mide analyses were performed using either 10% diethylene glycol succinate or 20% silicone oil on Chromosorb W, 80–100 mesh. For reductions of methyl cinnamate, most reactions utilized 2.0 g. of ester in 50 ml. of solvent. For reductions of β-bromostyrene, most reactions utilized about 1 g. of bromide in 20–60 ml. of solvent. All reactions were stirred continuously, either magnetically or mechanically. It was found that yields increased as the addition time of acid was lengthened. The following is a description of a typical reduction of methyl cinnamate. Into a mechanically stirred slurry of 5.0 g. of PADA in 50 ml. of dioxane in a N_2 atmosphere was dissolved 2.0 g. of ester. A solution of 1.3 g. of acetic acid in 5 ml. of dioxane was added over a period of about 30 min. After 9 hr. an equal amount of acid was slowly added. No yellow solids were noted after a total elapsed time of 19 hr. Analysis of the reaction mixture by v.p.c. showed only two peaks, identical in retention time with hydrocinnamate and cinnamate, whose areas, after correcting for differences in detector sensitivity, corresponded to 93% saturated and 7% unsaturated product.

Commercial β-bromostyrene contained 8% of the *cis* isomer[9] according to v.p.c. examination. This was corroborated by n.m.r. examination which showed parts of two vinylic AB patterns in a ratio close to 92:8, J_{AB} = 14 and 8 c.p.s., respectively. The bromide was distilled, recrystallized four times from methanol, freeze dried, and redistilled (b.p. 42° at 0.9 mm.) to afford ⩾99.4% *trans*-β-bromostyrene. Commercial propenylbenzene was distilled with only a small forerun being collected. A vapor phase chromatogram (10% diethylene glycol succinate, 135°) showed only two components in the ratio 97:3. The major component was assigned the *trans* configuration on the basis of a strong (C–H bending) absorption at 965 cm.$^{-1}$. Infrared spectra in the series $C_6H_5CH{=}CHX$ (X = Br, CH_3, OAc) indicate that the *trans* isomers have a ring C–H bending frequency at 730–750 cm.$^{-1}$, shifted to 770–790 cm.$^{-1}$ in the *cis* isomers.

Competitive reductions were performed in methanol using an equimolar mixture of β-bromostyrene and propenylbenzene and excess PADA. After about 25% of total olefin had been reduced, the mixture was analyzed by v.p.c., using calibration curves which had been prepared for both olefins and their saturated counterparts. The relative rate constants, k/k', for reduction of the bromides were taken as being equal to the ratio of reduced products.

Acknowledgment.—This investigation was supported in part by Public Health Service Research Grant No. GM12113-01 from the National Institutes of Health and in part by the University of Connecticut Research Foundation.

(9) T. Yoshino, Y. Manabe, and Y. Kibiucki, *J. Am. Chem. Soc.*, **86**, 4673 (1964); E. Grovenstein, *ibid.*, **75**, 2639 (1953); S. J. Cristol and W. K. Norris, *ibid.*, **75**, 2645 (1953).

Reductive Cleavage of Aryloxysilanes

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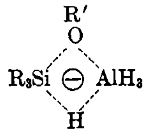
Hydrolysis in the presence of acid or base is the usual method for the removal of the trimethylsilyl group from aryloxysilanes.[1] However, in the course of our work it became necessary to remove the trimethylsilyl group from a number of compounds containing the aryloxytrimethylsilane grouping by an essentially nonhydrolytic means. A literature search failed to reveal any previous attempt to do this. Speier[2] subjected *p*-trimethylsilylphenoxytrimethylsilane to the action of hydrogen in the presence of a Raney nickel catalyst under pressure and at elevated temperatures, but the reaction resulted in the desired hydrogenation of the aromatic ring with the Si–O bond remaining intact.

The use of lithium aluminum hydride for the purpose of cleaving alkoxysilanes to silanes and alcohols has been reported on numerous occasions,[3–6] and there was no reason (except the lack of information) to suppose that aryloxysilanes would behave differently. This assumption was indeed correct, and we would like to report that the bond in question undergoes a facile cleavage in the presence of lithium aluminum hydride with almost quantitative yields. The reaction appears to proceed more readily than the reductive cleavage of alkoxysilane bonds since varying degrees of difficulty have been experienced[4,5b,7] with the latter cleavages. More difficult aryloxysilane cleavages can be accomplished at higher temperatures in *p*-dioxane.

In the examples given below trimethylsilane is produced as a side product, and this was trapped and identified. The aluminum complex formed during the reduction was destroyed with ice and dilute acid, since trimethylphenoxysilane and other silicon–carbon ethers not mentioned in this paper can be recovered unchanged from this mild treatment. Other techniques[8] could of course be used to recover the required products if even cold dilute acid cannot be tolerated.

It is not the purpose of this particular paper to comment in detail on the mechanism of this reaction.[9] However, it is interesting to note that 2,4,6-trichlorophenoxysilane undergoes rapid reductive cleavage of the silicon–oxygen bond at room temperature while trimethylphenoxysilane reacts at a much reduced rate, and hence the reaction appears to be facilitated by electron-withdrawing substituents in the aromatic ring. Sommer and his co-workers[4,5b] have postulated an S_Ni-Si quasi-cyclic mechanism for such reactions in nonpolar media which proceed *via* a four-center transition state. The complex so formed accommodates a negative charge within its structure. Thus,



if R′ is a phenyl group, it is to be expected that the complex formed during the rate-determining transition state would be stabilized (especially if the aromatic group contains electron-withdrawing substituents) and the reaction would be generally facilitated. Also, it can be argued that the electron withdrawal into the aromatic ring reduces the d_π-p_π bonding between silicon and oxygen. A resultant lowering of the activation

(1) C. Eaborn, "Organosilicon Compounds," Butterworth and Co. (Publishers) Ltd., London, 1960, p. 301.

(2) J. L. Speier, *J. Am. Chem. Soc.*, **74**, 1003 (1952).

(3) See ref. 1, p. 196.

(4) L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Series in Advanced Chemistry, McGraw-Hill Book Co., Inc., New York, N. Y., 1965, p. 51.

(5) (a) L. H. Sommer, C. L. Frye, G. A. Parker, and K. W. Michael, *J. Am. Chem. Soc.*, **86**, 3271 (1964); (b) L. H. Sommer, C. L. Frye, and G. A. Parker, *ibid.*, **86**, 3276 (1964).

(6) H. J. Emeleus and L. E. Smythe, *J. Chem. Soc.*, 609 (1958).

(7) H. Westermark, *Acta Chem. Scand.*, **8**, 1830 (1954).

(8) N. G. Gaylord, "Reduction with Complex Metal Hydride," Interscience Publishers, Inc., New York, N. Y., 1956, p. 1010.

(9) A more detailed paper will be published at a future date.

free energy associated with the concerted nucleophilic and electrophilic attacks at silicon and oxygen, respectively, would ensue.

Experimental Section[10]

Starting Materials.—Phenol, b.p. 182°, was distilled before use and 2,4,6-trichlorophenol, m.p. 68°, was recrystallized from glacial acetic acid.

Trimethylphenoxysilane.—This material was made from phenol (88.6 g., 0.94 mole) and chlorotrimethylsilane (153 g., 1.41 mole).[11] The silane (140 g., 84%) was purified by fractional distillation: b.p. 180°, lit.[11] b.p. 181.9-182.4°; n^{25}_{D} 1.4772, lit.[12] n^{25}_{D} 1.4753.

Reductive Cleavage of Trimethylphenoxysilane.—A suspension of lithium aluminum hydride (10 g., 0.26 mole) in 100 ml. of anhydrous ether was placed under a slight positive pressure of nitrogen and protected from moisture by using a sulfuric acid trap. To the stirred mixture was added trimethylphenoxysilane (84.2 g., 0.51 mole) in 80 ml. of ether at room temperature; no observable reaction took place. Anhydrous *p*-dioxane (180 ml.) was exchanged for the ether by the process of simultaneous addition and distillation. The mixture was then stirred at reflux temperature for 7 hr. After the unreacted lithium aluminum hydride was destroyed with an ethyl alcohol-ether mixture and cooled to 0°, the resulting mixture was poured onto an excess of dilute hydrochloric acid and ice. Product isolation was achieved by *quickly* extracting three times with 50-ml. portions of ether, washing the combined ethereal extract once with water, drying with sodium sulfate (overnight), and distilling the solvent. Fractional distillation of the crude product at reduced pressure gave phenol (40.5 g., 84%), b.p. 75° (10 mm.).

The identity and purity of the phenol was checked by comparison of infrared spectra and v.p.c. analysis with an authentic sample since its boiling point was very close to that of trimethylphenoxysilane.

A repeat of the above experiment was carried out using trimethylphenoxysilane (16.6 g., 0.1 mole), lithium aluminum hydride (2 g., 0.05 mole), and anhydrous ether (100 ml.), but this time the exit gases were passed through a trap cooled with isopropyl alcohol and Dry Ice. The mixture was stirred and heated at reflux temperature for 17 hr., after which time 7.5 g. of material had collected in the cold trap. Infrared analysis of the condensate (no solvent) indicated the presence of Me_3SiH,[13] since strong bands were present at 2145 and 1260 cm.$^{-1}$. The yield of phenol in this experiment was 9 g. (96%).

2,4,6-Trichlorophenoxysilane.—A solution of 2,4,6-trichlorophenol (50 g., 0.25 mole) and chlorotrimethylsilane (108.6 g., 1 mole) in 100 ml. of toluene was stirred at reflux temperature for 6 hr. using 1.6 g. of N,N-dimethylformamide as a catalyst.[14] The excess of chlorotrimethylsilane was distilled from the reaction mixture and the residue was fractionally distilled at reduced pressure to give 57 g. of impure product. Refractionation using a Nester-Faust Intermediate Laboratory spinning-band column gave 48.6 g. (70%) of the pure silane, b.p. 147° (20 mm.), n^{25}_{D} 1.5231.

Anal. Calcd. for $C_9H_{11}Cl_3OSi$: C, 40.30; H, 4.14. Found: C, 40.34; H, 4.13.

Reductive Cleavage of 2,4,6-Trichlorophenoxysilane.—A nitrogen atmosphere and a cold trap were incorporated in this experiment as previously described. 2,4,6-Trichlorophenoxysilane (40.5 g., 0.15 mole) was added dropwise to a stirred suspension of lithium aluminum hydride (2.85 g., 0.075 mole) in 100 ml. of anhydrous ether. An immediate exothermic reaction took place accompanied by a gas evolution. The rate of addition was adjusted so that the ambient temperature was approached. At the end of the addition (1 hr.), 4.3 g. of trimethylsilane had condensed in the trap. To ensure full reaction, the reaction was heated at reflux temperature for 5 hr., and a further quantity of trimethylsilane and ether was collected. The reaction complex was destroyed and ether extracted as previously described. The product, isolated by evaporating the water-free ethereal solution to dryness on a rotary evaporator under reduced pressure, consisted of 28.7 g. (97%) of reasonably pure 2,4,6-trichlorophenol, m.p. 66-67° (lit.[15] m.p. 68-69°).

Structure Proof of Trimethylsilane.[16]—The condensate from the last experiment was allowed to warm to −40°. At this temperature a stream of chlorine gas was passed through the mixture while the temperature was allowed to rise gradually over a 30-min. period to 5°. After standing overnight in a stoppered flask, the chlorinated mixture was fractionally distilled to give 7.5 g. of chlorotrimethylsilane, b.p. 56° (lit.[17] b.p. 57.3°). The infrared spectrum of this material corresponded exactly with that of an authentic sample.

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(10) All melting points and boiling points are uncorrected, and fractional distillations were carried out through a precision-built Vigreux column having an approximate ten-theoretical-plate equivalent as described by J. D. Ray [*Rev. Sci. Instr.*, **28** (3), 200 (1957)], unless otherwise stated.

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(14) R. J. N. Thiesse, German Patent 1,163,824 (1964).

(15) N. A. Lange, "Handbook of Chemistry," 10th Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1961, p. 704.

(16) A. G. Taylor and B. V. De G. Walden, *J. Am. Chem. Soc.*, **66**, 842 (1944).

(17) See ref. 1, p. 177.

Substituent Effects in Hydrolysis of Diaryl Carbonates

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In a previous paper[1] the rates of hydrolysis of diphenyl carbonate and phenyl benzoate were compared under acidic, basic, and "neutral" conditions, *i.e.*, without added acid or base. The present report describes the effect of substituents on the hydrolysis of symmetrical diaryl carbonates in neutral[2] and basic solution.

Basic Hydrolysis.—The second-order rate constants for reaction of substituted diaryl carbonates with hydroxide ion in 1:1 dioxane-water were measured at 20° by following the rate of appearance of the phenoxide ion spectrophotometrically, with the results shown in Table I. The reaction is quite sensitive to the electronic effects of the substituent, being accelerated by electron-withdrawing groups and retarded by electron-donating groups, as expected. The data for *meta* and *para* substituents were fitted to the Hammett equation,[3] using values of σ derived from the ionization constants of the substituted benzoic acids.[3]

TABLE I

RATES OF REACTION OF DIARYL CARBONATES WITH HYDROXIDE ION IN DIOXANE-WATER AT 20°

$$(XC_6H_4O)_2\,C{=}O + 4OH^- \rightarrow 2XC_6H_4O^- + CO_3^{2-} + H_2O$$

Substituent	*k*, l. mole^{-1} sec.$^{-1}$	Substituent	*k*, l. mole^{-1} sec.$^{-1}$
H	0.842	*m*-CH_3O	1.05
o-Cl	1.36	*p*-CH_3O	0.454
m-Cl	8.32	*m*-NO_2	155
p-Cl	7.48	*o*-CH_3	0.088
m-Br	7.60	*m*-CH_3	0.372
p-Br	7.95	*p*-CH_3	0.368

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(2) The term "neutral" solution is used throughout this paper to denote reaction in the absence of added acid or base and does not imply reaction at controlled pH.

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