anisidine,[4] using *m*-nitroaniline as the starting material, is long and tedious, and involves diazotization, hydrolysis, methylation, and reduction. Its preparation by rearrangement of the product from *o*-chloroanisole with sodium amide in liquid ammonia is not very convenient.[5] A convenient method of making *m*-anisidine, starting with *m*-aminophenol, has been reported by Reverdin,[6] and involves acylation of the amino group, followed by methylation with dimethyl sulfate and subsequent hydrolysis. However, in spite of the apparent simplicity of this method it has not been widely used by other workers, and in recent studies on the constitution of tazettine,[7] as lycoris alkaloid, the above described conventional method for the synthesis of *m*-anisidine was used.

We wish to report here the details of a single step synthesis of *m*-anisidine by direct methylation of the easily available and inexpensive *m*-aminophenol using dimethyl sulfate, as well as the results of reinvestigation of the earlier procedure of Reverdin.[6] The use of methyl *p*-toluenesulfonate as a methylating agent was also successful but offered no advantage.

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EXPERIMENTAL

m-Anisidine from m-Aminophenol. A mixture of *m*-aminophenol (25 g.), dimethyl sulfate, technical grade (50 g.), anhydrous potassium carbonate (100 g.), and potassium hydroxide (25 g.) was refluxed in anhydrous methyl ethyl ketone (500 ml.) for 120 hr. The cooled reaction mixture was poured into an excess of cold water and let stand overnight to decompose excess dimethyl sulfate. It was then extracted with ether and the ether extract dried and distilled to remove solvent. The oily residue was distilled under reduced pressure to give 25.5 g. (91%) of pale yellow *m*-anisidine, b.p. 81–86°/2 mm.

m-Anisidine from m-acetylaminophenol. A mixture of *m*-acetylaminophenol (43 g.), dimethyl sulfate, technical grade (50 g.) and anhydrous potassium carbonate (100 g.) was refluxed in anhydrous methyl ethyl ketone (500 ml.) for 48 hr. The mixture was then cooled, filtered, and the residual potassium carbonate washed with ether. The washings were combined with the filtrate and the solvents removed by distillation. The syrupy residue of *m*-acetaniside (a portion was crystallized from benzene petroleum ether to give colorless, shining crystals, m.p. 79–80°)[6] was hydrolyzed by refluxing with concentrated hydrochloric acid for 4 hr. The cooled mixture was made strongly alkaline with sodium hydroxide solution, and extracted with ether. Removal of the ether, subsequent to drying and distillation of the residue, gave 20 g. (57%) of pale yellow *m*-anisidine, distilling at 79° under 1 mm. pressure. The reaction time could be reduced to 6 hr., but the yield was lower.

m-Acetylaminophenol was methylated and hydrolyzed following the procedure of Reverdin. The yields were in order of 50–55% as against the 90% claimed by Reverdin.

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[4] D. A. Shirley, *Preparation of Organic Intermediates*, John Wiley and Sons, New York, N. Y., 1951, p. 213.

[5] H. Gilman and R. H. Kyle, *J. Am. Chem. Soc.*, **74**, 3028 (1952).

[6] F. Reverdin and A. de Luc, *Ber.*, **47**, 1537 (1914).

[7] H. Kondo, T. Ikada, and J. Taga, *Ann. Rept. ITSUU Lab. Japan*, **3**, 659 (1952); [*Chem. Abstr.* **47**, 7417 (1953)].

Analogs of Hexaphenylethane. VI. Triphenylgermyltriphenyltin[1]

Henry Gilman and Clare W. Gerow

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There has been reported only one organic compound containing a germanium-tin bond. This was triphenylgermyltrimethyltin reported by Kraus and Foster.[2] We have prepared triphenylgermyltriphenyltin as a member of a series to compare the strengths of the bonds between various Group IV-B elements. The preparation was carried out by coupling triphenylgermylpotassium with triphenyltin chloride according to the equation

$$(C_6H_5)_3GeK + (C_6H_5)_3SnCl \rightarrow (C_6H_5)_3GeSn(C_6H_5)_3 + KCl$$

The mode of addition was found to be important in this reaction, for it was found that when the triphenyltin chloride was added to the triphenylgermylpotassium a 60% yield of triphenylgermyltriphenyltin was isolated; however, when the triphenylgermylpotassium was added to the triphenyltin chloride only a mixture of products was formed which could not be separated into its components. A mixture was also formed when triphenyltinlithium was allowed to react with triphenylchlorogermane, and when triphenylgermyllithium was allowed to react with triphenyltin chloride. It is believed that the mixtures obtained above contain hexaphenyldigermane, triphenylgermyltriphenyltin, and possibly hexaphenylditin. The presence of hexaphenyldigermane and probably triphenylgermyltriphenyltin was confirmed by treating the mixture obtained from the reaction of triphenylgermyllithium and triphenyltin chloride with iodine. Hexaphenyldigermane, which is unaffected by iodine, was isolated in 46% yield and triphenyliodogermane was found in 14% yield. The triphenyliodogermane probably arose from the cleavage of triphenylgermyltriphenyltin, and the nonisolation of a tin compound was probably due to the cleavage of more than one phenyl group from the tin atom.

The above mixtures could have been formed from a coupling of the many species present in the

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[1] For paper V of this series see H. Gilman and C. W. Gerow, *J. Am. Chem. Soc.*, **78**, 5823 (1956).

[2] C. A. Kraus and L. S. Foster, *J. Am. Chem. Soc.*, **49**, 457 (1927).

reaction mixture due to a halogen-metal interconversion reaction between the triphenylgermyllithium and the triphenyltin chloride or between the triphenyltinlithium and the triphenylchlorogermane. Similar halogen-metal interconversion reactions have been observed between triphenylgermylpotassium and triphenylchlorosilane,[1] between triphenylmethylsodium and triphenylbromosilane,[3] and between triphenylsilylpotassium and triphenylchloromethane.[3]

Triphenylgermyltriphenyltin is a white solid melting at 284–286°; when heated above its melting point it decomposes. It is stable to oxygen in chloroform at room temperature. However, it is partially decomposed in refluxing xylene either in the presence or absence of air. In the former respect it is similar to triphenylgermyltriphenylsilane,[1] hexaphenyldisilane,[4] and hexaphenyldigermane,[5] all of which are unaffected by oxygen. The Ge—Sn bond is readily cleaved by iodine and organolithium reagents. In these reactions triphenylgermyltriphenyltin is entirely different from hexaphenyldisilane,[4] hexaphenyldigermane,[5] and triphenylgermyltriphenylsilane,[1] all of which are unaffected by both iodine and organolithium reagents. When triphenylgermyltriphenyltin is allowed to react with phenyllithium a mixture of tetraphenylgermane and tetraphenyltin apparently is formed. With butyllithium there is isolated, subsequent to carbonation, triphenylgermanecarboxylic acid and hexaphenyldigermane; however, no pure tin compound was found.

Triphenylgermyltriphenyltin is not extensively affected by sodium-potassium alloy unless an initiator such as tetrahydrofuran is added, in which case cleavage proceeds easily. In this respect the Ge—Sn bond is like the Ge—Ge bond in hexaphenyldigermane[5] which is not affected by sodium-potassium alloy unless an initiator is added. The Ge—Si[1] and Si—Si[6] bonds in triphenylgermyltriphenylsilane and hexaphenyldisilane are readily cleaved under the same conditions.

EXPERIMENTAL[7]

Preparation of triphenylgermyltriphenyltin. To an ether suspension of triphenylgermylpotassium prepared by the cleavage of 19.1 g. (0.05 mole) of tetraphenylgermane with sodium-potassium alloy, according to recent directions[5] there was added an ether suspension of 19.3 g. (0.05 mole) of triphenyltin chloride. After stirring overnight the mixture was poured into a saturated ammonium chloride solution, and then was filtered to give a solid melting over the range 250–275° with some decomposition. This material was crystallized twice from benzene to give 19.5 g. (60%) of product melting at 284–286°.

Anal. Calcd. for $C_{36}H_{30}GeSn$: GeSn, 29.25. Found: GeSn, 29.28, 29.46.

Using the same procedure, two other runs gave 26 and 64% yields. When the triphenylgermylpotassium was added to the triphenyltin chloride there was obtained a mixture from which no pure product could be isolated. A mixture was likewise formed when triphenylchlorogermane was allowed to react with triphenyltinlithium and when triphenylgermyllithium was allowed to react with triphenyltin chloride.

Cleavage experiments with triphenylgermyltriphenyltin. With oxygen. When 1.0 g. of triphenylgermyltriphenyltin was dissolved in 50 ml. of chloroform and dry air was passed through it for 24 hr. there was recovered 0.95 g. of starting material melting at 284–287°. When refluxing xylene was substituted for chloroform there was recovered only 0.6 g. of pure starting material. However, it is believed that the loss of material was due to decomposition by heat because when 5.0 g. of triphenylgermyltriphenyltin was refluxed for 24 hr. in 25 ml. of xylene in a nitrogen atmosphere only 4.5 g. of impure starting material was recovered.

With iodine. When a chloroform solution of iodine was added to 5.0 g. of triphenylgermyltriphenyltin dissolved in 50 ml. of chloroform, the color was dispelled immediately after each small addition. The iodine was added as long as the color was discharged at room temperature, then the mixture was heated to boiling and the addition was continued until a large excess of iodine was present. The solvent was removed by distillation to leave a liquid residue which was washed with petroleum ether (b.p. 60–70°) to give a quantitative yield of triphenyliodogermane melting at 155–157°. No tin compound was isolated.

When 1.12 g. (0.0044 mole) of iodine dissolved in 50 ml. of chloroform was added dropwise to 2.9 g. (0.0044 mole) of triphenylgermyltriphenyltin dissolved in 70 ml. of chloroform, the color was discharged immediately after each small addition during the first few drops. After about half of the iodine had been added the color took longer to disappear, and at this point the solution was heated to boiling and the remainder of the iodine was added dropwise. When the addition was complete the color of the solution was yellow. The chloroform was removed by distillation and the residue was washed with petroleum ether (b.p. 60–70°) to give 0.8 g. of insoluble solid melting over the range 260–275°. This material was washed with ether to give 0.6 g. of recovered starting material melting at 283–285°. The petroleum ether filtrate from above was cooled and there crystallized 2.05 g. of solid melting over the range 110–116°. Repeated crystallization of this material from petroleum ether (b.p. 60–70°) gave no pure product. It is believed that a mixture of triphenyliodogermane and triphenyltin iodide was present. An infrared spectrum of this mixture showed absorption peaks at 1090 $cm.^{-1}$ and 1070 $cm.^{-1}$, indicative of the phenylgermanium and phenyl-tin bonds.

With sodium-potassium alloy. The cleavage experiments with triphenylgermyltriphenyltin and sodium-potassium alloy were not clean-cut. Several cleavage experiments, however, indicate that reaction is not extensive. When 3.3 g. (0.005 mole) of triphenylgermyltriphenyltin was stirred 71 hr. with 0.6 ml. (0.012 g. atom of potassium) of sodium-potassium alloy in a small amount of ether there was recovered 2.5 g. (70%) of impure starting material melting over the range 260–295°. However, when the same amount of triphenylgermyltriphenyltin was stirred 70 hr. under the same conditions, except that 20 drops of tetrahydrofuran was added, the addition of propyl bromide to derivatize the products led to the isolation of 0.4 g. (26%) of hexaphenyldigermane and 1.6 g. of what is believed to be a mixture of triphenyl-*n*-propylgermane and triphenyl-*n*-propyltin melt-

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(5) H. Gilman and C. W. Gerow, *J. Am. Chem. Soc.*, **77**, 5509 (1955).

(6) H. Gilman and T. C. Wu, *J. Am. Chem. Soc.*, **73**, 4031 (1951).

(7) All melting points are uncorrected. Reactions involving reactive organometallic compounds were carried out in an atmosphere of dry, oxygen-free nitrogen.

ing over the range 77–82°. Repeated crystallization of this material from methanol gave no pure products. An infrared spectrum of this mixture showed absorption peaks at 1090 cm.$^{-1}$ and 1070 cm.$^{-1}$, which a large number of spectra have shown to be indicative of the phenyl-germanium and phenyl-tin bonds. The melting point of the mixture is consistent with what one might expect from a mixture of triphenyl-*n*-propylgermane and triphenyl-*n*-propyltin.

With phenyllithium. To an ether solution of phenyllithium prepared from 7.85 g. (0.05 mole) of bromobenzene there was added 3.27 g. (0.005 mole) of triphenylgermyltriphenyltin. After stirring overnight the mixture was hydrolyzed by the addition of water. Filtration then gave 3.52 g. of solid melting over the range 217–223°. From the ether layer there was obtained an additional 0.65 g. of solid melting over the range 222–226°. Repeated crystallization of these materials from benzene gave no pure products. It is believed a mixture of tetraphenylgermane and tetraphenyltin is present. The infrared spectrum of this mixture also showed absorption peaks at 1090 cm.$^{-1}$ and 1070 cm.$^{-1}$ indicative of the phenyl-germanium and phenyl-tin bonds. The melting point of the mixture is consistent with the melting point that Drew and Landquist[8] found for a mixture of tetraphenylgermane and tetraphenyltin in their studies on mixture melting points of the tetraphenyls of the Group IV-B elements; they reported a melting point of 223–224° for their synthetic mixture.

With butyllithium. To a suspension of 3.27 g. (0.005 mole) of triphenylgermyltriphenyltin in 20 ml. of ether there was added rapidly 10 ml. of a 0.1*N* solution of *n*-butyllithium. After stirring 24 hr. Color Test I[9] was positive and Color Test II[10] was negative. The mixture was then carbonated by pouring it into an ether–Dry-Ice slurry, and after warming to room temperature water was added and the alkaline layer was separated. The ether layer was extracted twice with 50 ml.-portions of 5% sodium hydroxide solution, and then the combined alkaline layers were acidified by the addition of concentrated hydrochloric acid. There precipitated a solid weighing 0.6 g. which was recrystallized from ethanol to give 0.16 g. (9%) of triphenylgermanecarboxylic acid melting at 186° with the evolution of carbon monoxide. The ether layer above was filtered to give 0.75 g. of solid melting over the range 300–320°. Recrystallization of this material from benzene gave 0.35 g. of hexaphenyldigermane melting at 338–340°. The ether solution was dried over anhydrous sodium sulfate and the solvent was removed by distillation to leave a residue which was washed with methanol to give 0.4 g. of material melting over the range 210–230°. Recrystallization of this material gave no pure products.

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Synthesis of Some Derivatives of Phenothiasilin, A Silicon Analog of Thiaxanthene

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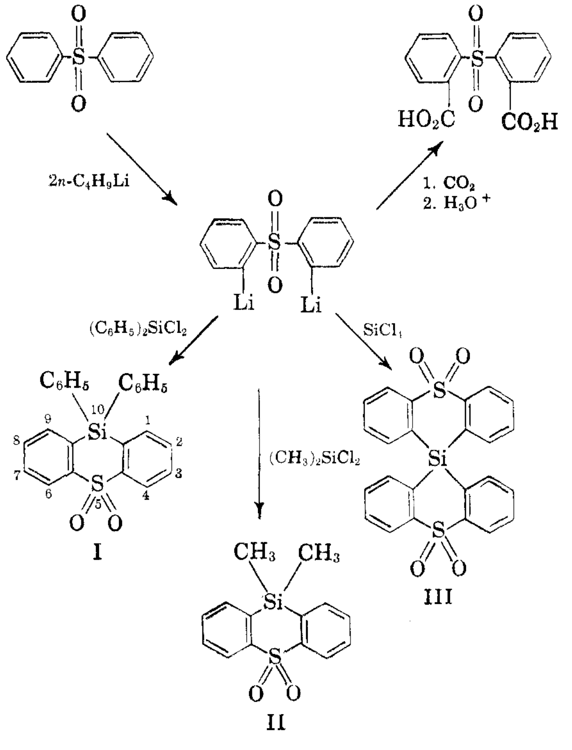
In view of the success attained in the preparation of several derivatives of phenoxasilin,[1] a silicon analog of xanthene, the synthesis of a new heterocyclic system in which silicon and sulfur were present as hetero atoms was undertaken. The compounds prepared were 10,10-diphenylphenothiasilin-5,5-dioxide (I) and 10,10-dimethylphenothiasilin-5,5-dioxide[2] (II), silicon analogs of 10,10-diphenylthiaxanthene-5,5-dioxide and 10,10-dimethylthiaxanthene-5,5-dioxide, respectively. A Fisher-Hirschfelder-Taylor model of phenothiasilin-5,5-dioxide indicated very little strain.

These phenothiasilin derivatives were prepared from the reaction of 2,2′-dilithiodiphenyl sulfone with the corresponding dichlorosilane. The dimetalation of diphenyl sulfone was carried out in accordance with the previously reported low-temperature procedure.[3] The identity of 2,2′-dilithiodiphenyl sulfone has been confirmed by its conversion to 2,2′-dicarboxydiphenyl sulfone.[3]



As in the syntheses of phenoxasilin derivatives[1]

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