbonyl fragment, RCHO (step **34** → **35**). To explain why $PhOCH(SiMe_3)Li$ undergoes rearrangement, while $PhOCH_2Li$ fragments, one could note the stabilizing influence of the Me_3Si group on the radical ion (**35**). Such stabilization would not be present in the radical anion of formaldehyde (**37a–c**).

Selectivity of Lithiation. From the behavior of these [(aryloxy)methyl]silanes, it is evident that at least three

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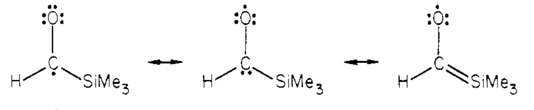
(7) As has been shown by U. Schöllkopf, H. Küppers, H. J. Traenckner, and W. Pitteroff, (*Justus Liebigs Ann. Chem.* **1967**, *704*, 120), (alkoxymethyl)lithium reagents, such as $MeOCH_2Li$, decompose to yield ethylene. Attempts to capture any intermediate methylene with cyclohexene were unsuccessful. Presumably, decomposition of the aggregate $(MeOCH_2Li)_x$ prevents escape of any carbene.

(8) For the lithiation and scission of THF into ethylene and lithium vinyloxide see Bates, R. B.; Kroposki, L. M.; Potter, D. E. *J. Org. Chem.* **1973**, *38*, 322.

(9) Eisch, J. J.; Tsai, M.-R. *J. Organometal. Chem.* **1982**, *225*, 5.

(10) Eisch, J. J. "Organometallic Syntheses"; Academic Press: New York, 1981; Vol 2, pp 96, 170, 174.



37a **37b** **37c**

sites of lithiation are important, namely, attack at the OCH_2, at silicon, and at the ortho position of the aryl group. From Table I it can be concluded that the desired lithiation at the OCH_2 group is best achieved with *sec*-BuLi or *n*-BuLi in THF. Chelating solvation of *n*-BuLi by TMEDA or glyme, however, forces lithiation to occur at silicon; this may be due to the greater steric demands of solvated reagents. On the other hand, media of lower solvating power than THF (ether or hexane) also favor attack at silicon. In these cases, the greater degree of association of $(n\text{-BuLi})_x$ (x = 4–6) may again cause a steric hindrance to OCH_2 attack. Finally, even in THF the less potent reagents, MeLi and PhLi, principally attack at silicon rather than at OCH_2. This preference might be ascribed to "softer" bases attacking a "softer" acid (silicon) rather than a "harder" acid (proton).

The significant amount of ortho lithiation with the [(*p*-methoxyphenoxy)methyl]silane **3b** may arise because the electron-donating *p*-methoxy group disfavors attack at the OCH_2 group. Although the *p*-nitro group in **3c** would be expected to foster lithiation, the oxidizing action of this group dominated over its acidifying effect.

α Elimination. When the lithium reagent attacked at silicon, the resulting $ArOCH_2Li$ underwent almost exclusively elimination, as studies with independently synthesized **13** proved. In the interaction between $PhOCH_2SiMe_3$ and PhLi in THF, small amounts of toluene, ethylbenzene, and *n*-butylbenzene were detected. These can be considered as phenyllithium-trapping products of the methylene and ethylene generated in the α elimination. Although the latter two could have also arisen from the THF, the toluene could come only from **13**. That the $O_2NC_6H_4OCH_2K$ generated from **3c** (eq 4) underwent protonation to $O_2NC_6H_4OCH_3$ before it underwent α elimination may be related to its solvent-separated ion pairing. Contact ion pairs seem to be more prone to elimination. For example, PhOCHLiPh undergoes >90% α elimination in ether, but in THF it gives >90% Wittig rearrangement.[11]

Experimental Section

General Procedures. All melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra (IR) were recorded on a Perkin-Elmer spectrometer Model 137 or Model 337, equipped with sodium chloride optics. Proton magnetic resonance spectra (^1H NMR) were obtained with a Varian spectrometer, Model A-60, on neat samples or on 10% solutions in pure solvents. The values are reported on the δ scale in parts per million with reference to internal or external tetramethylsilane, followed by the relative proton intensities and the coupling constants (J) in hertz. Vapor-phase chromatographic analysis (VPC) and isolations were carried out on an F & M chromatograph, Model 720, equipped with a 6 ft × 0.25 in. column of 10% SE-30 silicone gum rubber on Chromosorb P. Mass spectra of solids and liquids were obtained on a Varian MAT spectrometer, Model CH5, and those of gases on a Consolidated Electrodynamics instrument, Model CEC-21-620A. Elemental analyses were performed by the Spang Microanalytical Laboratory, Ann Arbor, MI.

All preparations and reactions involving air- and moisture-sensitive organometallic intermediates were conducted under an atmosphere of dry, oxygen-free nitrogen, with adherence to published procedures.[10] Solvents of reagent grade were used in all reactions. The anhydrous ethyl ether (Fisher) was used directly; the hexane and 1,2-dimethoxyethane were dried just before use by distilling from the sodium ketyl of benzophenone under a dry nitrogen atmosphere; the tetrahydrofuran (Baker) was stored overnight over sodium hydroxide pellets, then heated at reflux for 24 h over freshly cut pieces of sodium metal, distilled under a nitrogen atmosphere from the sodium, and finally redistilled from lithium aluminum hydride just prior to use; the dimethyl sulfoxide was stirred with calcium hydride and then subjected to distillation under reduced pressure.

Hydrolyses were generally conducted by the slow addition of a 5% aqueous HCl solution, and the organic product was extracted into ethyl ether. The solvent was removed after drying over anhydrous magnesium sulfate. The organolithium reagents were analyzed by established titrimetric procedures.[12]

Starting Materials. Phenyl (Trimethylsilyl)methyl Ether (3a). Fifty milliliters of dried dimethyl sulfoxide (Me_2SO) was added to the sodium hydride obtained by washing 2.0 g (50 mmol, 60% in oil) of sodium hydride with three 90-mL portions of anhydrous diethyl ether under nitrogen. To this suspension was added 5.7 g (50 mmol) of phenol in 50 mL of dried dimethyl sulfoxide (Me_2SO) by a pressure equalizing funnel, and the mixture was stirred at 25 °C for 8 h. Then 6.13 g (50 mmol) of (chloromethyl)trimethylsilane was added and stirring was continued for 8 h. After hydrolysis with distilled water and extraction with ether, the ether layer was washed several times with water, dried (magnesium sulfate), and concentrated to give a light-brown crude product. Fractional distillation afforded 7.8 g (87%) of the desired product: bp 83–84 °C (8 mm); ^1H NMR (neat) 0.00 (s, 9 H), 3.32 (s, 2 H), 6.63–7.25 ppm (m, 5 H); IR (neat) 3030 (w), 2970 (s), 1600 (s), 1490 (s), 1430 (s), 1290 (s), 1250 (s, br), 1165 (s), 1075 (m), 1025 (s), 850 (s, br), 750 (s), 690 cm^{-1} (s); mass spectrum, *m/e* 180 (P), 166 (P − CH_2), 136 (P − C_3H_8), 107 ($C_6H_5OCH_2$), 91 (C_7H_7), 77 (C_6H_5), 73 ($SiMe_3$). Anal. Calcd for $C_{10}H_{16}OSi$: C, 66.59; H, 9.50. Found: C, 66.55; H, 9.44.

Attempted Preparation of Phenyl Bis(trimethylsilyl)methyl Ether (11). By a known procedure dichlorobis(trimethylsilyl)methane[13] was prepared from dichloromethane, chlorotrimethylsilane, and *n*-butyllithium at −120 °C: bp 115–118 °C (58 mm); 62% yield; ^1H NMR (neat) 0.22 ppm. Further treatment of this product with *n*-butyllithium in THF at −110 °C and subsequent hydrolysis provided 71% of chlorobis(trimethylsilyl)methane:[14] bp 98–104 °C (64 mm); ^1H NMR (neat) 0.0.

The interaction of 2.0 g of sodium hydride (50 mmol) with 4.7 g (50 mmol) of phenol in 50 mL of anhydrous dimethyl sulfoxide was conducted at 25 °C for 8 h. Then 9.67 g (50 mmol) of chlorobis(trimethylsilyl)methane was added and stirring was continued for 8 h. Usual isolation yielded principally phenyl (trimethylsilyl)methyl ether (**3a**) and the starting chloride.

Phenyl (Triphenylsilyl)methyl Ether (9). (Chloromethyl)triphenylsilane was prepared from trichloro(chloromethyl)silane (10 mmol) in 15 mL of tetrahydrofuran and phenylmagnesium bromide (30 mmol) in 120 mL of the same solvent. After 2 h at reflux and 15 h at 25 °C the reaction mixture was hydrolyzed with aqueous NH_4Cl solution. Usual workup and crystallization of the crude product from absolute ethanol afforded 15 g of pure product: mp 113–114.5 °C (lit.[15] mp 113–114 °C); NMR ($CDCl_3$) δ 3.50 (s, 2 H), 7.28–7.85 (m, 15 H).

The interaction of 1.45 g of sodium hydride (30 mmol) with 2.82 g (30 mmol) of phenol in 40 mL of dimethyl sulfoxide was carried out at 25 °C for 8 h. Then 9.25 g (30 mmol) of (chloromethyl)triphenylsilane was added and the mixture stirred at 70–75 °C for 5 h. The usual workup gave a crude product that was washed with cold, absolute ethanol and then recrystallized from a chloroform–hexane mixture. The resulting product, **9**, was

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(11) Schöllkopf, U.; Eisert, M. *Justus Liebigs Ann. Chem.* **1963**, *664*, 76.

(12) Reference 10, pp 89–91.

(13) Bamford, W. R.; Paul, B. C. *J. Chem. Soc.* C **1967**, 1471.

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isolated in 55% yield (6.1 g) and melted at 142–142.5 °C: NMR ($CDCl_3$) δ 4.33 (s, 2 H), 6.87–7.85 (m, 20 H). Anal. Calcd for $C_{25}H_{22}OSi$: C, 81.80; H, 6.01. Found: C, 81.60; H, 5.82.

***p*-Methoxyphenyl (Trimethylsilyl)methyl Ether (3b).** A mixture of 7.5 g (60 mmol) of *p*-methoxyphenol, 7.8 g (66 mmol) of (chloromethyl)trimethylsilane, 10 g of powdered, anhydrous K_2CO_3, and 100 mL of anhydrous Me_2SO was heated on a steam bath for 27 h. The cooled mixture was admixed with water and ether and the resulting organic layer was separated and dried over anhydrous $MgSO_4$. After solvent removal the residue was chromatographed on silica gel with a hexane–ether gradient. With 6% ether the pure product was eluted, 9.4 g (68%). Recrystallization from hexane at −25 °C gave a melting point of 59–60 °C: NMR ($CDCl_3$, relative to $SiMe_3$) δ 0.0 (s, 9 H), 3.40 (s, 3 H), 6.72 (s, 4 H). Anal. Calcd for $C_{11}H_{18}O_2Si$: C, 62.81; H, 8.62. Found: C, 62.73; H, 8.62.

***p*-Nitrophenyl (Trimethylsilyl)methyl Ether (3c).** In a manner analogous to the preparation of **3b**, *p*-nitrophenol was converted into **3c** in a 93% yield on a 70-mmol scale. Recrystallization from hexane at −20 °C gave a melting point of 54–54.5 °C: NMR ($CDCl_3$, relative to $SiMe_3$) δ 0.0 (s, 9 H), 3.60 (s, 2 H), 6.93 (m, 2 H), 8.13 (m, 2 H). Anal. Calcd for $C_{10}H_{15}NO_3Si$: C, 53.30; H, 6.71. Found: C, 53.46; H, 6.67.

2-Naphthyl (Trimethylsilyl)methyl Ether (3d). On a 10-mmol scale, 2-naphthol was converted into **3d** by a procedure analogous to that for **3a**: NMR ($CDCl_3$, relative to $SiMe_3$) δ 0.0 (s, 9 H), 3.41 (s, 2 H), 6.96 (m, 4 s), 7.4 (m, 3 s). Anal. Calcd for $C_{14}H_{18}OSi$: C, 72.99; H, 7.87. Found: C, 73.10; H, 7.72.

9-Phenanthryl (Trimethylsilyl)methyl Ether (3e). By the method employed for **3a**, 9-phenanthrol was converted into **3e** in a 65% yield on a 13-mmol scale: NMR (CCl_4) δ 0.28 (s, 9 H), 3.7 (s, 2 H), 7.5 (m, 6 H), 8.4 (m, 3 H). Anal. Calcd for $C_{18}H_{20}OSi$: C, 77.09; H, 7.19. Found: C, 77.23; H, 7.33.

Tri-*n*-butyl(phenoxymethyl)tin (25). A mixture of 34.2 g (80 mmol) of tri-*n*-butyl(iodomethyl)tin,[16] 8.3 g (88 mmol) of phenol, and 12 g of powdered, anhydrous K_2CO_3 in 100 mL of anhydrous Me_2SO was stirred for 48 h at room temperature and for 20 h at 70–75 °C. The cooled mixture was diluted with 150 mL of a 1:1 ether–pentane mixture and the resulting suspension extracted with five 50-mL portions of water. The organic layer was dried over anhydrous $MgSO_4$, and the volatiles were evaporated. Chromatography on a silica gel column and elution with hexane yielded 23 g of **25**, which was pure by analytical and spectral criteria: NMR (CCl_4) δ 0.75–2.65 (m, 27 H), 4.1 (s, 2 H), 6.7–7.3 (m, 5 H). Anal. Calcd for $C_{19}H_{34}OSn$: C, 57.46; H, 8.63. Found: 57.19; H, 8.70.

Rearrangements of Phenyl (Trimethylsilyl)methyl Ether (3a). a. *n*-Butyllithium in Tetrahydrofuran. Under a nitrogen atmosphere 900 mg (5 mmol) of **3a** in 10 mL of anhydrous THF was placed in a serum-capped, two-necked flask also equipped with a nitrogen inlet. Then 10 mmol of *n*-butyllithium in hexane (2.2 M) was injected into the solution and the yellow solution stirred for 16 h at 25–30 °C. Hydrolysis with 6 N aqueous HCl, addition of ether, separation, drying, and evaporation of the organic phase gave an oil, whose GLC analysis (150 °C, on a 12-ft column prepared from 10% SE-30 on Chromosorb W) showed the presence of 57% of phenol, 41% of α-(trimethylsilyl)benzyl alcohol (**4a**) and 2% of **3a**. The product, **4a**, was collected and identified both by its NMR spectrum ($CDCl_3$, relative to $SiMe_3$ [δ 0.0 (s, 9 H), 2.3 (br s, 1 H), 4.42 (s, 1 H), 7.22 (s, 5 H)] and by heating a sample with alcoholic KOH solution. The latter reaction produced benzyl alcohol quantitatively.

When only 1 equiv was employed, the yield of **4a** was 30%; use of 3–6 equiv of the lithium reagent did not increase the yield of **4a**.

b. *n*-Butyllithium in Other Media. Comparable rearrangements in other solvents gave the following yields of **4a**: 3 equiv of *n*-BuLi in hexane for 6 h at reflux, no **4a** but only phenol; in glycol dimethyl ether, no **4a** and a 36:40 mixture of phenol and **3a**; in a 1:1 mixture of THF and ether, 16% of **4a**, 81% of phenol, and 3% of **3a**; in pure ether after 48 h, a 35:65 mixture of phenol and **3a**; and in pure *N,N,N′,N′*-tetramethylethylenediamine after 40 h, only phenol was produced quantitatively.

c. *sec*-Butyllithium in Tetrahydrofuran. A solution of 3.6 g (20 mmol) of **3a** in 80 mL of anhydrous THF was treated with 50 mmol of *sec*-butyllithium (1.5 M in cyclohexane) and the mixture stirred at 20–25 °C for 28 h. Usual hydrolysis workup gave 3.28 g (91%) of crude product. This product was heated for 2 h in a solution of 1.7 g of KOH dissolved in 30 mL of methanol. Dilution with water and ether, followed by the separation, drying, and evaporation of the organic layer, gave 1.8 g of crude product. Bulb-to-bulb distillation at 0.1 mm gave 1.4 g (64%) of pure benzyl alcohol (oven, 110 °C).

d. Phenyllithium in Tetrahydrofuran. A solution of 900 mg (5 mmol) of **3a** in 15 mL of anhydrous THF was treated with 10 mmol of phenyllithium in ethyl ether. After 96 h at 25–30 °C hydrolysis and GLC analysis showed the presence of 60% of phenol, 20% of trimethylphenylsilane, 25% of dimethyldiphenylsilane, and 25% of **3a**.

A solution of (2.8 mmol) of **3a** in 15 mL of anhydrous THF was allowed to react with 7.0 mmol of phenyllithium in ethyl ether for 16 h at 20–25 °C. The starting material was converted to the extent of 80% into a 1.0:0.8 mixture of trimethylphenylsilane and phenol. By GLC detection and separation, toluene, ethylbenzene, and *n*-butylbenzene were also identified. However, traces of ethylbenzene and *n*-butylbenzene were also detected from a control run of phenyllithium in THF, from which ether **3a** was omitted.

Attempted Rearrangements of Phenyl (Triphenylsilyl)methyl Ether (9). a. Methyllithium in Tetrahydrofuran. A solution of 1.25 g (2.0 mmol) of **9** in 15 mL of anhydrous THF at −78 °C was treated with 2.0 mmol of methyllithium in ethyl ether. Upon gradual warming the solution turned yellow at −10 °C and then orange at 25 °C. After a 16-h stirring period the reaction mixture was hydrolyzed with 5% aqueous HCl. Workup and isolation of the organic layer showed it to contain a 1.0:0.92:0.4 ratio of phenol, methyltriphenylsilane, and dimethyldiphenylsilane, as demonstrated by GLC separation and NMR spectroscopy. No starting ether **9** was present.

b. *n*-Butyllithium in Tetrahydrofuran. A solution of (2.8 mmol) of **9** in 15 mL of anhydrous THF at −78 °C was treated with 1 equiv of *n*-butyllithium in hexane and the resultant solution stirred at −30 °C for 6 h. Usual hydrolytic workup led to the isolation of 25% of phenol, 10% of pure, recrystallized *n*-butyltriphenylsilane (from 95% ethanol), and 60% of **9**. An NMR spectrum of the total crude organic product showed the absence of peaks ascribalbe to anisole (CH_3) or benzyl alcohol (CH_2).

When 2.8 mmol of **9** in 15 mL of anhydrous THF was treated with 5.6 mmol of *n*-butyllithium and the mixture then stirred at 20–25 °C for 16 h, usual workup showed the presence of a 1.0:0.95:0.2 ratio of phenol, *n*-butyltriphenylsilane, and di-*n*-butyldiphenylsilane. The starting ether **9** remained in 12%.

Attempted Rearrangement of Tri-*n*-butyl(phenoxymethyl)tin (25). A solution of 3.97 g (10 mmol) of **25** in 40 mL of anhydrous THF at −78 °C was treated with 6.9 mL of 1.6 M *n*-butyllithium (11 mmol) in hexane over the course of 5 min. After a further 10 min, 2.0 g (11 mmol) of solid benzophenone was added. The resultant, stirred mixture was allowed to come to 20–25 °C and then treated with aqueous NH_4Cl solution. Separation of the organic layer, drying over anhydrous Na_2SO_4, evaporation of the solvent, and column chromatography of the organic residue on silica gel with a hexane–ether gradient gave 3.5 g (100%) of tetra-*n*-butyltin and the alcohol product admixed with benzophenone. Recrystallization of the latter from hexane gave 1.42 g (49%) of 2-phenoxy-1,1-diphenylethanol (**27**), mp 99–100 °C. An additional 0.55 g of product could be obtained as a second crop (67% in all). NMR ($CDCl_3$) δ 3.50 (s, OH), 4.42 (s, 2 H), 6.75–7.6 (m, 15 H). Anal. Calcd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25. Found: C, 82.51; H, 6.07.

An identical run to the foregoing, except that the benzophenone was omitted, gave upon hydrolytic workup the same high yield of tetra-*n*-butyltin and 85% of phenol. During the solvent evaporation the temperature was kept below 30 °C. The crude reaction product, however, gave no NMR spectral peaks characteristic of anisole or benzyl alcohol.

Action of Bases on Para-Substituted Phenyl (Trimethylsilyl)methyl Ethers. a. *p*-Nitrophenyl Derivative 3c. Despite the use of reaction temperatures between −78 and −100 °C, *n*-butyllithium, *sec*-butyllithium, or lithium diiso-

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(16) Reference 10, pp 170–171.

propylamide (2.5 equiv in THF) gave none of the desired rearrangement. Even when the resulting dark-colored hydrolysis products were heated with alcoholic KOH solution (to convert any ArCHSiMe$_3$OH into ArCH$_2$OH), no *p*-nitrobenzyl alcohol could be detected. The only identifiable product was *p*-nitrophenol.

Heating **3c** (4 mmol) in 10 mL of anhydrous THF with 10 mmol of potassium *tert*-butoxide for 8 h and hydrolysis produced *p*-nitroanisole (35%).

Likewise, letting a suspension of 5 mmol of **3c**, 50 mmol of anhydrous KF, and 2.5 mmol of benzyltriethylammonium chloride in 25 mL of acetonitrile reflux for 24 h and then hydrolyzing gave only a 1:3 mixture of *p*-nitroanisole and **3c**.

b. *p*-Methoxyphenyl Derivative 3b. A solution of 840 mg (4 mmol) of **3b** in 30 mL of anhydrous THF at −78 °C was treated with 10 mmol of *n*-butyllithium in hexane. After 0.5 h at −78 °C the mixture was warmed up to 25 °C over 1 h and stirred a further 16 h. The crude product (309 mg) obtained after the usual hydrolytic workup consisted of over 60% of *p*-methoxyphenol, 10% of **3b**, and 30% of a mixture of 2-ethyl-4-methoxyphenol (**20**) and 4-methoxy-2-[2-(trimethylsilyl)ethyl]phenol (**21**). The latter two components were separated from each other by GLC and the IR spectrum of each displayed a broad band at 3350 cm^{-1}. **20**: NMR (CDCl$_3$) δ 1.12 (t, 3 H, $J = 7$ Hz), 2.74 (q, 2 H, $J = 7$ Hz), 3.96 (s, 3 H), 5.57 (br s, 1 H), 6.81 (br s, 3 H). **21**: NMR (CHCl$_3$) δ 0.20 (s, 9 H), 0.8–1.2 (m, 2 H), 2.6–2.9 (m, 2 H), 3.9 (s, 3 H), 4.67 (br s, 1 H), 6.81 (br s, 3 H). No NMR signals characteristic of *p*-dimethoxybenzene or of *p*-methoxybenzyl alcohols were observed in the hydrolysis products.

When 2 mmol of **3b** in 15 mL of anhydrous THF was treated with 5 mmol of *sec*-butyllithium for 16 h at 20–25 °C and then worked up by the usual acidic hydrolysis, a 28% conversion of **3b** to *p*-methoxyphenol was observed.

Rearrangement of 2-Naphthyl (Trimethylsilyl)methyl Ether (3d). A solution of 1.15 g (5 mmol) of **3d** in 40 mL of absolute THF at −78 °C was treated with 12.5 mmol of *sec*-butyllithium in cyclohexane. The reaction mixture was allowed to come to 20–25 °C and stirred there for 12 h. Treatment with water and ether and the usual workup gave an organic product, whose NMR spectrum showed the absence of **3d**. The product was heated to reflux with 600 mg of KOH in 15 mL of methanol for 8 h. Usual workup and column chromatography of the organic product on silica gel with a hexane–ether gradient yielded 62% of 2-naphthalenemethanol, mp 79–80 °C from hexane (lit.[17] 80–80.5 °C).

Rearrangement of 9-Phenanthryl (Trimethylsilyl)methyl Ether (3e). A solution of 2.6 g (8.8 mmol) of **3e** in 40 mL of absolute THF at −78 °C was treated with 23 mmol of *sec*-butyllithium in cyclohexane. The reaction mixture was allowed to come to 20–25 °C and stirred there for 12 h. Usual workup and column chromatography on silica gel gave 0.58 g (32%) of 9-phenanthrenemethanol, mp 148–149 °C (lit.[18] mp 149 °C).

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Registry No. **3a**, 75144-61-5; **3b**, 83693-52-1; **3c**, 83693-53-2; **3d**, 83693-54-3; **3e**, 83693-55-4; **4a**, 17876-95-8; **6a**, 108-95-2; **6b**, 150-76-5; **6c**, 100-02-7; **6d**, 135-19-3; **6e**, 484-17-3; **7**, 2344-80-1; **8**, 17067-65-1; **9**, 83693-56-5; **10**, 5926-35-2; **11**, 83693-57-6; **13**, 83693-58-7; **20**, 13391-32-7; **21**, 83693-59-8; **23**, 66222-29-5; **25**, 83693-60-1; **26**, 1461-25-2; **27**, 5432-02-0; **28**, 83693-61-2; **29**, 100-17-4; benzyl alcohol, 100-51-6; 2-naphthalenemethanol, 1592-38-7; 9-phenanthrenemethanol, 4707-72-6.

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Diels–Alder Reactions of Cycloalkenones. 1. Preparation and Structure of the Adducts[1]

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Uncatalyzed and aluminum chloride induced Diels–Alder reactions of 2-cyclopentenones, 2-cyclohexenones, and 2-cycloheptenones with 1,3-butadiene, isoprene, and (*E*)-piperylene are described. Structure analysis of the adducts and their hydrogenation products by standard means and ^{13}C NMR spectroscopy is presented.

For half a century the Diels–Alder reaction has served as one of the best methods of synthesis of six-membered carbocycles.[4] The ease of the cycloaddition of diene and dienophile (illustrated below, for example, by the production of 1,2,5,6-tetrahydrobenzaldehyde from the interaction of acrolein with 1,3-butadiene), the rapid accumulation of polyfunctionality in a relatively small molecular framework, the extraordinary stereochemical control of the cycloaddition, and the fair predictability of its regiochemistry have contributed to the popularity of the reaction in general organochemical synthesis. In the realm of natural products synthesis, in which a premium is put on the rapidity of construction of polyfunctional, highly bridged carbon, and heteroatom networks, the Diels–Alder reaction has left a special imprint. By the use of cyclic dienes and/or dienophiles facile syntheses of polycycles have emerged. In this connection, however, one highly desirable research goal has remained elusive, i.e., the synthesis of octalones and related bicyclic olefinic ketones by the reaction of conjugated dienes with conjugated cycloalkenones (e.g., the reaction between 1,3-butadiene and 2-cyclohexenone depicted below). Whereas, in principle,

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