during the first 20 minutes, then proceeded at a progressively more rapid rate. External heating was discontinued when the temperature reached 190°, and the reaction mixture was cooled and worked up according to the procedure described above. Devolatilization was accomplished to 180° under reduced pressure, then to 175° *in vacuo*. In addition to the volatiles (7.9 g., 27.2%), there was obtained polydiethylsilethylene, $n^{25}D$ 1.4977, viscosity (centistokes at 25°) 378.6, yield 16.6 g. (57.3%).

Anal. Calcd. for $(C_6H_{14}Si)_n$: C, 63.07; H, 12.35; Si, 24.58. Found: C, 63.15; H, 12.8; Si, 25.04; vinyl, 3.59. The average molecular weight, calculated from the residual vinyl content, was 753, and the degree of polymerization, 6.59.

The presence of the polysilethylene structure was confirmed by infrared analysis. Bands due to $Si-CH_2CH_2-Si$ were found at 8.82 and 9.45 μ. There were C_2H_5-Si bands at 6.86, 7.08 and 8.12 μ, and weak Si–H absorption appeared at 4.78 μ.

Fractionation of the volatile components afforded 1,1,4,4-tetraethyl-1,4-disilacyclohexane, b.p. 117–118° (6 mm.), $n^{25}D$ 1.4734, d^{25}_4 0.8610, yield 5.7 g. (19.7%).

Anal. Calcd. for $C_{12}H_{28}Si_2$: C, 63.07; H, 12.35; Si, 24.58; mol. wt., 228; *MR*D, 74.86. Found: C, 62.7; H, 12.55; Si, 24.63; mol. wt., 210; *MR*D, 74.52.

Examination of the infrared spectrum revealed the presence of $Si-CH_2CH_2-Si$ absorption at 8.82 and 9.45 μ; bands due to C_2H_5-Si were found at 8.11, 9.90 and 10.40 μ. There appeared to be no $CH_2{=}CH-Si$ or Si–H absorption.

Polydiphenylsilethylene and 1,1,4,4-Tetraphenyl-1,4-disilacyclohexane.—A mixture of 37.7 g. (0.179 mole) of diphenylvinylsilane and 0.18 g. of the Wagner catalyst was stirred accompanied by external heating for 4 hours. The monomer reacted slowly over the period of the first 3 hours, then more rapidly in the ensuing 30 minutes during which time the reaction temperature rose from 146.5 to 216°. The temperature then dropped to 183° during the final 30 minutes. The reaction mixture was worked up in the manner outlined previously. Devolatilization *in vacuo* to a pot temperature of 245° gave 1.8 g. (4.8%) of liquid volatiles. The residue solidified to a glass on cooling to room temperature. The material was taken up in toluene, filtered twice, then freed of toluene *in vacuo* at *ca.* 150° for 3 hours. There was obtained polydiphenylsilethylene, yield 23.2 g. (61.6%).

Anal. Calcd. for $(C_{14}H_{14}Si)_n$: C, 79.93; H, 6.71; Si, 13.35. Found: C, 79.55; H, 6.85; Si, 13.28.

The infrared spectrum showed the following absorption bands: $Si-CH_2CH_2-Si$, 8.85 and 9.50 μ; C_6H_5-Si, 7.01 and 9.00 μ; Si–H (weak), 4.73 μ.

Remaining on the filter from the filtration operations was a crude, crystalline solid amounting to 2.1 g. This material was twice resublimed *in vacuo* to afford 1,1,4,4-tetraphenyl-1,4-disilacyclohexane, m.p. 131–134.5° (uncor.), yield 0.55 g. (1.46%).

Anal. Calcd. for $C_{28}H_{28}Si_2$: Si, 13.35; mol. wt., 421. Found: Si, 13.05; mol. wt., 343.

Infrared analysis confirmed the proposed structure. The bands due to $Si-CH_2CH_2-Si$ were not apparent, but there was no evidence for $CH_2{=}CH-Si$ or Si–H, nor for $Si-CH(CH_3)-Si$. Bands at 7.00 and 8.98 μ indicated the presence of C_6H_5-Si.

Infrared data on the liquid volatiles showed these materials to be lower molecular weight, linear molecules.

Polymethylphenylsilethylene and 1,4-Dimethyl-1,4-diphenyl-1,4-disilacyclohexane.—A mixture of 30.5 g. (0.206 mole) of methylphenylvinylsilane and 0.21 g. of the Wagner catalyst was heated with stirring. After reaching 95°, the temperature rose to 255° during the following 3 minutes. The total heating period was 1 hour, by the end of which time the temperature had dropped to 164.5°. The reaction mixture was worked up in the usual way (devolatilization to 205° *in vacuo*) to yield 6.9 g. (22.6%) of volatiles. The polymeric residue was taken up in toluene and filtered twice to effect clarification. Toluene was then removed by heating *in vacuo* at *ca.* 150° for 3 hours to afford polymethylphenylsilethylene, $n^{25}D$ 1.5870, yield 18.8 g. (61.6%).

Anal. Calcd. for $(C_9H_{12}Si)_n$: C, 72.90; H, 8.16; Si, 18.94. Found: C, 71.8; H, 8.35; Si, 19.14.

Infrared analysis indicated the presence of the following bands: $Si-CH_2CH_2-Si$, 8.83 and 9.48 μ; C_6H_5-Si, 7.02 and 9.00 μ; CH_3-Si, 8.02 μ; Si–H (very weak), 4.75 μ.

The volatile portion of the polymerization mixture was fractionally distilled *in vacuo*. There was obtained 1,4-dimethyl-1,4-diphenyl-1,4-disilacyclohexane (probably a mixture of the two possible isomers), b.p. 135–137° (0.26–0.275 mm.), $n^{25}D$ 1.5692, d^{25}_4 1.0117, yield 6.0 g. (19.7%).

Anal. Calcd. for $C_{18}H_{24}Si_2$: C, 72.90; H, 8.16; Si, 18.94; mol. wt., 297; *MR*D, 96.08. Found: C, 71.3; H, 7.95; Si, 19.15; mol. wt., 262; *MR*D, 96.06.

Absorption bands characteristic of CH_3-Si and C_6H_5-Si were found to be present at 8.02 μ, and at 7.01, 9.75 and 10.02 μ, respectively, in the infrared spectrum.

Acknowledgment.—The author wishes to thank Dr. Lee Smith for the determination and interpretation of the infrared absorption spectra and Mr. Arnold Kolb for carrying out the other analytical phases of this work. He is also grateful to Drs. M. J. Hunter, J. F. Hyde and O. K. Johannson for the many valuable discussions.

MIDLAND, MICHIGAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Some Tetraarylsilanes Containing Functional Groups

BY HENRY GILMAN, CECIL G. BRANNEN AND ROBERT K. INGHAM

RECEIVED SEPTEMBER 26, 1955

A new method of introducing functional groups into tetraarylsilanes is presented. Triphenyl-(*p*-tolyl)-silane was brominated with N-bromosuccinimide to yield *p*-(triphenylsilyl)-benzyl bromide and *p*-(triphenylsilyl)-benzal bromide. The monobromination product was hydrolyzed to *p*-(triphenylsilyl)-benzyl alcohol and the alcohol was oxidized to *p*-(triphenylsilyl)-benzoic acid. The dibromination product was hydrolyzed to *p*-(triphenylsilyl)-benzaldehyde; treatment of this aldehyde with N-bromosuccinimide followed by hydrolysis gave *p*-(triphenylsilyl)-benzoic acid, a product also obtained by the chromic acid oxidation of triphenyl-(*p*-tolyl)-silane. Attempts to similarly brominate and oxidize tri-1-naphthyl-(*p*-tolyl)-silane were unsuccessful.

The introduction of functional groups to an aromatic ring of tetraphenylsilane has been achieved by the nitration of this compound.[1] This reaction, however, results in a mixture of isomers that are not easily separated. We are reporting a different and perhaps better method for the incorporation of such groupings, involving the lateral bromination of triphenyl-(*p*-tolyl)-silane using N-bromosuccinimide[2];

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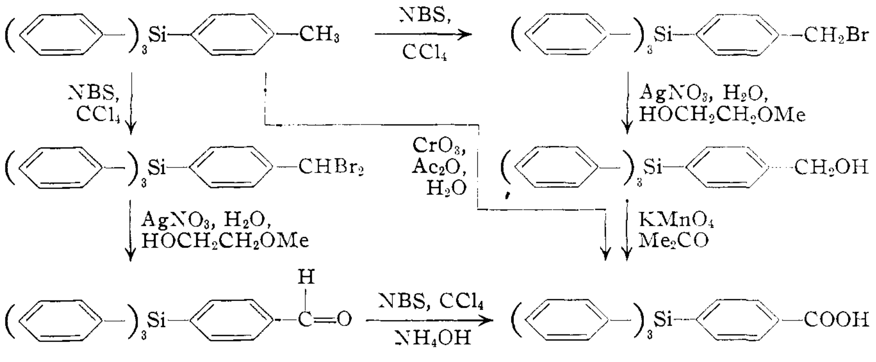
(1) A. Polis, *Ber.*, **19**, 1016 (1886); F. S. Kipping and L. L. Lloyd, *J. Chem. Soc.*, **79**, 449 (1901); D. Vorlander, *Ber.*, **55**, 1900 (1922); F. S. Kipping and J. C. Blackburn, *J. Chem. Soc.*, 2200 (1932); F. S. Kipping and N. W. Cusa, *ibid.*, 1089 (1935).

(2) *p*-(Triphenylsilyl)-benzyl bromide was reported by H. Gilman, R. K. Ingham and R. D. Gorsich, WADC Technical Report 53-426, Part I, Wright Air Development Center, 1953, p. 91. M. Maienthal, M. Hellmann, C. P. Haber, L. A. Hymo, S. Carpenter and A. J. Carr, THIS JOURNAL, **76**, 6392 (1954), recently have reported the preparation of this compound by a similar procedure.

depending upon the conditions, either mono- or dibromination may take place. The triphenyl-(*p*-tolyl)-silane can be prepared easily in good yields.[3]

The *p*-(triphenylsilyl)-benzyl bromide was readily converted to the corresponding alcohol by treatment with aqueous silver nitrate. *p*-(Triphenylsilyl)-benzaldehyde was obtained by dibromination of the methyl grouping of triphenyl-(*p*-tolyl)-silane followed by a similar treatment with aqueous silver nitrate.

p-(Triphenylsilyl)-benzoic acid was obtained by the oxidation of triphenyl-(*p*-tolyl)-silane, by the oxidation of *p*-(triphenylsilyl)-benzyl alcohol, and by the treatment of *p*-(triphenylsilyl)-benzaldehyde with N-bromosuccinimide followed by hydrolysis. An attempt to oxidize *p*-(triphenylsilyl)-benzaldehyde with hydrogen peroxide was not successful. It is interesting to note that while *p*-(triphenylsilyl)-benzoic acid melts at 213–214°, *p*-(triphenylstannyl)-benzoic acid melts at 166–168°[4] and *p*-(triphenylplumbyl)-benzoic acid melts at 256–258°.[5] Also, *p*-(triphenylsilyl)-benzyl alcohol has a melting point of 54–55°, while both *p*-(triphenylstannyl)-benzyl alcohol[4] and *p*-(triphenylplumbyl)-benzyl alcohol[5] melt at 98–100°.



Attempts to laterally brominate tri-1-naphthyl-(*p*-tolyl)-silane were unsuccessful. The failure of this method may have been due to the inability to purify the crude product; some bromination of the naphthalene nuclei may have occurred, or the free bromine that is formed in N-bromosuccinimide reactions may have cleaved one of the groups from the silane.

The decreased reactivity of the methyl grouping of tri-1-naphthyl-(*p*-tolyl)-silane is evidenced by its failure to undergo oxidation under the conditions employed for the oxidation of triphenyl-(*p*-tolyl)-silane.

Experimental[6]

p-(Triphenylsilyl)-benzyl Bromide.—Five grams (0.0143 mole) of triphenyl-(*p*-tolyl)-silane[3] was dissolved in about 300 ml. of commercial carbon tetrachloride, 2.54 g. (0.0143 mole) of finely powdered N-bromosuccinimide was added, and the mixture was refluxed for 24 hours. The N-bromosuccinimide had not disappeared from the bottom of the flask. A starch-iodide paper test for active bromine was positive. The use of ultraviolet irradiation for 15 minutes on the refluxing mixture induced complete reaction as evidenced by the disappearance of the N-bromosuccinimide and a negative active bromine test. After cooling and filtering, there was collected 1.35 g. (0.0136 mole, 95% recovery) of succinimide (mixed m.p.) melting at 122–123°. The white solid obtained after removing the solvent was dissolved in about 100 ml. of acetone, decolorized with charcoal, filtered, and set aside to crystallize slowly. In three crops, 4.5 g. (73%) of pure *p*-(triphenylsilyl)-benzyl bromide, m.p. 175–176°, was obtained.

Anal.[7] Calcd. for $C_{25}H_{21}BrSi$: Br, 18.62; Si, 6.53. Found: Br, 18.6; Si, 6.62, 6.60.

The preparation of this compound (m.p. 174–175°) by a similar procedure has been reported recently.[2]

Several attempts were made to treat highly purified samples of this compound with magnesium. However, the reaction failed to start and the silane was recovered unchanged even though the following precautions and devices were used: the apparatus was thoroughly dried; the ether used was especially dried with calcium hydride and filtered directly into a nitrogen-swept flask; magnesium-copper alloy and powdered magnesium as well as metal turnings activated by heating with iodine were used; and the usual crystal of iodine and drop of methyl iodide were added. This failure is surprising since benzyl halide types form the Grignard reagent with especial ease.

p-(Triphenylsilyl)-benzyl Alcohol.—Three grams (0.007 mole) of *p*-(triphenylsilyl)-benzyl bromide was dissolved in about 300 ml. of methyl Cellosolve (ethylene glycol monomethyl ether), 3.0 g. (0.017 mole) of silver nitrate dissolved in 40 ml. of water was added, and the mixture was refluxed for 30 minutes. The greenish precipitate was removed by filtration of the hot mixture, most of the solvent was distilled off at reduced pressure, and the remaining material was subjected to steam distillation. The residue was extracted with ether and the ethereal solution was dried over sodium sulfate. After removal of the ether, crystallization of the yellow viscous oil was induced by the addition of a few ml. of methanol and external cooling. There was thus obtained 1.95 g. (76%) of white crystals, m.p. 53–54°. An analytical sample melting at 54–55° was obtained by slow crystallization from methanol.

Anal. Calcd. for $C_{25}H_{22}OSi$: Si, 7.65; active hydrogen, 1.0. Found: Si, 7.53; active hydrogen (Zerewitinoff), 0.95.

Poor yields were obtained by hydrolyzing *p*-(triphenylsilyl)-benzyl bromide with potassium hydroxide in acetone or ethanol. A solution of 2.0 g. (0.0046 mole) of the silane in 100 ml. of acetone was mixed with a solution of 0.5 g. of potassium hydroxide in 2 ml. of water, and the resulting solution was refluxed for 30 minutes. After cooling this solution, about 300 ml. of ether was added and the acetone and inorganic salts were removed by several extractions with water. A gummy solid was obtained after removing the solvent from the organic layer. After several recrystallizations of the resulting oils from methanol, 0.2 g. (12%) of *p*-(triphenylsilyl)-benzyl alcohol, m.p. 52–53°, was isolated. A 10% yield of this alcohol was obtained by the same procedure when ethanol was used as a solvent rather than acetone.

p-(Triphenylsilyl)-benzal Bromide.—Five grams (0.0143 mole) of triphenyl-(*p*-tolyl)-silane was dissolved in 250 ml. of commercial carbon tetrachloride (the silicon compound was easily soluble at room temperature) and 5.2 g. (0.029 mole) of finely divided N-bromosuccinimide was added. After refluxing the mixture for 40 minutes while irradiating with a mercury-vapor lamp, a homogeneous solution was formed and a test for free bromine (starch–iodide paper) was negative. After cooling, 2.8 g. (96%) of succinimide was removed from the solution by filtration. The solvent

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[3] H. Gilman, C. G. Brannen and R. K. Ingham, This Journal, **77**, 3916 (1955).

[4] H. Gilman and C. E. Arntzen, *J. Org. Chem.*, **15**, 994 (1950).

[5] H. Gilman and D. S. Melstrom, This Journal, **72**, 2953 (1950).

[6] All melting points are uncorrected.

[7] The silicon analyses were carried out by the procedure of H. Gilman, B. Hofferth, H. W. Melvin and G. E. Dunn, This Journal, **72**, 5767 (1950).

was removed from the filtrate to give a slightly yellow solid. This solid was dissolved in 75 ml. of ethyl acetate which, on cooling, gave 3.30 g. of white crystals, m.p. 180–182°. The filtrate was diluted with an equal volume of petroleum ether (b.p. 90–115°) to give a second portion of 2.4 g., m.p. 177–180°. Recrystallization from 100 ml. of 1:1 ethanol–ethyl acetate gave 5.3 g. (73%) of *p*-(triphenylsilyl)-benzal bromide melting at 184–184.5°.

Anal. Calcd. for $C_{25}H_{20}Br_2Si$: Br, 31.5; Si, 5.52. Found: Br, 30.0; Si, 5.65, 5.64.

p-(Triphenylsilyl)-benzal bromide was also made by the action of N-bromosuccinimide on the monobromo derivative. A mixture of 4.00 g. (0.0093 mole) of *p*-(triphenylsilyl)-benzyl bromide, 150 ml. of carbon tetrachloride and 1.66 g. (0.0093 mole) of N-bromosuccinimide was refluxed with stirring and ultraviolet irradiation for 30 minutes. After cooling and removing the succinimide by filtration, the solvent was removed from the filtrate. The residue was crystallized from a 1:1 acetone–petroleum ether (b.p. 90–110°) mixture to yield 1.6 g. (34%) of a white solid melting at 184–184.5°. This material showed no depression of melting point when mixed with an analyzed sample of *p*-(triphenylsilyl)-benzal bromide.

p-(Triphenylsilyl)-benzaldehyde.—Five grams (0.0099 mole) of *p*-(triphenylsilyl)-benzal bromide was dissolved in hot commercial methyl Cellosolve and a mixture of 5.0 g. (0.03 mole) of silver nitrate in about 40 ml. of water was added dropwise, with stirring, to the refluxing solution over a period of 10 minutes. The silver bromide precipitated immediately. After the mixture was stirred for an additional 20 minutes to insure the removal and subsequent reaction of any of the bromosilicon compound that might have been entrapped in the precipitate, the green solid was removed by filtration of the hot mixture. The solvent was removed from the filtrate by distillation at reduced pressure, and the residual yellow oil dissolved in 75 ml. of ethanol. After standing for 2 days, 1.40 g. of white solid, m.p. 110–111°, was obtained and an additional 1.00 g., m.p. 108–110°, was obtained after reducing the volume to 30 ml. The final yield was 67%. The analytical sample melted at 110–111°.

Anal.. Calcd. for $C_{25}H_{20}OSi$: Si, 7.70. Found: Si, 7.78, 7.72.

This aldehyde was also prepared in good over-all yields (79%) by starting with triphenyl-(*p*-tolyl)-silane and not isolating the intermediate dibromosilicon compound formed after treatment with N-bromosuccinimide. This procedure was carried out in the same manner as described above. It was found necessary to change the solvent after the first step in the reaction sequence. When carbon tetrachloride was used throughout the reaction, a 60% yield of the dibromosilicon compound was isolated instead of the expected aldehyde. Possibly this was because of the extreme immiscibility of water and carbon tetrachloride. Although some silver bromide was formed, the two-phase system apparently allowed very little reaction of the silver ions with the halogen compound.

Employing the procedure of Shriner and Fuson,[8] a 98% yield of *p*-(triphenylsilyl)-benzaldoxime, melting at 194–195°, was obtained from *p*-(triphenylsilyl)-benzaldehyde and hydroxylamine hydrochloride.

Anal. Calcd. for $C_{25}H_{21}NOSi$: N, 3.70; Si, 7.38. Found: N, 3.56, 3.62; Si, 7.24, 7.28.

The thiosemicarbazone of *p*-(triphenylsilyl)-benzaldehyde was obtained from the reaction of this aldehyde with thiosemicarbazide.[9] A 62% yield of white crystals melting at 234–235° was obtained after the crude product was recrystallized from a 6:1 ethanol–ethyl acetate mixture.

Anal. Calcd. for $C_{26}H_{23}N_3SSi$: S, 7.32; Si, 6.40. Found: S, 7.21, 7.28; Si, 6.28, 6.31.

p-(Triphenylsilyl)-benzoic Acid. A. Oxidation of Triphenyl-(p-tolyl)-silane.—Triphenyl-(*p*-tolyl)-silane, 1.80 g. (0.0052 mole), was suspended in a mixture of 100 ml. of glacial acetic acid and 30 ml. of acetic anhydride and 3 ml. of concd. sulfuric acid were added, followed by 10 g. (0.1 mole) of anhydrous chromium trioxide (Baker and Adamson, 98% pure) in three portions. The reaction flask was immersed in a large water-bath maintained at 17 ± 2°. After stirring for 15 minutes, the dark green mixture was poured rapidly onto about 500 g. of crushed ice and stirred for several minutes. About 300 ml. of water was added and the resulting white solid was removed by filtration. This solid, melting at 195–197° after recrystallization from 300 ml. of petroleum ether (b.p. 90–110°), weighed 1.6 g. and had a melting point of 213–214°. The yield was 81%.

Anal. Calcd. for $C_{25}H_{20}O_2Si$: Si, 7.37; neut. equiv., 380; active hydrogen, 1.00. Found: Si, 7.38, 7.30; neut. equiv., 377; active hydrogen (Zerewitinoff), 1.02, 1.1.

The above procedure is a modification of the directions for the oxidation of *p*-nitrotoluene to the corresponding aldehyde.[10] The only essential difference was that of changing the reaction temperature from 0 to 17°. When this reaction was carried out at 0° in the manner outlined above, no products could be obtained from the oils and tars. Several unsuccessful attempts were made to oxidize triphenyl-(*p*-tolyl)-silane with potassium permanganate in acetone.

B. From p-(Triphenylsilyl)-benzyl Alcohol and Potassium Permanganate.—One gram (0.0027 mole) of *p*-(triphenylsilyl)-benzyl alcohol was dissolved in 200 ml. of acetone (previously treated with permanganate), 1.5 g. (0.009 mole) of potassium permanganate was added, and the mixture was refluxed for 18 hours. At the end of this period, no permanganate remained. The manganese dioxide was removed by filtration, and the residue was washed twice with fresh boiling acetone. The solvent was removed from the combined filtrates, and the white residue was dissolved in about 100 ml. of petroleum ether (b.p. 90–110°). No solid separated from this solution after standing for 5 days. The solvent was replaced with ether and the ethereal solution was extracted with concd. ammonium hydroxide. About 0.2 g. of white solid melting at 184–187° was obtained after acidifying the aqueous layer. Recrystallization from petroleum ether (b.p. 90–110°) gave 0.12 g. (12%) of crystals melting at 203–205°. A mixed melting point with an analyzed specimen of *p*-(triphenylsilyl)-benzoic acid showed no depression.

C. From p-(Triphenylsilyl)-benzaldehyde and N-Bromosuccinimide Followed by Hydrolysis.—Six grams (0.0165 mole) of *p*-(triphenylsilyl)-benzaldehyde was dissolved in 300 ml. of commercial carbon tetrachloride, 3.0 g. (0.0169 mole) of finely powdered N-bromosuccinimide was added, and the mixture was refluxed, with stirring, for 20 minutes while irradiating the flask with a mercury arc lamp. After cooling and filtering off the succinimide, the solvent was removed from the red-colored filtrate by the use of a steam-bath and vacuum pump. The solid was white when first formed but turned black after 15 minutes while the last traces of solvent were being removed. This solid was taken up in ether and the ethereal solution was extracted with concd. ammonium hydroxide. The addition of about 50 ml. of saturated sodium chloride solution broke the resulting emulsion and precipitated a white solid between the layers. This solid was filtered off and combined with the solid obtained by acidifying the basic aqueous layer. Recrystallization from petroleum ether (b.p. 90–110°) gave 1.2 g. (19%) of white solid, m.p. 212–214°. This material was shown to be *p*-(triphenylsilyl)-benzoic acid by a mixed melting point determination.

D. From p-(Triphenylsilyl)-benzaldehyde and Hydrogen Peroxide (Attempted).—Three grams (0.00825 mole) of *p*-(triphenylsilyl)-benzaldehyde in 50 ml. of acetone was added dropwise, with stirring, at 70° to a solution containing 0.4 g. of sodium hydroxide and 10 ml. of 30% hydrogen peroxide. After stirring for 10 minutes, 10 ml. of 30% hydrogen peroxide in 50 ml. of acetone was added and the mixture was refluxed for 10 minutes. The solution was acidified and steam distilled. After extracting the residue with ether, the ethereal layer was extracted with concd. ammonium hydroxide. No solid was obtained from the acidified aqueous layer. The solvent was removed from the neutral ethereal layer to obtain a red-brown oil. Attempts to induce crystallization from ethanol, petroleum ether, benzene and acetone were unsuccessful. No identifiable products were isolated from the various fractions.

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(8) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1947, p. 249.

(9) N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," Thomas Y. Crowell Co., New York, 1947, p. 249.

(10) S. V. Lieberman and R. Connor in A. H. Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 441.

p-(Tri-1-naphthylsilyl)-benzyl Bromide (Attempted).—The procedure for obtaining p-(triphenylsilyl)-benzyl bromide from triphenyl-(p-tolyl)-silane and N-bromosuccinimide was employed. Fifteen grams (0.03 mole) of tri-1-naphthyl-(p-tolyl)-silane was dissolved in 600 ml. of carbon tetrachloride, 5.35 g. (0.03 mole) of finely powdered N-bromosuccinimide was added, and the mixture was refluxed, with stirring, for 30 minutes while irradiating the reaction flask with a mercury vapor lamp. The N-bromosuccinimide had disappeared from the bottom of the flask and a test for active bromine was negative. After cooling and filtering off the succinimide, the solvent was removed from the filtrate to give a yellow oil. Digestion of this oil with about 200 ml. of petroleum ether (b.p. 90–110°), followed by filtration, gave 14.0 g. of yellow solid melting over the range 150–155°. Even after several recrystallizations from ethanol, ethyl acetate and petroleum ether (b.p. 90–110°), the melting point range could not be raised above 160–165°.

This experiment was repeated twice with essentially the same negative results.

p-(Tri-1-naphthylsilyl)-benzoic Acid (Attempted).—Several attempts were made to oxidize tri-1-naphthyl-(p-tolyl)-silane with chromium trioxide by the same procedure that was used to prepare p-(triphenylsilyl)-benzoic acid from triphenyl-(p-tolyl)-silane. A typical experiment is described. Ten grams (0.02 mole) of tri-1-naphthyl-(p-tolyl)-silane was suspended in 400 ml. of glacial acetic acid and 6.0 g. (0.06 mole) of chromium trioxide was added in small portions to the stirred mixture. After stirring for an additional hour, the green solution was poured onto crushed ice and filtered. There resulted an 80% recovery of tri-1-naphthyl-(p-tolyl)-silane as evidenced by the mixed melting point method.

In a similar experiment the mixture was refluxed for 15 minutes and a 15% recovery of the starting organosilicon compound was obtained. Extraction of the organic material with potassium and ammonium hydroxide followed by neutralization of the aqueous layer did not reveal any acid. (It was expected that some benzoic or phthalic acid might be formed from oxidation of cleavage products.)

Three runs were made in which 1, 3 and 10 ml. of concd. sulfuric acid were added to the respective mixtures which were all stirred at room temperature throughout the reaction. Tri-1-naphthyl-(p-tolyl)-silane was not isolated from these attempts but the resulting oils and tars resisted purification. These latter substances apparently were not acidic. Essentially the same negative results were obtained by using sulfuric acid at 50 and 100° except that some charring occurred at 100°

AMES, IOWA

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, DREXEL INSTITUTE OF TECHNOLOGY]

Esters in Organogermanium "Conversion Series"

BY HERBERT H. ANDERSON

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A systematic investigation of the ester group in the organogermanium "conversion series" for reactions using silver salts, together with other reactions, now makes available a single conversion series for germanium including esters. The properties of eleven new diisopropylgermanium derivatives, chiefly esters, are reported.

Conversion series, in which the appropriate silver salt converts an organometallic compound to any other organometallic compound to the right of it in the series, are available for silicon,[1] tin,[2] germanium[3] and phosphorus.[4] Previous results showed conversion of organogermanium iodide, bromide or chloride to the acetate, cyanide to isothiocyanate and isothiocyanate to isocyanate.[3] Recent papers on organosilicon and organotin compounds demonstrated the conversion of cyanides, isothiocyanates, isocyanates and sulfides to esters.[1,2]

In the present paper there is presented an investigation of the ester group in the organogermanium conversion series. An organogermanium ester forms almost quantitatively from silver acetate and the organogermanium iodide, sulfide, bromide, hydride, cyanide, chloride, isothiocyanate or isocyanate; the oxide gives the ester in approximately 60% yield; the ester does not form from the fluoride. On the basis of this and previously published work,[3] the single conversion series for organogermanium compounds, using silver salts, is as follows: I $\rightarrow$ S $\rightarrow$ Br $\rightarrow$ CN $\rightarrow$ (NCS and Cl) $\rightarrow$ NCO $\rightarrow$ (O and OCOR) $\rightarrow$ F. Here the isothiocyanate and chloride are paired, although the mixture at equal mole fractions contains 20% organogermanium isothiocyanate and 80% chloride; oxide and ester are paired since neither replaces the other completely; hydride is omitted since silver hydride is so unstable.

There is no adequate explanation for these conversion series. As Eaborn[5] points out, the relative positions of organosilicon oxide and sulfide in the organosilicon conversion series are inconsistent with the relative solubilities of silver oxide and silver sulfide, compared with those of the silver halides. Moreover, all series should be identical if the solubilities of the silver salts were the only factor; however, no two of the four known series[1,2,4] are identical.

Experimental

I. **Preparation of New Esters.**—Table I lists the properties of the new compounds prepared, and also the temperatures of distillations.

Equipment included distilling units with 10/30 standard taper ground joints on all units and accessories, micropipets for the measurement of a liquid and the subsequent titration of the available acidity,[6] and transfer micropipets.

Starting Materials.—The slow addition of 1100 ml. of 1.3 M isopropylmagnesium chloride to 67 g. of germanium tetrachloride was followed by decomposition with water, two hours after the final addition of the Grignard reagent. After washing the reaction mixture with water to remove magnesium salts, the organometallic layer was shaken with excess aqueous sodium hydroxide and extracted with hexane, which was later removed by distillation. Further distillation under 9 mm. pressure yielded 15 g. of $(i\text{-}C_3H_7)_3GeOH$, b.p. 90–92°; subsequent distillation under 1 mm. pressure furnished a 10-g. mixture boiling as high as 126°, and finally

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(1) H. H. Anderson and H. Fischer, *J. Org. Chem.*, **19**, 1296 (1954).

(2) H. H. Anderson and J. A. Vasta, *ibid.*, **19**, 1300 (1954).

(3) H. H. Anderson, THIS JOURNAL, **73**, 5439, 5800 (1951); **74**, 2371 (1952); **75**, 814 (1953).

(4) H. Hubner and G. Wehrhane, *Ann.*, **128**, 254 (1863); H. H. Anderson, THIS JOURNAL, **64**, 1757 (1942). The conversion series for phosphorus needs further investigation for completion.

(5) C. Eaborn, *J. Chem. Soc.*, 3077 (1950).

(6) H. H. Anderson, THIS JOURNAL, **71**, 1801 (1949); *Anal. Chem.*, **24**, 579 (1952).