[CONTRIBUTION FROM DIAMOND ORDNANCE FUZE LABORATORIES AND NATIONAL BUREAU OF STANDARDS]

The Preparation of Some Aryl Silanes[1]

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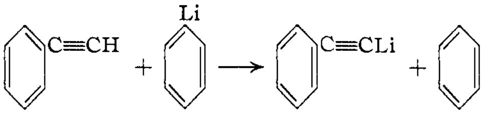
Grignard reagents and organolithium compounds have been used to prepare dibenzyldiphenylsilane, tribenzylphenylsilane, triphenyl-(*p*-tolyl)-silane, diphenyldi-(*p*-tolyl)-silane, phenyltri-(*p*-tolyl)-silane, diphenyldi-(phenylethynyl)-silane, tetra-(phenylethynyl)-silane, and dimethylphenylchlorosilane. Dimethylphenylchlorosilane was reduced with $LiAlH_4$ to dimethylphenylsilane. Triphenyl-(*p*-tolyl)-silane was brominated with N-bromosuccinimide to yield *p*-(α-bromotolyl)-triphenylsilane. The adduct from lithium and anthracene was treated with trimethylchlorosilane to produce a compound with the proposed structure of 9-trimethylsilyl-9,10-dihydroanthracene.

Introduction

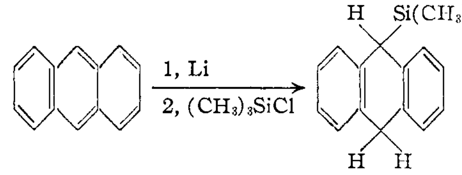
During an investigation of certain chemical and physical properties of aryl silanes, eleven new compounds were prepared. For the most part the standard procedures of using Grignard reagents or organolithium compounds with the appropriate chlorosilanes were used. A slight variation of this method was employed in the preparation of phenylethynylsilanes. The procedure followed here was an adaptation of the method of Gilman and Nobis[4] for the synthesis of triphenyl-(phenylethynyl)-silane where the lithium compound was prepared by a lithium–hydrogen exchange reaction between phenyllithium and phenylacetylene.



Dimethyldichlorosilane was treated with one mole of phenylmagnesium bromide and the product was assumed to be dimethylphenylchlorosilane on the basis of its chlorine content and its reduction with lithium aluminum hydride to dimethylphenylsilane. Reduction of similar chlorosilanes has been reported by Benkeser, Landesman and Foster.[5]

Bromination with N-bromosuccinimide has been applied to silanes by the preparation of *p*-(α-bromotolyl)-triphenylsilane from triphenyl-(*p*-tolyl)-silane.

The addition of alkali metals to aromatic hydrocarbons, including anthracene, was first reported by Schlenk and his co-workers.[6,7] Scott and his co-workers[8] and more recently Brook, Cohen and Wright,[9] reported that this reaction is facilitated by employing solvents, such as dimethyl ether, dimethoxyethane and tetrahydrofuran. The adduct prepared by adding lithium to anthracene was expected to contain atoms of lithium in the 9- and 10-positions of the middle ring. This adduct was expected to react with trimethylchlorosilane to form 9,10-di-(trimethylsilyl)-9,10-dihydroanthracene. The final product actually isolated was 9-trimethylsilyl 9,10-dihydroanthracene



Experimental[10]

Dibenzyldiphenylsilane.—Benzylmagnesium chloride was prepared according to Gilman and Catlin[11] from 253 g. (2 moles) of benzyl chloride and 48.6 g. (2 g. atoms) of magnesium in 1,000 ml. of ether. To this solution 168.6 g. (0.66 mole) of diphenyldichlorosilane was added dropwise at 0°. After the addition was completed, the mixture was refluxed for 24 hours. The ether was removed by distillation and the residue heated in an oil-bath at 130° for 72 hours. After cooling the mixture, ether was added again and the mixture was hydrolyzed with 600 ml. of 6% HCl at 0°. The ether layer was separated, washed with water and aqueous sodium carbonate and dried over $CaCl_2$. The ether was then removed by distillation and the remaining oil cooled to −25°. Crystallization proved to be difficult and was aided by seeding and extended cooling. The yield of crude product was 190 g. (78%). The material was recrystallized from ether. The melting point was 61°.

Anal. Calcd. for $C_{26}H_{24}Si$: C, 85.7; H, 6.6; Si, 7.7. Found: C, 85.6; H, 6.7; Si, 7.8.

This material also can be purified by molecular distillation. Under these conditions the product remains a viscous, colorless liquid, which crystallizes on exposure to air.

Tribenzylphenylsilane.—Benzylmagnesium chloride was prepared from 9.6 g. (0.395 g. atom) of magnesium and 50.2 g. (0.395 mole) of benzyl chloride in 50 ml. of ether. This solution was added dropwise to 21.2 g. (0.108 mole) of phenyltrichlorosilane in 50 ml. of ether. The mixture was refluxed for 18 hours and the ether distilled off. The residue was heated for 5 hours at 130°, cooled, and 200 ml. of ether added. The mixture was then hydrolyzed by dropwise addition of 200 ml. of 6% hydrochloric acid. The ether layer was separated, washed with sodium carbonate and dried. After removing the ether by distillation, the oily residue was distilled in a molecular still under high vacuum. The yield of viscous liquid was 22.3 g. (59%). This liquid was difficult to crystallize but by repeated distillation, cooling and seeding, a product melting at 130° was obtained.

Anal. Calcd. for $C_{27}H_{26}Si$: C, 85.7; H, 6.9. Found: C, 85.3; H, 7.2.

Triphenyl-(*p*-tolyl)-silane.—Under an argon atmosphere *p*-tolyllithium was prepared[12] by dissolving 128 g. (0.75 mole) of *p*-bromotoluene in 600 ml. of ether and adding 9.3

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[2] Diamond Ordnance Fuze Laboratories.

[3] National Bureau of Standards.

[4] H. Gilman and J. F. Nobis, THIS JOURNAL, **72**, 2629 (1950).

[5] R. A. Benkeser, H. Landesman and D. J. Foster, *ibid.*, **74**, 649 (1952).

[6] W. Schlenk, J. Appenrodt, A. Michael and A. Thal, *Ber.*, **47**, 473 (1914).

[7] W. Schlenk and E. Bergmann, *Ann.*, **463**, 91 (1928).

[8] N. D. Scott, J. F. Walker and V. L. Hansley, THIS JOURNAL, **58**, 2442 (1936).

[9] A. G. Brook, H. L. Cohen and G. F. Wright, *J. Org. Chem.*, **18**, 447 (1953).

[10] The C, H, Si and Br analyses were performed by Mr. R. A. Paulson and Mr. L. Machlan.

[11] H. Gilman and W. E. Catlin, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 458.

[12] L. A. Walter, *Org. Syntheses*, **23**, 83 (1943).

g. (1.5 g. atoms) of lithium.[12] The mixture was stirred at room temperature for 3 hours and then refluxed an additional hour. A slurry of 210 g. (0.75 mole) of triphenylchlorosilane and 600 ml. of ether was added while stirring. The mixture was stirred at the reflux temperature for 12 hours and cooled to room temperature. The mixture was then poured into 10% HCl, filtered, and the solid extracted with benzene. The benzene layer was evaporated to dryness, giving 130 g. (55% yield) of crystals melting at 130–139°. Crystallization from a mixture of ethyl acetate and methyl alcohol gave white crystals melting at 141–143°.

Anal. Calcd. for $C_{25}H_{22}Si$: C, 85.7; H, 6.3. Found: C, 85.5; H, 6.4.

Diphenyldi-(*p*-tolyl)-silane.—To a mixture of 800 ml. of ether and 14 g. (2 g. atoms) of lithium was added 171 g. (1 mole) of *p*-bromotoluene dissolved in 200 ml. of ether. With continued stirring, 127 g. (0.5 mole) of diphenyldichlorosilane in 200 ml. of ether was added and the solution refluxed for 3 hours. The excess lithium was removed by adding 30 ml. of 10% HCl. The mixture was filtered and the ether was evaporated from the filtrate, leaving 170 g. (92% yield) of a tan solid melting at 103–108°. Recrystallization from alcohol gave white crystals melting at 119–120°.

Anal. Calcd. for $C_{26}H_{24}Si$: C, 85.7; H, 6.6. Found: C, 85.6; H, 6.7.

Phenyltri-(*p*-tolyl)-silane.—*p*-Tolyllithium was prepared from lithium sand and *p*-bromotoluene. A solution of 0.48 mole of this compound in 500 ml. of ether was added dropwise to 25.4 g. (0.12 mole) of phenyltrichlorosilane in 350 ml. of ether with stirring. The contents of the reaction flask and the dropping funnel were kept under an atmosphere of dry nitrogen during the addition. The mixture was refluxed for 24 hours. Then it was cooled to 0° and 600 ml. of 6% hydrochloric acid was added slowly over a period of 2 hours. The mixture was filtered, yielding 27 g. (68%) of crude product melting at 183.5–184.5°. This material was recrystallized from a mixture of ethyl acetate and methanol (2:1) giving a pure white compound, m.p. 185.5–186.5°.

Anal. Calcd. for $C_{27}H_{26}Si$: C, 85.7; H, 6.9; Si, 7.4. Found: C, 85.6; H, 7.0; Si, 7.7.

Brook and Gilman[13] reported a melting point of 180–182° for this compound.

Diphenyldi-(phenylethynyl)-silane.—Lithium phenylacetylide was made from 0.13 mole of lithium phenyl in 100 ml. of ether and 13.2 g. (0.13 mole) of phenylacetylene. This solution was added under an atmosphere of helium to 17.8 g. (0.070 mole) of diphenyldichlorosilane in 50 ml. of ether. The mixture was refluxed with stirring for 20 hours, cooled and acidified with 200 ml. of 6% hydrochloric acid. The ether layer was removed, washed with sodium carbonate and dried. After removing the solvent the oily residue was seeded and kept at −20° until most of the material had crystallized; yield 7 g. (26%). The crude material was recrystallized repeatedly from benzene and petroleum ether until a sharp melting point of 80° was obtained.

Anal. Calcd. for $C_{28}H_{20}Si$: C, 87.4; H, 5.2. Found: C, 87.1; H, 5.3.

Tetra-(phenylethynyl)-silane.—The above procedure was applied using 10.4 g. (0.075 mole) of silicon tetrachloride in 50 ml. of ether and 0.295 mole of lithium phenylacetylide in 200 ml. of ether. After hydrolysis, ether extraction and drying, the solvent was evaporated and the residue crystallized at −20°; yield 10 g. (37%). Recrystallization from benzene–petroleum ether gave a product with a melting point of 198°.

Anal. Calcd. for $C_{32}H_{20}Si$: C, 88.9; H, 4.7. Found: C, 88.9; H, 4.6.

Dimethylphenylchlorosilane.—Phenylmagnesium bromide in ether was prepared from 26 g. (1.1 g. atoms) of magnesium and 181 g. (1.1 moles) of bromobenzene in 450 ml. of ether.[14] This reagent was transferred to a 500-ml. separatory funnel and a 3-liter, three-necked flask was attached to the funnel. A solution of 750 ml. of ether and 129 g. (1 mole) of dimethyldichlorosilane was added to the flask and cooled to −10° by a bath of Dry Ice and acetone. The Grignard reagent in the funnel was added to the flask with stirring over a period of 1.5 hours. The mixture was then kept at room temperature for 8 hours, followed by filtration to remove that part of the $MgCl_2$ which had precipitated. The filtrate was concentrated by distilling off most of the ether and again filtered to remove additional $MgCl_2$ which had precipitated. The filtrate was then distilled and 99 g. of a colorless liquid boiling over a range from 192 to 204° was collected. This product was fractionally distilled through a bead-packed column and a center-cut, boiling from 192 to 194°, was analyzed for chlorine by titrating the HCl formed on hydrolysis.

Anal. Calcd. for $C_8H_{11}SiCl$: Cl, 20.7. Found: Cl, 20.3.

Dimethylphenylsilane.—A solution of 99 g. (0.58 mole) of dimethylphenylchlorosilane in 250 ml. of ether was added with stirring to a solution of 11.4 g. (0.3 mole) of $LiAlH_4$ in 750 ml. of ether. The mixture was refluxed for 2 hours and then the excess $LiAlH_4$ was hydrolyzed with 5% HCl. The ether layer was washed first with 10% acetic acid and then five times with water, and the washings were discarded. The ether was removed by distillation and the product, 58 g. (78.5% yield), was distilled at 158–164°. Fractionation gave a center-cut of b.p. 158°, $n^{20}D$ 1.4992.

Anal. Calcd. for $C_8H_{12}Si$: C, 70.5; H, 8.9. Found: C, 70.6; H, 9.0.

***p*-(α-Bromotolyl)-triphenylsilane.**—A mixture of 15 g. (0.043 mole) of triphenyl-(*p*-tolyl)-silane and 7.6. g. (0.043 mole) of N-bromosuccinimide in 100 ml. of CCl_4 and 0.05 g. of benzoyl peroxide was refluxed for 4 hours. The solution was filtered while still hot. After cooling and refiltering, 15 g. (81% yield) of white crystals was obtained. Recrystallization from alcohol produced crystals melting at 174–175°.

Anal. Calcd. for $C_{25}H_{21}SiBr$: Br, 18.6. Found: Br, 18.9, 19.0.

9-Trimethylsilyl-9,10-dihydroanthracene.—To a mixture of 13.5 g. (0.075 mole) of anthracene in 500 ml. of tetrahydrofuran was added 2.1 g. (0.3 g. atom) of lithium. The solution was kept under an argon atmosphere and stirred for 6 hours. The color of the solution rapidly became green and changed to a dark brown as the lithium reacted. To the solution 16.3 g. (0.15 mole) of trimethylchlorosilane was added at room temperature and stirring was continued for an additional 10 hours. About 400 ml. of the tetrahydrofuran was distilled out of the solution and, after cooling the solution, 6 g. of LiCl crystals was removed by filtration. The solution was further concentrated by distillation until all the solvent was removed and there remained 14 g. (74% yield) of crude product. This product distilled at 160–175° (5 mm.) and became partly solid after standing at room temperature. Two crystallizations from methyl alcohol produced white crystals melting at 112–113°. The molecular weight of the compound determined by the Rast method was 258; the calculated molecular weight of trimethylsilyldihydroanthracene is 252.

Anal. Calcd. for $C_{17}H_{20}Si$: C, 80.9; H, 8.0. Found: C, 80.8; H, 8.0.

WASHINGTON, D. C.

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[13] A. G. Brook and H. Gilman, THIS JOURNAL, **76**, 2333 (1954).

[14] C. F. H. Allen and S. Converse, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 221.