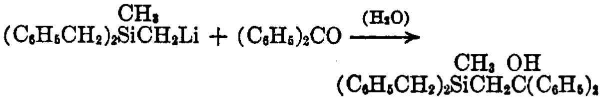
pared in a high yield from (chloromethyl)trimethylsilane and lithium in *n*-pentane.[1] This intermediate proved to be quite versatile for the preparation of other carbon-functional organosilicon compounds. No R_3SiCH_2Li compounds have been reported in which two of the R groups are phenyl or benzyl.

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



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

III

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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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

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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.

of hydrocyanic acid" with a tertiary amine,[1,2] by thermal decomposition of formamidine hydrochloride or trimerization of the free base,[3] or by trimerization of ethyl formimidate.[4] Other methods have been summarized by Smolin and Rapoport.[5] We now wish to describe a new and convenient method for the preparation of small quantities of *s*-triazine by the dehydration of formamide.

Although *s*-triazine is formed in the thermal decomposition of thioformamide,[6] Grundmann and Kreutzberger have shown that thermal dehydration of formamide itself leads only to the monomer, hydrocyanic acid.[2] We have now found that when formamide is mixed with a suitable dehydrating agent such as calcium carbide (or calcium nitride, calcium hydride, lithium carbide, etc.) and the mixture is heated, *s*-triazine is readily formed.

Several anhydrous transition metal halides, such as nickelous bromide, cobaltous chloride, and ferric chloride, when dissolved in the formamide in concentrations up to 10%, serve to improve the yield. Ferric chloride is especially useful since it also inhibits formation of black, tarry HCN polymer. A side reaction which reduces the efficiency of the preparation regardless of the order of addition is the base-catalyzed decomposition of formamide to carbon monoxide and ammonia. About 30% of the starting material is lost in this way. Unwanted byproducts which tend to distill from the reaction mixture with the triazine and to cause decomposition should be removed from the product before collection. This can be accomplished by passing the triazine vapor through a short column of Linde molecular sieve.

EXPERIMENTAL

Preparation of s-triazine. The apparatus consisted of a three-neck flask fitted with an addition buret, a nitrogen inlet, and a curved adapter outlet (packed with a 3-in. column of Linde molecular sieve Type 4A) leading to a chilled receiver. To 10.0 g. of pulverized calcium carbide maintained at 100° was added dropwise 10 ml. of a filtered solution of formamide containing approximately 10% anhydrous ferric chloride. The product sublimed immediately from the red-brown residue which formed. The reaction flask was subsequently heated to *ca.* 150° to obtain more product. A total of 1.17 g. of *s*-triazine was collected (19% yield based on the formamide added). The product was identified by melting point (82–83° uncorrected), infrared,[7] and mass spectroscopic analysis.

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[1] L. E. Hinkel and R. T. Dunn, *J. Chem. Soc.*, 1834 (1930).

[2] C. Grundmann and A. Kreutzberger, *J. Am. Chem. Soc.*, **76**, 5646 (1954).

[3] F. C. Schaefer, I. Hechenbleikner, G. A. Peters, and V. P. Wystrach, *J. Am. Chem. Soc.*, **81**, 1466 (1959).

[4] F. C. Schaefer and G. A. Peters, *J. Org. Chem.*, **26**, 2778 (1961).

[5] E. M. Smolin and L. Rapoport, *s-Triazines and Derivatives*, Interscience Publishers, Inc., New York, 1959, pp. 9–10.

[6] R. Willstätter and T. Wirth, *Ber.*, **42**, 1908 (1909).

[7] J. E. Lancaster, R. F. Stamm, and N. B. Colthup, *Spectrochim. Acta*, **17**, 155 (1961).

Synthesis and Properties of 4-Methyl-2-oxo-1,2-benzopyran-7-yl β-D-Galactoside (Galactoside of 4-Methylumbelliferone)

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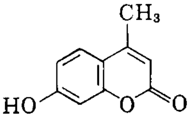
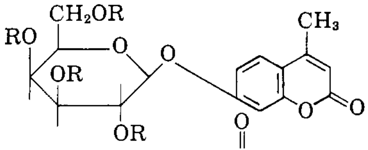
Mead, Smith, and Williams[1] observed that while 4-methylumbelliferone (I) fluoresced strongly in ultraviolet light at a *p*H 9–10, its conjugates showed little or no fluorescence. These workers were, therefore, able to show that the glucuronide of I, isolated from urine, served as a highly sensitive substrate for the determination of glucuronidase levels. Robinson[2] extended the fluorimetric method to the glucoside of I and Marsh and Levy[3] described the conversion of the glucoside to the glucuronide. Finally Leaback and Walker[4] described methylumbelliferyl 2-acetamido-2-deoxy-β-D-glucoside. We wish to report the synthesis of the galactoside (III).[4a] Fluorometric analysis showed the product to be substantially free of I.



I



II. $R = CH_3\overset{O}{\overset{\|}{C}}-$
III. R = H

EXPERIMENTAL[5]

Methylumbelliferyl tetra-O-acetyl-β-D-galactopyranoside (II). A mixture of 11.5 g. (0.065 mole) of I (Eastman Kodak), m.p. 188–189°, and of 19.0 g. (0.0462 mole)[6] of 2,3,4,6-tetra-*O*-acetyl-α-D-galactosyl bromide[7] was suspended in

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[1] J. A. R. Mead, J. N. Smith, and R. T. Williams, *Biochem. J.*, **60**, XV (1955); *Biochem. J.*, **61**, 569 (1955).

[2] D. Robinson, *Biochem. J.*, **63**, 39 (1956).

[3] C. A. March and G. A. Levy, *Nature*, **178**, 589 (1956).

[4] D. H. Leaback and P. G. Walker, *Biochem. J.*, **78**, 151 (1961).

[4a] The utilization of this substrate for the estimation of β-D-galactosidase levels in cell cultures will be described by A. A. Tytell and A. I. Shepartz (**Federation Proc. 21**, 1962).

[5] Analyses were carried out by Mr. R. Boos and his associates and the infrared spectra were determined by Messrs. R. Walker and N. Allan. The rotations were measured by Dr. D. Williams.

[6] The molar ratios employed are those of R. D. Robinson.[2]

[7] R. G. Hansen, W. J. Rutter, and P. Krichevsky, *Biochemical Preparations*, **4**, 1 (1955).