[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

An Allyl Displacement of a Benzyl Group from Di- and Tribenzylsilane

BY HENRY GILMAN AND RICHARD A. TOMASI

RECEIVED JULY 24, 1958

The displacement of a benzyl group from dibenzylsilane and tribenzylsilane by allylmagnesium chloride in tetrahydrofuran has been demonstrated. The solvent effect of the tetrahydrofuran was shown to be an important factor in the displacement reaction. Attempts to extend the replacement of an R group from triphenyl-, tri-γ-phenylpropyl-, tetraphenyl- and tetrabenzyl-silanes proved unsuccessful. The preparation and physical constants for benzyl-, dibenzyl- and allyldibenzyl-silanes are described.

Kipping[1] observed changes other than the displacement of chloride in reactions between trialkylchlorosilanes and alkyl Grignard reagents. For example, the reaction between methylmagnesium iodide and benzylethylpropylchlorosilane yielded a mixture of products which indicated the possibility of a methyl group displacing ethyl and propyl groups. Robiso and Kipping[2] concluded that a benzyl group was displacing an ethyl group in the reaction between benzylmagnesium chloride and ethyltrichlorosilane since dibenzyldichlorosilane and tribenzylchlorosilane were obtained as by-products. However, in a later paper, Challenger and Kipping[3] stated that the formation of tribenzylchlorosilane (and presumably dibenzyldichlorosilane) probably was due to the presence of silicon tetrachloride in the ethyltrichlorosilane and not to the displacement of an ethyl group by a benzyl group. They further stated that from a longer experience with silicon compounds such displacements do not occur.

The present investigation indicates that a displacement reaction of type (1) occurs in tetrahydrofuran (THF).

$$\mathrm{CH_2{=}CHCH_2MgCl + (C_6H_5CH_2)_2RSiH \longrightarrow C_6H_5CH_2MgCl + (CH_2{=}CHCH_2)(C_6H_5CH_2)RSiH} \qquad \mathrm{R = C_6H_5CH_2 \text{ or } H} \quad (1)$$

The first indication of the displacement of a benzyl group was observed when allylmagnesium chloride was allowed to react with tribenzylsilane in refluxing THF. The mixture of products obtained yielded no allyltribenzylsilane. Although an appreciable amount of tribenzylsilane was recovered, some lower boiling fractions contained R_3SiH, where at least one of the R groups was the allyl group as indicated by infrared spectra. It was thought that these fractions might possibly contain allyldibenzylsilane. This was established by comparison with allyldibenzylsilane prepared by an independent synthesis. Using a published method[4] for selective reactions of the silicon hydrogen group with organometallic compounds, allyldibenzylsilane was synthesized according to the reaction

$$\mathrm{CH_2{=}CHCH_2MgCl + (C_6H_5CH_2)_2SiH_2 \longrightarrow (CH_2{=}CHCH_2)(C_6H_5CH_2)_2SiH} \quad (2)$$

A by-product from reaction 2 was tribenzylsilane. The presence of significant amounts of tribenzylsilane as an impurity in the dibenzylsilane is precluded by the fact that an analytical sample of the latter was used in the reaction. The following steps are postulated for the formation of tribenzylsilane in reaction 2.

$$\mathrm{CH_2{=}CHCH_2MgCl + (C_6H_5CH_2)_2SiH_2 \longrightarrow C_6H_5CH_2MgCl + (CH_2{=}CHCH_2)(C_6H_5CH_2)SiH_2} \quad (3)$$

$$\mathrm{C_6H_5CH_2MgCl + (C_6H_5CH_2)_2SiH_2 \longrightarrow (C_6H_5CH_2)_3SiH} \quad (4)$$

Benzylmagnesium chloride was found to react with dibenzylsilane to give tribenzylsilane in good yield in THF, but not with tribenzylsilane to form tetrabenzylsilane to any detectable extent. The reaction between allylmagnesium chloride and tribenzylsilane in THF is formulated in reaction 5.

$$\mathrm{CH_2{=}CHCH_2MgCl + (C_6H_5CH_2)_3SiH \longrightarrow C_6H_5CH_2MgCl + (CH_2{=}CHCH_2)(C_6H_5CH_2)_2SiH} \quad (5)$$

The formation of a benzyl-type Grignard reagent was established by carbonation of the reaction mixture and subsequent isolation and identification of phenylacetic acid.

In order to test the effect of temperature on the displacement, reaction 5 was carried out in refluxing xylene after most of the THF was removed by distillation. The yield of phenylacetic acid, after carbonation, was not appreciably different from when the reaction was carried out in THF alone. The role of the THF in the reaction seemed to be more important than increased reaction temperature.

The solvent effect of the THF was further exemplified by the fact that the displacement reaction does not take place when allylmagnesium bromide[5] is refluxed with tribenzylsilane in an ether solution or in refluxing xylene where most of the ether has been removed by distillation.

No displacement occurred when tetrabenzylsilane was treated with allylmagnesium chloride in THF, as no solid acid was isolated when the reaction mixture was carbonated.

In an attempt to extend the displacement reaction, allylmagnesium chloride was refluxed with triphenylsilane in THF. After carbonation, no benzoic acid was isolated, indicating that a phenyl group was not displaced. However, the formation of allyltriphenylsilane[4] might indicate that the displacement of hydride ion occurs at a faster rate than the displacement of a phenyl group. As was the case with tetrabenzylsilane, no displacement was observed when tetraphenylsilane was treated with allylmagnesium chloride in refluxing THF. Furthermore, a γ-phenylpropyl group was not displaced from tri-γ-phenylpropylsilane[6] by allylmagnesium chloride in THF.

---

[1] F. S. Kipping, *J. Chem. Soc.*, **91**, 717 (1907).

[2] R. Robison and F. S. Kipping, *ibid.*, **93**, 439 (1908).

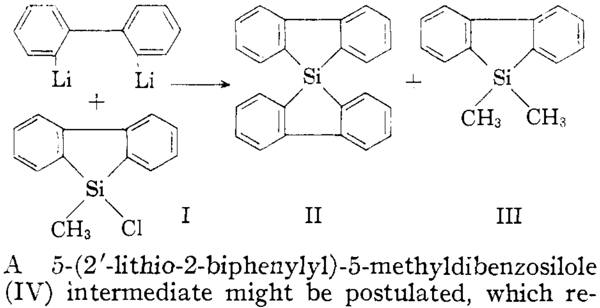
[3] F. Challenger and F. S. Kipping, *ibid.*, **97**, 143 (1910).

[4] H. Gilman and E. A. Zuech, THIS JOURNAL, **79**, 4560 (1957).

[5] H. Gilman and J. H. McGlumphy, *Bull. soc. chim. France*, **43**, 1322 (1928).

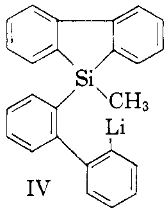
[6] E. A. Zuech, unpublished studies.

Recently, in this Laboratory, what may be analogous displacement reactions have been observed in cyclization reactions with organolithium reagents.[7] In the dibenzosilole[7a] series, treatment of 5-chloro-5-methyldibenzosilole (I) with 2,2′-dilithiobiphenyl in ether gave almost equimolar amounts of 5,5′-spirobi-(dibenzosilole) (II) and 5,5-dimethyldibenzosilole (III).



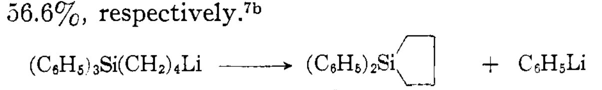
I II III

A 5-(2′-lithio-2-biphenylyl)-5-methyldibenzosilole (IV) intermediate might be postulated, which reacts intramolecularly forming II and methyllithium.



IV

The methyllithium thus formed could react with I to yield III. Similarly, 4-lithiobutyltriphenylsilane (V), prepared by the reaction of 4-bromobutyltriphenylsilane (VI) and lithium in ether, reacted intramolecularly to form 1,1-diphenylsilacyclopentane (VII) and phenyllithium in yields of 50.4 and 56.6%, respectively.[7b]



V VII

When the Grignard reagent of VI was prepared in ether, no cyclization or formation of phenylmagnesium bromide was detected.[7b] Related cleavages of silicon–carbon bonds by RM compounds, other than Grignard reagents, also have been observed.[8]

Experimental[9]

Allylmagnesium Halide and Tribenzylsilane. A. In Refluxing THF.—To 18.2 g. (0.06 mole) of tribenzylsilane in 25 ml. of THF was added rapidly 0.08 mole of allylmagnesium chloride[10] in 80 ml. of THF solution. The reaction mixture was refluxed for 96 hr. and hydrolyzed by the addition of 50 ml. of dilute acid. The organic layer was separated, dried over sodium sulfate, and the solvent removed by distillation. The products were distilled under reduced pressure, and the first fraction was collected between 134–148° (0.9 mm.), wt. 4.3 g. A second fraction was collected at 152–154° (0.9 mm.), wt. 4.4 g. (24.3%), which solidified and was identified by mixed melting point and infrared spectrum as recovered tribenzylsilane. The first fraction was redistilled twice and yielded 2.1 g. (13.9%) of slightly impure allyldibenzylsilane, $n^{20}\mathrm{D}$ 1.5668, which was identified by comparison of infrared spectra and refractive indices with those of pure allyldibenzylsilane.

B. Carbonation after Refluxing in THF.—The reaction was carried out in a manner similar to A, except that the reaction mixture was refluxed for 168 hr., and carbonated by pouring onto a slurry of Dry Ice and ether. After hydrolysis with dilute acid, the acidic layer was washed three times with ether and discarded. The combined ether washings and organic layer were extracted four times with aqueous alkali. The basic layer was acidified and extracted four times with ether. The ether extracts were dried over sodium sulfate and the solvent removed by evaporation to yield 2.3 g. (29.4%) of impure acid, m.p. 65–74°. After two recrystallizations from petroleum ether (b.p. 60–70°), 0.65 g. (8.0%) of acid, m.p. 76–77°, and 1.1 g. (13.2%), of acid, m.p. 74–77°, were obtained. The acid was identified as phenylacetic acid by infrared spectrum and mixed melting point.

An attempt to separate the products in the organic layer yielded complex mixtures. The infrared spectra of these products showed strong absorption bands at 3.3, 3.4, 4.7 and 6.1 μ indicating the presence of aromatic C–H, aliphatic C–H, Si–H, and C–C double bonds, suggesting the presence of $(C_6H_5CH_2)(CH_2{=}CHCH_2)RSiH$, where R may be a benzyl or an allyl group.

C. Carbonation after Refluxing in THF–Xylene.—The reaction was carried out as in B, with the exception that before refluxing for 168 hr., 100 ml. of xylene was added, and most of the THF removed by distillation until the temperature of the distillate was 100°. The carbonation and work-up were identical to those described in part B. One and seven-tenths grams (20.8%) of a solid acid, m.p. 72–77°, was obtained from the basic layer. This acid was recrystallized twice from petroleum ether (b.p. 60–70°) and yielded 1.3 g. (15.9%) of slightly impure phenylacetic acid, m.p. 76–78°, which was identified by mixed melting point and infrared spectrum.

D. Carbonation after Refluxing in Ether.—One hundred ml. of an ethereal solution containing 0.08 mole of allylmagnesium bromide was refluxed with 18.2 g. (0.06 mole) of tribenzylsilane for 168 hr. The carbonation and work-up were identical to those in reaction B. No solid acid was obtained from the basic extract. The organic layer yielded 16.3 g. (89.8%) of recovered tribenzylsilane, m.p. 89–91°, and another 1.5 g. (8.2%), of impure tribenzylsilane, m.p. 80–91°, which were identified by infrared spectra and mixed melting points.

E. Carbonation after Refluxing in Ether–Xylene.—The reaction was carried out as in reaction D, with the exception that before refluxing for 168 hr., 100 ml. of xylene was added and most of the ether removed by distillation until the temperature of the distillate was 100°. No phenylacetic acid was isolated after carbonation. Tribenzylsilane was recovered from the organic layer; 14.2 g. (78%), m.p. 89–91°, and 3.0 g. (16.4%), m.p. 80–90°, identified by infrared spectra and mixed melting points.

Dibenzylsilane.—To 102 g. (0.6 mole) of silicon tetrachloride in 250 ml. of ether was added 1.04 moles of benzylmagnesium chloride in 1750 ml. of ether at a rate which maintained gentle refluxing. The reaction mixture was stirred overnight, the magnesium salts removed by filtration under nitrogen pressure, and the salts washed with a total of 500 ml. of ether. The mixture of chlorosilanes[11] obtained was reduced[12] to a mixture of silanes by the addition of the combined ether washings and filtrate to 26.6 g. (0.6 mole) of lithium aluminum hydride suspended in 200 ml. of ether at a rate which maintained gentle refluxing. The reaction mix-

---

(7) (a) H. Gilman and R. D. Gorsich, THIS JOURNAL, **80**, 1883, 3243 (1958); (b) D. Wittenberg and H. Gilman, *ibid.*, **80**, 2677 (1958).

(8) (a) H. Gilman, R. A. Benkeser and G. E. Dunn, *ibid.*, **72**, 1689 (1950); (b) R. D. Gorsich, unpublished studies; (c) A. G. Brook and H. Gilman, THIS JOURNAL, **76**, 2333 (1954); (d) H. Gilman and T. C. Wu, *ibid.*, **75**, 2509 (1953); (e) R. A. Benkeser and D. J. Foster, *ibid.*, **74**, 4200 (1952); (f) R. A. Benkeser, H. Landesman and D. J. Foster, *ibid.*, **74**, 648 (1952); (g) R. A. Benkeser and D. J. Foster, *ibid.*, **74**, 5314 (1952); (h) C. R. Hauser and C. R. Hance, *ibid.*, **74**, 1856 (1952).

(9) All melting points and boiling points are uncorrected. Reactions involving Grignard reagents were carried out in an atmosphere of dry, oxygen-free nitrogen. The THF was dried by refluxing over sodium metal for at least 24 hours and distilled, immediately before use, from lithium aluminum hydride. The ether and xylene were dried by storage over sodium wire.

(10) Prepared according to unpublished directions of Theodore Soddy. The method is essentially that of H. Gilman and J. H. McGlumphy (ref. 5), except that THF is used as the solvent and allyl chloride is used instead of allyl bromide. Allylmagnesium chloride is soluble in THF at approximately 1 *M* concentration.

(11) G. Martin and F. S. Kipping, *J. Chem. Soc.*, **95**, 306 (1909).

(12) A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach and H. I. Schlesinger, THIS JOURNAL, **69**, 2642 (1947).

ture was allowed to cool, and hydrolyzed by pouring cautiously upon a mixture of cracked ice and 50 ml. of concd. sulfuric acid. The ether layer was separated immediately, washed three times with 100-ml. portions of water, and dried over calcium sulfate. After removal of the solvent by distillation, the products were distilled under reduced pressure and 87.1 g. (68.5%) of impure dibenzylsilane, n^{20}_{D} 1.5731, was obtained. On redistillation, 53.8 g. (32.6%) of slightly impure dibenzylsilane was collected, b.p. 174–180° (25–29 mm.), n^{20}_{D} 1.5740. Further distillation yielded 15.0 g. (11.8%) of pure dibenzylsilane, b.p. 160° (14 mm.), n^{20}_{D} 1.5746, d^{20}_{4} 0.9917.

Anal. Calcd. for $C_{14}H_{16}Si$: Si, 13.22; *MR*D, 70.30. Found: Si, 13.16, 12.98; *MR*D, 70.72.

From lower boiling fractions, benzylsilane was isolated and identified, b.p. 65–68° (35–40 mm.), n^{20}_{D} 1.5208, d^{20}_{4} 0.8922.

Anal. Calcd. for $C_7H_{10}Si$: Si, 22.98; *MR*D, 41.49. Found: Si, 22.83, 22.40; *MR*D, 41.66.

Some tribenzylsilane was obtained from the distillation residue.

Allyldibenzylsilane.—To 12.8 g. (0.06 mole) of dibenzylsilane in 25 ml. of THF was added rapidly 0.08 mole of allylmagnesium chloride[10] in 80 ml. of THF solution. The reaction mixture was refluxed for 16 hr., and hydrolyzed by the slow addition of 50 ml. of dilute acid. The organic layer was separated and the aqueous layer washed twice with ether. The combined organic layer and ether washings were dried over calcium sulfate and the solvents removed by distillation. The products were distilled under reduced pressure to give 3.1 g. (20.5%) of allyldibenzylsilane, b.p. 130–134° (0.8 mm.), n^{20}_{D} 1.5690, d^{20}_{4} 0.9855.

Anal. Calcd. for $C_{17}H_{20}Si$: Si, 11.13; *MR*D, 84.01. Found: Si, 11.02, 10.94; *MR*D, 83.92.

A higher boiling fraction and the distillation residue were recrystallized from petroleum ether (b.p. 60–70°) to give 3.0 g. (16.5%) of tribenzylsilane, m.p. 89–91°, which was identified by mixed melting point and infrared spectrum.

Benzylmagnesium Chloride and Dibenzylsilane.—To 3.7 g. (0.017 mole) of dibenzylsilane in 50 ml. of THF was added 0.017 mole of benzylmagnesium chloride in 25 ml. of THF solution. The reaction mixture was refluxed for 15 min., after which Color Test I[13] was slightly positive. Color Test I was strongly positive after another equivalent of the Grignard reagent was added and the mixture refluxed for 20 hr. The reaction mixture was worked up in a manner similar to that used in the preceding experiment. Crude tribenzylsilane, m.p. 84–89°, wt. 4.4 g. (82.7%), was obtained by crystallization from petroleum ether (b.p. 60–70°). Upon recrystallization, 3.8 g. (71.5%) of tribenzylsilane, m.p. 89–91°, was obtained and identified by mixed melting point. No tetrabenzylsilane was isolated.

Carbonation after Refluxing Allylmagnesium Chloride[10] and Triphenylsilane in THF.—Allylmagnesium chloride (0.07 mole) in 75 ml. of THF was added to 15.6 g. (0.06 mole) of triphenylsilane, the reaction mixture refluxed for 168 hr., and carbonated. The products obtained from the carbonation were worked up in a manner similar to previously described carbonation reactions. There was no solid acid obtained from the basic extract. From the organic layer, after removal of the solvents, 12.4 g. (67.8%) of allyltriphenylsilane,[4] m.p. 89–90°, was obtained after crystallization from ethanol. The identification was made by mixed melting point and infrared spectrum.

Carbonation after Refluxing Allylmagnesium Chloride[10] and Tetrabenzylsilane in THF.—Tetrabenzylsilane (15.7 g., 0.04 mole) and 0.06 mole of allylmagnesium chloride in 90 ml. of THF were refluxed for 168 hr., and carbonated. No phenylacetic acid was isolated, and 14.3 g. (91.1%) of tetrabenzylsilane, m.p. 126–128°, was recovered.

Carbonation after Refluxing Allylmagnesium Chloride[10] and Tetraphenylsilane in THF.—Allylmagnesium chloride (0.06 mole) in 90 ml. of THF, and 13.44 g. (0.04 mole) of tetraphenylsilane were refluxed 168 hr. and carbonated. No benzoic acid was isolated, and 12.1 g. (90%) of tetraphenylsilane, m.p. 236–238°, was recovered.

Carbonation after Refluxing Allylmagnesium Chloride[10] and Tri-γ-phenylpropylsilane[6] in THF.—Tri-γ-phenylpropylsilane (15.4 g., 0.04 mole) and 0.05 mole of allylmagnesium chloride in 65 ml. of THF were refluxed for 168 hr. and carbonated. No γ-phenylbutyric acid was isolated.

Acknowledgment.—This research was supported in part by the United States Air Force under Contract AF 33(616)-3510 monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright–Patterson AFB, Ohio. The authors wish to express their appreciation to Dr. V. A. Fassel, Mr. E. M. Layton, Mr. R. Kniseley, Miss E. Conrad and Miss S. Trusdell of the Institute of Atomic Research, Ames, Iowa, for infrared spectra.

AMES, IOWA

---

[13] H. Gilman and F. Schulze, THIS JOURNAL, **47**, 2002 (1925).

[CONTRIBUTION FROM THE RESEARCH CENTER, HERCULES POWDER CO.]

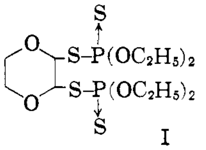
Two Organophosphorus Derivatives of *p*-Dioxane with Insecticidal and Acaricidal Activity[1]

BY W. R. DIVELEY, A. H. HAUBEIN, A. D. LOHR AND P. B. MOSELEY

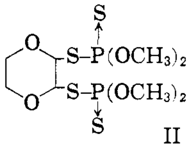
RECEIVED MAY 15, 1958

Two organophosphorus derivatives of *p*-dioxane, namely, 2,3-*p*-dioxanedithiol S,S-bis-(O,O-diethyl phosphorodithioate) (I), and the corresponding methyl ester II, were found to be exceptionally toxic to certain insects and mites. These compounds may be synthesized from 2,3-dichloro-*p*-dioxane and the appropriate O,O-dialkyl hydrogen phosphorodithioates in the presence of molecular equivalents of certain bases or catalytic quantities of certain catalysts, or from *p*-dioxene and bis-(dialkoxyphosphinothioyl) disulfide in the presence of catalytic quantities of iodine. The products made from O,O-diethyl hydrogen phosphorodithioate contained about 70% of the ethyl ester I as a mixture of *cis* and *trans* isomers (2:3 ratio) which were isolated using partition chromatography and tentatively assigned configurations based on chemical, physical and biological data. A mechanism involving ionic intermediates is proposed for the formation of these isomers.

During the course of a systematic search for compounds with pesticidal activity, two organophosphorus derivatives of *p*-dioxane, namely, 2,3-*p*-dioxanedithiol S,S-bis-(O,O-diethyl phosphorodithioate) (I), and the corresponding methyl ester II, were found to be exceptionally toxic to certain pests.[2]



I



II

The pesticidal activity of one of these compounds, the ethyl ester I, also known as Delnav,[3] is reported

---

[1] Presented in part before the Division of Agricultural and Food Chemistry at the 131st Meeting of the American Chemical Society, Miami, Fla., April, 1957.

[2] W. R. Diveley and A. D. Lohr, U. S. Patent 2,725,328 (1955).

[3] Delnav is a registered trademark of Hercules Powder Co.