20 hr.; maximum pressure attained was 90 p.s.i.g. The vessel was cooled and pressured to 200 p.s.i.g. with purified, dry nitrogen to facilitate removal of the products. The contents of the vessel were then charged to a distillation flask held at Dry Ice temperature. Distillation of the product under purified nitrogen at 10 mm. gave 0.51 mole (71 g.) of butyldichloroborane, b. +4° (10 mm.), and 0.59 mole (94.5 g.) of dibutylchloroborane, b. 54° (10 mm.). Both products are colorless when first distilled and are pyrophoric in air. Both products hydrolyze violently in water.

Butylfluoroisopropoxyborane.—Butyldifluoroborane (0.25 mole, 24.6 g.) and 0.25 mole (34.7 g.) of dichlorobutylborane were charged to a stirred flask at −40°. Isopropyl alcohol (0.50 mole, 35 g.) was added dropwise in 30 minutes. Hydrogen chloride was evolved. Distillation gave two major fractions: butylfluoroisopropoxyborane, b. 60° (100 mm.), 0.17 mole (24.6 g.), 34%, and butyldiisopropoxyborane, b. 105° (100 mm.), 0.13 mole (24.8 g.), 27%. The entire preparation was performed under an atmosphere of purified, dry nitrogen.

Anal. Calcd. for $C_7H_{16}OBF$: C, 57.5; H, 11.0; B, 7.41; F, 13.2. Found: C, 58.9; H, 11.7; B, 7.6; F, 12.5; Cl, 0.0. Calcd. for $C_{10}H_{23}O_2B$: C, 64.5; H, 12.4; B, 5.82. Found: C, 64.2; H, 12.4; B, 6.7; F, 0.9.

Butylcyclohexyloxyfluoroborane.—Butyldichloroborane (0.14 mole, 20 g.), and 0.15 mole (16 g.) of difluorobutylborane were charged to a flask equipped with a stirrer. Cyclohexanol (0.35 mole, 33.5 g.) was added dropwise in 30 minutes at about −80° and the solution was allowed to come to room temperature. During this time hydrogen chloride was removed with a nitrogen sweep. Calcium carbonate, 2 g., was then added and stirring was continued an additional 2 hr. Distillation gave 0.049 mole (9 g.) of butylcyclohexyloxyfluoroborane, b.p. 60–65° (10 mm.), 21%, and 0.12 mole (30.5 g.) of butyldicyclohexyloxyborane, b.p. 156–160° (1 mm.), 50%. Butylcyclohexyloxyfluoroborane tends to disproportionate to butyldicyclohexyloxyborane and butyldifluoroborane during distillation. Traces of acid catalyze this disproportionation. The entire preparation was performed under an atmosphere of purified, dry nitrogen.

Anal. Calcd. for $C_{10}H_{20}OBF$: C, 64.5; H, 10.8; F, 10.2; B, 5.81. Found: C, 65.1; H, 11.4; F, 12.1; B, 4.3; Cl, <0.2. Calcd. for $C_{16}H_{31}O_2B$: C, 73.7; H, 11.7; B, 4.06. Found: C, 74.8; H, 12.1; B, 4.1; Cl, <0.2; F, <0.5.

EMERYVILLE, CALIF.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Preparation of Some Derivatives of Phenoxasilin, a Silicon Analog of Xanthene

BY KATASHI OITA AND HENRY GILMAN

RECEIVED AUGUST 8, 1956

The dimetalation of diphenyl ether with *n*-butyllithium yielded 2,2′-dilithiodiphenyl ether. From the reaction of 2,2′-dilithiodiphenyl ether with diphenyldichlorosilane, dimethyldichlorosilane and silicon tetrachloride there were obtained 10,10-diphenylphenoxasilin, 10,10-dimethylphenoxasilin and 10,10′-spirobiphenoxasilin, respectively. 10,10-Diphenylphenoxasilin and 10,10′-spirobiphenoxasilin were cleaved by lithium in dioxane to yield *o*-hydroxyphenyltriphenylsilane and bis-(*o*-hydroxyphenyl)-diphenylsilane, respectively.

In a Fisher–Hirschfelder–Taylor model of 5,5-diphenyldibenzosilole[1] the silicon–carbon bonds which are part of the 5-membered cyclic system are under a considerable strain. We are reporting the synthesis of a new heterocyclic system in which the strain is alleviated by the presence of an oxygen atom in the central, 6-membered, cyclic system. The compounds prepared were 10,10-diphenylphenoxasilin (I), 10,10-dimethylphenoxasilin (II) and 10,10′-spirobiphenoxasilin (III),[2] silicon analogs of 9,9-diphenylxanthene, 9,9-dimethylxanthene and 9,9′-spirobixanthene, respectively.

In both the dibenzosilole and phenoxasilin syntheses the key reaction was that of an 2,2′-dilithium compound and an appropriate dichlorosilane (silicon tetrachloride for the spiro compound). In the preparation of 5,5-diphenyldibenzosilole the intermediate, 2,2′-dilithiobiphenyl, was prepared by a halogen–metal interconversion reaction of *n*-butyllithium and 2,2′-dibromobiphenyl. For phenoxasilin derivatives the corresponding dilithium intermediate, 2,2′-dilithiodiphenyl ether, was prepared by the dimetalation of a more accessible reagent, diphenyl ether, with *n*-butyllithium. 2,2′-Dilithiodiphenyl ether may prove to be the reagent of choice for preparing other diphenyl ether derivatives with substituents in the 2,2′-positions.

In order to prove that dimetalation of diphenyl ether occurred in the 2,2′-positions, the dilithium compound was carbonated and the product so formed was acidified to yield 2,2′-dicarboxydiphenyl ether, confirmed by a mixed melting point with an authentic specimen.[3] The infrared spectra of the phenoxasilin derivatives synthesized, also supported, the 2,2′-positions of dimetalation. 10,10-Diphenylphenoxasilin had strong absorption bands at 13.2 and 13.5 μ, characteristic of an *ortho* disubstituted benzene and a monosubstituted benzene, respectively, but the only aromatic-substitution band present in 10,10-dimethylphenoxasilin and 10,10′-spirobiphenoxasilin was that of *ortho* disubstituted benzene at 13.2 μ.

The cleavage of compounds I and III with metallic lithium in dioxane[4] to yield *o*-hydroxyphenyltriphenylsilane and bis-(*o*-hydroxyphenyl)-diphenylsilane, respectively, is not a rigorous proof for the assigned structures I and III, but it supports them. The identity of *o*-hydroxyphenyltriphenylsilane from the cleavage reaction was established by a mixed melting point determination with the compound prepared from the reaction of *o*-hydroxyphenyllithium and triphenylchlorosilane[5] and by a comparison of their infrared spectra.

Bis-(*o*-hydroxyphenyl)-diphenylsilane could not be isolated from the reaction of *o*-hydroxyphenyllithium and diphenyldichlorosilane. However, this is not too surprising since forcing conditions were used even in the direct preparation of *o*-hydroxy-

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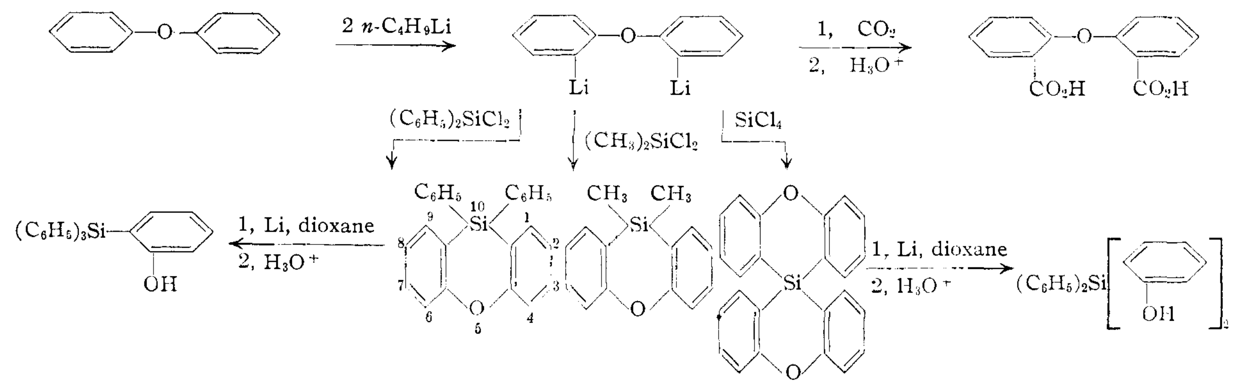
(1) H. Gilman and R. D. Gorsich, THIS JOURNAL, **77**, 6380 (1955).

(2) The names and the numbering system used herein were recommended by the editorial staff of *Chemical Abstracts*.

(3) Kindly provided by Mr. S. H. Eidt of this Laboratory.

(4) H. Gilman and D. L. Esmay, THIS JOURNAL, **75**, 2947 (1953).

(5) H. W. Melvin, unpublished studies.



I II III

phenyltriphenylsilane.[5] The identification of bis-(o-hydroxyphenyl)-diphenylsilane is supported by the similarity of its infrared spectrum to that of o-hydroxyphenyltriphenylsilane, the probable mechanism of the cleavage reaction employed[4] and the structure of compound III.

The elementary analysis and the infrared spectrum for each of the reaction products obtained do not necessarily exclude the possibility of a polymeric structure. Molecular weight determinations proved that compounds I, II and III are monomers.

For obtaining maximum yields of monomeric phenoxasilin derivatives the concentration of both 2,2′-dilithiodiphenyl ether and an appropriate dichlorosilane should be low during the entire reaction period. In order to maintain this favorable condition, dilute solutions were used and the two reagents were added simultaneously. The reaction mixture was vigorously stirred at reflux temperature during the addition period. Since the exact concentration of 2,2′-dilithiodiphenyl ether was less than that of the dichlorosilane by an unknown amount, the dilithium compound was added at a more rapid rate.

Quantitative yields of 2,2′-dilithiodiphenyl ether from the reaction of diphenyl ether and n-butyllithium were not obtained; therefore, a mixture of silanediols and silanols was present after hydrolysis of the reaction mixture. These products were removed chromatographically on activated alumina.

Although both 5,5-diphenyldibenzosilole (m.p. 148–149°)[1] and 10,10-diphenylphenoxasilin (m.p. 178–179°) melted at a lower temperature than their carbon analogs, 9,9-diphenylfluorene (m.p. 222°)[6] and 9,9-diphenylxanthene (m.p. 199°),[7] the melting point of 10,10′-spirobiphenoxasilin (m.p. 284–285°) was almost identical with that for 9,9′-spirobixanthene (m.p. 283–284°).[6]

Experimental[8]

2,2′-Dicarboxydiphenyl Ether.—A reaction mixture consisting of 17.0 g. (0.10 mole) of diphenyl ether and 0.25 mole of n-butyllithium in 194 ml. of an ethereal solution was stirred at the ether-reflux temperature for 72 hr. The mixture was carbonated by pouring it jetwise upon a well-stirred, ether–Dry Ice slurry, although Color Test II[9] was still slightly positive. The carbonated mixture was allowed to stand until the evolution of carbon dioxide ceased; then it was stirred thoroughly with water. The aqueous layer was separated from the ethereal layer, heated on a steam-plate to remove any residual ether, cooled, acidified and filtered to yield 19.56 g. of crude 2,2′-dicarboxydiphenyl ether melting over the range 190–209°. The product was purified by fractional recrystallizations from methyl ethyl ketone and from a mixture of methyl ethyl ketone and benzene to yield 6.03 g. (23.4%) of 2,2′-dicarboxydiphenyl ether melting at 224–227°. A purer sample (m.p. 227–228°) obtained by another recrystallization from a mixture of methyl ethyl ketone and benzene when mixed with an authentic specimen of 2,2′-dicarboxydiphenyl ether (m.p. 228.5–229.5°)[3] melted at 227.5–229°.

10,10-Diphenylphenoxasilin (I).—An ethereal solution of 2,2′-dilithiodiphenyl ether was prepared by stirring at the ether-reflux temperature 42.5 g. (0.25 mole) of diphenyl ether in 250 ml. of ether with 0.525 mole of n-butyllithium in 421 ml. of ether. This was diluted to 700 ml. with more ether; then a 200-ml. portion of it was added to 100 ml. of ether in a 2-liter flask. The contents of the flask were heated to a gentle reflux and stirred, and during a period of 40 minutes the remaining ethereal solution of 2,2′-dilithiodiphenyl ether and 125 ml. of an ethereal solution of 65.2 g. (0.25 mole) of diphenyldichlorosilane in 200 ml. of ether were added simultaneously. The remainder of the diphenyldichlorosilane–ether solution was added in 1 hr. After 10 hr. of stirring at the ether-reflux temperature Color Test I[10] became negative. The reaction mixture was hydrolyzed with 300 ml. of water and the two phases were separated. The ethereal solution was dried over anhydrous calcium sulfate and then chromatographed on 80–200 mesh, activated alumina with ether as an eluant. The removal of the ether from the eluate left a white solid mixed with a viscous oil. The material was filtered through a sintered glass Büchner funnel, washed thoroughly with petroleum ether (b.p. 60–70°) and dried to give 34.2 g. of white product melting over the range 168–176°. One recrystallization from petroleum ether (b.p. 77–115°) yielded 30.1 g. (34.4%) of 10,10-diphenylphenoxasilin melting at 175.6–178.5°. The analytical sample obtained from successive recrystallizations from petroleum ether (b.p. 77–115°) and ethyl acetate melted at 178–179°.

Anal. Calcd. for $C_{24}H_{18}OSi$: Si, 8.00; mol. wt., 350. Found: Si, 7.86, 7.75; mol. wt., 338, 328.

The infrared spectrum determined as a carbon disulfide solution showed strong absorption bands at 13.2 and 13.5 μ, characteristic of an *ortho* disubstituted benzene and a monosubstituted benzene, respectively.

The analytical sample volatilized[11] at 420° with no apparent decomposition. At 455° volatilization was complete, leaving no residue.

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[6] R. G. Clarkson and M. Gomberg, THIS JOURNAL, **52**, 2881 (1930).

[7] A. Schönberg and W. Asker, *J. Chem. Soc.*, 609 (1946).

[8] All melting points reported herein are uncorrected and all reactions were carried out in an atmosphere of dry, oxygen-free nitrogen.

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

[10] H. Gilman and F. Schulze, *ibid.*, **47**, 2002 (1925).

[11] Volatility was determined by inserting a melting point capillary containing a small amount of a sample into a copper block which was heated with a bunsen flame. The volatilization temperature was arbitrarily taken as the temperature at which approximately one-eighth of an inch of condensate appeared in the capillary tube above the block.

Cleavage of 10,10-Diphenylphenoxasilin with Lithium in Dioxane.—A mixture of 7.0 g. (0.02 mole) of 10,10-diphenylphenoxasilin, 0.42 g. (0.06 g. atom) of lithium wire cut into small pieces, and 50 ml. of purified dioxane[12] was vigorously stirred at reflux temperature for 12 hr. The reddish-brown reaction mixture, which gave a negative Color Test I, was poured into ice and hydrochloric acid. The product obtained upon filtration and air-drying weighed 6.93 g. and melted over the range 200–233°. This material was dissolved in benzene and chromatographed on activated alumina. After eluting with benzene the chromatogram was extracted with methanol in a Soxhlet extraction apparatus. The methanol extract was concentrated, cooled and filtered to give 3.74 g. of a product melting over the range 232.5–237°. One recrystallization from a mixture of ethyl acetate and petroleum ether (b.p. 77–115°) yielded 2.65 g. (37.7%) of *o*-hydroxyphenyltriphenylsilane melting at 236–239°. Recrystallization from a mixture of ethanol and water raised the melting point to 237.5–239°. Recrystallization from carbon tetrachloride did not change the melting point. A mixed melting point with *o*-hydroxyphenyltriphenylsilane (m.p. 236–239°) prepared from the reaction of *o*-hydroxyphenyllithium and triphenylchlorosilane[5] was 236–239°. The infrared spectra of these two samples determined in carbon disulfide solutions showed the same absorption bands. Absorption bands at 2.9, 3.3, 13.2 and 13.6 μ, characteristic of an hydroxyl group, an aromatic C–H, an *ortho* disubstituted benzene and a monosubstituted benzene, respectively, were present.

10,10′-Spirobiphenoxasilin (III).—Into a 1-liter flask containing 200 ml. of ether was added 100 ml. of a suspension of 2,2′-dilithiodiphenyl ether prepared from the reaction of 34 g. (0.2 mole) of diphenyl ether and 0.42 mole of *n*-butyllithium in 500 ml. of ether. The remaining 2,2′-dilithiodiphenyl ether suspension and about three-fifths of a solution of 17.0 g. (0.1 mole) of silicon tetrachloride in 100 ml. of ether were added simultaneously over a period of 95 minutes to the reaction mixture. Initially the heat of reaction was sufficient to maintain a gentle reflux. When the refluxing subsided, external heating sufficient to maintain the refluxing was applied. Two hours after completion of the addition of the silicon tetrachloride solution, Color Test I was negative. The reaction mixture was hydrolyzed by pouring upon crushed ice and subsequently filtering. The precipitate obtained was digested with water, filtered, digested with hot benzene, cooled, filtered and air-dried to yield 7.26 g. (20%) of 10,10′-spirobiphenoxasilin melting at 284–286°. One recrystallization from a mixture of benzene and toluene gave 6.61 g. of the pure compound melting at 284–285°. The ethereal layer from the mother liquor was separated and the ether was removed. The resulting residue was digested with benzene, cooled, filtered, digested with water, filtered and air-dried to give 4.04 g. of a product melting over the range 273–281°. One recrystallization from benzene yielded 2.42 g. (6.65%) of pure 10,10′-spirobiphenoxasilin, m.p. 284–285°. The total yield of the pure compound was 24.8%.

Anal. Calcd. for $C_{24}H_{16}O_2Si$: Si, 7.70; mol. wt., 364. Found: Si, 7.85, 7.80; mol. wt., 362, 341.

The infrared spectrum measured in a carbon disulfide solution had a strong absorption band at 13.2 μ, indicative of an *o*-disubstituted benzene, but none in the region of 13.5 μ, thereby showing the absence of a monosubstituted benzene group in the compound.

The analytical sample melted at 284–285° forming a clear, colorless melt. It volatilized completely at 460° without leaving any residue. When the condensate was melted back into the bottom of the capillary and remelted, the melting point was undepressed.

Cleavage of 10,10′-Spirobiphenoxasilin with Lithium in Dioxane.—A reaction mixture consisting of 3.64 g. (0.01 mole) of 10,10′-spirobiphenoxasilin, 0.42 g. (0.06 g. atom) of lithium wire, and 50 ml. of purified dioxane was heated to a gentle reflux and vigorously stirred for 16 hr. The reaction mixture was cooled and hydrolyzed with a mixture of ice and hydrochloric acid, and then about one-half of the solvent was removed by evaporation. The remaining liquid was separated from the sticky residue by careful decantation. This residue was dissolved in benzene, dried over anhydrous sodium sulfate and chromatographed on activated alumina with benzene as an eluant. The zone of the chromatogram which fluoresced strongly under ultraviolet light was extruded and extracted with methanol in a Soxhlet extraction apparatus. The methanol extract was diluted with an equal volume of water, concentrated and filtered to yield 2.11 g. of material melting over the range 205–210°. The crude product was recrystallized twice from carbon tetrachloride and once from petroleum ether (b.p. 77–115°) to give 0.64 g. (17.4%) of bis-(*o*-hydroxyphenyl)-diphenylsilane melting at 206–207°.

Anal. Calcd. for $C_{24}H_{20}O_2Si$: Si, 7.65. Found: Si, 7.63, 7.40.

Its infrared spectrum determined as a carbon disulfide solution was very similar to that for *o*-hydroxyphenyltriphenylsilane. Absorption bands were at 2.9, 13.2 and 13.5 μ, characteristic of a hydroxyl group, an *o*-disubstituted benzene and a monosubstituted benzene, respectively.

The volatilization temperature of this compound, which formed a clear, colorless melt, was 300°. The pale yellow color of the condensate and of the liquid residue at its volatilization temperature indicated slight decomposition. At 400° there was still some pale yellow, glassy residue.

Attempted Direct Preparation of Bis-(*o*-hydroxyphenyl)-diphenylsilane.—To an ethereal suspension (cooled to 0°) of *o*-hydroxyphenyllithium prepared from the reaction of 0.4 mole of *n*-butyllithium and 34.6 g. (0.2 mole) of *o*-bromophenol[13] was added a solution of 19 g. (0.075 mole) of diphenyldichlorosilane in 25 ml. of ether. After 2 hr. of stirring at the ether-reflux temperature the ether was distilled during 8 hr. until a temperature of approximately 60° was reached. The mixture was stirred at this temperature for 24 hr., then hydrolyzed and the two layers were separated. Acidification of the aqueous layer resulted in the formation of a small amount of dark oil possessing a phenolic odor. The ethereal phase was concentrated and acidified to give a product which was filtered and washed with petroleum ether (b.p. 60–70°) to yield 7.24 g. of a product melting over the range 150–195°. This material when purified by recrystallizing once from carbon tetrachloride and twice from a mixture of benzene and petroleum ether (b.p. 77–115°) weighed 3.12 g. and melted at 158–159°. A mixed melting point with an authentic specimen of diphenylsilanediol (m.p. 158–161°)[14] melted over the range 151–156° with shrinkage from 120°.

The percentage of silicon found in this, as yet unidentified, compound was 11.0%. The calculated values for bis-(*o*-hydroxyphenyl)-diphenylsilane, *o*-hydroxyphenyldiphenylsilanol and symmetrical bis-(*o*-hydroxyphenyl)-tetraphenyldisiloxane are 7.65, 9.60 and 9.75%, respectively.

10,10-Dimethylphenoxasilin (II).—Into a 1-liter flask was added about one-third of an ethereal suspension (313 ml.) containing approximately 0.143 mole of 2,2′-dilithiodiphenyl ether. The mixture was heated to a gentle reflux and stirred while the remaining suspension was added over a period of 35 minutes. The simultaneous addition of a solution of 18.5 g. (0.043 mole) of dimethyldichlorosilane in 100 ml. of ether required 65 minutes. The reaction mixture was stirred at reflux temperature for 4 hr. and then allowed to stand overnight. Then it was hydrolyzed with water, treated with Norit-A, filtered, and the two phases were separated. The ethereal layer was dried over anhydrous sodium sulfate and chromatographed on activated alumina with ether as an eluant. The oil remaining after removing the solvent from the eluate was distilled *in vacuo*. The fraction weighing 18.99 g., b.p. 90–185° (0.1–0.2 mm.), was redistilled under atmospheric pressure. The combined fractions boiling over the range 292–297° weighed 15.85 g. When an attempt was made to determine the freezing point of the best fraction by cooling it in an acetone–Dry Ice-bath, the liquid solidified. This solid was used to induce crystallization in the other fractions which upon filtration weighed 12.4 g. and melted over the range 69–77°. Successive recrystallizations from ethanol and methanol yielded 8.10 g. (25.1%) of pure 10,10-dimethylphenoxasilin melting at 78.5–79°.

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[12] The dioxane was purified by the procedure of K. Hess and H. Frahm, *Ber.*, **71**, 2627 (1938), as reported in L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., New York, N. Y., 1941, p. 369.

[13] H. Gilman and C. E. Arntzen, This Journal, **69**, 1537 (1947).

[14] Kindly provided by Mr. R. D. Gorsich of this Laboratory.

Anal.[15] Calcd. for $C_{14}H_{14}OSi$: C, 74.5; H, 6.24; mol. wt., 226. Found: C, 74.20, 74.14; H, 6.24, 6.28; mol. wt., 226, 218.

The infrared spectrum determined in a carbon disulfide solution had absorption bands at 3.3, 3.4 and 13.2 μ, indicating the presence of an aromatic C–H, an aliphatic C–H and an *o*-disubstituted benzene, respectively. An absorption band at 13.5 μ, characteristic of a monosubstituted benzene, was absent.

Acknowledgment.—The authors wish to express their appreciation to the Materials Laboratory, Wright Air Development Center, Wright–Patterson Air Force Base, Ohio, for financial assistance. They also are grateful to the Institute for Atomic Research, Iowa State College, and Dr. V. A. Fassel and Mr. R. McCord for the actual determination of the spectra.

AMES, IOWA

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[15] The silicon analyses by ignition with sulfuric acid according to the procedure of H. Gilman, B. Hofferth, H. W. Melvin and G. E. Dunn, THIS JOURNAL, **72**, 5767 (1950), gave low erratic results, probably because of the dimethylsilyl group present.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Reactions of Triphenylgermyllithium, Triphenylgermylpotassium and Triphenylgermane with Some Olefins

BY HENRY GILMAN AND CLARE W. GEROW

RECEIVED AUGUST 2, 1956

It has been found that triphenylgermyllithium and triphenylgermylpotassium add to the olefinic linkage in 1,1-diphenylethylene to form 1,1-diphenyl-2-triphenylgermylethane, but neither adds to *trans*-stilbene. In addition, triphenylgermyllithium reacts with octadecene-1 to form triphenyl-*n*-octadecylgermane. With benzalacetophenone, triphenylgermyllithium forms 2-phenyl-2-triphenylgermylethyl phenyl ketone. Triphenylgermane, with peroxide catalyst, reacts with octadecene-1 to give triphenyl-*n*-octadecylgermane and with triphenylallylgermane to give 1,3-bis-(triphenylgermyl)-propane. The authentic preparations of triphenyl-*n*-octadecylgermane and 1,1-diphenyl-2-triphenylgermylethane are given as well as the syntheses of previously unreported triphenylallylgermane and triphenylchloromethylgermane.

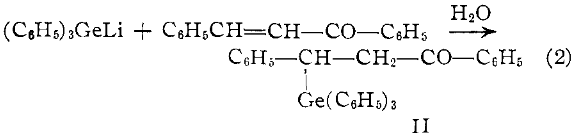
In connection with studies in this Laboratory to determine the relative reactivity of triphenylgermylmetallic compounds, to find new methods of introducing germanium into organic molecules and to compare the thermal stabilities of analogous organosilicon and organogermanium compounds, the reactions with olefins were investigated.

We have found that both triphenylgermylpotassium and triphenylgermyllithium add to the olefinic bond in 1,1-diphenylethylene to give 1,1-diphenyl-2-triphenylgermylethane (I).

$$(C_6H_5)_3GeM + (C_6H_5)_2C{=}CH_2 \xrightarrow{H_2O} \underset{\textstyle \text{I}}{(C_6H_5)_2CH{-}CH_2Ge(C_6H_5)_3} \quad (1)$$

However, unlike triphenylsilylpotassium[1] and triphenylsilyllithium,[2] neither triphenylgermylpotassium nor triphenylgermyllithium added to the olefinic linkage of *trans*-stilbene. This failure to react with *trans*-stilbene may be due to steric factors because of the larger size of the germanium atom. It is not believed that either triphenylsilylpotassium or triphenylsilyllithium is more reactive than the analogous germanium compounds, because triphenylgermyllithium has been found to add to octadecene-1, while triphenylsilylpotassium fails to react under the same conditions.[3] The reaction of triphenylgermyllithium with olefins is not universally applicable, however, for this reagent was apparently unreactive toward both cyclohexene and octene-1.

With benzalacetophenone, under comparable conditions, triphenylgermyllithium reacted to give a compound believed to be 2-phenyl-2-triphenylgermylethyl phenyl ketone (II).



$$(C_6H_5)_3GeLi + C_6H_5CH{=}CH{-}CO{-}C_6H_5 \xrightarrow{H_2O} C_6H_5{-}\underset{\textstyle Ge(C_6H_5)_3}{\underset{|}{CH}}{-}CH_2{-}CO{-}C_6H_5 \quad (2)$$

II

Elemental analysis supported this conclusion and infrared analysis indicated the presence of the carbonyl group and the absence of an hydroxyl group. It is not known whether the product was obtained by means of a 1,4- or a 3,4-addition, but it seems altogether probable that 1,4-addition took place.[4] If such is the case, then it is possible to determine to some degree the relative reactivity of triphenylgermyllithium as compared to other organometallic reagents. It has been found that the extent of 1,4-addition to benzalacetophenone might be used as a measure of the relative reactivities of various organometallic reagents.[5] It was found that the more reactive phenylmetallic reagents such as phenylcalcium iodide and phenylpotassium underwent exclusively 1,2-addition to benzalacetophenone. Phenylsodium gave mostly the 1,2-addition product with a small amount of the 1,4-addition product, and phenyllithium gave a larger amount of the 1,4-addition product than did phenylsodium along with 69% of the 1,2-addition product. Phenylmanganese iodide, triphenylaluminum, diphenylzinc and diphenylberyllium gave exclusively the 1,4-addition product. Phenylmagnesium bromide is reported to give the 1,4-addition product exclusively.[6] In the light of this reaction alone, triphenylgermyllithium would be classified as being less reactive than phenyllithium

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[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] T. C. Wu, unpublished studies.

[4] For a discussion of 1,4- and 3,4-additions to conjugated unsaturated systems see H. Gilman, "Organic Chemistry," Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 511 and 672.

[5] H. Gilman and R. H. Kirby, THIS JOURNAL, **63**, 2046 (1941).