methyl bromide) held in an ice bath at 0°. After addition was complete the reaction mixture was stirred at room temperature for 10 hr. and then allowed to stand for 8 hr. The product was worked up as in the preparation of I except for the addition of a few pellets of sodium hydroxide (the solution was pale yellow before the solvent ether was removed). After distilling a forerun of about 4 ml. a main fraction of 90 g. (49%) of very slightly yellow product was obtained, b.p. 34.1–34.5°/8.0 mm. A small quantity of dark brown, lachrymatory residue was left. Careful refractionation[9] gave 80 g. (44%) of product of constant boiling point and refractive index, b.p. 37.5°/8.0 mm., n_D^{25} 1.4453, d_4^{25} 1.2315, M_R Calcd.[10] 39.32, M_R found 39.16.

Anal. Calcd. for $C_6H_{13}OBr$: C, 39.80; H, 7.24; Br, 44.13. Found:[11] C, 39.91; H, 7.10; Br, 43.96.

This compound, in contrast to I and those previously studied,[3a] was found neither to lose HBr nor to commence to fume in moist air at temperatures up to its normal boiling point (about 162°). It was found, however, to undergo peroxidation quite easily upon standing.

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(9) We continued to distill over sodium hydroxide pellets though they seemed not to be necessary.

(10) Using Eisenlohr's atomic refractions. See K. Fajans in A. Weissberger, *Physical Methods of Organic Chemistry*, 2nd ed., Part Two, Interscience Publishers, Inc., New York, New York, 1949, p. 1163.

(11) Analysis by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

Some Reactions of RX Compounds with Triphenylsilyllithium in Tetrahydrofuran

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Incidental to a study of some silyllithium compounds with epoxides, [1] a significant difference was noted in the behavior of epichlorohydrin and epibromohydrin toward triphenylsilyllithium in tetrahydrofuran. The particular difference that concerns us here involves the formation of hexaphenyldisilane. The yield of this product from the epibromohydrin reaction was 68.6%; and essentially none of it was obtained from the reaction with epichlorohydrin. The formation of this coupling product may be due, at least in part, to a halogen-metal interconversion reaction.[2]

This unusual secondary coupling reaction suggested an examination of other related types. Reactions are now reported of triphenylsilyllithium with *n*-butyl chloride, *n*-butyl bromide, *n*-dodecyl chloride, allyl chloride, cyclopentyl chloride, 1,3-dichloropropane, and 1,3-dibromopropane. The pronounced effect of the nature of the halogen is reflected in the reactions with *n*-butyl chloride and *n*-butyl bromide.

$$(C_6H_5)_3SiLi + n\text{-}C_4H_9Br \longrightarrow (C_6H_5)_3SiSi(C_6H_5)_3\ (60\%) + (C_6H_5)_3SiC_4H_9\text{-}n\ (10\%)$$

Under corresponding conditions, *n*-butyl chloride gave a 75% yield of the "primary" coupling product, *n*-butyltriphenylsilane. Related variations occur with mono and polyhalogenated aromatic compounds,[3] in which the secondary coupling product (hexaphenyldisilane) is formed in some cases in yields close to 90%.

EXPERIMENTAL

Reaction of triphenylsilyllithium with n-butyl chloride. A solution of triphenylsilyllithium (0.05 mole) in tetrahydrofuran was added dropwise to 4.63 g. (0.05 mole) of *n*-butyl chloride. The reaction was exothermic and Color Test I was negative immediately after the addition. Work-up of the reaction mixture gave a solid residue which was crystallized from methanol, yielding 11.8 g. (75%) of *n*-butyltriphenylsilane, m.p. 89–90°; identified by a mixed melting point determination with an authentic sample, and by comparison of infrared spectra.

Reaction of triphenylsilyllithium with n-butyl bromide. A solution of triphenylsilyllithium (0.025 mole) in tetrahydrofuran was added dropwise to 3.42 g. (0.025 mole) of *n*-butyl bromide. The reaction was exothermic and Color Test I was negative immediately after addition. Subsequent to hydrolysis by dilute sulfuric acid, 3.90 g. (60%) of hexaphenyldisilane was isolated, m.p. 349–350°. Work-up of the organic layer gave an oily residue which was chromatographed on alumina. Using petroleum ether (b.p. 60–70°) as an eluant, there was obtained 0.8 g. (10%) of *n*-butyltriphenylsilane, m.p. 90–91°, after recrystallization from methanol. A mixed melting point determination with the compound obtained from the reaction of triphenylsilyllithium with *n*-butyl chloride was not depressed, and their infrared spectra were superimposable.

Reaction of triphenylsilyllithium with n-dodecyl chloride. A solution of triphenylsilyllithium (0.026 mole) in tetrahydrofuran was added dropwise to 5.30 g. (0.026 mole) of *n*-dodecyl chloride. The reaction was exothermic and Color Test I was negative immediately after addition. Work-up gave a solid which was recrystallized twice from methanol to yield 3.20 g. (28.7%) of *n*-dodecyltriphenylsilane, m.p. 65–67°; identified by mixed melting point determination with an authentic sample and by infrared spectra.

Reaction of triphenylsilyllithium with allyl chloride. A solution of triphenylsilyllithium (0.025 mole) in tetrahydrofuran was added dropwise to 1.91 g. (0.025 mole) of allyl chloride. The reaction was exothermic and Color Test I was negative immediately after the addition. The work-up gave a solid residue which was chromatographed on alumina. Using petroleum ether (b.p. 60–70°) and carbon tetrachloride as the eluants there was isolated 4.20 g. (56%) of allyltriphenylsilane, m.p. 90–91°, after recrystallization from petroleum ether (b.p. 60–70°); identified by a mixed melting point determination with an authentic sample. In addi-

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(1) H. Gilman, D. Aoki, and D. Wittenberg, *J. Am. Chem. Soc.*, in press.

(2) H. Gilman and D. H. Miles, *J. Am. Chem. Soc.*, **80**, 611 (1958); A. G. Brook, H. Gilman, and L. S. Miller, *J. Am. Chem. Soc.*, **75**, 4759 (1953); A. G. Brook and S. Wolfe, *J. Am. Chem. Soc.*, **79**, 1431 (1957); D. Seyferth, *J. Am. Chem. Soc.*, **79**, 2738 (1957); R. A. Benkeser and R. G. Severson, *J. Am. Chem. Soc.*, **73**, 1424 (1951); A. G. Brook and H. Gilman, *J. Am. Chem. Soc.*, **76**, 278 (1954); O. H. Johnson and D. M. Harris, *J. Am. Chem. Soc.*, **72**, 5566 (1950); and H. Gilman and C. W. Gerow, *J. Am. Chem. Soc.*, **78**, 5823 (1956).

(3) Studies by Glen Dappen. Details of reactions of silylmetallic compounds with a wide variety of halogenated compounds will be reported later.

tion, there was obtained 0.40 g. (6%) of triphenylsilanol; identified by infrared spectra.

Reaction of triphenylsilyllithium with cyclopentyl chloride. A solution of triphenylsilyllithium (0.05 mole) in tetrahydrofuran was added dropwise to 5.23 g. (0.05 mole) of cyclopentyl chloride. The reaction was exothermic, but to a lesser extent than with primary halides. Color Test I was positive after addition. The reaction mixture was stirred at refluxing temperature for 18 hr. after which Color Test I was negative. Subsequent to hydrolysis, 1.2 g. (9.3%) of hexaphenyldisilane, m.p. 356–357°, was isolated. Work-up of the organic layer gave a solid residue which was chromatographed on alumina. From petroleum ether (b.p. 60–70°) as an eluant there was obtained 6.50 g. (40%) of cyclopentyltriphenylsilane, m.p. 112–116°, after recrystallization from ethanol. The product was identified by a mixed melting point determination with an authentic sample, and infrared spectra.

Reaction of triphenylsilyllithium with 1,3-dichloropropane. A solution of triphenylsilyllithium (0.05 mole) in tetrahydrofuran was added dropwise to 2.83 g. (0.025 mole) of 1,3-dichloropropane. The reaction was exothermic, and Color Test I was negative immediately after addition. Work-up gave a solid residue, which was recrystallized from petroleum ether (b.p. 60–70°), yielding 10.25 g. (73%) of 1,3-bis(triphenylsilyl)propane, m.p. 132–133.5°. Recrystallization from the same solvent raised the melting point to 133–134°. Infrared spectrum supported the structure of the product.

Anal. Calcd. for $C_{39}H_{36}Si_2$: Si, 10.02. Found: Si, 10.00, 9.92.

Reaction of triphenylsilyllithium with 1,3-dibromopropane. A solution of triphenylsilyllithium (0.04 mole) in tetrahydrofuran was added dropwise to 4.04 g. (0.02 mole) of 1,3-dibromopropane. The reaction was exothermic, and Color Test I was negative immediately after addition. Subsequent to hydrolysis, 7.4 g. (71.5%) of hexaphenyldisilane, m.p. 355–357°, was isolated. A very small amount of the residue, which was obtained after work-up of the organic layer, has failed to give any pure product.

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Cyanoethylation of Trichlorosilane

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The reaction of trichlorosilane and acrylonitrile in the presence of tertiary amines has been reported by Nozakura and Konotsune[1] and also by Prober and Cooper[2] to give 3-trichlorosilylpropionitrile (I). This product has also been reported[3] to have been prepared from the same reagents in the presence of triphenylphosphine.

While evaluating various catalysts for the reaction of acrylonitrile and trichlorosilane, several amides were found to promote the formation of I. The reactants were heated to reflux for 24 hr. or longer in the presence of two mole percent of the amide. The table lists the yields of I obtained with various amides. None of these amides promoted cyanoethylation of methyldichlorosilane. The product in each case had the same melting point as that reported by Nozakura and Konotsune,[1] who related the structure of their product to the known 3-trimethylsilylpropionamide.[4] The isomeric 2-trichlorosilylpropionitrile was not detected in any of the mixtures although its properties[5] should have made its detection very easy.

Treatment of I with ethanol and pyridine gave the known 3-triethoxysilylpropionitrile (II)[1] in good yields, and 3-methyldichlorosilylpropionitrile (III)[2] was prepared from I and methyl magnesium bromide. Hydrolysis of I and III gave polysiloxane resins and fluids.

The accepted mechanism for base-catalyzed cyanoethylation reactions[6] would lead one to expect trichlorosilane, polarized as $Cl_3Si^+H^-$,[7] to yield 2-trichlorosilylpropionitrile. Contrary to such expectations, certain catalysts bring about almost exclusive formation of 3-trichlorosilylpropionitrile. These catalysts are not the strong bases used in common cyanoethylations, but have been found among special classes of compounds which form relatively stable complexes with chlorosilanes.

Tertiary amines,[8,9] phosphines,[9] arsines,[9] and amides[10] form complexes involving the *d*-orbitals of silicon. These complexes are the probable reactive intermediates leading to 3-trichlorosilylpropionitrile.

To see if the amine hydrochlorides formed by decomposition of amide complexes[11] were catalyt-

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