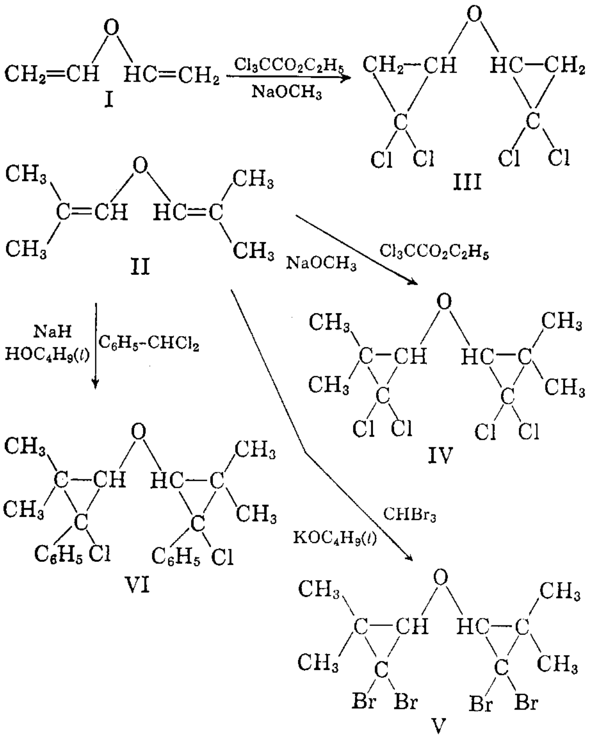

would have the additional advantage of greater reactivity toward carbene additions.[4] The method used for the preparation of III was also satisfactory for the synthesis of bis(2,2-dichloro-3,3-dimethylcyclopropyl) ether (IV), which was a white crystalline solid, melting point 132–133°. The addition of dibromocarbene, generated from bromoform and potassium *tert*-butoxide, to II furnished bis-(2,2-dibromo-3,3-dimethylcyclopropyl) ether (V), which melted at 123°. The best results for the synthesis of bis(2-chloro-2-phenyl-3,3-dimethylcyclopropyl) ether (VI) were obtained by the addition of benzal dichloride to a petroleum ether solution of II containing an equivalent amount of sodium hydride and a small amount of *tert*-butyl alcohol. The crystalline VI melted 144–145°.

In all the carbene addition reactions of the divinyl ethers, no attempts were made to isolate the labile mono-adducts. Compounds III, IV, V, and VI all exhibited infrared spectra in which vinyl ether absorption was absent and medium absorption in the 1000–1021-cm.$^{-1}$ region, purportedly characteristic of a cyclopropane ring, was present.

EXPERIMENTAL[5]

Bis(2,2-dichlorocyclopropyl) ether (III). To a solution containing 14 g. (0.20 mole) of divinyl ether[6] and 24.5 g. (0.42 mole) of sodum methoxide in olefin free petroleum ether was slowly added with stirring 76.8 g. (0.2 mole) of ethyl trichloroacetate. After the addition was complete, the solution was stirred for 48 hr., poured into water, and the organic phase was separated. The aqueous phase was extracted with ether and the ether layer was combined with the organic phase and the total solution was dried over anhydrous sodium sulfate. The solution was then filtered and the low boiling components were removed on a steam bath. The remaining material was evaporatively distilled to yield 7 g. (16%) of III, b.p. 85–90° (0.2 mm.), n_D^{25} 1.4978, d^{20} 1.3855.

Anal. Calcd. for $C_6H_6Cl_4O$: C, 30.65; H, 2.84; Cl, 60.00. Found: C, 30.57, H, 2.84; Cl, 59.85.

Bis(2,2-dichloro-3,3-dimethylcyclopropyl) ether (IV). To a solution containing 12.6 g. (0.1 mole) of diisobutenyl ether[7] and 11.88 g. (0.22 mole) of sodium methoxide in olefin free petroleum ether was slowly added with stirring 42 g. (0.22 mole) of ethyl trichloroacetate. After the addition was complete, the solution was stirred for 48 hr., poured into water, and the organic phase was separated. The aqueous layer was extracted with chloroform and the combined chloroform extract and organic phase were dried over anhydrous sodium sulfate. The solution was then filtered and the low boiling components were removed by vacuum concentration. A white solid crystallized, which on recrystallization from ether yielded 5.8 g. (20%) of IV, m.p. 132–133°.

Anal. Calcd. for $C_{10}H_{14}Cl_4O$: C, 41.12; H, 4.83; Cl, 48.57. Found: C, 41.26; H, 4.94; Cl, 48.29.

Bis(2,2-dibromo-3,3-dimethylcyclopropyl) ether (V). To a solution containing 12.6 g. (0.1 mole) of diisobutenyl ether and 24.6 g. (0.22 mole) of potassium *t*-butoxide in olefin free petroleum ether was slowly added with stirring 55.6 g. (0.22 mole) of bromoform. The products were isolated by a procedure similar to isolation of IV. The solid material which resulted was recrystallized from ether and yielded 12.5 g. (25.6%) of V, m.p. 123°.

Anal. Calcd. for $C_{10}H_{14}Br_4O$: C, 25.68; H, 3.24; Br, 67.80. Found: C, 25.67; H, 2.99; Br, 67.93.

Bis(2-chloro-2-phenyl-3,3-dimethylcyclopropyl) ether (VI). To 6.3 g. (0.05 mole) of diisobutenyl ether, 3 g. of *t*-butyl alcohol, and 2.4 g. (0.1 mole) of sodium hydride in hexane was added slowly and with stirring 16.1 g. (0.1 mole) of benzal dichloride. The product was isolated by a procedure similar to that used in isolation of IV. The remaining solid was recrystallized from petroleum ether and yielded 5.0 g. (26.6%) of VI, m.p. 144–145° dec.

Anal. Calcd. for $C_{22}H_{24}Cl_2O$: C, 70.40; H, 6.45; Cl, 18.89. Found: C, 70.20; H, 6.60; Cl, 18.87.

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(5) Melting points and boiling points are uncorrected. Spectra were determined on a Perkin-Elmer Model 137 double beam infrared spectrophotometer. Analyses were carried out by Drs. Weiler and Strauss, Oxford, England, and Alfred Bernhardt, Mulheim, Germany.

(6) The authors wish to acknowledge gifts of generous quantities of divinyl ether from Merck & Co., Chemical Division, Rahway, N. J.

(7) Prepared according to the procedure given in ref. 3.

Some Organolithium Compounds Containing Silicon

HENRY GILMAN AND RICHARD D. GORSICH

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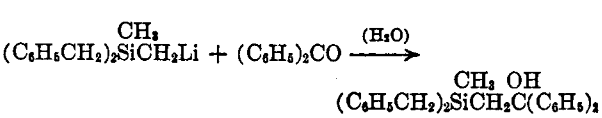
As an approach to the synthesis of high molecular weight, unsymmetrical molecules, we have briefly examined the synthetic utility of R_3SiCH_2Li reagents where two of the R groups are different. Previously, trimethylsilylmethyllithium was prepared in a high yield from (chloromethyl)trimethylsilane and lithium in *n*-pentane.[1] This intermediate proved to be quite versatile for the preparation of other carbon-functional organosilicon compounds. No R_3SiCH_2Li compounds have been reported in which two of the R groups are phenyl or benzyl.

(Chloromethyl)methyldibenzylsilane (I) and (chloromethyl)methyldiphenylsilane[2] (II) were synthesized by allowing one mole of (chloromethyl)methyldichlorosilane to interact with two moles of benzylmagnesium chloride and phenyllithium, respectively. The former compound could not be obtained pure. Although the impurity did not interfere with the formation of the organolithium compound, it probably affected the yield.

$$Cl_2\overset{CH_3}{Si}CH_2Cl + 2\ C_6H_5CH_2MgCl \longrightarrow (C_6H_5CH_2)_2\overset{CH_3}{Si}CH_2Cl$$

I

Impure I reacted smoothly with lithium ribbon in refluxing *n*-pentane to give, after treatment of the reaction mixture with benzophenone, [(methyldibenzylsilyl)methyl]diphenylmethanol (III) in a 66% yield. On the other hand, II did not react with lithium in *n*-pentane, but the reaction did proceed



$$(C_6H_5CH_2)_2\overset{CH_3}{Si}CH_2Li + (C_6H_5)_2CO \xrightarrow{(H_2O)} (C_6H_5CH_2)_2\overset{CH_3}{Si}CH_2\overset{OH}{C}(C_6H_5)_2$$

III

in refluxing benzene to give 31% of [(methyldiphenylsilyl)methyl]diphenylmethanol subsequent to derivatization with benzophenone.

EXPERIMENTAL[3]

(Chloromethyl)methyldibenzylsilane. A diethyl ether solution containing 0.60 mole of benzylmagnesium chloride and 20 g. (0.123 mole) of (chloromethyl)methyldichlorosilane was refluxed for 2 days. A dense precipitate formed. The mixture was hydrolyzed with 5% hydrochloric acid. The organic layer was separated, dried, and the solvent distilled. The oily residue was distilled under reduced pressure to give 4.2 g. of forerun, mainly bibenzyl, followed by 24.81 g. (74%) of impure product, b.p. 107–108° (0.005 mm.), n_D^{20} 1.5712, d_4^{20} 1.067.

Anal. Calcd. for $C_{16}H_{19}ClSi$: Si, 8.30; MR, 83.9. Found: Si, 8.80, 9.01; MR, 84.4.

All attempts to purify the compound were unsuccessful.

(Chloromethyl)methyldiphenylsilane. Seven hundred milliliters of an ethereal solution containing 0.765 mole of phenyllithium was added dropwise to a stirred solution of 60 g. (0.368 mole) of (chloromethyl)methyldichlorosilane in 125 ml. of ether. The mixture was worked up as described in the preceding experiment. The residual oil was distilled to give 76 g. (84%) of colorless liquid, b.p. 100–102° (0.012 mm.), n_D^{20} 1.5810, d_4^{20} 1.106; reported[2] n_D^{25} 1.5785, d^{25} 1.101.

[(Methyldibenzylsilyl)methyl]diphenylmethanol. A mixture of 2.67 g. (0.385 g.-atom) of finely cut lithium ribbon, 4.0 g. (0.0145 mole) of (chloromethyl)methyldibenzylsilane, and 55 ml. of *n*-pentane was refluxed for 18 hr. The excess lithium was filtered off and a solution of 2.73 g. (0.015 mole) of benzophenone in 40 ml. of *n*-pentane was added to the organolithium solution. After the addition was complete, the mixture was hydrolyzed with water, and diethyl ether was added to clear up the organic layer which was separated and dried over sodium sulfate. Distillation of the solvents from the organic layer left a solid which was crystallized from petroleum ether (b.p. 60–70°) to give 4.03 g. (66%) of product, m.p. 105.5–106.5°.

Anal. Calcd. for $C_{29}H_{30}OSi$: C, 82.42; H, 7.16; Si, 6.64. Found: C, 82.62; H, 7.13; Si, 6.62, 6.72.

The infrared spectrum of the compound in carbon disulfide showed an absorption band at 2.75 μ characteristic of a C—OH bond.

[(Methyldiphenylsilyl)methyl]diphenylmethanol. Three grams (0.433 g.-atom) of finely cut lithium ribbon, 6.0 g. (0.0243 mole) of (chloromethyl)methyldiphenylsilane, and 50 ml. of benzene were refluxed for 11.5 hr. The organolithium solution was filtered and allowed to react with 4.43 g. (0.024 mole) of benzophenone in 50 ml. of benzene. The mixture was hydrolyzed and worked up as described in the preceding experiment. The crude product was distilled to give a small amount of forerun followed by 4.35 g. (45%) of material, b.p. 180–186° (0.005 mm.). The distillate was crystallized twice from petroleum ether (b.p. 60–70°) and once from 95% ethanol to give 2.96 g. (31%) of white needles, m.p. 89–90°.

Anal. Calcd. for $C_{27}H_{26}OSi$: Si, 7.11. Found: Si, 7.00, 6.92.

The infrared spectrum of the compound in carbon disulfide solution showed an absorption band at 2.75 μ characteristic of a C—OH bond.

An attempt to prepare (methyldiphenylsilyl)methyllithium in *n*-pentane was unsuccessful.

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[1] L. H. Sommer, R. M. Murch, and F. A. Mitch, *J. Am. Chem. Soc.*, **76**, 1619 (1954).

[2] This has been prepared previously from phenylmagnesium bromide and (chloromethyl)methyldichlorosilane; J. L. Speier, Jr., U. S. Patent **2,550,205** (1951); Dow Corning Corporation, British Patent **635,733** (1950); *Chem. Abstr.*, **44,** 6876 (1950).

[3] All melting points are uncorrected and all reactions involving organometallic compounds were carried out under an atmosphere of dry, oxygen-free nitrogen in sodium dried solvents.

A New Preparation of *s*-Triazine

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s-Triazine is usually prepared in one of the following ways: by reaction of the "sesquichloride