under nitrogen, and the container was purged with nitrogen every 2 days.

Diaryl aminophosphinic acids. The preparation of (3,4-*dichloro-phenylamino)-4'-hydroxybenzylphosphinic* is given as typical example for the synthesis of this class of compounds. Physical properties and analyses of all aminophosphinic acids prepared are shown in Table IV.

The Schiff's base from 3,4-dichloroaniline and *p*-hydroxybenzaldehyde was prepared by boiling equimolar amounts of the reactants in benzene, with azeotropic removal of water, followed by filtration and recrystallization from benzene. To 80 g. (0.3 mole) of this Schiff's base in 200 ml. ethanol heated to 65° was added 21 g. 95% hypophosphorous acid (0.3 mole). The reaction mixture was refluxed for 2.5 hr. The solution was then cooled, 48 g. of 50% sodium hydroxide (0.6 mole) was added dropwise, and the reaction mixture evaporated to dryness on the water bath under vacuum. The residue was agitated with 300 ml. of warm water, cooled, and extracted with ether until the ether layer appeared completely colorless. From eight to nine extractions were required. The aqueous portion was freed from residual ether by heating and bubbling nitrogen through it. After cooling, the aqueous solution was added dropwise, with rapid stirring, to 300 ml. of 3*N* hydrochloric acid. The precipitated phosphinic acid was filtered and redissolved in aqueous sodium hydroxide, the solution again extracted with ether, and the phosphinic acid reprecipitated by adding to aqueous hydrochloric acid as shown above. After filtration, washing with water, and drying *in vacuo* over phosphorus pentoxide 52 g. (52% yield) of a light yellow powder was obtained, m.p. 147–149°.

Long-chain alkylaryl aminophosphinic acids. The preparation of *N-dodecylaminobenzylphosphinic acid* is a typical example, and is given as below: *Method A.* A mixture of 55.5 g. (0.3 mole) dodecylamine and 32 g. benzaldehyde (0.3 mole) in 150 ml. benzene was heated under reflux until the calculated amount of water had separated in the Stark and Dean trap. The solution of the Schiff's base was then cooled to 50°, and 21 g. of 95% hypophosphorous acid (0.3 mole) was added dropwise. The temperature rose to 63° and the color became slightly darker. After 2.5 hr. heating under reflux, the solution became turbid. It was cooled, diluted with three volumes of ether, and allowed to stand overnight at −10°. The precipitate was filtered, redissolved in hot benzene, filtered to remove turbidity, and reprecipitated by dilution with ether and cooling to −10°. After filtration washing with ether, and drying over phosphorus pentoxide, 98 g. (96% yield) of a white crystalline powder was obtained, m.p. (recrystallized from ethanol) 198°.

Method B. Using the same amounts and proportions of reactants as in Method A, the hypophosphorous acid was added to the benzene solution of dodecylamine, followed by addition of benzaldehyde. The mixture was heated under reflux until the calculated amount of water had separated. After cooling, the viscous and turbid reaction mixture was diluted with 3 volumes of ether and worked up as described in Method A. Only 76 g. (75% yield) of phosphinic acid was obtained, m.p. (from ethanol) 197–198°.

Acknowledgment. The authors are indebted to Mrs. B. C. Brown for technical assistance in a portion of this work and to Mr. D. Noel for the bacteriological evaluations.

CHICAGO 9, ILL.

[CONTRIBUTION FROM THE RESEARCH AND ENGINEERING DIVISION, MONSANTO CHEMICAL CO.]

The Dimerization of Vinyl- and Allylsilanes with Trialkylaluminums[1]

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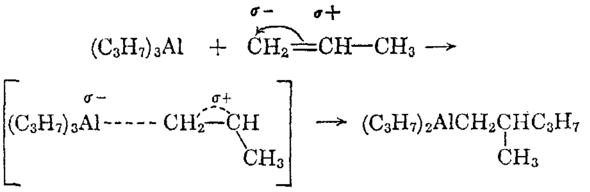
Received January 6, 1961

Vinyl- and allyltriorganosilanes dimerize when heated at 200° with small amounts of triisobutylaluminum. The structures of the dimers from allyltriphenylsilane and vinyltriphenylsilane were established by conversion to saturated products which were compared with material prepared by alternate syntheses.

The dimerization of monoalkyl substituted ethylenes with trialkylaluminums was discovered by Ziegler and associates.[2] A variety of α-olefins can be dimerized to compounds of predictable structure—*i.e.*, propylene to 2-methylpent-1-ene, but-1-ene to 2-ethylhex-1-ene, etc. The probable mechanism for this dimerization[3] involves the approach of the π electrons of the olefinic double bond to the vacant *p* orbital of aluminum of the trialkylaluminum. A concerted shift of one of the alkyl groups attached to aluminum with its pair of electrons to satisfy the developing positive center on carbon and relief of the partial negative center about aluminum results in the formation of a new branched chain substituent on aluminum. The reaction can be represented with tri-*n*-propylaluminum and propylene as below:



$$(C_3H_7)_3Al + \overset{\sigma-}{CH_2}{=}\overset{\sigma+}{CH}-CH_3 \rightarrow$$

$$\left[(C_3H_7)_3\overset{\sigma-}{Al}\text{-----}CH_2\text{--}\overset{\sigma+}{CH}(CH_3)\right] \rightarrow (C_3H_7)_2AlCH_2\underset{CH_3}{\underset{|}{C}}HC_3H_7$$

The displacement of the so formed branched 2-methylpentyl group from aluminum takes place by a similar type approach of propylene toward aluminum but, rather than alkyl migration, transfer of a hydride ion from the tertiary β-carbon center is favored and tri-*n*-propylaluminum and 2-methylpent-1-ene are generated.

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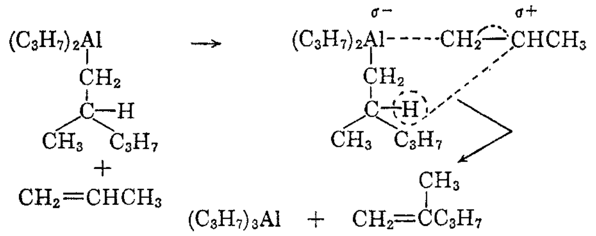
[1] Presented at the Frederick F. Blicke Symposium of the Division of Medicinal Chemistry at the 138th National Meeting of the American Chemical Society, New York N. Y., September 1960.

[2] K. Ziegler, *Angew. Chem.*, 64, 323 (1952).

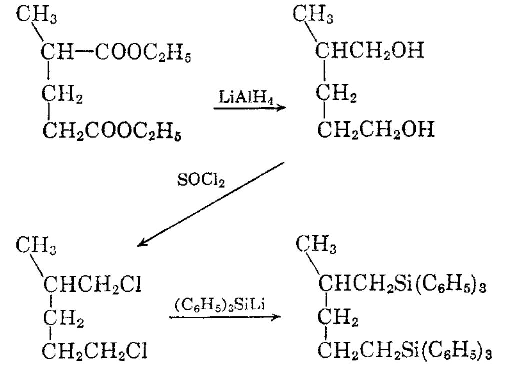
[3] R. Robinson, *Chem. Age (London)*, 74, 997 (1956).



The aluminum trialkyl can be employed in rather low concentrations but strictly speaking is not a true catalyst.

It was of interest to determine if monosubstituted ethylenes which contained atoms other than carbon might not also produce dimers when reacted with trialkylaluminums at elevated temperatures. This paper reports our investigations of the reactions of vinyl- and allylsilanes with triisobutylaluminum. Polymers prepared from olefinically unsaturated silanes with aluminum trialkyl-titanium tetrachloride catalysts have been investigated in these laboratories and also reported by Natta *et al.*[4] In our study, vinyltrimethyl-, vinyltriethyl- and vinyltriphenylsilane as well as allyltrimethyl- and allyltriphenylsilane were dimerized with small amounts of trialkylaluminums. Triisobutylaluminum was employed as the aluminum alkyl reactant since a displacement reaction would generate the desired silicon containing trialkylaluminum and the isobutylene liberated would be inert. Generally, the reactions were conducted at 200° for twelve to twenty-four hours. The lower boiling dimers could be examined by vapor phase chromatography and indicated the reactions to be productive of predominantly single products and not mixtures of several isomeric dimers. The allylsilane dimers appear to be those one would predict from the known art of α-olefins.[5]

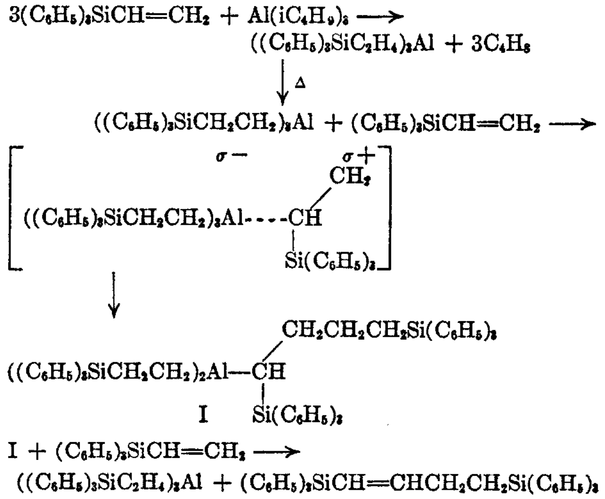
$$2R_3SiCH_2CH{=}CH_2 \xrightarrow{AlR'_3} R_3SiCH_2CH_2CH_2CCH_2SiR_3$$
$$R = \text{methyl, phenyl}$$



The infrared spectra of the allyltriphenylsilane dimer was found to be, allowing for the unsaturation, very similar to 1,5-bis(triphenylsilyl)-2-methylpentane, which was synthesized by an alternate route involving classical reactions. Further evidence for the structure of the allyltriphenylsilane dimer was obtained by an olefin exchange reaction[6] involving the dimer and triisobutylaluminum followed by a cleavage of the resulting carbon-aluminum bond with acetic acid. This resulted in a low yield of material whose infrared spectra was identical to 1,5-bis(triphenylsilyl)-2-methylpentane.

The dimers obtained from the vinylsilanes deviated from those expected in analogy to α-olefins. A closer investigation of the reaction of vinyltriphenylsilane with triisobutylaluminum was therefore made.

The first step in the reaction of vinyltriphenylsilane and triisobutylaluminum involves liberation of isobutylene and formation of tris(triphenylsilylethyl)aluminum. This was established by ethanolysis of the reaction product of the two components which had been heated at 140°, ethyltriphenylsilane being identified as the product. The position of attachment of the aluminum atom in respect to the silicon atom—*i.e.*, α or β—was not established. Examples of the anti-Markownikoff addition of phenyllithium[7] and hydrogen chloride[8] to vinyltriorganosilanes and the mixture of products obtained upon hydroboration of vinyltrimethylsilane[9] suggest the aluminum atom may be attached to either the α or β carbon atom in respect to the silicon atom or more probably is a mixture of both. The displacement of isobutylene from triisobutylaluminum with styrene is known to furnish a mixture in which the aluminum atom is attached to



$$3(C_6H_5)_3SiCH{=}CH_2 + Al(iC_4H_9)_3 \longrightarrow ((C_6H_5)_3SiC_2H_4)_3Al + 3C_4H_8$$

$$I + (C_6H_5)_3SiCH{=}CH_2 \longrightarrow ((C_6H_5)_3SiC_2H_4)_3Al + (C_6H_5)_3SiCH{=}CHCH_2CH_2Si(C_6H_5)_3$$

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(4) G. Natta, G. Mazzonti, P. Longi, and F. Bernardini, *J. Polymer Sci.*, **31**, 181 (1958).

(5) K. Ziegler, H. G. Gellert, K. Zosel, E. Holzkamp, J. Schneider, M. Söll, and W. R. Kroll. *Ann.*, **629**, 121 (1960).

(6) K. Ziegler, H. Martin, and F. Krupp, *Ann.*, **629**, 14 (1960).

(7) L. F. Cason and H. G. Brooks, *J. Am. Chem. Soc.*, **74**, 4582 (1952); *J. Org. Chem.*, **19**, 1278 (1954).

(8) L. H. Sommer, D. L. Bailey, G. M. Goldberg, C. E. Buck, T. S. Bye, F. J. Evans, and F. C. Whitmore, *J. Am. Chem. Soc.*, **76**, 1613 (1954).

(9) D. Seyferth, *J. Am. Chem. Soc.*, **81**, 1844 (1959).

both the α- and β-carbon atoms.[10] It was not important to this study to determine the position of attachment as, under the dimerization reaction conditions (200°), the aluminum atom behaved as if it were attached to the terminal carbon atom.[11]

When vinyltriphenylsilane reacted with tris(triphenylsilylethyl)aluminum at 200°, 1,4-bis(triphenylsilyl)but-1-ene was the dimer obtained. The saturation of the double bond was accomplished by "hydroalumination" followed by cleavage of the carbon-aluminum bond with butanol. The 1,4-bis(triphenylsilyl)butane obtained in this manner was identical to that obtained from the reaction of 1,4-dichlorobutane and triphenylsilyllithium and completely different from 1,3-bis(triphenylsilyl)butane. We therefore are lead to believe that 1,4-bis(silyl)but-1-enes are formed when vinylsilanes are dimerized with alkylaluminums.

EXPERIMENTAL

All boiling points and melting points are uncorrected values. Reactions involving aluminum alkyls were conducted in thoroughly dried, nitrogen filled, and blanketed reactors. Vinyltrimethylsilane was purchased[12] material which was redistilled [b.p. 55° (741 mm.)] vinyltriphenylsilane [b.p. 180–190° (1.3–1.5 mm.)] was prepared from triphenylchlorosilane[13] and the vinyl Grignard reagent[14]; vinyltriethylsilane [b.p. 144–145 (743 mm.)] from vinyltrichlorosilane and the ethyl Grignard reagent; allyltrimethylsilane [b.p. 80–84° (747 mm.)] from trimethylchlorosilane[13] and the allyl Grignard reagent[15]; and allyltriphenylsilane [b.p. 176–178° (0.3 mm.) from triphenylchlorosilane[13] and the allyl Grignard reagent.[15]

1,4-Bis(trimethylsilyl)but-1-ene. A mixture of vinyltrimethylsilane (50 g.; 0.5 mole) and triisobutylaluminum (2 g.; 0.01 mole) was heated in a sealed reactor at 200° for 12 hr. The cooled reaction mixture was diluted with about an equal volume of ether and then shaken out with a 25-ml. portion of 10% sulfuric acid followed by two 20-ml. portions of water. The ether solution was dried over anhydrous magnesium sulfate and the solvent removed by distillation. The dimer, b.p. 81–83° (17 mm.), was obtained in 64% yield; n_D^{25} 1.4354.

Anal. Calcd. for $C_{10}H_{24}Si_2$: C, 59.90; H, 12.07; Si, 28.02. Found: C, 59.97; H, 12.08; Si, 27.52.

1,4-Bis(trimethylsilyl)but-1-ene. A mixture of vinyltriethylsilane (25 g.; 0.175 mole) and triisobutylaluminum (1 g.; 0.05 mole) was heated at reflux. Initially the pot temperature at reflux was 145°, but gradually increased so that after 60 hr. heating, no reflux was noted when the pot was maintained at 200°. The reaction mixture was worked up as described above. The dimer, b.p. 171–173° (15 mm.); n_D^{25} 1.4653, was obtained in 56% yield.

Anal. Calcd. for $C_{16}H_{32}Si_2$: C, 67.57; H, 12.76; Si, 19.76; mol. wt., 284.6. Found: C, 67.70; H, 12.92; Si, 19.58; mol. wt., (freezing point in benzene) 285.

2-Triphenylsilylmethyl-5-triphenylsilylpent-1-ene. A mixture of allyltrimethylsilane (95 g.; 0.83 mole) and triisobutylaluminum (5 g.; 0.025 mole) was heated in a sealed reactor at 200° for 27 hr. The mixture was distilled and 65 g. (68%) of dimer, b.p. 96–100° (14 mm.), was obtained. An analytical sample was redistilled; b.p. 109–110° (22 mm.); n_D^{25} 1.4439.

Anal. Calcd. for $C_{12}H_{28}Si_2$: C, 63.07; H, 12.35; mol. wt., 228.5. Found: C, 63.25; H, 12.25; mol. wt. (freezing point in benzene) 228.

1,4-Bis(triphenylsilyl)but-1-ene. A mixture of vinyltriphenylsilane (28.6 g.; 0.1 mole) and triisobutylaluminum (1 g.; 0.005 mole) was heated at 195°. As the silane melted foaming and gas evolution was noted which would be indicative of an olefin exchange reactions.[6] After heating at 195° for 24 hr., the reaction mixture solidified at reaction temperature. The reaction mixture was quenched by a short heating period with 50 ml. of ethanol at reflux and allowed to cool. The crystalline solid was separated by filtration and recrystallized from benzene. There was obtained 18 g. (64%) of colorless, crystalline product, m.p. 240°.

Anal. Calcd. for $C_{40}H_{36}Si_2$: C, 83.88; H, 6.33; Si, 9.82. Found: C, 83.86; H, 6.37; Si, 10.09.

2-Triphenylsilylmethyl-5-triphenylsilylpent-1-ene. Allyltriphenylsilane (57 g.; 0.188 mole) and triisobutylaluminum (2 g.; 0.01 mole) were heated together at 200°. Initially a short period of effervescence of liberated isobutylene was noted. After heating for 24 hr., the cooled mixture was taken up in the minimum amount of ether. Chilling the ether solution in Dry Ice furnished 27 g. of crude dimer, m.p. 99–101°. Recrystallizations from ethanol furnished 20 g. (36%) of dimer, m.p. 108°.

Anal. Calcd. for $C_{42}H_{40}Si_2$: C, 83.93; H, 6.71; Si, 9.35. Found: C, 84.03; H, 6.80; Si, 9.11.

3-(Trimethylsilyloxy)-1-chlorobutane. A solution of 4-chlorobutan-2-ol[16] (21.6 g.; 0.2 mole), trimethylchlorosilane (21.6 g.; 0.2 mole) and 200 ml. of dry benzene was treated with anhydrous ammonia until the odor of ammonia persisted in the reaction mixture. The precipitated ammonium chloride was separated by filtration. Distillation of the filtrate furnished 20.2 g. (56%) of the silyl ether, b.p. 59–60° (21 mm.); n_D^{25} 1.4174.

Anal. Calcd. for $C_7H_{17}ClOSi$: C, 46.50; H, 9.48; Cl, 19.62. Found: C, 46.00; H, 9.35; Cl, 19.48.

3-Hydroxybutyltriphenylsilane. A solution of 3-(trimethylsilyloxy)-1-chlorobutane (3.6 g.; 20 mmole) in 20 ml. of tetrahydrofuran was treated dropwise with 20 mmoles of triphenylsilyllithium[17] in tetrahydrofuran. Upon completion of the addition the test for organolithium compound[18] was negative. The tetrahydrofuran was removed by distillation and the residue treated with 50 ml. of ether followed by 30 ml. of water and 10 ml. of concentrated hydrochloric acid and the mixture agitated for 24 hr. The two phases were separated and the organic phase dried. Evaporation of solvent furnished a solid residue which yielded 5.5 g. (83%) of crystalline solid, m.p. 105–106° when recrystallized from isooctane.

Anal. Calcd. for $C_{22}H_{24}OSi$: C, 79.45; H, 7.28. Found: C, 79.28; H, 7.36.

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(10) (a) G. Natta, P. Pino, G. Mazzonti, P. Longi, and F. Bernardini, *J. Am. Chem. Soc.*, **81**, 2561 (1959). (b) L. I. Zakharkin and V. V. Gavrilenki, *Izvest. Akad. Nauk. S.S.S.R., Otdel. Khim. Nauk.*, 1507 (1959).

(11) This would be the position of most expected stability. Migration of aluminum atoms attached to internal carbon atoms of straight chain hydrocarbons have been observed by others at elevated temperature [see L. I. Zakharkin and O. Yu. Okhlobystin, *Izvest. Akad. Nauk., S.S.S.R., Otdel. Khim. Nauk.*, 1278 (1958)].

(12) Available from Peninsular Chemical Co., Gainesville, Fla.

(13) Purchased from the Dow-Corning Corp., Midland, Mich.

(14) H. Normant, *Compt. Rend.*, **239**, 1510 (1954).

(15) M. S. Karasch and C. F. Fuchs, *J. Org. Chem.*, **9**, 359 (1944).

(16) F. Sondheimer and R. B. Woodward, *J. Am. Chem. Soc.*, **75**, 5438 (1953).

(17) H. Gilman and G. D. Lechtenwalter, *J. Am. Chem. Soc.*, **80**, 608 (1958).

(18)(a) H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925); (b) G. Wittig, *Angew. Chem.*, **53**, 243 (1940).

3-Chlorobutyltriphenylsilane. An equimolar mixture of 3-hydroxybutyltriphenylsilane and pyridine (30 mmoles) was treated dropwise with thionyl chloride (30 mmoles) and then heated for 20 min. on a steam bath. The reaction mixture was diluted with 50 ml. of benzene and then shaken out with two 10-ml. portions of dilute hydrochloric acid and finally with water. The benzene was removed by distillation and the resulting crude solid taken up in hexane and chromatographed on alumina, hexane being used as eluent. The product was recrystallized from methanol and 8 g. (76%) of solid, m.p. 73.5–74° resulted.

Anal. Calcd. for $C_{22}H_{23}ClSi$: C, 75.30; H, 6.59. Found: C, 75.08; H, 6.60.

1,3-Bis(triphenylsilyl)butane. 3-Chlorobutyltriphenylsilane (10 mmoles) in 10 ml. of tetrahydrofuran was treated with triphenylsilyllithium[17] (10 mmoles) in tetrahydrofuran. The test for organolithium compound[18] was negative immediately following the addition. The tetrahydrofuran was removed by distillation and the residue recrystallized from isobutanol. There was obtained 3.8 g. (67%) of product, m.p. 163–164°.

Anal. Calcd. for $C_{40}H_{38}Si_2$: C, 83.55; H, 6.66. Found: C, 83.06; H, 6.86.

1,4-Bis(triphenylsilyl)butane. 1,4-Dichlorobutane (15 mmoles) reacted with triphenylsilyllithium[17] (30 mmoles) in tetrahydrofuran. The tetrahydrofuran was removed by distillation and the residue suspended in 200 ml. of ether. The ether suspension was shaken out with water, dried, and the ether removed by distillation. Recrystallization of the resulting crude product from hexane resulted in 5.5 g. (64%) of pure product, m.p. 215–216° (reported[19] m.p. 215–216°).

1,4-Bis(triphenylsilyl)butane from the vinyltriphenylsilane dimer. A mixture of 1,4-bis(triphenylsilyl)but-1-ene (3.5 g., 6 mmoles) in 50 ml. of *o*-xylene was treated with triisobutylaluminum (2 g.; 10 mmoles) and the resulting mixture heated to reflux. As reflux temperature was approached, isobutylene was liberated and evolution persisted for about 5 min. at reflux temperature. The mixture was refluxed for an additional 15 min. after evolution of gas had terminated. The cool reaction mixture was treated with 2 ml. of isobutyl alcohol and additional gas was evolved. A crystalline solid separated and recrystallization from benzene furnished 2.2 g. (63%) of 1,4-bis(triphenylsilyl)butane, m.p. 215–216°.[19] A mixed melting point with the sample of 1,4-bis(triphenylsilyl)butane prepared as above melted at 215–216° and the infrared spectra of the two samples were identical.

α-Methylglutaric acid and ethyl α-methylglutarate. Ethyl methylmalonate was treated with methyl acrylate as described by Floyd and Miller.[20] The triester product was distilled [b.p. 110–120° (0.8–1.0 mm.)] and this product was heated at reflux for 12 hr. with 12*N* hydrochloric acid. The α-methylglutaric acid was obtained by thermally decarboxylating the tricarboxylic acid and distilled at 190–205° (20 mm.) [reported[21] b.p. 222° (61 mm.). α-Methylglutaric acid was esterified with ethanol employing anhydrous hydrogen chloride as a catalyst. The ethyl α-methylglutarate distilled at 124–130° (18 mm.), n_D^{25} 1.4220 [reported[22] b.p. 122–125° (15 mm.)].

Anal. Calcd. for $C_{10}H_{18}O_4$: C, 59.38; H, 8.97. Found: C, 59.33; H, 9.12.

2-Methyl-1,5-pentanediol. Lithium aluminum hydride (0.4 mole) in 100 ml. of anhydrous ether was treated with a solution of ethyl α-methylglutarate (0.3 mole) in 200 ml. of anhydrous ether. An additional 100 ml. of ether was added to the reaction mixture and it was refluxed for 2 hr. The mixture was hydrolyzed with 50 ml. of 10% sulfuric acid and 100 ml. of water. The aqueous layer was separated, saturated with sodium chloride, and continuously extracted with methylene chloride. Evaporation of the dried original ether layer and the methylene chloride extracts furnished an oil which was distilled. The diol was collected at 143–145° (19 mm.), n_D^{25} 1.4511, weight 18.5 g. (53% yield).

Anal. Calcd. for $C_6H_{14}O_2$: C, 60.95; H, 11.94. Found: C, 61.36; H, 12.07.

The bisphenylurethan was prepared and recrystallized from carbon tetrachloride, m.p. 116–117°.

Anal. Calcd. for $C_{20}H_{24}O_4N_2$: C, 67.40; H, 6.79. Found: C, 67.31; H, 6.97.

2-Methyl-1,5-dichloropentane. A mixture of 2-methyl-1,5-pentanediol (11.8 g., 0.1 mole) and pyridine (1 ml.) was treated dropwise with thionyl chloride (47.6 g., 0.4 mole). The mixture was stirred for 1 hr. at room temperature and finally 3 hr. at reflux. The reaction mixture was treated dropwise with 100 ml. of ice water and the separated organic layer taken up in ether. The ether solution was shaken out with dilute sodium hydroxide solution and finally water and dried. The ether was removed and attempts to distill the dichloro product at atmospheric pressure failed because of excessive foaming. The product (10.8 g., 70% yield) was distilled, b.p. 85–86° (21 mm.), n_D^{25} 1 4555.

Anal. Calcd. for $C_6H_{12}Cl_2$: C, 46.47; H, 7.80; Cl, 45.73. Found: C, 46.72; H, 7.91; Cl, 45.34.

2-Methyl-1,5-bis(triphenylsilyl)pentane. 2-Methyl-1,5-dichloropentane (15 mmoles) was treated with triphenylsilyllithium (30 mmoles) in tetrahydrofuran. Work-up furnished a 63% yield of bis-silane, m.p. 126–127° after recrystallization from ethanol.

Anal. Calcd. for $C_{42}H_{42}Si_2$: C, 83.65; H, 7.02. Found: C, 83.60; H, 7.05.

2-Methyl-1,5-bis(triphenylsilyl)pentane from the allyltriphenylsilane dimer. A mixture of 2-triphenylsilylmethyl-5-triphenylsilylpent-1-ene (1.8 g., 3 mmoles), triisobutylaluminum (0.6 g., 3 mmoles) and 15 ml. of *o*-xylene was heated at reflux for 1.5 hr. The cooled reaction mixture was treated with 1 ml. of glacial acetic acid and stirred for a short period. The mixture was shaken out with 25 ml. of dilute sulfuric acid and then washed with water and dried. Removal of the solvent furnished an oil which was chromatographed over alumina, employing hexane as an eluent. There was obtained 200 mg. (10%) of crude 2-methyl-1,5-bis(triphenylsilyl)pentane, m.p. 117–118° (from isooctane). The melting point was raised to 118–120° by recrystallization from ethanol, and the infrared spectra of this material and that obtained by the alternate synthesis were identical. A mixed melting point of the two samples melted at 120–124°.

Dayton 7, Ohio

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(19) D. Wittenberg and H. Gilman, *J. Am. Chem. Soc.*, **80**, 2677 (1958).

(20) D. E. Floyd and S. E. Miller, *J. Org. Chem.*, **16**, 882 (1951).

(21) K. Auwers, *Ann.*, **292**, 132 (1896).

(22) G. R. Clemo and K. N. Welch, *J. Chem. Soc.*, 2621 (1928).