[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Addition of Silylmetallic Compounds to the Azo and Azomethine Linkage

BY DIETMAR WITTENBERG, M. V. GEORGE, T. C. WU, DAVID H. MILES AND HENRY GILMAN

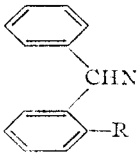
RECEIVED APRIL 2, 1958

Triphenylsilylpotassium (I) and triphenylsilyllithium (II) are shown to add to the azomethine linkage of benzophenone anil to form N,1,1,1-tetraphenyl-N-(diphenylmethyl)-silylamine (VIII), an abnormal addition product. From the reaction of I and II with azobenzene, N,N'-diphenyl-N-(triphenylsilyl)-hydrazine (XI) was isolated; XI was also obtained, together with N,N'-diphenyl-N,N'-bis-(triphenylsilyl)-hydrazine (XII), from the reaction of N,N'-dilithio-N,N'-diphenylhydrazine and chlorotriphenylsilane.

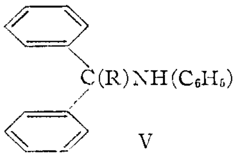
The high reactivity of silylmetallic compounds has been shown by several reactions. Triphenylsilylpotassium (I) and triphenylsilyllithium (II) have been reported to add to the ethylenic linkage of *trans*-stilbene.[1,2] Whereas II adds normally to the carbonyl group of aliphatic ketones to form α-silylcarbinols,[3] the reaction of I and II with benzophenone gives rise to abnormal addition products,[4,5] in which the silicon atom is bonded to the oxygen.

While organolithium compounds generally add in a 1,2-position to pyridine,[6] and only benzylmagnesium chloride[7] and allylmagnesium bromide[8] gave low yields of 1,4-addition products, II has been shown to undergo exclusively 1,4-addition to this heterocycle.[9]

One of the most distinctly different types of reactions shown by Grignard reagents and organolithium compounds is with the azomethine linkage of benzophenone anil (III). It has been shown[10] that phenylmagnesium bromide does not react with III in ether, but under forced conditions a lateral-nuclear 1,4-addition occurs to give N-(*o*-phenyldiphenylmethyl)-aniline (IV, where R is C_6H_5). Phenyllithium, however, reacts with III in ether to give a 1,2-addition product, namely, N-(triphenylmethyl)-aniline (V, where R is C_6H_5).[11]

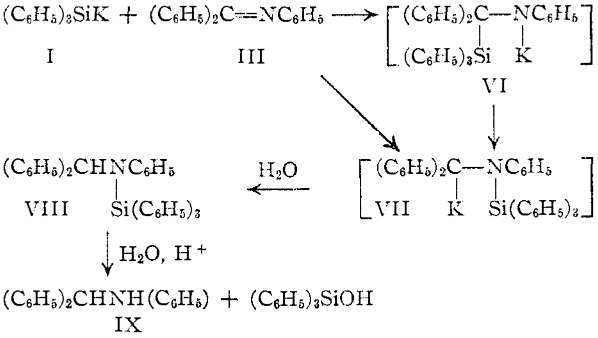


IV



V

It seemed of interest to study the reaction of I and II with benzophenone anil (III), in order to find out which course of addition is preferred in the case of silylmetallic reagents. However, the product m.p. 194-195°, which was obtained from both reactions in high yields, was shown to be *Zerewitinoff* inactive. Its infrared spectrum indicated the absence of any N-H bond. Therefore, its possible structure could be neither IV nor V (where R is $(C_6H_5)_3Si$–). Acid hydrolysis, which yielded N-(diphenylmethyl)-aniline (IX) and triphenylsilanol, confirmed its structure as N-1,1,1-tetraphenyl-N-(diphenylmethyl)-silylamine (VIII).



The compound may have been formed by a direct "abnormal" addition of I or II to the azomethine linkage of III. But, more likely, a "normal" addition to VI, immediately followed by rearrangement to VII may be assumed to have taken place.

In an excellent study, Brook[12] recently showed the rearrangement of phenyl-substituted α-silylcarbinols to the corresponding alkoxysilanes under the influence of catalytic amounts of base. A similar rearrangement[13] of phenyl-substituted α-silylmethylamines to the corresponding silylamines would explain the formation of VIII.

Attempts to prepare VIII by an independent method have so far been unsuccessful. N-(Diphenylmethyl)-aniline did not react with chlorotriphenylsilane in ether at room temperature[14] or in boiling pyridine. Nor could the desired compound be obtained from N-lithio-N-(diphenylmethyl)-aniline and chlorotriphenylsilane in refluxing toluene. Since the reaction of II with alkylamines had been found[15] to give excellent yields of substituted silylamines, II was allowed to react with N-(diphenylmethyl)-aniline. Color Test I[16a] was found to be negative, but the initially

---

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

(2) A. G. Brook, K. M. Tai and H. Gilman, *ibid.*, **77**, 6219 (1955).

(3) H. Gilman and G. D. Lichtenwalter, *ibid.*, **80**, 2680 (1958).

(4) H. Gilman and T. C. Wu, *ibid.*, **75**, 2935 (1953).

(5) H. Gilman and G. D. Lichtenwalter, *ibid.*, **80**, 607 (1958).

(6) K. Ziegler and H. Zeiser, *Ber.*, **63**, 1847 (1930); *Ann.*, **485**, 174 (1931).

(7) W. L. C. Veer and S. Goldschmdit, *Rec. trav. chim.*, **65**, 793 (1946); R. A. Benkeser and D. S. Holton, THIS JOURNAL, **73**, 5861 (1951).

(8) H. Gilman, J. Eisch and T. Soddy, *ibid.*, **79**, 1245 (1957).

(9) D. Wittenberg and H. Gilman, *Chemistry & Industry*, 390 (1958).

(10) H. Gilman, J. E. Kirby and C. R. Kinney, THIS JOURNAL, **51**, 2252 (1929); see also, R. C. Fuson, R. J. Lokken and R. L. Pedrotti, *ibid.*, **78**, 6064 (1956).

(11) H. Gilman and R. H. Kirby, *ibid.*, **55**, 1265 (1933); see also, J. Eisch and H. Gilman, *Chem. Revs.*, **57**, 525 (1957).

(12) A. G. Brook, THIS JOURNAL, **80**, 1886 (1958).

(13) Further experimental results concerning "abnormal" addition reactions of silylmetallic compounds as well as corresponding rearrangement reactions will be presented later.

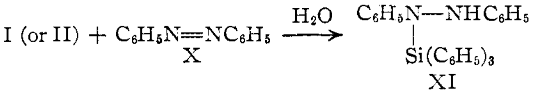
(14) Based on the procedure of R. O. Sauer and R. H. Hasak, *ibid.*, **68**, 241 (1946).

(15) H. Gilman and G. D. Lichtenwalter, unpublished studies.

(16) (a) H. Gilman and F. Schulze, THIS JOURNAL, **47**, 2002 (1925). (b) For the reaction of silicon hydrides with lithium amides see H. Gilman, B. Hofferth, H. W. Melvin, Jr., and G. E. Dunn, *ibid.*, **72**, 5767 (1950).

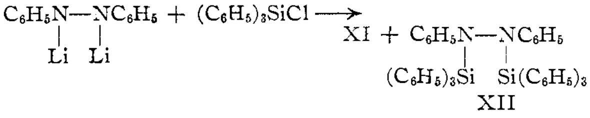
formed products, triphenylsilane and the lithium derivative of IX, did not further couple[16b] with the formation of lithium hydride and VIII.

Whereas phenylmagnesium bromide, phenyllithium and phenylsodium react at room temperatures with azobenzene (X) to yield hydrazobenzene and biphenyl,[17] the low temperature addition of phenyllithium to X gives a 20% yield of triphenylhydrazine.[18] The latter compound was obtained in mediocre yields from the reaction of azobenzene with the highly reactive phenylpotassium and phenylcalcium iodide,[17] respectively. The silylmetallic compounds I and II added smoothly to the azo linkage of X to give N,N′-diphenyl-N-(triphenylsilyl)-hydrazine (XI) in 67 and 74% yields, respectively.



$$\text{I (or II)} + \underset{\text{X}}{C_6H_5N{=}NC_6H_5} \xrightarrow{H_2O} \underset{\text{XI}}{\underset{Si(C_6H_5)_3}{C_6H_5N{-}NHC_6H_5}}$$

Compound XI could not be obtained from the reaction of hydrazobenzene with chlorotriphenylsilane in refluxing pyridine.[19] However, N,N′-dilithio-N,N-diphenylhydrazine, prepared by lithium additon to azobenzene[20] in tetrahydrofuran, coupled smoothly with chlorotriphenylsilane and gave a 67.9% yield of XI, together with a small amount of N,N′-diphenyl-N,N′-bis-(triphenylsilyl)-hydrazine[21] (XII).



$$C_6H_5N(Li){-}N(Li)C_6H_5 + (C_6H_5)_3SiCl \longrightarrow \text{XI} + \underset{\text{XII}}{(C_6H_5)_3Si{-}N(C_6H_5){-}N(C_6H_5){-}Si(C_6H_5)_3}$$

Experimental[22]

Reaction of Triphenylsilylpotassium with Benzophenone Anil.—A solution of 5.1 g. (0.02 mole) of benzophenone anil in 50 ml. of ether was added, within a period of one minute, to a triphenylsilylpotassium suspension[23] in ether (prepared from 0.01 mole of hexaphenyldisilane) containing the excess alloy. There was practically no heat evolved during the addition, although the reaction mixture rapidly became deep brownish-red. After stirring for 24 hr. at room temperature the reaction mixture was hydrolyzed and filtered. There was obtained 8.4 g. of ether-insoluble material, m.p. 193–195°. Concentration of the ether solution yielded 0.4 g. of product, melting at 194.5–195°. The combined product was recrystallized from benzene to give 8.4 g. (81%) of N,1,1,1-tetraphenyl-N-(diphenylmethyl)-silylamine (VIII) in colorless crystals, m.p. 193.5–195°. The infrared spectrum of the compound showed no absorption band in the region 2.0–3.2 μ, indicating the absence of an N–H group in the molecule. The compound also was shown to be Zerewitinoff-inactive.

Anal. Calcd. for $C_{37}H_{31}NSi$: C, 85.84; H, 6.04; N, 2.70; Si, 5.42. Found: C, 85.64; H, 6.26; N, 2.88; Si, 5.40, 5.34.

A similar experiment was made, in which the excess alloy of the triphenylsilylpotassium suspension had been removed by the amalgamation procedure,[23] before it was treated with benzophenone anil. Under these conditions, however, only a 58% yield of the product VIII was obtained.

No pure product has so far been isolated from the reaction of triphenylsilylpotassium or triphenylsilyllithium with benzalaniline at room temperature. Reaction at lower temperatures may be indicated.

Reaction of Triphenylsilyllithium with Benzophenone Anil.—A solution of 0.067 mole of triphenylsilyllithium[24] in tetrahydrofuran was added slowly to 17.3 g. (0.067 mole) of benzophenone anil. Heat was evolved during the addition and Color Test I[15] was found negative thereafter. Hydrolysis with dilute sulfuric acid gave a yellow organic layer and a blue water layer. The organic layer, on addition of ether, deposited 28.2 g. (81.5%) of pale yellow crystals, m.p. 190–193°. Two recrystallizations from benzene gave pure N,1,1,1-tetraphenyl-N-(diphenylmethyl)-silylamine, m.p. 193.5–194.5°. A mixed melting point with the compound obtained in the previous experiment was undepressed.

Hydrolytic Cleavage of N,1,1,1-Tetraphenyl-N-(diphenylmethyl)-silylamine.—Six grams (0.0116 mole) of N,1,1,1-tetraphenyl-N-(diphenylmethyl)-silylamine was refluxed for 10 min. with a mixture of 100 ml. of 95% ethanol and 3 ml. of concd. hydrochloric acid. The reaction mixture was neutralized with aqueous ammonium hydroxide, and the solvents removed on a steam-bath. The residue was chromatographed on alumina. Elution with carbon tetrachloride and benzene gave a colorless oil, which was subsequently dissolved in methanol. On cooling, 1.8 g. (61%) of N-(diphenylmethyl)-aniline was obtained in colorless crystals, m.p. 56–58°. The compound was identified by mixed melting point and infrared spectra. Elution with methanol gave a product, which was recrystallized from petroleum ether (b.p. 100–110°) to give 1.4 g. (45%) of triphenylsilanol, m.p. 148–151°, identified by mixed m.p. and infrared spectra.

Attempted Preparation of N,1,1,1-Tetraphenyl-N-(diphenylmethyl)-silylamine. A. From N-(Diphenylmethyl)-aniline and Triphenylsilyllithium.—A solution of 0.0085 mole of triphenylsilyllithium[24] in tetrahydrofuran was added slowly to 2.2 g. (0.0085 mole) of N-(diphenylmethyl)-aniline.[25] Color Test I[15] was found negative immediately after the addition. A sample was withdrawn, hydrolyzed and some ether added to the organic layer. Since no precipitate was formed (the expected compound VIII is only very slightly soluble in ether and should have precipitated), the reaction mixture was refluxed for 24 hr. The work-up by hydrolysis, addition of some ether, extraction with water, drying of the organic layer with sodium sulfate and the removal of the solvents, left an oil, which was found to be completely soluble in cold petroleum ether (b.p. 60–70°), indicating the absence of the desired product. The solution was chromatographed on alumina. With petroleum ether (b.p. 60–70°) 1.55 g. (70%) of triphenylsilane was obtained, m.p. 42–45°. Elution with carbon tetrachloride gave an oil, which was dissolved in methanol, and gave on cooling 1.45 g. (66%) of N-(diphenylmethyl)-aniline, m.p. 53–56°. A mixed melting point with the starting material was not depressed.

B. From N-(Diphenylmethyl)-aniline and Chlorotriphenylsilane.—A solution of 1.5 g. (0.0058 mole) of N-(diphenylmethyl)-aniline and 1.75 g. (0.006 mole) of chlorotriphenylsilane in 8 ml. of dry pyridine was refluxed for one hour. The mixture was subsequently poured on ice. The oily precipitate was washed with 20 ml. of methanol to leave 0.35 g. of insoluble material, m.p. 209–219°. Recrystallization from cyclohexane raised the m.p. to 225–228°. A

---

(17) H. Gilman and J. C. Bailie, *J. Org. Chem.*, **2**, 84 (1937); see also F. M. Beringer, J. A. Farr, Jr., and S. Sands, THIS JOURNAL, **75**, 3984 (1953).

(18) P. F. Holt and B. P. Hughes, *J. Chem. Soc.*, 764 (1954); 1320 (1955); see also G. Wittig, *Angew. Chem.*, **53**, 241 (1940).

(19) U. Wannagat and W. Liehr, *Angew. Chem.*, **69**, 783 (1957), reported the formation of N-phenyl-N′-(triphenylsilyl)-hydrazine from the corresponding reaction of phenylhydrazine and chlorotriphenylsilane, but these authors were also unsuccessful, even under forced conditions, in replacing a second, phenylsubstituted aminehydrogen atom by a silyl grouping.

(20) J. W. Reesor and G. F. Wright, *J. Org. Chem.*, **22**, 375 (1957); see also W. Schlenk and E. Bergmann, *Ann.*, **463**, 1 (1928).

(21) A detailed study of the reactions of hydrazine–lithium compounds with chlorosilanes will be the subject of a forthcoming publication.

(22) All melting points are uncorrected. Reactions involving organometallic compounds were carried out in an atmosphere of dry, oxygen-free nitrogen. Silicon analyses were carried out according to the procedure of H. Gilman, H. W. Melvin, Jr., and G. E. Dunn, THIS JOURNAL, **72**, 5767 (1950).

(23) Prepared according to the directions of H. Gilman and T. C. Wu, *J. Org. Chem.*, **18**, 753 (1953).

(24) H. Gilman and G. D. Lichtenwalter, THIS JOURNAL, **80**, 608 (1958).

(25) Prepared according to H. Gilman, J. E. Kirby and C. R. Kinney, *ibid.*, **51**, 2252 (1929).

mixed melting point with hexaphenyldisiloxane was not depressed. N-(Diphenylmethyl)-aniline and triphenylsilanol were obtained by chromatography of the methanol-soluble part of the reaction mixture.

C. **From N-Lithio-N-(diphenylmethyl)-aniline and Chlorotriphenylsilane.**—To a stirred solution of 10.0 g. (0.039 mole) of N-(diphenylmethyl)-aniline in 100 ml. of ether was added 0.036 mole of *n*-butyllithium in ether. The reaction was slightly exothermic and both Color Test I and Color Test IIA[26] were negative within 5 min. The color of the solution had changed from yellow to red. After the addition of 8.8 g. (0.03 mole) of chlorotriphenylsilane, the mixture was refluxed for 72 hr. The ether was then replaced by toluene, and the mixture stirred at toluene reflux for 48 hr. The work-up by hydrolysis, addition of ether, extraction with water, drying of the organic layer with Drierite, and removal of the solvents by distillation, gave an oily residue. Washing with 50 ml. of dry ether left 1.0 g. of undissolved hexaphenyldisiloxane, m.p. 225–227° (mixed m.p.). No crystalline compound was isolated from the ether solution.

Reaction of Triphenylsilylpotassium with Azobenzene.—A suspension of triphenylsilylpotassium in ether was prepared from 0.01 mole of hexaphenyldisilane and amalgamated in the usual manner.[23] A solution of 3.6 g. (0.02 mole) of azobenzene in 30 ml. of ether was added to this suspension over a period of one min. There was no appreciable amount of heat evolved, although the color of the mixture changed to reddish-brown. After 18 hr. of stirring at room temperature, the reaction mixture was hydrolyzed and the organic layer filtered to remove a trace of gray precipitate. Removal of the solvent left 8.2 g. of reddish-orange residue, melting at 90° to a gel. The crude product was dissolved in a hot mixture of 25 ml. of benzene and 50 ml. of petroleum ether (b.p. 60–70°). Concentration of this solution to about 50-ml. volume and cooling yielded 5.7 g. of a crystalline compound, m.p. 138–141°. Concentration of the mother liquor gave a second crop, 0.8 g., m.p. 132–138°. Further evaporation of the mother liquor to dryness and recrystallization of the residue from petroleum ether (b.p. 60–70°) yielded 0.7 g. (13%) of triphenylsilanol (mixed m.p.), melting at 150–152°. The combined first two fractions were recrystallized from ethanol to give 5.9 g. (67%) of N,N′-diphenyl-N-(triphenylsilyl)-hydrazine, as colorless, shining prisms, m.p. 140–141°.

Anal. Calcd. for $C_{30}H_{26}N_2Si$: C, 81.41; H, 5.92; N, 6.33; Si, 6.34. Found: C, 81.19; H, 6.11; N, 6.57; Si, 6.40, 6.48.

In a second experiment, the same procedure and quantities of reagents were used, although the excess of alloy present in the triphenylsilylpotassium suspension was not removed by amalgamation. A 36% yield of N,N′-diphenyl-N-(triphenylsilyl)-hydrazine and a 32% yield of hexaphenyldisiloxane were obtained, the latter presumably being formed by the hydrolysis of unchanged triphenylsilylpotassium.

Reaction of Triphenylsilyllithium with Azobenzene.—A solution of 0.050 mole of triphenylsilyllithium[24] in 60 ml. of tetrahydrofuran was added slowly to 9.1 g. (0.050 mole) of azobenzene. Heat was evolved during the addition and Color Test I[15] was found to be negative immediately thereafter. The work-up by hydrolysis, addition of some ether, extraction with water, drying of the organic layer with sodium sulfate and the removal of the solvents left a yellow oil. This was treated with 100 ml. of methanol to give 16.4 g. (74%) of methanol-insoluble N,N′-diphenyl-N-(triphenylsilyl)-hydrazine, m.p. 136–138°. Recrystallization from a mixture of benzene and petroleum ether (b.p. 60–70°) raised the m.p. to 140–141°. A mixed m.p. with the compound obtained in the previous experiment was not depressed.

N,N′-Diphenyl-N-(triphenylsilyl)-hydrazine. A. From Hydrazobenzene and Chlorotriphenylsilane (Attempted).—A solution of 4.3 g. (0.020 mole) of hydrazobenzene and 5.9 g. (0.020 mole) of chlorotriphenylsilane in 15 ml. of dry pyridine was refluxed for one hour. The mixture was subsequently poured on ice. The oily precipitate was washed with 50 ml. of methanol to give 2.2 g. of insoluble residue, m.p. 218–220°. Recrystallization from cyclohexane raised the m.p. to 225–228°. A mixed m.p. with hexaphenyldisiloxane was not depressed.

B. **From N,N′-Dilithio-N,N′-diphenylhydrazine and Chlorotriphenylsilane.**—A mixture of 4.6 g. (0.025 mole) of azobenzene and 0.7 g. (0.1 g. atom) of finely cut lithium wire in 100 ml. of tetrahydrofuran (distilled immediately before use from lithium aluminum hydride) was stirred for 12 hr. at room temperature. At this time the solution, which showed a deep green color in the beginning, had become deep yellow. The solution of N,N′-dilithio-N,N′-diphenylhydrazine was filtered through glass wool into an addition funnel and subsequently added during a period of 30 min. to 14.7 g. (0.050 mole) of chlorotriphenylsilane. The mixture was stirred for one hour at room temperature . After hydrolysis with 100 ml. of water and extraction with 200 ml. of ether, the organic layer was dried and the solvents removed. The oily residue was recrystallized repeatedly from a mixture of benzene and petroleum ether (b.p. 60–70°) to give 7.5 g. (67.9%) of N,N′-diphenyl-N-(triphenylsilyl)-hydrazine, m.p. 138–139°. The compound gave no melting point depression with a compound obtained from the reaction of triphenylsilylpotassium and azobenzene.

From the mother liquor, 4.7 g. (16.8%) of N,N′-diphenyl-N,N′-bis-(triphenylsilyl)-hydrazine, m.p. 265–266°, was obtained.

Anal. Calcd. for $C_{48}H_{40}N_2Si_2$: C, 82.24; H, 5.75; N, 3.99; Si, 8.02. Found: C, 82.05; H, 5.90; N, 4.22; Si, 7.90.

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 A.F.B., Ohio. Infrared analyses were obtained through the courtesy of the Institute for Atomic Research, Iowa State College, and special acknowledgment is made to Dr. V. A. Fassel, Mr. M. Margoshes, Mr. R. Kniseley, Miss E. Conrad and Miss S. Truesdell for the spectra.

AMES, IOWA

---

[26] H. Gilman and J. Swiss, THIS JOURNAL, **62**, 1847 (1940).