[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Addition of Silyllithium Compounds Containing Methyl and Phenyl Groups to Benzophenone in Tetrahydrofuran

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From the reaction of triphenylsilyllithium, methyldiphenylsilyllithium or dimethylphenylsilyllithium with benzophenone in tetrahydrofuran was obtained an addition product in which the silicon atom was bonded to the oxygen. Benzopinacol was obtained in small amounts from the latter two reagents and benzhydrol from the third.

The mode of addition of triphenylsilylpotassium[1] and triphenylgermyllithium[2a] to benzophenone and to formaldehyde has been investigated. Triphenylsilylpotassium reacted with benzophenone to give the "abnormal" addition product I, and with formaldehyde to give the "normal" adduct II. Triphenylgermyllithium added "normally" to both carbonyl compounds.

$(C_6H_5)_3SiOCH(C_6H_5)_2$ I $(C_6H_5)_3SiCH_2OH$ II

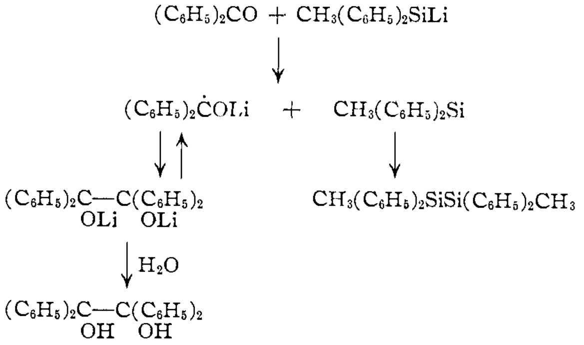
It has been postulated[1] that compound I may have formed as the result of a "normal" addition of triphenylsilylpotassium to benzophenone followed by a rearrangement. This concept is consistent with evidence accumulated recently by Brook[2b] who in excellent studies has succeeded in preparing triphenylsilyldiphenylcarbinol and has shown that under the mildest basic conditions this compound rearranges to benzhydryloxytriphenylsilane (I).

In view of some unusual reactions which have been carried out[3] recently in this Laboratory using tetrahydrofuran (THF) as a solvent, we have investigated the mode of addition of triphenylsilyllithium (III), methyldiphenylsilyllithium (IV) and dimethylphenylsilyllithium (V), the preparation of which has been reported,[4] to benzophenone in this solvent. It was of interest to compare the mode of addition of these silylmetallic compounds to benzophenone in THF with the mode of addition of triphenylsilylpotassium to benzophenone in diethyl ether.[1] Lithium was chosen as the metal to be used in this investigation since the preparation and properties of the silyllithium compounds in THF have been studied.[4] The "abnormal" addition products I, VI and VII were obtained.

$CH_3(C_6H_5)_2SiOCH(C_6H_5)_2$ VI $(CH_3)_2C_6H_5SiOCH(C_6H_5)_2$ VII

The structures were assigned on the basis of the infrared spectra. Compound I was identical to the compound previously obtained[1] from the reaction of triphenylsilylpotassium with benzophenone in diethyl ether. The spectra of VI and VII were similar to the spectrum of I except for bands at 8.0 and 12.7 μ attributable to the Si–CH_3 group. A broad band at 9.5 μ was found in all three cases, showing the presence of a Si–O bond.

Benzhydrol was reported[1] as a product of the reaction of triphenylsilylpotassium with benzophenone. Although we obtained no benzhydrol from the reaction of either III or IV with benzophenone, V reacted with benzophenone to give some benzhydrol, which may have formed by hydrolysis of VII. IV and V reacted with benzophenone to give small amounts of benzopinacol. Using the reaction of IV with benzophenone as an illustration, the formation of benzopinacol can be pictured as



$$\begin{tikzcd}[column sep=small] & (C_6H_5)_2CO + CH_3(C_6H_5)_2SiLi \arrow[d] & \\ (C_6H_5)_2\dot{C}OLi \arrow[d, shift right] & + & CH_3(C_6H_5)_2Si \arrow[d] \\ \underset{OLi\quad OLi}{(C_6H_5)_2C{-}C(C_6H_5)_2} \arrow[u, shift right] \arrow[d, "H_2O"] & & CH_3(C_6H_5)_2SiSi(C_6H_5)_2CH_3 \\ \underset{OH\quad OH}{(C_6H_5)_2C{-}C(C_6H_5)_2} & & \end{tikzcd}$$

Benzopinacol has been obtained from the reaction of benzophenone with triphenylmethylsodium[5] and with triphenylmethylmagnesium bromide.[6]

Experimental[7]

Materials.—III, IV and V were prepared by the method described recently.[4] Eastman Kodak Co. white label benzophenone was used in all reactions. THF was dried by distillation, first from sodium wire and then from lithium aluminum hydride.

Triphenylsilyllithium (III) and Benzophenone.—To a stirred solution of 7.05 g. (0.0386 mole) of benzophenone in 100 ml. of THF was added dropwise a solution of III prepared from 10.0 g. (0.0193 mole) of hexaphenyldisilane and 0.7 g. (0.1 g.-atom) of lithium in 100 ml. of THF. The reaction mixture at first became blue-green, but gradually turned brown as the addition progressed; 10 hr. after the addition was complete, Color Test I[8] was negative. The reaction mixture was hydrolyzed with water, and the layers were separated. The organic layer was combined with ether extracts of the aqueous layer and dried over sodium sulfate. Evaporation of solvents left an oil which crystallized from ethanol to give 8.6 g. (50%) of I, m.p. 83–84°, identified by a mixture melting point and comparison of the infrared spectrum with an authentic sample of I (m.p. 83–84°).[1] Concentration of the mother liquor gave another 1.2 g. (7%) of impure I, m.p. 80–84°. Evaporation of ethanol left an oil which crystallized from petroleum ether (b.p. 60–70°) to give 0.35 g. of triphenylsilanol, m.p. 152–155° (mixture melting point).

Methyldiphenylsilyllithium (IV) and Benzophenone.—To a stirred solution of 2.76 g. (0.0152 mole) of benzophenone in 50 ml. of THF was added dropwise a solution of IV prepared from 3.0 g. (0.0076 mole) of 1,2-dimethyl-1,1,2,2-tetraphenyldisilane and 0.7 g. (0.1 g.-atom) of lithium in 45

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(1) H. Gilman and T. C. Wu, THIS JOURNAL, **75**, 2935 (1953).

(2) (a) H. Gilman and C. W. Gerow, *ibid.*, **77**, 5740 (1955); (b) A. G. Brook, private communication.

(3) (a) H. Gilman and B. J. Gaj, *J. Org. Chem.*, **22**, 447 (1957); (b) H. Gilman and T. S. Soddy, *ibid.*, **22**, 1121 (1957); (c) H. Gilman and T. S. Soddy, *ibid.*, in press.

(4) H. Gilman and G. D. Lichtenwalter, THIS JOURNAL, in press.

(5) W. Schlenk and R. Ochs, *Ber.*, **49**, 608 (1916).

(6) W. E. Bachmann, THIS JOURNAL, **53**, 2758 (1931).

(7) All reactions were carried out under an atmosphere of dry nitrogen using oven-dried glassware. All melting points are uncorrected.

(8) H. Gilman and F. Schulze, THIS JOURNAL, **47**, 2002 (1925).

ml. of THF. The blue color acquired by the reaction mixture gradually changed to brown as the addition continued. After the addition was complete, Color Test I[8] was weakly positive. The reaction mixture was stirred for 3 hr. at room temperature and subsequently hydrolyzed with water. The organic layer was combined with ether extracts of the aqueous layer and dried over sodium sulfate. Evaporation of solvents left an oil which was dissolved in petroleum ether (b.p. 60–70°). On cooling, 0.15 g. of crystals, m. 160–170°, was deposited. These were recrystallized from petroleum ether (b.p. 60–70°) to give a small quantity of needles, m.p. 174–175°. A mixture melting point with an authentic sample of benzopinacol was not depressed, and the infrared spectra were identical. The petroleum ether from which the benzopinacol had deposited was evaporated. The resulting oil was dissolved in ethanol, from which 0.21 g. of white solid, m. 125–140°, was deposited. This material was recrystallized from ethanol to give 0.1 g. of diamond-shaped crystals, m.p. 142–144°, which was identified as 1,2-dimethyl-1,1,2,2-tetraphenyldisilane by a mixture melting point with an authentic sample. The ethanol solution, from which the 1,2-dimethyl-1,1,2,2-tetraphenyldisilane was isolated, was concentrated and chilled. There was deposited 1.09 g. (19%) of needles, m.p. 63–64°. Recrystallization from ethanol did not change the melting point. On the basis of an infrared spectrum which showed a broad Si–O band at 9.5 μ and Si–CH_3 bands at 8.0 and 12.7 μ, this product was assigned the structure of VI.

Anal. Calcd. for $C_{26}H_{24}OSi$: Si, 7.38. Found: Si, 7.35, 7.42.

Dimethylphenylsilyllithium (V) and Benzophenone.—To a solution of 6.75 g. (0.0370 mole) of benzophenone in 75 ml. of THF was added dropwise a solution of V prepared from 5.0 g. (0.0185 mole) of 1,1,2,2-tetramethyl-1,2-diphenyldisilane and 0.7 g. (0.1 g.-atom) of lithium in 75 ml. of THF; 10 hr. after the addition was complete, Color Test I[8] was negative. The reaction mixture was hydrolyzed with water. The organic layer was combined with ether extracts of the aqueous layer and dried over sodium sulfate. Evaporation of solvents left an oil which was dissolved in petroleum ether (b.p. 60–70°). There was formed 0.5 g. of diamond-shaped crystals, m. 170–176°. This material was recrystallized from benzene to give 0.25 g. of crystals, m.p. 181–183°, identified as benzopinacol on the basis of a mixture melting point and a comparison of the infrared spectrum with that of an authentic sample.

Evaporation of the petroleum ether from which the benzopinacol had deposited left an oil which was distilled at 0.05 mm. Two main fractions were collected. The first, 3.57 g., b.p. 104–107°, was dissolved in petroleum ether (b.p. 60–70°) and chilled. There was formed 0.4 g. (6%) of crystals, m.p. 67–68°, which was shown to be benzhydrol by a mixture melting point with an authentic sample and a comparison of the infrared spectra. The petroleum ether from which the benzhydrol had crystallized was evaporated. The presence of benzophenone in the resulting oil was shown by the formation of a 2,4-dinitrophenylhydrazone, 1.3 g., m.p. 238–240°. The infrared spectrum of the oil from which the benzophenone had been removed indicated the presence of some 1,1,2,2-tetramethyl-1,2-diphenyldisilane, but none was isolated.

The second fraction from the distillation consisted of 2.9 g., b.p. 139–143°, $n^{20}{}_{\mathrm{D}}$ 1.5705. This was redistilled at 0.05 mm. to give 2.36 g. (20%) of VII, b.p. 145–147°, $n^{20}{}_{\mathrm{D}}$ 1.5708. This oil crystallized slowly on standing for several days and melted at 36–38°. The infrared spectrum showed peaks at 9.5 μ (Si–O) and 8.0 μ (Si–CH_3). The product was too soluble in common solvents to be recrystallized.

Anal. Calcd. for $C_{21}H_{22}OSi$: C, 79.19; H, 6.96; *MR*,[9] 99.01. Found: C, 79.27, 79.17; H, 6.98, 6.86; *MR*, 99.19.

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[9] The values used in the calcd. *MR* were those of Vogel, *et al.*, *Chem. Ind.* (*London*), 358 (1950); and Vogel, *et al.*, *Chem. Ind.* (*London*), 19 (1953).

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Cleavage of Symmetrically Substituted Disilanes by Lithium in Tetrahydrofuran

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The cleavage of symmetrically substituted disilanes containing methyl and phenyl groups by lithium in tetrahydrofuran is reported. From $(CH_3)_2C_6H_5SiSiC_6H_5(CH_3)_2$ was obtained $(CH_3)_2C_6H_5SiLi$ while $CH_3(C_6H_5)_2SiSi(C_6H_5)_2CH_3$ gave $CH_3(C_6H_5)_2SiLi$. Derivatives were prepared with chlorotrimethylsilane and with chlorotriphenylsilane under conditions where the chlorosilane was present in excess. Addition of chlorotriphenylsilane to either silylmetallic resulted in a halogen–metal interconversion reaction in which hexaphenyldisilane and other coupling products were obtained.

The formation of silylmetallic compounds in which the metal is sodium, potassium or lithium has been reported by several investigators. Triphenylsilylpotassium was prepared[1] by Benkeser and Severson by way of the cleavage of phenylisopropyltriphenylsilane by sodium–potassium alloy in diethyl ether. Subsequent to this work, the formation of triphenylsilylpotassium was demonstrated[2] as a result of the cleavage of hexaphenyldisilane by sodium–potassium alloy in diethyl ether. The desirability of eliminating the use of sodium–potassium alloy led to an investigation[3] which showed that hexaphenyldisilane was cleaved readily by lithium, sodium or potassium in ethylene glycol dimethyl ether (GDME). These triphenylsilylmetallic solutions, however, suffered from a serious disadvantage in that they were unstable over extended periods of time.

As an extension of the study of the formation and reactions of silylmetallic compounds, we have carried out cleavages of symmetrically substituted disilanes containing methyl and phenyl groups by lithium in tetrahydrofuran (THF).

Solutions of II in THF were found to be fairly stable over extended periods of time at room temperature, a distinct advantage over the use of GDME as a solvent. The yield of the derivative 1,1,1-trimethyl-2,2,2-triphenyldisilane, prepared by

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[1] R. A. Benkeser and R. G. Severson, THIS JOURNAL, **73**, 1424 (1951).

[2] H. Gilman and T. C. Wu, *ibid.*, **73**, 4031 (1951).

[3] (a) A. G. Brook and H. Gilman, *ibid.*, **76**, 278 (1954); (b) see also A. G. Brook, *Chem. in Can.*, **7**, 43 (1955).