

the first two. The first band was treated by elution and the second by extrusion and extraction with ethanol. The material from the first band crystallized readily from benzene, *n*-heptane as yellow needles with a slight greenish cast, m.p. 194–195°. The yield was 0.19 g., 31.59% on a dinitro basis.

Anal. Calcd. for $C_{12}H_8O_2N_2$: N, 10.77. Found: N, 10.73.

After extrusion and extraction with 95% ethanol, the material from the second band was crystallized from chloroform-*n*-heptane as shiny plates of pale yellow color, m.p. 226–228°. The yield was 0.073 g., 12% on a dinitro basis. When the compounds from the first and second bands were oxidized using chromic acid, and the products separately mixed with *p*-nitrobenzoic acid and heated, no lowering of the m.p. was observed. This shows that the second nitro group enters the phenolic ring.

Anal. Calcd. for $C_{12}H_8O_3N_2$: N, 10.77. Found: N, 10.56.

Further nitration of 3,4'- and 5,4'-dinitro-2-hydroxybiphenyl to 3,5,4'-tri-nitro-2-hydroxybiphenyl. A sample (0.208 g.) of the compound from the first band was dissolved in 10 ml. of glacial acetic acid and nitrated at room temperature with 1.0 ml. (0.0023 mole) nitric acid. A stock of this nitrating mixture was made up by mixing 1.3 ml. of fuming nitric acid and 8.7 ml. of glacial acetic acid. The mixture was set aside for 2 hr. and poured into 25 ml. of ice water. The yellow precipitate was collected on the filter, washed free of acid with water, and taken up in benzene. The benzene solution was twice taken to dryness with added *n*-heptane and the residue redissolved in 15 ml. of benzene. Addition of an equal volume of *n*-heptane caused a precipitate of brown-yellow needles m.p. 162–163° following recrystallization. A mixed melting point with 3,5,4'-trinitro-2-hydroxybiphenyl, previously prepared, showed no depression. A sample of the compound from the second band (0.186 g.) was dissolved in 10 ml. of glacial acetic acid and nitrated at room temperature with 1 ml. of the nitrating mixture previously described. The reaction mixture was refluxed on the water bath for 30 min. The product was worked up in the same manner as that described for the material from band 1. The purified product melted 161–163°. The melting point was not lowered by admixture with previously prepared 3,5,4'-trinitro-2-hydroxybiphenyl.

Further nitration of 2'-nitro-2-hydroxybiphenyl. A sample of 2'-nitro-2-hydroxybiphenyl (0.25 g., 0.0012 mole) was dissolved in 5 ml. of nitromethane and 1 ml. of nitration mixture (0.0012 mole nitric acid) added dropwise at room temperature. The nitrating mixture was made up with 0.5 ml. of fuming nitric acid and 9.5 ml. of nitromethane. There was immediate darkening of the reaction mixture and a moderate increase in temperature. The reaction mixture was set aside for 2 hr. and poured into 25 ml. of ice water. The precipitated material was prepared for the column in the usual manner. The first band, when eluted, gave 0.06 g. of starting material. The second band was extruded and extracted with 95% ethanol. Crystallization from hot benzene,*n*-heptane gave pale yellow fernlike leaflets which, when heated, showed a change of state above 200° forming rectangular plates, m.p. 228–229°, yield 0.09 g., 40.95%. This product was assumed to be either the 3,2'- or the 5,2'-dinitro derivative.

Further nitration of 2'-nitro-2-hydroxybiphenyl in glacial acetic acid. A sample of 2'-nitro-2-hydroxybiphenyl (0.25 g., 0.0012 mole) was dissolved in 5 ml. of glacial acetic acid and nitrated with 4 ml. of a nitrating mixture made up of 0.5 ml. fuming nitric acid dissolved in 9.5 ml. glacial acetic acid (0.0047 mole nitric acid). The reaction mixture darkened at once and a precipitate came down during the latter part of the addition period. The product was worked up as usual and placed on the column. Three bands developed of which the first was narrow, dim yellow in color and moved, under moderate elution with benzene, with sufficient speed to enable extrusion of a second band which was the principal one. This was the only band from which material could be isolated. The material from this band crystallized readily from benzene,*n*-heptane as yellow needles, m.p. 152–153°. The weight was 0.17 g., 48.02%. These yellow, needlelike crystals were assumed to be 3,5,2'-trinitro-2-hydroxybiphenyl. A sample of these crystals when oxidized with chromic acid formed a product whose m.p. of 146–147° approximated that of *o*-nitrobenzoic acid.

Anal. Calcd. for $C_{12}H_7O_3N_3$: N, 13.77. Found: N, 13.60.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Cleavage Studies of Some Organogermanium Compounds

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n-Butyltriethylgermane, benzyltriethylgermane, and 2-biphenyltriethylgermane were prepared and characterized. *n*-Octadecyldiphenyl-2-phenylethylgermane was prepared *via* two independent routes from diphenyl-2-phenylethylgermyllithium and *n*-octadecyl bromide or from *n*-octadecyldiphenylgermyllithium and 2-phenylethyl bromide.

The cleavage of tetraethylgermane was investigated under a variety of experimental conditions. When lithium wire or lithium dispersion was employed, there was little evidence of reaction; but when sodium-potassium alloy was used, it appeared that triethylgermylpotassium was formed but immediately reacted in some unknown manner with the solvent. Attempts were also made to cleave other R_4Ge and $R_3R'Ge$ compounds.

The only trialkylgermylmetallic compound which has been successfully synthesized and characterized is triethylgermylpotassium,¹ prepared from hexaethylgermane and potassium in ethylamine.

Triphenylgermylmetallic reagents have been more completely investigated. Kraus and Foster²

cleaved hexaphenyldigermane with sodium in ammonia, forming triphenylgermylsodium. Triphenylgermyllithium was prepared initially by the cleavage of triethylsilyltriphenylgermane in ethylamine.³ The preparation of triphenylgermyl-

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

(3) C. A. Kraus and W. K. Nelson, *J. Am. Chem. Soc.*, **56**, 195 (1934).

(1) C. A. Kraus and E. A. Flood, *J. Am. Chem. Soc.*, **54**, 1635 (1932).

potassium and -lithium, *via* the cleavage of hexaphenyldigermene in ethylene glycol dimethyl ether or in diethyl ether in the presence of catalytic amounts of tetrahydrofuran or bromobenzene, have been reported more recently.⁴ These investigators also found they could cleave tetraphenyldigermene under essentially the same conditions.⁵

A review of the preparation of the corresponding silylmetallic compounds has appeared,⁶ as well as a summary of the authors' attempts to prepare trialkylsilylmetallic compounds by the metallic cleavage of hexaalkyldisilanes and trialkyltriaryldisilanes. Inasmuch as the germanium-carbon bond energy is less than the silicon-carbon bond energy, 63 kcal/mole^{7a} vs. 68 kcal/mole,^{7b} it was felt that a trialkylgermylmetallic compound might be prepared where efforts to synthesize the corresponding silylmetallic compounds had been only partially successful.

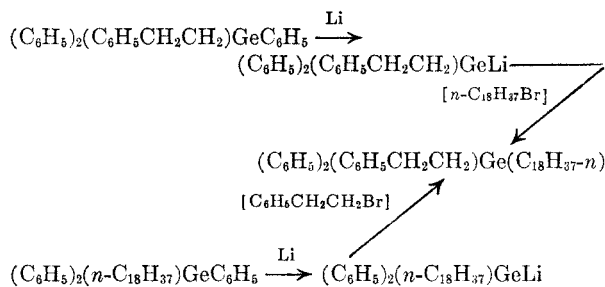
Tetraethylgermane was prepared from germanium tetrabromide and ethylmagnesium bromide according to published procedures¹ in yields varying from 35 to 80% of the theoretical. Hexaethyldigermene was isolated as a by-product during the preparation of the tetrasubstituted compound.⁸ Maximum yield of the digermene was 8%. Substitution of germanium tetrachloride for the tetrabromide did not alter the yield of products significantly. However, the use of ethyllithium rather than the Grignard reagent did affect the course of the reaction radically, giving rise to only a 12% yield of tetraethylgermane and 8.6% of hexaethyldigermene in addition to a large amount of unidentified polymeric material.

Attempts to cleave tetraethylgermane using lithium wire or lithium dispersion proved unsuccessful, a high recovery of starting material being realized. A variety of solvents as well as a number of initiators was investigated. When sodium-potassium alloy was employed as cleaving agent, there was no recovery of starting material. Cleavage may have occurred followed by immediate reaction of the germylpotassium reagent with the solvent, but none of these possible products were isolated. The results of these attempted cleavages are summarized in Tables I and II.

The cleavage of tetra-*n*-butyl-, tetra-*n*-octyl-, tetrabenzyl-, and tetrakis(2-phenylethyl)germane was also investigated.

Another approach to the preparation of trialkyl-

germylmetallic reagents involved the step-wise cleavage of phenyl groups from a tetrasubstituted germane with lithium in ethylene glycol dimethyl ether and derivatization of the germyllithium intermediates so formed with alkyl halides. *n*-Octadecyltriphenylgermane and triphenyl-2-phenylethylgermane were prepared and cleaved, followed by addition of 2-phenylethyl bromide and *n*-octadecyl bromide, respectively, to give *n*-octa-



decyldiphenyl-2-phenylethylgermane. However, the yields were too low to make the process synthetically attractive. An attempt to cleave tri-*n*-hexylphenylsilane was unsuccessful.

n-Butyltriethylgermane, benzyltriethylgermane, and 2-biphenyltriethylgermane were prepared from chlorotriethylgermane and the appropriate organometallic reagent and their physical properties determined so the compounds could serve as reference materials.

EXPERIMENTAL⁹

Tetraethylgermane. The technique of Kraus and Flood¹ was used, employing ethylmagnesium bromide and germanium tetrabromide in diethyl ether. In nine preparations, the yield varied from 35 to 80% of the theoretical with an average yield of 50%. In the later runs, hexaethyldigermene,¹ b.p. 61–62° (0.007 mm.), *n*_D²⁰ 1.4960, was isolated in about 8% yield.

The use of ethyllithium, in hopes of increasing the yield of the digermene, resulted in low yields of both tetraethylgermane (12%) and hexaethyldigermene (8.6%) in addition to a large amount of polymeric material.¹⁰

n-Butyltriethylgermane. To a stirred solution of 5.6 g. (0.029 mole) of chlorotriethylgermane in ether was added 0.032 mole of *n*-butyllithium.¹¹ A white solid appeared suspended in the liquid shortly after addition was begun and heat was evolved. After addition was complete, the mixture was stirred overnight.

Hydrolysis was effected with ice water, and the aqueous layer was separated and extracted three times with ether before being discarded. Distillation of the organic material, after drying over sodium sulfate, afforded 3.93 g. of crude product, b.p. 175–182°. Redistillation gave 3.21 g. (51.1%) of pure *n*-butyltriethylgermane, b.p. 181–181.5°, *n*_D²⁰ 1.4475.

(9) All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen in sodium-dried solvents. Melting and boiling points reported herein are uncorrected.

(10) O. H. Johnson and D. M. Harris, *J. Am. Chem. Soc.*, **72**, 5564 (1950), report 60% yields of hexaphenyldigermene from germanium tetrachloride and phenylmagnesium bromide.

(11) 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 C. W. Gerow, *J. Am. Chem. Soc.*, **77**, 5509 (1955); *J. Am. Chem. Soc.*, **77**, 5740 (1955).

(5) H. Gilman and C. W. Gerow, *J. Am. Chem. Soc.*, **77**, 4675 (1955).

(6) H. Gilman, R. K. Ingham, and A. G. Smith, *J. Org. Chem.*, **18**, 1743 (1953). See also A. G. Brook, *Chem. in Can.*, **43** (1955).

(7) (a) M. L. Huggins, *J. Am. Chem. Soc.*, **75**, 4123 (1953). (b) M. L. Huggins, *J. Am. Chem. Soc.*, **75**, 4126 (1953).

(8) See some recent related studies by Seyferth, *J. Am. Chem. Soc.*, **79**, 2738 (1957).

Anal. Calcd. for $C_{10}H_{24}Ge$: Ge, 33.51. Found: Ge, 33.28.

Benzyltriethylgermane. To a stirred solution of 5.8 g. (0.03 mole) of chlorotriethylgermane in ether was added 0.033 mole of benzylmagnesium chloride. A solid formed and a small amount of heat⁶ was generated during the addition. Work-up as described above resulted in the isolation of 5.94 g. (79%) of benzyltriethylgermane, b.p. 78–81° (1.0 mm.), n_D^{20} 1.5178.

Anal. Calcd. for $C_{13}H_{22}Ge$: Ge, 28.97. Found: Ge, 29.15.

2-Biphenyltriethylgermane. An ethereal solution of 0.067 mole of 2-biphenyllithium was added to 11.5 g. (0.059 mole) of chlorotriethylgermane at such a rate as to maintain gentle reflux. After addition was complete, the mixture was stirred at reflux for 12 hr. before being hydrolyzed and worked up. Two distillations of the organic material afforded 11.5 g. (62.4%) of 2-biphenyltriethylgermane, b.p. 150–152° (3.3 mm.), n_D^{20} 1.5697.

Anal. Calcd. for $C_{18}H_{24}Ge$: Ge, 23.20. Found: Ge, 23.06, 23.00.

Attempted cleavage of tetraethylgermane. (a) With lithium wire. Seven attempts were made to cleave tetraethylgermane using lithium wire under a variety of conditions.

Color Test I¹² was taken at regular intervals and was usually negative. Sometimes toward the end of the extended cleavage reactions, the Color Test was weakly positive, possibly indicative of the formation of triethylgermyllithium and ethyllithium which would be expected to exhibit a positive Color Test; but in light of the high recovery of starting material, this could also have been due to the presence of very finely subdivided lithium metal which is known to give a weak Color Test I.

The results are summarized in Table I.

TABLE I

ATTEMPTED CLEAVAGE OF TETRAETHYLGERMANE WITH LITHIUM WIRE IN ETHYLENE GLYCOL DIMETHYL ETHER

Run	Initiator	Reaction Time, Hr.	Temp., °C.	Derivatizing Agent	Recovery of Et_4Ge , %
1	...	8	25	H ₂ O	72
2	...	12	80	H ₂ O	72
3	...	48	80	H ₂ O	35
4	...	60	80	(C ₆ H ₅) ₃ SiCl	0
5	Tetrahydrofuran	8	80	H ₂ O	70
6	Bromobenzene	30	80	H ₂ O	72
7	Ethyl bromide	30	80	H ₂ O	50

(b) *With lithium dispersion.* A mixture of 5 ml. (4.9 g., 0.026 mole) of tetraethylgermane and 0.38 g. (0.055 g.-atom) of lithium contained in 1.27 g. of a lithium dispersion in xylene (courtesy of Lithium Corporation of America) and 40 ml. of xylene was stirred for 4 days at room temperature. A brown color developed in the solution during this time.

Addition of excess *n*-butyl bromide caused gentle refluxing. Following hydrolysis with water and the usual work-up, fractional distillation failed to yield any identifiable material.

(c) *With sodium-potassium alloy.* Nineteen attempts were made to cleave tetraethylgermane with sodium-potassium alloy using a variety of solvents, reaction times and temperatures, and initiators. In most cases colors were observed during the reaction and work-up, but no material isolated was identified. It is possible that triethylgermylpotassium

formed and immediately reacted in some unknown manner with the solvent or initiator, where one was used.

The sodium-potassium alloy contained sodium and potassium in the ratio of 1 to 5 by weight. In some of the first reactions, the excess alloy was amalgamated with mercury before derivatization, but later runs were treated with a large excess of derivatizing agent in lieu of amalgamation.

In all reactions, 5 ml. (4.9 g., 0.026 mole) of tetraethylgermane, 5 ml. of solvent, and 4 ml. of Na-K alloy (0.08 g.-atom of potassium) were stirred together. During the first 30 min. an additional 25 ml. of solvent was added as well as 0.5 ml. of initiator, where one was used. Following the usual work-up, final distillation was achieved through a 4-in. Vigreux column.

The details of the reactions are summarized in Table II.

TABLE II

ATTEMPTED CLEAVAGE OF TETRAETHYLGERMANE WITH SODIUM-POTASSIUM ALLOY

Run	Solvent ^a	Initiator	Reaction Time, hr.	Temp., °C.	Derivatizing Agent
1	Et ₂ O	...	1	25	(C ₆ H ₅) ₃ SiCl
2	Et ₂ O	...	24	25	(C ₆ H ₅) ₃ SiCl
3	Et ₂ O	...	36	35	H ₂ O
4	Et ₂ O	...	72	25	(C ₆ H ₅) ₃ SiCl
5	Et ₂ O	Bromobenzene	12	25	(C ₆ H ₅) ₃ SiCl
6	GDME ^b	...	144	85	H ₂ O
7	GDME	Bromobenzene	108	25	<i>n</i> -C ₄ H ₉ Br
8	GDME	Bromobenzene	48	85	<i>n</i> -C ₄ H ₉ Br
9	GDME	Bromobenzene	96	85	H ₂ O
10	(<i>n</i> -C ₄ H ₉) ₂ O	...	100	140	<i>n</i> -C ₄ H ₉ Br
11	Benzene	...	168	75	<i>n</i> -C ₄ H ₉ Br
12	Xylene	...	48	135	<i>n</i> -C ₄ H ₉ Br
13	Xylene	...	48	135	C ₆ H ₅ CH ₂ Cl
14	Dioxane	...	72	100	<i>n</i> -C ₄ H ₉ Br
15	Et ₃ N	...	2.5	25	<i>n</i> -C ₄ H ₉ Br
16	Et ₃ N	...	72	25	<i>n</i> -C ₄ H ₉ Br
17	Et ₃ N	...	2	25	(C ₆ H ₅) ₃ SiCl
18	Et ₃ N	...	2	25	(C ₆ H ₅) ₃ -GeCl
19	THF ^c	...	2	25	<i>n</i> -C ₄ H ₉ Br

^a Recent studies by Dr. M. V. George of this laboratory indicate tetrahydrofuran may be a better solvent for the cleavage reactions inasmuch as it exhibits greater stability toward cleavage by silylmetallic intermediates. ^b Ethylene glycol dimethyl ether. ^c Tetrahydrofuran.

*Cleavage of tetra-*n*-butylgermane. (Attempted). (a) With lithium.* After a mixture of 6.02 g. (0.02 mole) of tetra-*n*-butylgermane, 1.2 g. (0.173 g.-atom) of lithium and 10 ml. of ethylene glycol dimethyl ether had been stirred for 96 hr. the mixture was black, but Color Test I was negative. Water was added to hydrolyze the mixture; the black color was dissipated and heat was evolved. Distillation of the residue which remained after the usual work-up and removal of solvents afforded 5.52 g. (92%) of starting material boiling 110–113° (0.7 mm.).

(b) *With sodium-potassium alloy.* After a mixture of 3.01 g. (0.01 mole) of tetra-*n*-butylgermane, 1.1 ml. (0.022 g.-atom of potassium) of sodium-potassium alloy and 20 ml. of ethylene glycol dimethyl ether had been stirred 115 hr., the alloy was still bright and the mixture slightly grey. The alloy was amalgamated and the suspension transferred to an addition funnel; thereafter, it was added rapidly to 5.9 g. (0.02 mole) of chlorotriphenylsilane dissolved in the same

solvent. There was no evidence of reaction. After stirring overnight, water was added and the mixture worked up as usual. The residue remaining after removal of the ether was washed with petroleum ether (b.p. 60–70°) to give 5.3 g. of insoluble solid melting over the range of 148–155°. This was recrystallized from the same solvent to give 3.6 g. (66%) of triphenylsilanol (mixture m.p.) melting 155–157°. The original petroleum ether filtrate was distilled to give 3.0 g. (100%) of starting material, boiling 148° (11 mm.).

*Cleavage of Tetra-*n*-octylgermane. (Attempted).* After stirring a mixture of 5.3 g. (0.01 mole) of tetra-*n*-octylgermane, 1.3 g. (0.186 g.-atom) of lithium and 10 ml. of ethylene glycol dimethyl ether for 18 hr., a reddish color had developed and Color Test I was positive; after 67 hr. the red solution was pipetted into a dropping funnel and added to 7.7 g. (0.02 mole) of bromotriphenylgermane dissolved in 25 ml. of GDME. The red color was dissipated immediately. After stirring for 4 hr., water was added and the mixture was extracted with ether and filtered to give 2.6 g. of solid melting at 186–189°. The ether solution was dried and the solvents distilled to leave a residue which was washed with petroleum ether (b.p. 60–70°) to give 2.5 g. of insoluble solid melting over the range 160–188°. The two solids were recrystallized from chloroform-petroleum ether (b.p. 60–70°) to yield 4.3 g. (68%) of hexaphenyldigermoxane, melting 184–185°. The original ether filtrate was distilled to give 3.57 g. (67%) of starting material, b.p. 223° (0.015 mm.).

Cleavage of tetrabenzylgermane. (Attempted). Five g. (0.0114 mole) of tetrabenzylgermane, 0.8 g. (0.12 g.-atom) of lithium and 10 ml. of ethylene glycol dimethyl ether were stirred for 3 min., a red-brown color developing, accompanied by evolution of heat. After stirring 5 hr. Color Test I was positive so the mixture was pipetted into a dropping funnel and added to 2.54 g. (0.023 mole) of ethyl bromide. Heat was generated and the dark color dissipated. After stirring overnight, water was added, and the mixture worked up as usual. Distillation of the material remaining after removal of solvents gave fractions having the following boiling ranges: 212–216° (0.08 mm.), 216–221° (0.08 mm.), below 186° (0.005 mm.), and 186–198° (0.005 mm.). No tribenzylethylgermane¹³ was isolated.

Cleavage of tetrakis(2-phenylethyl)germane. (Attempted). After stirring a mixture of 4.9 g. (0.01 mole) of tetrakis(2-phenylethyl)germane, 1.3 g. (0.19 g.-atom) of lithium and 25 ml. of ethylene glycol dimethyl ether for 68 hr., the color was dark brown and Color Test I was positive. The solution was pipetted into a dropping funnel and added rapidly to 5.9 g. (0.02 mole) of chlorotriphenylsilane dissolved in GDME. Heat was evolved and the dark color dissipated. After stirring overnight, water was added and the mixture extracted with ether. The ether was dried and the solvents distilled to leave a residue which gave 5.1 g. (97%) of triphenylsilanol, m.p. 142–149°. Recrystallization from petroleum ether (b.p. 60–70°) gave 4.5 g., m.p. 151–153°. The original petroleum ether filtrate was distilled to give 4.8 g. (100%) of crude starting material, m.p. 42–44°. Recrystallization from ethyl alcohol gave 3.8 g. of pure starting material, m.p. 48.5–50°.

Triphenyl-2-phenylethylgermane. To a stirred solution of 7.4 g. (0.04 mole) of 2-phenylethyl bromide in 35 ml. of ethylene glycol dimethyl ether was added a 60-ml. solution of triphenylgermyllithium, prepared from 12.14 g. (0.02 mole) of hexaphenyldigermene in GDME.⁴ Ten min. after addition was complete, Color Test I was negative. The mixture was hydrolyzed with 100 ml. of a saturated ammonium chloride solution. A white solid which separated at the interface was filtered off before the aqueous layer was separated, extracted three times with ether and discarded. This white material weighed 16.19 g. and melted over the range 143–146°. Two recrystallizations from petroleum ether (b.p. 60–70°) gave 9.83 g. (60%) of triphenyl-2-phenylethylgermane, m.p. 147–149°. Reduction in volume of the

mother liquor resulted in the isolation of another 1.7 g. (10.6%) of product.

Anal. Calcd. for C₂₈H₂₄Ge: C, 76.34; H, 5.91. Found: C, 76.38, 76.24; H, 6.08, 5.95.

Another run, exactly as above except that the triphenylgermyllithium from 0.03 mole of hexaphenyldigermene was interacted with 0.06 mole of 2-phenylethyl bromide, resulted in the isolation of 24 g. of crude product. One recrystallization from ethanol gave 18 g. (73%) of triphenyl-2-phenylethylgermane.

**n*-Octadecyltriphenylgermane.* To a stirred solution of 20.0 g. (0.06 mole) of *n*-octadecyl bromide in 60 ml. of ethylene glycol dimethyl ether was added an 80-ml. solution of triphenylgermyllithium prepared from 0.03 mole of hexaphenyldigermene in GDME.⁴ The reaction mixture warmed slightly during the addition and 5 min. after addition was complete, Color Test I was negative. The mixture was hydrolyzed with 100 ml. of saturated ammonium chloride solution and the solid which appeared at the interface was filtered off. This material weighed 28.78 g. and melted from 76 to 79°. Recrystallization of this solid from ethanol gave 23.29 g. (70%) of pure *n*-octadecyltriphenylgermane, m.p. 76.5–77.5°. Several grams of less pure material was isolated upon concentration of the mother liquor. A mixture m.p. with an authentic sample¹⁴ was not depressed.

**n*-Octadecyldiphenyl-2-phenylethylgermane. (a) From *n*-octadecyldiphenylgermyllithium and 2-phenylethyl bromide.* A mixture of 11.13 g. (0.02 mole) of *n*-octadecyltriphenylgermane, 50 cm. (1.5 g., 0.22 g.-atom) of finely cut lithium wire and 15 ml. of ethylene glycol dimethyl ether was stirred for 5 hr. Shortly after stirring was begun, a green color developed to be gradually replaced by a red-brown color as cleavage proceeded and an additional 35 ml. of GDME was added. At the end of the cleavage period, Color Test I was positive and the reagent was pipetted into an addition funnel.

The germyllithium reagent was added over a 10-min. period to a stirred solution of 3.7 g. (0.02 mole) of 2-phenylethyl bromide in 40 ml. of GDME. Color Test I was negative immediately upon completion of addition. The mixture was hydrolyzed with a saturated ammonium chloride solution and worked up in the usual manner. After removal of all the solvents, there remained an oil. Distillation resulted in the recovery of 2.37 g. (21%) of starting material and 1.19 g. of solid, m.p. 34–36°. Recrystallization of this waxy solid from methanol gave 1.03 g. (17.6% based on unrecovered starting material) of *n*-octadecyldiphenyl-2-phenylethylgermane, m.p. 34.5–36°.

Anal. Calcd. for C₂₈H₃₆Ge: Ge, 12.40. Found: Ge, 12.98, 12.47.

An infrared spectrum of the compound, as a carbon disulfide solution, had bands at 3.3, 3.5, and 9.2 μ , characteristic of aromatic C—H, aliphatic C—H and the germanium—phenyl bonds, respectively.

*(b) From diphenyl-2-phenylethylgermyllithium and *n*-octadecyl bromide.* A mixture of 4.09 g. (0.01 mole) of triphenyl-2-phenylethylgermane, 75 cm. (2.25 g., 0.32 g.-atom) of finely cut lithium wire and 10 ml. of GDME was stirred for 3.5 hr. About 10 min. after stirring was begun, a yellow-green color developed and was gradually replaced by a red-brown color as cleavage progressed and an additional 40 ml. of GDME was added. At the end of the cleavage period, the germyllithium reagent was pipetted into an addition funnel and added slowly to a stirred solution of 3.33 g. (0.01 mole) of *n*-octadecyl bromide in GDME. Immediately after addition was complete, Color Test I was negative. Hydrolysis was effected with a saturated ammonium chloride solution and the usual method of work-up was employed. Distillation of the material remaining after the solvents had been stripped off resulted in the recovery of a

(13) H. Bauer and K. Burschkes, *Ber.*, **67**, 1041 (1934).

(14) H. Gilman and C. W. Gerow, *J. Am. Chem. Soc.*, **79**, 342 (1957).

small amount of *n*-octadecyl bromide, 2.74 g. (67%) of unreacted triphenyl-2-phenylethylgermane and 0.63 g. of product boiling over the range 180–185° at 0.005 mm. Recrystallization of this latter fraction from methanol gave 0.5 g. (28.6%) based on unrecovered starting material) of *n*-octadecyldiphenyl-2-phenylethylgermane, m.p. and mixture m.p. 34.5–35.5°.

*Cleavage of tri-*n*-hexylphenylgermane. (Attempted).* A mixture of 2.03 g. (0.005 mole) of tri-*n*-hexylphenylgermane, 0.3 g. (0.043 g.-atom) of lithium and 7 ml. of ethylene glycol dimethyl ether was stirred for 24 hr. to yield a deep red solution giving a positive Color Test I. The solution was pipetted into a dropping funnel and added to 1.7 g. (0.01 mole) of *n*-hexyl bromide dissolved in 20 ml. of GDME. After stirring 5 min., Color Test I was negative. Water was added and the mixture extracted with ether. The ether portions were dried and the solvents distilled to leave a residue

which was distilled under reduced pressure to give 1.3 g. (65%) of starting material, b.p. 186–188° (0.7 mm.), n_D^{20} 1.4959.

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Acid-Catalyzed Addition of Phosphine to Olefins

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Phosphine adds to olefins in the presence of non-oxidizing acid catalysts to give good yields of monoalkylphosphines and small amounts of dialkylphosphines. Reaction takes place readily at 30 to 60° under 20 to 40 atmospheres of phosphine. Because tertiary olefins react most easily, a carbonium ion mechanism seems likely. Nearly stoichiometric amounts of catalyst are needed because monoalkylphosphines react with the catalyst to form monoalkylphosphonium salts.

Phosphine adds to olefins in the presence of acid catalysts.¹ This addition is particularly interesting because phosphine is intermediate in basicity between two other hydrides: hydrogen sulfide and ammonia. Hydrogen sulfide reacts stepwise with olefins in the presence of acid catalysts to yield mercaptans and thioethers.² Because olefins are more basic than hydrogen sulfide or mercaptan, a carbonium ion intermediate can form easily and only a small amount of catalyst is needed. By contrast, no carbonium ion can form in the presence of ammonia. However, weakly basic derivatives of ammonia, such as urea, permit carbonium ions to form and can add to olefins with acid catalysts.³

The addition of phosphine to olefins has therefore been studied to determine qualitatively the relation of phosphine to hydrogen sulfide and ammonia in the presence of acid catalysts. Olefin reactivity was studied with primary, tertiary,⁴ cyclic, and substituted olefins with methanesulfonic acid as catalyst. As catalysts, mineral acids, carboxylic acids, sulfonic acids, hydrogen halides, and Lewis acids were tested with a polypropene as the olefin. The effects of temperature and catalyst

concentration were measured with methanesulfonic acid and a polypropene. Product distribution between mono- and dialkylphosphine was determined with typical olefins.

EXPERIMENTAL

Phosphine was prepared by adding water to a mixture of phosphorus and phosphorus tetraiodide⁵ at 80° and scrubbing the evolved gases with aqueous sodium hydroxide. The scrubbed gases were dried in a coil cooled in Dry Ice and condensed in a pressure vessel cooled in liquid nitrogen. The mass spectrum showed the product to be pure phosphine.

Ten olefins were studied. Propene, dodecene-1, isobutene, and 2-ethylhexene-1 were commercial materials. C₁₂-polypropene was fractionated from a mixture of polypropenes obtained by polymerization with phosphoric acid. This fraction contained about 85% tertiary olefins. Polybutenes were obtained by polymerizing mixed butenes and butanes with aluminum chloride. Fractions containing an average of 26 and 65 carbon atoms were used. Two cyclic olefins, 1-methylcyclopentene-1 and 4-methylcyclohexene-1 were synthesized. A mixture of the two di-isobutene isomers was chlorinated and the product was fractionated to isolate the unsaturated monochloride.

Detailed studies were carried out with C₁₂-polypropene because of its stability toward acids. This stability was demonstrated by stirring a sample with an equimolar amount of methanesulfonic acid for 16 hr. at 85° and distilling the recovered olefins. A plot of the refractive index and boiling point at 5% increment of the distillation showed no significant variation from a similar distillation of untreated C₁₂-polypropylene. Also, no measurable polymeri-

(1) H. C. Brown, U. S. Patent 2,584,112 (1952).

(2) W. A. Proell and W. F. Wolff, U. S. Patent 2,615,786 (1952).

(3) H. C. Brown, U. S. Patent 2,548,585 (1951).

(4) Olefins in which one of the carbon atoms of the double bond is also bonded to two other carbon atoms; isobutene is the simplest example.

(5) W. C. Fernelius, "Inorganic Synthesis, Vol. II", McGraw-Hill Book Co., Inc., New York, New York, 1946, p. 41.