Previously tested hydrocarbons with a single phenyl-phenyl linkage include such compounds as biphenyl,[1a] fluorene,[1a] phenanthrene,[1b] and pyrene[1b] (0.10, 0.12, 0.16, and 0.21, respectively). Table I shows the remarkable value of 0.87 for 1,1'-binaphthyl along with 0.25 for 2,2'-binaphthyl and 0.24 for the closely related perylene. Some partially hydrogenated terphenyls and quaterphenyls having only two benzenoid nuclei also give surprisingly high values and will be reported later along with the corresponding aromatic compounds.

Included in Table I are a number of interesting functional derivatives of biphenyl. Among these are two solutes related to p-terphenyl (RPH 0.97[1b]). Previously[1e] we have reported a value of 0.16 for 4-biphenylyl phenyl ether. In Table I Compound 2, in which the three rings are separated by a —CH₂— group, gives no response within the limits of our measuring system. Compound 9 with an —NH— function separating the rings shows a value of 0.63. The temptation to attribute this high value to resonance interaction between rings is discouraged by the low value of the corresponding oxygen compound. To date no theoretical explanation involving the hydrogen attached to the nitrogen separating the rings has been proposed, although there are other examples that lend appeal to this line of thought. Compare, for example, 4-biphenylyldiphenylamine[1f] (0.39) with Compound 9 and bis-4-biphenylylamine[1f] (0.95) with bis-4-biphenylylphenylamine[1f] (0.61). Even Compound 10, with little opportunity for any sort of interaction between the rings and the secondary amine function, affords a measurable response. In all of these cases consideration of the values of the oxygen analogs is discouraging in that the diaryl ethers have poor values and the phenolic hydroxyl group is known to be an undesirable function in all instances examined thus far.[1b]

The encouraging results for the dimethylamino and methoxy derivatives tested (Compounds 3,4,5,-7, and 11) seem to indicate that these functions give rise to enhanced scintillation in compounds which are otherwise poor solutes in spite of the fact that they have little, if any, effect on molecules which are otherwise good scintillators. The simple aminophenanthrenes are the first derivatives of this system reported, and the pulse heights (0.20 and 0.23) indicate good potential for this nucleus. Synthesis and examination of more complex derivatives will almost certainly be rewarding.

The values reported in Table I were measured in the pulse height analyzer previously described,[1b] and all were measured at a concentration of 3 g./l. in toluene. All values are relative to 2,5-diphenyloxazole which is assigned the arbitrary value of 1.00.

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## Some Compounds in the Tri-n-hexylgermane Series

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Because the information in the literature on the higher aliphatic germanium compounds[1] is meager, a study of such types has recently been initiated in this laboratory. The preparations and physical properties of some compounds of the tri-n-hexylgermane series are reported herein, including tetra-n-hexylgermane, phenyltri-n-hexylgermane, tri-n-hexylbromogermane, bis(tri-n-hexylgermanium) oxide, tri-n-hexylchlorogermane, tri-n-hexyliodogermane and tri-n-hexylgermane.

Tetra-n-hexylgermane was prepared by the reaction of germanium tetrachloride with an excess of n-hexyllithium. Tri-n-hexylbromogermane was obtained directly from germanium tetrachloride and 3.3 equivalents of n-hexylmagnesium bromide, although the product obtained by this method cannot be completely freed of di-n-hexyldibromogermane. The ready displacement by bromide ion of the chloride ion from the expected initial product, tri-n-hexylchlorogermane, finds a parallel in the preparation of the corresponding iodide from either the chloride or the bromide by the action of sodium iodide in acetone solution. The high rate

$$R_3GeCl + NaI \longrightarrow R_3GeI + NaCl$$
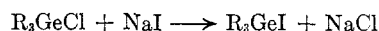
of reaction of trialkylhalogermanes compared to tertiary butyl halides in bimolecular nucleophilic displacement reactions can be partially ascribed to the relative unimportance of steric hindrance at the large central germanium atom. Also, germanium is less electronegative than carbon.[2] This suggets a polarization of the alkyl-germanium bonds which would tend to lower the electron density at the central atom thereby speeding S_N2 reactions.

(1) For a comprehensive review see: O. H. Johnson, Chem. Revs., 48, 259 (1951), and more recently, H. H. Anderson, J. Am. Chem. Soc., 73, 5800 (1951); J. Am. Chem. Soc., 75, 814 (1953); R. Fuchs, L. O. Moore, D. Miles, and H. Gilman, J. Org. Chem., 21, 1113 (1956).

(2) M. L. Huggins, J. Am. Chem. Soc., 75, 4123 (1953).

TABLE I

Physical Properties of Tri-n-hexylgermane Compounds

Compound[e]	B.P., °C at 0.5 mm.	n_D at t°	Den. at t°	Formula	Germanium % Calcd.	Found
R$_4$Ge	158–161	1.4567/27	0.908/27	C$_{24}$H$_{52}$Ge	17.6	17.4
						17.2
R$_3$GeBr	143–145	1.4763/27	1.117/26	C$_{18}$H$_{39}$GeBr[a]	17.8	17.8
R$_3$GeC$_6$H$_5$	160–165	1.4984/22	0.972/25	C$_{24}$H$_{44}$Ge	17.9	17.9
						17.9
(R$_3$Ge)$_2$O	210–211[b]	1.4645/25	0.963/25	C$_{36}$H$_{78}$Ge$_2$O	21.6	21.8
						21.9
R$_3$GeCl	138–139	1.4661/20	0.989/20	C$_{18}$H$_{39}$GeCl[c]		
R$_3$GeI	154–155	1.4935/26	1.188/26	C$_{18}$H$_{39}$GeI[d]		
R$_3$GeH	122–125	1.4565/21	0.917/25	C$_{18}$H$_{40}$Ge	22.1	22.4
						22.4

[a] *Anal.* Calcd.: Br, 19.59. Found: Br, 21.8. This indicates a composition of 82% tri-n-hexylbromogermane and 18% di-n-hexyldibromogermane. [b] B.p. at 0.04 mm. gauge pressure. [c] *Anal.* Calcd.: Cl, 9.76. Found: Cl, 9.72. [d] *Anal.* Calcd.: I, 27.59. Found: I, 27.62. [e] R represents an n-hexyl group.

Pure tri-n-hexylchlorogermane was obtained by basic hydrolysis of the impure bromide, fractional distillation of the resulting oxide, and treatment of the oxide with concentrated hydrochloric acid. Tri-n-hexylbromogermane reacted with phenyllithium to give phenyltri-n-hexylgermane, and with lithium aluminum hydride to give tri-n-hexylgermane.

EXPERIMENTAL

Tetra-n-hexylgermane. n-Hexyllithium was prepared[3] by the addition over a two-hour period of 128 ml. (0.907 mole) of n-hexyl bromide in 100 ml. of anhydrous ether to a mixture of 13.9 g. (2.0 gram atoms) of lithium wire cut into pieces 5–10 mm. in length, and 400 ml. of anhydrous ether. A dry nitrogen atmosphere was maintained. The reaction was started at room temperature, then was cooled to −30° during the two-hour addition period, and finally was stirred at 0° for two hours more. The resulting solution was shown by the double titration procedure[4] to contain 0.62 mole of n-hexyllithium (68%). This was added to a solution of 14.8 ml. (0.13 mole) of germanium tetrachloride in 100 ml. of ether, at 0° (over a 1-hr. period) and then the mixture was stirred for two hours. Hydrolysis was effected with ice water, the layers were separated and the ether layer dried over magnesium sulfate, and the solvent was distilled. Fractional distillation of the residue through a Vigreux column gave 7.2 g. (14%) of product, b.p. 158–161° at 0.5 mm.

Anal. Calcd. for C$_{24}$H$_{52}$Ge: MR, 124.7. Found: MR, 123.9.

Tri-n-hexylbromogermane. To 19.4 ml. (0.17 mole) of germanium tetrachloride was added 0.56 mole of n-hexylmagnesium bromide obtained from 14.6 g. of magnesium and 84.4 ml. of n-hexylbromide. The suspension was filtered, and the liquid was distilled. First, solvent and unchanged n-hexyl bromide came over, followed by 28.0 g. (40%) of product, b.p. 143–145° at 0.5 mm.

Anal. Calcd. for C$_{18}$H$_{39}$GeBr: MR, 104.8. Found: MR, 103.1.

An additional 15.4 g. of material which boiled at 145–160° at 0.5 mm. appeared to be a mixture of tri-n-hexyl-bromogermane and tetra-n-hexylgermane.

Halogen analysis of halogermanes. A sample of the halogermane (0.2 g.) was weighed into a dry Erlenmeyer flask. This was heated nearly to boiling with 0.5 g. of calcium car-

bonate and 50 ml. of distilled water for 10 min. After the flask was cooled, the contents were titrated by the Mohr method against 0.1N silver nitrate solution using 0.05 g. of sodium chromate as an indicator. A blank containing calcium carbonate, sodium chromate, and water was titrated, and the volume of silver nitrate used was subtracted from the volume required by the sample.

Phenyltri-n-hexylgermane. A solution of 0.045 mole of phenyllithium in ether solution was added to 8.2 g. (0.02 mole) of tri-n-hexylbromogermane in 100 ml. of toluene. The ether was distilled until the vapor reached 110°, and the residue was refluxed overnight. The mixture, after hydrolysis and isolation by the method used for tetra-n-hexylgermane, gave 6.1 g. (75%) of product boiling at 160–165° at 0.5 mm.

Anal. Calcd. for C$_{24}$H$_{44}$Ge: MR, 121.1. Found: MR, 122.0.

Bis(tri-n-hexylgermanium) oxide. Fifteen g. of the higher boiling fraction of impure tri-n-hexylbromogermane was stirred for 0.5 hr. with 100 ml. of aqueous 10% potassium hydroxide solution cooled in ice. After the addition of 75 ml. of isopropyl ether, the organic layer was separated, washed with water, and dried. Distillation through a semimicro column gave 4.3 g. (35%) of a liquid, b.p. 210–211° at 0.04 mm.

Anal. Calcd. for C$_{36}$H$_{78}$Ge$_2$O: MR, 193.4. Found: MR, 192.8.

A total of 7.0 g. (57%) of product distilled over the range from 204–212° at 0.04 mm.

Tri-n-hexylchlorogermane. To concentrated hydrochloric acid (15 ml.) was added 3.6 g. of bis(tri-n-hexylgermanium) oxide, and the mixture was stirred for 30 hr. The product was extracted twice with hexane, and the combined extracts were dried over magnesium sulfate. Distillation afforded 2.62 g. (74%) of product boiling at 138–139° at 0.5 mm.

Anal. Calcd. for C$_{18}$H$_{39}$GeCl: MR, 102.0. Found: MR, 101.9.

Tri-n-hexyliodogermane. A solution of 7.5 g. of sodium iodide in 50 ml. of acetone was mixed with 2.6 g. of tri-n-hexylchlorogermane. Precipitation of sodium chloride began almost immediately. After overnight standing the addition of 50 ml. of hexane caused the unchanged sodium iodide to precipitate. The orange solid was separated by filtration during which contact with air was minimized. Distillation of the filtrate gave 1.8 g. (56%) of a colorless liquid, b.p. 154–155° at 0.5 mm.

Anal. Calcd. for C$_{18}$H$_{39}$GeI: MR, 109.8. Found: MR, 112.6.

This sample of tri-n-hexyliodogermane became brown after standing for several days.

Tri-n-hexylgermane. To 2 g. of lithium aluminum hydride dissolved in 75 ml. of anhydrous ether was added a solution

(3) H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn, and L. S. Miller, *J. Am. Chem. Soc.*, 71, 1499 (1949).

(4) H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, 66, 1515 (1944).

of 9.5 g. of tri-*n*-hexylbromogermane in 40 ml. of ether. The mixture was refluxed for 4 hr. and was allowed to stand overnight. Unchanged lithium aluminum hydride was then precipitated by the addition of 100 ml. of petroleum ether (b.p. 77–115°) followed by distillation of the ethyl ether. The solution was filtered and then distilled. After a fore-run came over at 95–122° at 0.5 mm., 2.0 g. (26%) of product was collected, b.p. 122–125° at 0.5 mm.

Anal. Calcd. for $C_{18}H_{40}Ge$: MR, 97.1. Found: MR, 97.4.

The pure product does not evolve hydrogen at a noticeable rate when treated with dilute alcoholic potassium hydroxide solution, although triphenylgermane reacts readily. The infrared absorption spectrum shows a peak at 1980 cm.$^{-1}$ due to the Ge–H bond.

Acknowledgment. This research was supported 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 AFB, Ohio.

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Cleavage of the Silicon-Silicon Bond of Hexaphenyldisilane. IV[1]

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The silicon-silicon bond of hexaphenyldisilane is much more stable than the carbon-carbon bond of hexaphenylethane. Unlike the carbon analog, hexaphenyldisilane is not cleaved by oxygen,[3,4] iodine,[4] sodium in xylene or dioxane,[1c] or sodium amalgam in ether.[1c] Nevertheless, the silicon-silicon bond of hexaphenyldisilane has been cleaved by sodium-potassium alloy in ether,[1c,5] lithium in tetrahydrofuran,[1a] lithium and sodium in ethylene glycol dimethyl ether,[1b] potassium in di-*n*-butyl ether,[1c] and rubidium or cesium in ether.[5]

In an extension to the studies of the cleavage reactions of the silicon-silicon bond of hexaphenyldisilane, a number of other reagents have been studied. It was found that sodium cleaved the disilane in liquid ammonia. Although iodine does not react with hexaphenyldisilane,[4] bromine was found to effect slow cleavage of the silicon-silicon bond in carbon tetrachloride to give bromotriphenylsilane. For example, 33% of pure bromo-

triphenylsilane was isolated in a period of 42 hr., and a 55% yield of bromotriphenylsilane was formed in 6 days. This observation further demonstrates that the silicon-silicon bond of hexaphenyldisilane is more stable than the central carbon-carbon bond of hexaphenylethane since the latter compound reacts readily with iodine due to dissociation.

Hexaphenyldisilane has been treated with a number of oxidizing agents as well as lithium aluminum hydride, but no cleavage reaction of the silicon-silicon bond was observed. In most cases, a nearly quantitative recovery of the starting material was obtained. When chromic acid was employed, some oxidation occurred yielding a sirupy product.

EXPERIMENTAL[6]

Reaction of hexaphenyldisilane with bromine. A suspension containing 10 g. (0.019 mole) of hexaphenyldisilane, 3.4 g. (0.021 mole) of bromine, and 250 ml. of carbon tetrachloride was refluxed with constant stirring for 42 hr. The solvent and the unchanged bromine were removed by distillation to leave a solid residue (10.8 g.) melting at 100° to a turbid liquid. The crude product was boiled with 200 ml. of petroleum ether (b.p. 60–70°), filtered hot, and cooled. The insoluble solid (4.1 g.) melting at 346–354° was recrystallized from dioxane to give 3.6 g. (36%) of hexaphenyldisilane (mixed melting point). The filtrate was concentrated twice to collect 6.2 g. (47%) of solid melting at 115–118°. Two recrystallizations from petroleum ether (b.p. 60–70°) yielded 4.3 g. (33%) of crystals melting at 118–120°. A mixed melting point determination with an authentic specimen of bromotriphenylsilane was not depressed.

In a second experiment, the hexaphenyldisilane was allowed to react with bromine in refluxing carbon tetrachloride for 6 days. The reaction mixture was worked up according to the procedure described in the previous paragraph to give a 19% recovery of hexaphenyldisilane and a 65% yield of crude, and a 55% yield of pure bromotriphenylsilane.

Reaction of hexaphenyldisilane with sodium in liquid ammonia. Sodium, 0.35 g. (0.015 g.-atom), was cut into small pieces and dropped into about 50 ml. of liquid ammonia at −50°. To this deep blue solution thus formed there was added 2.6 g. (0.005 mole) of hexaphenyldisilane in one portion. The reaction mixture was stirred for 6 hr. at −50°. It was observed that some brown precipitate had formed although the color was somewhat masked by the deep blue color due to the excess sodium in liquid ammonia. The cooling bath was removed and ammonia was allowed to evaporate as the reaction mixture warmed to room temperature. A small amount of ethanol was added to the pale gray residue to destroy the excess sodium. Water was then added, and the mixture was filtered to give 1.6 g. of solid which softened at 120° but did not melt completely until 360°. This was boiled with a solution of benzene and ethanol and filtered hot. There was obtained, as the insoluble residue, 0.1 g. (4%) of hexaphenyldisilane (mixed melting point) melting at 360–362°. The filtrate was cooled to give 0.8 g. of solid melting at 150–200°. This was shaken with a small amount of cold ethanol and filtered to separate 0.4 g. of solid melting at 230–234°. One recrystallization from benzene raised the melting point to 233–235°. A mixed melting point determination with tetraphenylsilane was not depressed. The yield was 0.3 g. (9%). The ethanolic solution was evaporated to dryness, and the residue was recrystallized from petroleum ether (b.p. 60–70°) to give 0.4 g. (11%) of triphenylsilanol melting at 151–152°. Evaporation of the solvent from the

(1) (a) For Part III of this series see H. Gilman and G. D. Lichtenwalter, *J. Am. Chem. Soc.*, **80**, 608 (1958); (b) for Part II see A. G. Brook and H. Gilman, *J. Am. Chem. Soc.*, **76**, 278 (1954); (c) for Part I see H. Gilman and T. C. Wu, *J. Am. Chem. Soc.*, **73**, 4031 (1951).

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(6) All melting points are uncorrected.