This material was heated under vacuum at 100° for 1 hr. prior to analysis.

Anal. Calcd. for $C_{52}H_{46}O_4Si_4$: C, 73.79; H, 5.43; Si, 13.26. Found: C, 73.97, 73.98; H, 5.63, 5.54; Si, 13.20, 13.15.

The infrared spectrum showed the bands at 5.8 and 8.2 μ characteristic of the acetate group.[16] The n.m.r. spectrum gave a ratio of aromatic to aliphatic protons of 6.57 (calculated value, 6.67). The methyl groups gave the expected singlet which appeared at 8.28 τ.

From 1,1,2,2,3,3,4,4-Octaphenyltetrasilane (III) and Mercuric Acetate.—A mixture of 3.0 g. (0.0041 mole) of 1,1,2,2,3,3,4,4-octaphenyltetrasilane and 2.58 g. (0.0082 mole) of mercuric acetate in 100 ml. of glacial acetic acid was refluxed for 12 hr. Filtration of the cooled reaction mixture gave 1.3 g. (79%) of mercury and 3.3 g. (95.5%) of a white solid, m.p. 205–230°. Recrystallization of this material from benzene–petroleum ether (b.p. 60–70°) afforded 2.5 g. (72%) of product, m.p. 233–235°. A mixture melting point with an authentic sample of 1,4-diacetoxy-1,1,2,2,3,3,4,4-octaphenyltetrasilane was not depressed and the infrared spectra were superimposable.

From 1,4-Dichloro-1,1,2,2,3,3,4,4-octaphenyltetrasilane (IV) and Acetic Anhydride.—A mixture of 5.0 g. (0.00625 mole) of 1,4-dichloro-1,1,2,2,3,3,4,4-octaphenyltetrasilane in 50 ml. of acetic anhydride was refluxed for 24 hr. Filtration gave 4.0 g. (80%) of unchanged starting material, m.p. 185–187° (m.m.p.). Evaporation of the solvent from the filtrate gave 0.85 g. (16%) of white solid, m.p. 230–235°. Recrystallization from benzene–petroleum ether (b.p. 60–70°) afforded 0.75 g. (14%) of product, m.p. 233–235° (m.m.p.).

Hydrolysis of 1,4-Diacetoxy-1,1,2,2,3,3,4,4-octaphenyltetrasilane (II).—A mixture of 3.0 g. (0.0035 mole) of 1,4-diacetoxy-1,1,2,2,3,3,4,4-octaphenyltetrasilane and 50 ml. of *ca.* 0.5 *N* hydrochloric acid was refluxed for 48 hr. Filtration gave 2.5 g. (91.2%) of white solid, m.p. 230–234°. Recrystallization from benzene–petroleum ether (b.p. 60–70°) raised the melting point to 234–236° (87%). A mixture melting point with an authentic sample of monoxide was not depressed. The infrared spectrum showed the strong band at 10.45 μ previously reported for this strained cyclic siloxane.[13]

Reaction of Hexaphenyldisilane with Mercuric Acetate (Attempted).—A mixture of 5.2 g. (0.01 mole) of hexaphenyldisilane and 6.37 g. (0.02 mole) of mercuric acetate in 100 ml. of sodium-dried benzene was refluxed for 72 hr. Filtration gave 8.0 g. of solid, m.p. 270° dec. This material was extracted with hot water and filtered to give 5.0 g. (96%) of recovered starting material, m.p. 365–367° (m.m.p.).

Reaction of Decaphenylcyclopentasilane[9] with Mercuric Acetate (Attempted).—A mixture of 10.0 g. (0.011 mole) of decaphenylcyclopentasilane and 7.01 g. (0.022 mole) of mercuric acetate in 100 ml. of sodium-dried benzene was refluxed for 72 hr. Filtration gave 11.0 g. of solid, m.p. 275° dec. Extraction of this material with acetone followed by filtration gave 8.5 g. (85%) of recovered starting material, m.p. 456–462° (m.m.p.). No other pure materials could be isolated.

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(16) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., Methuen and Co., Ltd., London, 1958, pp. 179, 189.

The Preparation of a Di-Grignard Reagent from 2,2'-Dibromodibenzyl

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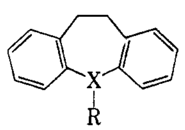
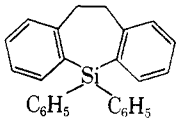
Incidental to an interesting study concerned with the preparation of 10,11-dihydro-5-phenyldibenz[*b,f*]arsepin (I) and the analogous phosphepin (II), it was reported[1] that a di-Grignard reagent could not be prepared from 2,2'-dibromodibenzyl (III) in diethyl ether. In view of the subsequently established successes in preparing some Grignard reagents in tetrahydrofuran by the general procedure of H. Normant,[2] we examined this solvent as a reaction medium in place of diethyl ether.



I, X = As, R = C_6H_5–
II, X = P, R = C_6H_5–

We now wish to report that III reacts with magnesium in tetrahydrofuran to give a soluble di-Grignard reagent. Carbonation of this di-Grignard compound gave a 68% yield of dibenzyl-2,2'-dicarboxylic acid.[3] In addition, reaction of the di-Grignard reagent with dichlorodiphenylsilane yielded the previously described 10,11-dihydro-5,5-diphenyldibenzo[*b,f*]silepin (IV).[4] The yield of IV, although low, was comparable to that obtained employing 2,2'-dilithiodibenzyl[3] and dichlorodiphenylsilane.



IV

Experimental[5]

Dibenzyl-2,2'-dicarboxylic Acid.—Five milliliters of a solution of 5 g. (0.0147 mole) of 2,2'-dibromodibenzyl in 50 ml. of tetrahydrofuran was added to 2.43 g. (0.1 g.-atom) of magnesium and 2–3 drops of ethyl iodide. The reaction mixture was refluxed for 5–10 min. at which time a gray color developed and color test I[6] was positive. The external heat was removed and the addition was continued at a rate sufficient to maintain an exothermic reaction. After dissipation of the heat of reaction, the mixture was stirred for 1 hr., decanted through a glass wool plug into a Dry Ice–ether slurry, and allowed to warm to room temperature. Extraction of the organic layer with dilute base followed by acidification yielded 2.5 g. (68%) of dibenzyl-2,2'-dicarboxylic acid, m.p. 229–231° (lit.[3] m.p. 226–228°).

10,11-Dihydro-5,5-diphenyldibenzo[*b,f*]silepin.—A tetrahydrofuran solution containing 0.014 mole of the di-Grignard reagent was slowly added to 3.54 g. (0.014 mole) of dichlorodiphenylsilane in 40 ml. of tetrahydrofuran. Color test I[5] was strongly positive after addition. The reaction mixture was refluxed gently for 24 hr. at which time the color test was negative. Acid hydrolysis followed by the usual work-up gave an oil which was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave 0.51 g. (10%) of product, m.p. 174–175°, after one recrystallization from ethanol–petroleum ether (b.p. 60–70°). A mixture melting point with a known sample[4] was not depressed and the infrared spectra were identical.

We have found that the n.m.r. spectrum of this compound contains a sharp singlet at 6.83 τ with a relative area consistent with the presence of four benzylic protons. In addition, the aromatic

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(1) F. G. Mann, I. T. Millar, and B. B. Smith, *J. Chem. Soc.*, 1130 (1953).

(2) See H. Normant, "Alkenylmagnesium Halides" in "Advances in Organic Chemistry," Vol. II, R. A. Raphael, E. C. Taylor, and H. Wynberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, pp. 1–65.

(3) R. C. Fuson, *J. Am. Chem. Soc.*, **48**, 835 (1926).

(4) R. D. Gorsich, Ph.D. thesis, Iowa State University, 1957.

(5) Reactions involving organometallic reagents were carried out under an atmosphere of dry, oxygen-free nitrogen. The tetrahydrofuran was dried over sodium wire and distilled from lithium aluminum hydride immediately before use. All melting points are uncorrected.

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

protons appeared as a broad multiplet and the ratio of aromatic-aliphatic protons was found to be 4.56 (theoretical, 4.5).

10,11-Dihydro-5,5-diphenyldibenzo[*b,f*]silepin.[4]—To a stirred solution of 4.5 g. (0.026 mole) of 2,2′-dibromodibenzyl in 40 ml. of ether was added 38 ml. of an ethereal solution containing 0.52 mole of *n*-butyllithium,[7] while cooling with an ice bath. The mixture was stirred at room temperature for 4 hr. and then was added, during 45 min., to a stirred solution of 6.23 g. (0.0246 mole) of dichlorodiphenylsilane in 50 ml. of ether. The mixture was hydrolyzed and the organic layer was worked up in the usual manner. The residual material was washed with petroleum ether (b.p. 60–70°) and an insoluble substance was filtered off. This was dissolved in benzene and chromatographed on a column of alumina to give 1.36 g. (15%) of product, m.p. 170–172°. Recrystallization from petroleum ether (b.p. 77–115°) raised the melting point to 172.5–174°.

Anal. Calcd. for $C_{26}H_{22}Si$: C, 86.15; H, 6.12; Si, 7.74. Found: C, 86.49, 86.30; H, 6.32, 6.34; Si, 7.70.

The petroleum ether (b.p. 60–70°) was removed from the first filtrate, and the residue was distilled under reduced pressure to give two unidentified fractions and 4.1 g. of residue which could not be further purified.

Acknowledgment.—This research was supported in part by the United States Air Force under contract AF 33(616)-6463 monitored by the Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson AFB, Ohio.

[7] H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn, and L. S. Miller, *J. Am. Chem. Soc.*, **71**, 1499 (1949).

The Reduction of 3-Ethyl-3-methylvaleronitrile by Grignard Reagents in the Presence of Ferric Chloride[1]

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In an attempt to catalyze the reaction of *t*-butylmagnesium chloride with 3-ethyl-3-methylvaleronitrile, it was observed that the nitrile was reduced in reasonable yields to the corresponding aldehyde.

Hauser and Humphlett[2] predicted that the Grignard reagent should be capable of reducing nitriles, but were not able to isolate hexanal from the reaction of *t*-butylmagnesium chloride with hexanenitrile. Mosher and co-workers[3] reinvestigated the reaction and studied the action of ethyl, isopropyl, and *t*-butyl Grignard reagents on trimethylacetonitrile. They found that the amount of reduction product increased while normal addition decreased as branching of the Grignard reagent increased. However, the yields of trimethylacetaldehyde obtained amounted to only 5–17% as the reaction temperature was varied from 35–150°.

When 3-ethyl-3-methylvaleronitrile was treated with *t*-butylmagnesium chloride in the present investigation, no reaction occurred in refluxing ether for up to 139 hours. The introduction of a small amount of ferric chloride, however, caused a fairly rapid change in the infrared absorption spectrum of a hydrolyzed sample of the reaction mixture. After continued heating, there was obtained 31% of 3-ethyl-3-methylvaleraldehyde.

Further study of the reaction of 3-ethyl-3-methylvaleronitrile with *t*-butylmagnesium chloride in the presence of ferric chloride did not lead to improved yields of the aldehyde. When isobutylmagnesium iodide was substituted for *t*-butylmagnesium chloride, 3-ethyl-3-methylvaleraldehyde resulted in 51% yield.

The reaction of trimethylacetonitrile with *t*-butylmagnesium chloride and ferric chloride was examined briefly. Trimethylacetaldehyde was isolated in 20% yield along with traces of carbonyl and hydroxyl containing compounds.

An attempt to reduce hexanenitrile by means of *t*-butylmagnesium chloride and ferric chloride afforded *t*-butyl pentyl ketone plus tarry condensation products.

Experimental[4]

Reaction of 3-Ethyl-3-methylvaleronitrile with *t*-Butylmagnesium Chloride and Ferric Chloride.—A Grignard reagent, prepared from 24.3 g. (1 g.-atom) of magnesium and 102 g. (1.1 moles) of *t*-butyl chloride in 350 ml. of anhydrous ether, was added during 1 hr. to a mixture of 25 g. (0.2 mole) of 3-ethyl-3-methylvaleronitrile, 3 g. of ferric chloride, and 100 ml. of anhydrous ether. The reaction mixture was stirred and refluxed for 200 hr., and hydrolyzed with 1:1 cold hydrochloric acid. The ether layer was separated, washed, dried, and concentrated in the usual manner. The residue was distilled through a 25-cm. helices-packed column to give 8 g. (31%) of 3-ethyl-3-methylvaleraldehyde, b.p. 165–170°, $n^{25}{}_D$ 1.4258, plus an uncharacterized high-boiling residue.

Anal. Calcd. for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 74.54; H, 12.20.

Its 2,4-dinitrophenylhydrazone melted at 88–89° after recrystallization from ethanol.

Anal. Calcd. for $C_{14}H_{20}N_4O_4$: C, 54.53; H, 6.54. Found: C, 54.30; H, 6.34.

Reaction of 3-Ethyl-3-methylvaleronitrile with Isobutylmagnesium Iodide and Ferric Chloride.—A titrated[5] ether solution of 0.45 mole of isobutylmagnesium iodide was added dropwise to a mixture of 25 g. (0.2 mole) of 3-ethyl-3-methylvaleronitrile, 3 g. of ferric chloride, and 100 ml. of anhydrous ether. The resulting mixture was stirred and refluxed for 186 hr., and then hydrolyzed and worked up as in the previous experiment. There was obtained 13.1 g. (51%) of 3-ethyl-3-methylvaleraldehyde, b.p. 165–170°, $n^{25}{}_D$ 1.4257. The high-boiling residue (10.5 g.) was not investigated.

Reaction of Trimethylacetonitrile with *t*-Butylmagnesium Chloride and Ferric Chloride.—A mixture of 1.26 moles of *t*-butylmagnesium chloride and 0.75 g. of ferric chloride in 500 ml. of anhydrous ether was stirred for 0.5 hr., and then a solution of 41.5 g. (0.5 mole) of trimethylacetonitrile in 100 ml. of dry ether was added during 2 hr. The reaction mixture was stirred and refluxed for 28 hr., hydrolyzed with hydrochloric acid, and worked up in the usual fashion. There was obtained 3.6 g. of trimethylacetaldehyde, b.p. 60–70°, $n^{20}{}_D$ 1.3809–1.3827; the corresponding 2,4-dinitrophenylhydrazone melted at 203–207° (lit.[3] m.p. 205–207°). An additional 5 g. of trimethylacetaldehyde, codistilled with the ether, was recovered as the 2,4-dinitrophenylhydrazone. The total yield of trimethylacetaldehyde was 8.6 g. (20%). The aqueous phase from the hydrolysis of the original reaction mixture was extracted continuously for 2 days with 250 ml. of ether. After drying and evaporating the ether, a trace of residue was left. It showed characteristic infrared absorptions for hydroxyl and carbonyl groups.

Reaction of Hexanenitrile with *t*-Butylmagnesium Chloride and Ferric Chloride.—A solution of approximately 2 moles of *t*-butylmagnesium chloride in 700 ml. of anhydrous ether was added dropwise to a mixture of 48.5 g. (0.5 mole) of hexanenitrile, 3 g. of ferric chloride, and 150 ml. of dry ether. The reaction mixture

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[1] This work was supported by grant no. 918-A from the Petroleum Research Fund.

[2] C. R. Hauser and W. J. Humphlett, *J. Org. Chem.*, **15**, 359 (1950).

[3] H. S. Mosher and W. T. Mooney, *J. Am. Chem. Soc.*, **73**, 3948 (1951); E. J. Blanz, Jr., and H. S. Mosher, *J. Org. Chem.*, **23**, 492 (1958).

[4] All melting and boiling points are uncorrected. The carbon-hydrogen analyses were performed by the Weiler and Strauss Laboratories, Oxford, England.

[5] H. Gilman, P. D. Wilkinson, W. P. Fishel, and C. H. Meyers, *J. Am. Chem. Soc.*, **45**, 150 (1923).