were taken. The second proved to be practically pure diethylacetamide hydrobromide (1:1) and the fifth proved to be the 1:1 hydrobromide of N-(*t*-butyl)-acetamide (from the infrared spectra). The mother liquid from the fifth crop on evaporation yielded a mixture of the pure amides. The complex is apparently unstable in the crystalline state, relative to the 1:1 amide salts.

The infrared spectra of equimolar mixtures of acetic acid and diethylacetamide, acetic acid and diethylacetamide hydrobromide, and trichloroacetic acid with the diethylacetamide were equal to the sum of the spectra of the components, *i.e.*, no intense absorption bands characteristic of the 2:1 complexes were noted.

Bromination of Cyclohexene.—A solution of cyclohexene (1.64 g., 0.02 mole) in chloroform (35 ml.) was cooled to −60° and a solution of $A_2 \cdot HBr_3$ (III) (9.42 g., 0.02 mole) in chloroform (75 ml.) was slowly added with suitable precautions to keep the stirred mixture anhydrous. The solution added was decolorized practically instantaneously. The solution was washed with dilute sodium bisulfite, then extracted continuously with water for several hours at 20° to remove the amide (A). The chloroform was dried and removed and the product distilled at 46–47° (0.5 mm.) to yield 3.1 g. (0.0128 mole, 64%) of dibromocyclohexane, m.p. −3°, $n^{25}\text{D}$ 1.5495 (lit.[24] m.p. −8 to −4°, $n^{25}\text{D}$ 1.5490 to 1.5507). A comparison of the infrared spectrum with those of authentic samples of *cis*- and *trans*-1,2-dibromocyclohexane[6] showed that the product was exclusively the *trans* isomer. The products from the reaction of cyclohexene with bromine in chloroform at −60°, or with the bromine-dioxane complex[5] at −60°, were also exclusively *trans*-1,2-dibromocyclohexane.[6]

Acknowledgment.—The author wishes to thank Mr. Charles B. Davidson and Mr. William J. Considine for carrying out some of the experiments reported in this paper.

[24] S. Winstein, THIS JOURNAL, **64**, 2792 (1942).

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF TORONTO AND IOWA STATE COLLEGE]

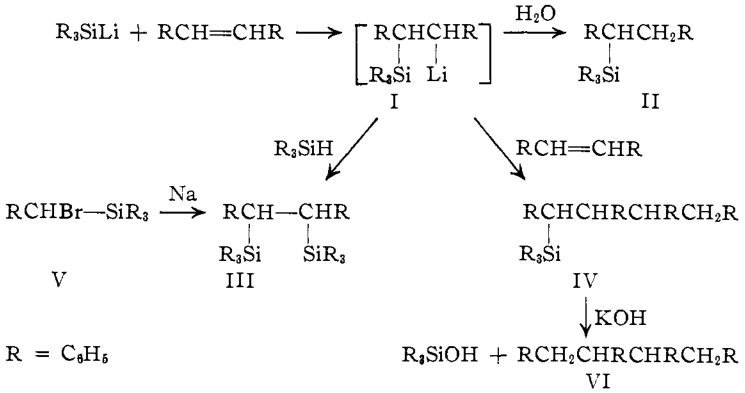
The Reactions of Triphenylsilyllithium with Stilbene

BY A. G. BROOK, K. M. TAI AND HENRY GILMAN

RECEIVED JULY 5, 1955

The addition of triphenylsilyllithium to *trans*-stilbene yields a variety of products, from which 1,2-bis-(triphenylsilyl)-1,2-diphenylethane and 1-triphenylsilyl-1,2,3,4-tetraphenylbutane have been isolated and identified. In connection with the structure proof of these compounds the identity of 1,2,3,4-tetraphenylbutane, m.p. 89–91°, has been confirmed by several varied syntheses.

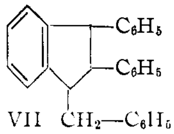
The addition of triphenylsilylpotassium in ether to *trans*-stilbene yields after hydrolysis the expected 1-triphenylsilyl-1,2-diphenylethane (II).[1] It was therefore surprising to find that the addition of the analogous triphenylsilyllithium, dissolved in ethylene glycol dimethyl ether,[2] to *trans*-stilbene did not yield this product, but instead gave a number of more complex products including 1,2-bis-(triphenylsilyl)-1,2-diphenylethane (III) and 1-triphenylsilyl-1,2,3,4-tetraphenylbutane (IV) and much polymeric material which contained silicon.



The constitution of III was established by alkaline cleavage, the only products isolated being bibenzyl and triphenylsilanol. The question of the location of the triphenylsilyl groups was settled when the same compound was produced by Wurtz coupling of α-bromobenzyltriphenylsilane (V), confirming the structure as 1,2-bis-(triphenylsilyl)-1,2-diphenylethane.

Alkaline cleavage of the other product isolated IV yielded triphenylsilanol and a hydrocarbon melting at 89–91°, which analysis suggested was 1,2,3,4-tetraphenylbutane (VI). This same compound (VI), in agreement with Bergmann,[3] was isolated from the reduction of tetraphenylthiophene with sodium and amyl alcohol, together with 1,2-diphenyl-3-benzylhydrindene (VII) (m.p. 180–182°). The same two compounds (VI, VII) were also produced by the reduction of 1,2,3,4-tetraphenylbutadiene-1,3 with sodium and amyl alcohol following published directions,[4] although these authors isolated only VII from this reaction to which they, after others,[5] incorrectly assigned the structure of tetraphenylbutane. Finally hydrogenation of tetraphenylbutadiene at high pressures yielded only VI. Thus it seems certain that the hydrocarbon melting at 89–91° is tetraphenylbutane, and hence the silicon compound from which it was isolated probably has the structure of 1-triphenylsilyl-1,2,3,4-tetraphenylbutane.

The complex nature of the reaction products makes it impossible to speculate with certainty about the mechanism of the reaction. However the formation of the dimer IV and of the polymeric material which con-



VII

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[1] H. Gilman and T. C. Wu, THIS JOURNAL, **75**, 234 (1953).

[2] A. G. Brook and H. Gilman, *ibid.*, **76**, 278 (1954).

[3] E. Bergmann, *J. Chem. Soc.*, 505 (1936).

[4] L. I. Smith and H. H. Hoehn, THIS JOURNAL, **63**, 1184 (1941).

[5] E. S. Wallis and F. H. Adams, *ibid.*, **55**, 3850 (1933).

tained silicon suggests that the enhanced solvent action of ethylene glycol dimethyl ether permits the initial adduct I to behave as an active organometallic reagent which can add to further stilbene molecules as has been observed in other cases.[6]

The formation of III is best accounted for by the reaction of the organometallic I with triphenylsilane which would be formed by reaction of triphenylsilyllithium with ethylene glycol dimethyl ether. Unpublished studies from these laboratories show that this reagent does react rapidly with this ether, 40–50% cleavage occurring in a few hours, and triphenylsilane is among the products isolated.

Treatment of tolan under similar conditions with triphenylsilyllithium yields a large amount of polymeric material containing silicon, and a small amount of 1,2-bis-(triphenylsilyl)-1,2-diphenylethane (III). Formation of this product suggests that 2 moles of triphenylsilyllithium added across the triple bond of tolan.

Experimental[7]

Reaction of Triphenylsilyllithium with Stilbene.—To the triphenylsilyllithium prepared from 25.2 g. (0.05 mole) of hexaphenyldisilane and 0.4 g. (0.057 g. atom) of lithium in 100 ml. of ethylene glycol dimethyl ether was added 18.0 g. (0.1 mole) of stilbene in 150 ml. of benzene, after removal of the excess lithium. Heat was evolved and the system changed from dark brown to a dark red-black. The mixture was stirred at room temperature for 24 hours, hydrolyzed with water, and 10 g. of white solid, m.p. 220–240°, was filtered off. Recrystallization twice from benzene yielded 9.0 g. (26%) of 1,2-bis-(triphenylsilyl)-1,2-diphenylethane, m.p. 250–252°.

Anal. Calcd. for $C_{50}H_{42}Si_2$: C, 85.9; H, 6.03; Si, 8.03. Found: C, 86.1; H, 6.16; Si, 8.02.

The aqueous layer of the filtrate was extracted 3 times with 100-ml. portions of benzene, and the combined nonaqueous layers, after drying, were evaporated under reduced pressure to yield an oily solid. Recrystallization from petroleum ether (b.p. 75–115°) gave 8.7 g. of crude product, m.p. 118–125°. Further recrystallization from the same solvent yielded 7.4 g. (24%) of white 1-triphenylsilyl-1,2,3,-4-tetraphenylbutane, m.p. 155–157°.

Anal. Calcd. for $C_{46}H_{40}Si$: C, 89.0; H, 6.46; Si, 4.53. Found: C, 89.1; H, 6.50; Si, 4.77.

Concentration of the mother liquors failed to yield further solid material. Evaporation to dryness yielded a viscous pale-yellow sirup which was essentially unchanged after chromatography on alumina, using petroleum ether as the eluent. It could be distilled in part from 130–170° at 0.7 mm. pressure, and the viscous oil resulting burnt freely on the spatula to leave a white residue, indicating silicon. This material was not worked up further.

A second run using the same quantities of reagents, but only a 4-hr. reaction period gave essentially the same results. However when 0.026 mole of triphenylsilyllithium was treated with 0.013 mole of stilbene and the reaction was stirred for only 0.5 hour before hydrolysis, the yields of product were somewhat decreased and only 2% of 1,2-bis-(triphenylsilyl)-1,2-diphenylethane, m.p. 250–252°, and 16% of 1-triphenylsilyl-1,2,3,4-tetraphenylbutane, m.p. 154–157°, were obtained, together with much polymeric material. When the reaction was carried out in a minimum of ethylene glycol dimethyl ether, to which 8 volumes of diethyl ether was added, none of the high melting material III was obtained and the yield of IV was about 15%.

Reaction of Triphenylsilyllithium with Tolan.—To 0.011 mole of triphenylsilyllithium in 13 ml. of ethylene glycol dimethyl ether was added 1.0 g. (0.0056 mole) of tolan in 15 ml. of benzene. The reaction mixture, which turned a dark red-black color, was stirred for 0.5 hour, and then was hydrolyzed. It was worked up essentially as described above to yield 0.31 g. (8%) of 1,2-bis-(triphenylsilyl)-1,2-diphenylethane, m.p. 250–252°, identical with the material described above, and much polymeric material which contained silicon.

Cleavage of 1,2-Bis-(triphenylsilyl)-1,2-diphenylethane (III).—A mixture of 2.0 g. (0.0028 mole) of III, 55 ml. of dioxane, 25 ml. of methyl Cellosolve, 2.0 g. of potassium hydroxide and 3 ml. of water were refluxed for 5.5 hr. After 1 hour the system was homogeneous. The solution was evaporated to dryness under reduced pressure, and after neutralization with dilute hydrochloric acid, the white solid which formed was taken up in ether, the ether solution was dried, and was then evaporated to dryness under reduced pressure. The residue was recrystallized from petroleum ether (b.p. 60–70°) to yield a total of 1.25 g. (80%) of triphenylsilanol, m.p. 149–151°, identified by mixed melting point and infrared spectrum. The mother liquors, after evaporation to dryness and recrystallization of the residue from ethanol–water yielded 0.35 g. (67%) of bibenzyl, m.p. 51–52°, identified by mixed melting point with an authentic specimen.

Synthesis of 1,2-Bis-(triphenylsilyl)-1,2-diphenylethane from α-Bromobenzyltriphenylsilane.—A solution of 5.0 g. (0.0117 mole) of α-bromobenzyltriphenylsilane[8] in 35 ml. of benzene was refluxed with 0.5 g. (0.022 g. atom) of sodium. During the first few minutes the sodium surface turned black and a white solid began to precipitate. Since the sodium appeared to remain coated and the reaction appeared to cease, 35 ml. of xylene was added and the benzene was distilled off until the boiling point was 115°. The solution became dark brown in color. After 12-hr. reflux the system was cautiously hydrolyzed with water, neutralized with acid, and then filtered. The 0.75 g. (19%) of white solid melted at 240–243° and after recrystallization from toluene–petroleum ether (b.p. 90–100°) melted at 249–252° and failed to depress the melting point when admixed with 1,2-bis-(triphenylsilyl)-1,2-diphenylethane. From the xylene layer of the filtrate was isolated an additional 0.34 g. (9%) of III, 0.34 g. of a compound, m.p. 235–238°, presumed to be the second possible diastereoisomer of III, and 2.0 g. (40%) of recovered α-bromobenzyltriphenylsilane.

Cleavage of 1-Triphenylsilyl-1,2,3,4-tetraphenylbutane (IV).—A mixture of 2.0 g. (0.0032 mole) of IV, 2.0 g. of potassium hydroxide, 3 ml. of water, 35 ml. of dioxane and 15 ml. of methyl Cellosolve was refluxed for 16 hr. The homogeneous system was evaporated to dryness, neutralized with dilute acid, and extracted with ether which was dried. After removal of the ether the residue was recrystallized from petroleum ether (b.p. 60–70°) to yield 0.35 g. (39%) of triphenylsilanol, m.p. 148–150°, identified by mixed melting point, a total of 0.85 g. (73%) of white needles, m.p. 85–88°, and 0.1 g. (5%) of recovered starting material, identified by mixed melting point. Recrystallization of the needles from ethanol gave 0.8 g. of material, m.p. 89–91°, believed to be 1,2,3,4-tetraphenylbutane.

Anal. Calcd. for $C_{28}H_{26}$: C, 92.8; H, 7.2; mol. wt., 362. Found: C, 92.6; H, 7.3; mol. wt. (Rast), 340.

The infrared spectrum of the hydrocarbon showed no characteristic absorption bands, other than those associated with phenyl groups attached to a hydrocarbon chain.

Preparation of Tetraphenylbutane. A. From Tetraphenylthiophene.—Reduction of 5.0 g. (0.0129 mole) of tetraphenylthiophene[9] with sodium and amyl alcohol following the procedure of Bergmann[3] yielded 1.65 g. (36%) of 1,2-diphenyl-3-benzylhydrindene, m.p. 181–182°, and a total of 1.04 g. (22%) of white needles, m.p. 85–90°, which after recrystallization from methanol melted at 89–91°. A mixed melting point with the tetraphenylbutane described above was not depressed.

B. From Tetraphenylbutadiene.—1,2,3,4-Tetraphenylbutadiene-1,3, m.p. 183–184°, was prepared by the method of Smith and Hoehn[4] (76% yield) and by the method of Orechoff[10] (59%). The two products were identical, as established by mixed melting point. To 0.7 g. (0.00195 mole) of tetraphenylbutadiene in 25 ml. of refluxing amyl alcohol was added 2.0 g. of sodium over 2 hr. The reaction mixture was poured into excess 50% acetic acid. A precipitate of 0.35 g. (50%) of white needles, m.p. 179–182°, was filtered off and recrystallized from ethanol–chloroform (2:1) to yield

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(6) K. Ziegler, H. Grimm and R. Willer, *Ann.*, **542**, 90 (1939); K. Ziegler and H. Kleiner, *ibid.*, **473**, 57 (1929).

(7) All melting points are uncorrected. All reactions were carried out under dry, oxygen-free nitrogen.

(8) C. R. Hauser and C. R. Hance, THIS JOURNAL, **74**, 5091 (1952).

(9) E. Baumann and M. Klett, *Ber.*, **24**, 3307 (1891).

(10) A. Orechoff, *ibid.*, **47**, 89 (1914).

0.23 g. (35%) of 1,2-diphenyl-3-benzylhydrindene, m.p. 180–182°, identical with the high melting material derived from reduction of tetraphenylthiophene.

The filtrate from above was steam distilled. A gummy residue remained which after recrystallization from methanol yielded 0.25 g. (36%) of white needles, m.p. 88–90°, identical with the tetraphenylbutane isolated above.

The same two products were isolated when 3.0 g. (0.0084 mole) of tetraphenylbutadiene in 30 ml. of ether, 10 ml. of ethylene glycol dimethyl ether and 20 ml. of benzene were stirred for 3 hours with 0.5 g. of lithium. The dark-brown solution was poured rapidly into ethanol. A total of 0.93 g. (34%) of 1,2-diphenyl-3-benzylhydrindene, m.p. 180–182°, was isolated and identified by mixed melting point with the above samples. From the filtrate was isolated 0.90 g. (30%) of tetraphenylbutane, m.p. 89–91°, identical with the other samples isolated above.

C. By Hydrogenation of Tetraphenylbutadiene.—A solution of 0.35 g. (0.00098 mole) of tetraphenylbutadiene in 35 ml. of pure dioxane was treated over 22 hr. in the presence of Raney nickel with hydrogen at 1300 p.s.i. Removal of the dioxane led to the recovery of 0.17 g. (48%) of the starting material, m.p. 183–184°, identified by mixed melting point, and 0.21 g. of white needles, m.p. 85–88°, which after recrystallization from methanol yielded 0.17 g. (48%) of tetraphenylbutane, m.p. 89–90°, identical with the material isolated above.

Acknowledgment.—Part of this research was supported by a grant to A. G. B. from the National Research Council of Canada.

TORONTO, CANADA
AMES, IOWA

[CONTRIBUTION FROM THE VENEREAL DISEASE EXPERIMENTAL LABORATORY, U. S. PUBLIC HEALTH SERVICE, SCHOOL OF PUBLIC HEALTH, UNIVERSITY OF NORTH CAROLINA]

Magnesium Salts of Arylphosphonic Acids. The Preparation of *o*-Nitrophenylphosphonic Acid[1]

BY LEON D. FREEDMAN AND G. O. DOAK

RECEIVED JUNE 23, 1955

A number of arylphosphonic acids, previously prepared in this Laboratory, were tested to determine whether they form insoluble magnesium salts. It was found that most of these acids yield no precipitates with magnesia mixture in the cold, but, when heated with magnesia mixture, form voluminous precipitates. Arylphosphonic acids containing bulky *o*-substituents do not form insoluble magnesium salts. This fact permitted the isolation of *o*-nitrophenylphosphonic acid from the mixture of isomers obtained by nitrating phenylphosphonic acid.

It has long been known that most arsonic acids when heated with magnesia mixture yield insoluble magnesium salts.[2] This reaction has often proved useful in the isolation and purification of arsonic acids. In 1941, Bauer[3] noted an analogous reaction with *p*-chloro- and *p*-aminophenylphosphonic acids. Since we had available a considerable number of arylphosphonic acids, the preparation of which has been described in recent communications[4] from this Laboratory, it seemed of interest to determine which of these compounds react with magnesia mixture.

A sample of the phosphonic acid,[5] dissolved in dilute aqueous ammonia, was treated with magnesia mixture. The resulting solution was allowed to stand at room temperature for five minutes and then boiled for one minute. The following results were obtained: (1) Only two compounds, *p*-biphenylylphosphonic and 2-hydroxy-4-nitrophenylphosphonic acids, yielded insoluble magnesium salts at room temperature. (2) Compounds containing *o*-methyl, *o*-amino, *o*-hydroxy or *o*-fluoro substituents gave sparse precipitates on heating; compounds containing other *ortho* substituents did not form insoluble magnesium salts either at room temperature or when heated. (3) With one exception, every compound that did not contain an *ortho* substituent gave a copious precipitate on heating. The exception was *m*-carboxyphenylphosphonic acid which failed to give a precipitate with magnesia mixture.

The Preparation and Properties of *o*-Nitrophenylphosphonic Acid.—The above results indicate that bulky *ortho* substituents (such as C_2H_5, CH_3O, COOH, Cl, Br and I) inhibit the formation of insoluble magnesium salts of arylphosphonic acids. It occurred to us that this effect might be used to bring about the separation of *o*-substituted phosphonic acids from mixtures with *m*- and *p*-isomers. In general, the separation of pure phosphonic acids from a mixture of these acids has proved to be extremely difficult.[6] Kosolapoff[6a] has reported that the nitration of diethyl phenylphosphonate produced a mixture of the corresponding *o*- and *m*-nitrophenylphosphonates, which he was unable to separate by fractional distillation. Furthermore, after these esters had been hydrolysed, he was unable to separate the free acids from the mixture. It was felt that it would be of interest to isolate the pure *o*-isomer, especially since the preparation of *o*-nitrophenylphosphonic acid by other methods never has been accomplished.[4a,d]

Using Kosolapoff's procedure,[6a] we prepared a mixture of isomers of nitrophenylphosphonic acid. This material was dissolved in dilute aqueous am-

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[1] The organophosphorus nomenclature used in this paper is that proposed by the Organic Division's Advisory Committee on the Nomenclature of Organic Phosphorus Compounds; *cf. Chem. Eng. News*, **30**, 4515 (1952).

[2] See, for example, W. M. Dehn, *Am. Chem. J.*, **33**, 101 (1905); P. Ehrlich and A. Bertheim, *Ber.*, **40**, 3292 (1907).

[3] H. Bauer, THIS JOURNAL, **63**, 2137 (1941).

[4] (a) G. O. Doak and L. D. Freedman, *ibid.*, **73**, 5658 (1951); (b) **74**, 753 (1952); (c) **75**, 683 (1953); (d) L. D. Freedman, H. Tauber, G. O. Doak and H. J. Magnuson, *ibid.*, **75**, 1379 (1953); (e) H. H. Jaffé, L. D. Freedman and G. O. Doak, *ibid.*, **75**, 2209 (1953); (f) G. O. Doak and L. D. Freedman, *ibid.*, **75**, 6307 (1953); (g) H. H. Jaffé, L. D. Freedman and G. O. Doak, *ibid.*, **76**, 1548 (1954); (h) L. D. Freedman and G. O. Doak, *ibid.*, **77**, 173 (1955).

[5] Every phosphonic acid described in ref. 4 was used. We also tested *o*-tolylphosphonic acid, which was kindly made available to us by Dr. G. M. Kosolapoff of the Ross Chemical Laboratory, Alabama Polytechnic Institute.

[6] (a) G. M. Kosolapoff, *ibid.*, **71**, 4021 (1949); (b) V. L. Bell, Jr., and G. M. Kosolapoff, *ibid.*, **75**, 4901 (1953).