EXPERIMENTAL

α,α-Dimethyldiglycolamide.[2] To a refluxing suspension of 19.5 g. (0.5 mole) of sodium amide in 300 cc. of ether was added dropwise ethyl α-hydroxyisobutyrate (66.0 g., 0.5 mole). After refluxing 45 min. longer to expel the ammonia ethyl bromoacetate (83.5 g., 0.5 mole) was added dropwise during 30 min. The stirred mixture was refluxed 2 hr. Water was added and the dried ether layer was distilled to yield 23.0 g. of product, b.p. 125–128° (13 mm.). This was dissolved in a solution of 25 cc. of liquid ammonia in 175 cc. of ethanol. The solution was heated in a pressure bottle 5 days at 70–80°. The solution was concentrated to 100 cc. and chilled to give 15.4 g. of crude amide, m.p. 160–162°. One crystallization from ethanol gave the pure product, m.p. 162–163°.

Anal. Calcd. for $C_8H_{12}N_2O_3$: N, 17.48. Found: N, 17.51.

2,2-Dimethyl-3,5-morpholinedione.[2] The above amide (14.3 g., 0.09 mole) was heated at 200° (60 mm.) for 30 min. The temperature of the bath was raised to 260° whereupon the imide distilled at 20 mm. pressure and solidified in the receiver. The product was triturated with sodium bicarbonate solution to give 6.3 g., m.p. 73–76°. One recrystallization from benzene-ligroin yielded 5.0 g. of pure product, m.p. 74–76°.

Anal. Calcd. for $C_6H_9NO_3$: N, 9.79. Found: N, 9.75.

α,α-Diethyldiglycolic acid.[2] To a stirred suspension of 2.4 g. of sodium hydride in 100 cc. of dry benzene was added during 25 minutes 16.0 g. (0.10 mole) of ethyl α-ethyl-α-hydroxybutyrate and the stirring continued 40 min. until a clear yellow solution resulted. Ethyl bromoacetate (18.4 g., 0.11 mole) was added dropwise and the mixture was refluxed for 2 hr. Water was added. The organic layer was dried and distilled to give 9.2 g. of colorless oil, b.p. 152–157° (22 mm.). A total of 90.7 g. of this oil was dissolved in 340 cc. of hot hydrochloric acid (Sp. gr. 1.18) and the solution was heated 16 hr. in a steam bath. The solution was concentrated to 200 cc. and chilled. The crystalline product (41.5 g.) had m.p. 140–147° and was suitable for preparation of the ammonium salt. A small sample was crystallized twice from ethyl acetate to give the pure acid, m.p. 146–148°.

Anal. Calcd. for $C_8H_{14}O_5$: C, 50.52; H, 7.42. Found: C, 50.58; H, 7.50.

2,2-Diethyl-3,5-morpholinedione.[2] A solution of 28.5 g. (0.15 mole) of α,α-diethyldiglycolic acid in 90 cc. ammonia water (Sp. gr. 0.90) was evaporated to dryness. The resulting salt was heated at 190° for 25 minutes at a pressure of 50 mm. The bath temperature was raised to 210° and the pressure was lowered to 14 mm., whereupon the product distilled and crystallized. It was triturated with sodium bicarbonate solution and recrystallized from a mixture of isopropyl alcohol and water to give 10.4 g. of the imide, m.p. 62–63°.

Anal. Calcd. for $C_8H_{13}NO_3$: N, 8.18. Found: N, 8.18.

Methyl ethylphenylhydroxyacetate.[1] Ethylphenylhydroxy-acetic acid[4] (11.4 g., 0.063 mole) was refluxed for 2.5 hr. with 60 cc. of methanol containing 0.3 cc. of sulfuric acid. The mixture was treated with 50 cc. of water and 50 cc. of saturated sodium bicarbonate solution. The solution was saturated with salt and extracted with ether. From the aqueous layer there was obtained unchanged acid (0.48 g.) and from the ether extract 11.11 g. of the ester, b.p. 86–88° (0.9 mm.), n_D^{25} 1.5080.

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 67.98; H, 7.37.

Methyl α-ethyl-α-phenyl-α-carbethoxymethoxyacetate.[1] In a nitrogen atmosphere methyl ethylphenylhydroxyacetate (18.8 g., 0.097 mole) was added dropwise during 2 hr. to a rapidly stirred suspension of sodium hydride (1.9 g., 0.08 mole) in 200 cc. of dry benzene at room temperature. Nearly all of the sodium hydride dissolved after stirring 6.5

hr. Complete solution was then effected by refluxing for 1.5 hr. To the stirred solution at room temperature was added dropwise ethyl bromoacetate (13.4 g., 0.08 mole). After stirring overnight the reaction mixture was refluxed for 1 hr., cooled and treated with 100 cc. of cold water. Less than 0.002 mole of hydrogen ions was required for neutrality. The benzene layer was washed with sodium bicarbonate solution, dried, and distilled, yield 14.7 g. (65.6%), b.p. 133–135.5° (0.7 mm.), n_D^{25} 1.4945.

Anal. Calcd. for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19. Found: C, 64.09; H, 7.11.

α-Ethyl-α-phenyldiglycolamide.[1] A solution of the above ester (4.2 g., 0.015 mole) in 100 cc. of anhydrous methanol contained in a pressure bottle was saturated at −5° with dry ammonia gas. The bottle was capped and allowed to stand for a week at 45–55°. Removal of the solvent afforded a quantitative yield of crude diamide, m.p. 169–173°. Recrystallization from methanol-ether gave the pure product, m.p. 175° (dec.).

Anal. Calcd. for $C_{12}H_{16}N_2O_3$: C, 60.99; H, 6.82; N, 11.86. Found: C, 60.90; H, 6.87; N, 11.86.

2-Ethyl-2-phenyl-3,5-morpholinedione.[1] The above amide was pyrolyzed at 210–220° to yield an amber oil which was dissolved in hot methanol and treated with boneblack to remove color. Hot water was added to the filtrate to the point of incipient precipitation. The crude imide (0.7 g., m.p. 115–125°) separated from the cold solution. This was crystallized from methanol-water to give 0.67 g. (73%) of the pure product, m.p. 124–125°.

Anal. Calcd. for $C_{12}H_{13}NO_3$: C, 65.75; H, 5.97; N, 6.39. Found: C, 65.87; H, 5.97; N, 6.41.

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Scission of the Silicon-Silicon Bond in Halogenated Polysilanes by Organometallic Reagents

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Cleavage of the silicon-silicon bond by organometallic reagents has been long known. First reports of cleavages of this nature were by Friedel and Ladenburg,[1–3] who demonstrated that treatment of hexaiododisilane with diethylzinc gave a mixture of tetraethylsilane and hexaethyldisilane. Shortly thereafter it was reported[4] that tetraphenyldisilane was the sole product from the reaction of hexachlorodisilane, chlorobenzene, and sodium. No yields or experimental details were mentioned. From the reaction of hexachlorodisilane with methyl magnesium iodide, Martin[5] obtained oils which he postulated were mixtures of monosilanes containing methyl and chloro groups. From hexachlorodisilane

(4) A. McKenzie and A. Ritchie, *Ber.*, **70B**, 33 (1937).

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(1) C. Friedel and A. Ladenburg, *Compt. rend.*, **68**, 923 (1869).
(2) C. Friedel and A. Ladenburg, *Ann.*, **203**, 251 (1880).
(3) C. Friedel and A. Ladenburg, *Ann. Chim. Phys.*, [5] **19**, 401 (1880).
(4) L. Gattermann and K. Weinlig, *Ber.*, **27**, 1946 (1894).
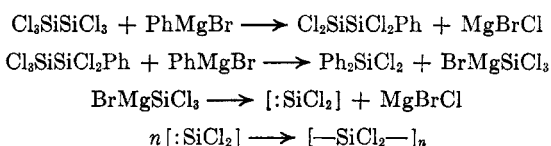(5) G. Martin, *Ber.*, **46**, 2442, 3294 (1913).

and phenylmagnesium bromide, dichlorodiphenylsilane was isolated.[6]

In a series of three papers,[7-9] Schumb and coworkers investigated the reactions of chlorinated polysilanes, notably hexachlorodisilane, with organometallic reagents. It was found[7] that hexasubstituted disilanes could not be prepared under Wurtz-type coupling conditions by treatment of alkyl or aryl halides with sodium in the presence of hexachlorodisilane. In each case, only the tetrasubstituted monosilane was obtained. When reactions were carried out[9] using preformed organosodium compounds and hexachlorodisilane, the main products isolated were the hexasubstituted disilanes. Some tetrasubstituted monosilanes were also isolated. Better yields of the hexasubstituted disilanes were obtained using Grignard reagents[8] instead of organosodium compounds. From the reaction of octachlorotrisilane with phenylmagnesium bromide, only hexaphenyldisilane and tetraphenylsilane were isolated. On this basis, it was postulated[8] that the instability of the silicon-silicon bond in halogenated polysilanes increases as the number of silicon atoms increases.
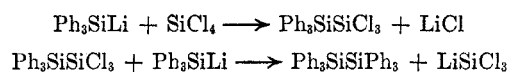
From the reaction of hexachlorodisilane with p-xenyllithium there was obtained[10] a mixture of tetraxenylsilane and hexaxenyldisilane. Similarly, from hexachlorodisilane and p-tolyllithium, tetra-p-tolylsilane was isolated[11] in 42% yield. From hexachlorodisilane and 2,2'-biphenylenedilithium there was obtained 5,5'-spirobi[dibenzosilole] and a large amount of resinous material.[12] When triphenylsilyllithium is allowed to react with silicon tetrachloride, hexaphenyldisilane is obtained along with a large quantity of polymer.[13] Since it is known that hexaphenyldisilane is not cleaved by phenyllithium in ether[14] it may be assumed that a totally halogenated or partially halogenated disilane is the species undergoing cleavage. It seems possible that a number of halogenated disilanes may cleave.

In an attempt to prepare 1,1,2,2-tetraphenyldisilane by the reaction of 4 moles of phenylmagnesium bromide with one mole of hexachlorodisilane, followed by reduction with lithium aluminum hydride, diphenylsilane was isolated. In a subsequent experiment, in which no reduction with lithium aluminum hydride was carried out, dichlorodiphenylsilane was isolated in 7% yield along with a trace of tetraphenylsilane and a large amount of resin. Thus we suggest that the first step of the reaction may be the formation of pentachlorophenyldisilane. Cleavage of this compound by phenylmagnesium bromide could give rise to dichlorodiphenylsilane and an intermediate species, trichlorosilylmagnesium bromide. Disproportionation of the trichlorosilylmagnesium bromide would give a dichlorosilane, which would then polymerize to give polymeric $SiCl_2$, which appears to be analogous to the material isolated by Schmeisser and Schwarzmann.[15]

$$Cl_3SiSiCl_3 + PhMgBr \longrightarrow Cl_2SiSiCl_2Ph + MgBrCl$$

$$Cl_3SiSiCl_2Ph + PhMgBr \longrightarrow Ph_2SiCl_2 + BrMgSiCl_3$$

$$BrMgSiCl_3 \longrightarrow [:SiCl_2] + MgBrCl$$

$$n[:SiCl_2] \longrightarrow [-SiCl_2-]_n$$

Polymeric resins were also obtained in some recently reported studies.[12,13] Also, the results[13] involving the formation of hexaphenyldisilane from the reaction of excess triphenylsilyllithium with silicon tetrachloride would suggest that initially 1,1,1-trichloro-2,2,2-triphenyldisilane is formed. Cleavage of this compound with triphenylsilyllithium would give hexaphenyldisilane and the intermediate trichlorosilyllithium.

$$Ph_3SiLi + SiCl_4 \longrightarrow Ph_3SiSiCl_3 + LiCl$$

$$Ph_3SiSiCl_3 + Ph_3SiLi \longrightarrow Ph_3SiSiPh_3 + LiSiCl_3$$

EXPERIMENTAL[16]

Reaction of hexachlorodisilane with phenylmagnesium bromide (Run 1). To a stirred solution of 63.7 g. (0.237 mole) of hexachlorodisilane in 100 ml. of ether was added 745 ml. of an ethereal solution containing 0.95 mole of phenylmagnesium bromide. After stirring overnight, the reaction mixture gave a positive Color Test I.[17] The ether was distilled and replaced by benzene. After heating for several hours at the benzene reflux temperature, Color Test I was negative. The reaction mixture was cooled and treated with 4.75 g. (0.125 mole) of lithium aluminum hydride suspended in ether. After a short reflux period, the reaction mixture was treated with ethyl acetate and then aqueous ammonium chloride. The only product identified was 17.6 g. of crude diphenylsilane, b.p. 82–86° (0.6 mm.), which on redistillation boiled at 123–126° (11 mm.).[18] The infrared spectrum showed a strong Si–H band at 4.8μ, but the product was badly contaminated with biphenyl.

Run 2. In this experiment, 290 ml. of an ethereal solution containing 0.335 mole of phenylmagnesium bromide was added to a solution of 22.6 g. (0.0837 mole) of hexachloro-

(6) R. Schwarz and W. Sexauer, *Ber.*, **59**, 333 (1926).

(7) W. C. Schumb, J. Ackerman, and C. M. Saffer, *J. Am. Chem. Soc.*, **60**, 2486 (1938).

(8) W. C. Schumb and C. M. Saffer, *J. Am. Chem. Soc.*, **61**, 363 (1939).

(9) W. C. Schumb and C. M. Saffer, *J. Am. Chem. Soc.*, **63**, 93 (1941).

(10) H. Gilman and G. E. Dunn, *J. Am. Chem. Soc.*, **73**, 5077 (1951).

(11) H. Gilman and T. C. Wu, *J. Am. Chem. Soc.*, **75**, 3762 (1953).

(12) H. Gilman and R. D. Gorsich, *J. Am. Chem. Soc.*, **80**, 3243 (1958).

(13) D. Wittenberg, M. V. George, and H. Gilman, *J. Am. Chem. Soc.*, **81**, 4812 (1959).

(14) G. E. Dunn, unpublished studies. However, unpublished studies by B. J. Gaj have shown that a solvent like tetrahydrofuran can have a significant effect.

(15) M. Schmeisser and M. Schwarzmann, *Z. Naturforsch.*, **11b**, 228 (1956).

(16) Organometallic reactions were carried out under an atmosphere of dry, oxygen-free nitrogen. Melting points are uncorrected.

(17) H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

(18) Reported 75–76° (0.5 mm.), R. A. Benkeser, H. Landesman, and D. J. Foster, *J. Am. Chem. Soc.*, **74**, 648 (1952).

disilane in 100 ml. of ether. The ether was distilled and the resulting paste was heated at about 50° for 3 hr. Color Test I was then negative. Petroleum ether (b.p. 60–70°) was added. Filtration gave a clear solution which on cooling deposited an oil. After stripping off the petroleum ether, distillation of the residue gave three main fractions.

The first, b.p. 169–180° (20 mm.), 3.24 g. (7.6%), was redistilled at 15 mm. and boiled at 165–167°. The infrared spectrum of this oil was identical with that of an authentic specimen of dichlorodiphenylsilane. Further confirmation that the product was dichlorodiphenylsilane was obtained by treatment of 1.22 g. of the chlorosilane with p-biphenylyl-lithium. There was obtained 1.86 g. (81%) of di-p-biphenyl-yldiphenylsilane, m.p. 169–171° (reported[19] 169–170°). A mixed melting point with an authentic specimen of di-p-biphenylyldiphenylsilane was not depressed.

A second fraction distilled over the range 229–240° (20 mm.) and weighed 3.45 g. This was recrystallized from petroleum ether (b.p. 60–70°) and melted partially at 97°, indicative of the possible presence of chlorotriphenylsilane. Distillation of this solid gave no pure products.

A third fraction distilled over the range 185–215° (0.3 mm.), 7.1 g., and crystallized on standing. Recrystallization from petroleum ether (b.p. 60–70°) gave 3.5 g., melting at 125–128° (partial). Several recrystallizations did not sharpen the melting point. One g. of this material was treated with excess methyllithium. Hydrolysis, followed by work-up in the usual way, gave some solid, m.p. 133–143°. This was dissolved in hot petroleum ether (b.p. 60–70°) and chromatographed on an alumina column to give 0.3 g. of solid, m.p. 140–142° (cloudy). A mixed melting point with 1,2-dimethyl-1,1,2,2-tetraphenyldisilane was not depressed.

A small amount of tetraphenylsilane was scraped from the condenser walls after the distillation and recrystallized from benzene, m.p. 236°.

The distillation residue consisted of a large amount of brown polymer which, though insoluble in most common solvents, dissolved slowly in benzene.

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(19) L. Spialter, D. C. Priest, and C. W. Harris, *J. Am. Chem. Soc.*, **77**, 6227 (1955).

Magnesium Salts of Aromatic Arsonic Acids. The Nitration of Benzenearsonic Acid
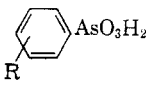
LEON D. FREEDMAN AND G. O. DOAK

Magnesium salts of most phosphonic acids are soluble at room temperature but are precipitated on heating.[1] However, arylphosphonic acids con-

(1) L. D. Freedman and G. O. Doak, *J. Am. Chem. Soc.*, **77**, 6221 (1955); see also *Chem. Revs.*, **57**, 479 (1957).

taining bulky *ortho* substituents do not form insoluble magnesium salts either at room temperature or when heated. This fact permitted the isolation of o-nitrophenylphosphonic acid from the mixture of isomers obtained by nitrating phenylphosphonic acid.[1] It has been known for over half a century that the magnesium salts of arsonic acids are more soluble in cold water than in hot.[2] And, indeed, the fact that atoxyl[3] yields a precipitate with magnesia mixture only upon boiling was cited by Ehrlich and Bertheim[4] as evidence that atoxyl is an arsonic acid derivative. However, a survey of the literature revealed very little information concerning the effect of the substituents on the solubility of magnesium salts of aromatic arsonic acids.[5] Since we had available in this laboratory a number of aromatic arsonic acids, it was of interest to determine whether the generalizations previously noted[1] for arylphosphonic acids were also valid for the analogous arsonic acids.

A sample of each arsonic acid listed in Table I was dissolved in dilute aqueous ammonia and treated with magnesia mixture exactly as described for the phosphonic acids.[1] The following results were obtained: (1) Only one arsonic acid (N-p-toluylarsanilic acid) gave an insoluble magnesium salt at room temperature. (2) o-Toluenearsonic and o-bromobenzenearsonic acids gave sparse precipitates on heating; all other compounds

TABLE I

ARSONIC ACIDS STUDIED

R =

R	
H	p-NHCOCH₃
o-,m,p-NO₂	p-AsO₃H₂
o-,m,p-Cl	p-NHCH₂COOCH₃
o-,p-Br	p-NHCOC₆H₄CH₃-p'
o-,p-CH₃	2-NO₂-6-CH₃
m-,p-SO₂NH₂	2-NO₂-3-COOH
m-COOH	3-NO₂-4-NH₂
p-COOCH₃	3-NO₂-4-OH
o-C₆H₅	3-NO₂-4-COOH
p-NH₂	3-NH₂-4-(CH₂)₃COOH
p-OH	

(2) W. M. Dehn, *Am. Chem. J.*, **33**, 101 (1905).

(3) "Atoxyl" is a trivial name for the sodium salt of arsanilic acid. It was first prepared by A. Bechamp, *Compt. rend.*, **56**, 1172 (1863), and was originally believed to be an anilide of arsenic acid.

(4) P. Ehrlich and A. Bertheim, *Ber.*, **40**, 3292 (1907).

(5) L. Benda, *J. prakt. Chem.*, **95**, 75 (1917), reported that several anthraquinonearsonic acids yield precipitates with magnesia mixture in the cold. H. Schmidt, *Ann.*, **421**, 159 (1920), found that o-nitrobenzenearsonic acid does not give any precipitate on boiling with magnesia mixture, the magnesium salt separating only on prolonged standing at room temperature. G. O. Doak, H. Eagle, and H. G. Steinman, *J. Am. Chem. Soc.*, **64**, 1064 (1942), state that certain diarsonic acids give insoluble magnesium salts in the cold, whereas the magnesium salts of monoarsonic acids usually precipitate only on heating.