perature was maintained below 50° by cooling. The mixture was allowed to stand overnight and filtered to remove ammonium chloride. The filtrate was concentrated under reduced pressure, and the residual slush was dissolved in 100 ml. of water. The solution was made alkaline with 40% sodium hydroxide solution and the resulting mixture was extracted with three 40-ml. portions of chloroform. The combined extracts were washed with water, dried with anhydrous sodium sulfate and distilled under reduced pressure to obtain 16.0 g. (47%) of the ester, b.p. 193–194° (1 mm.), $n^{25}\text{D}$ 1.4748.

Anal. Calcd. for $C_{15}H_{27}O_6P$: C, 53.88; H, 8.14. Found: C, 53.92; H, 8.38.

Tris-(2-carbethoxyethyl)-phosphine Sulfide.—Under a nitrogen atmosphere 5.0 g. of tris-(2-carbethoxyethyl)-phosphine was added in one portion to a stirred mixture of 0.5 g. of sulfur and 30 ml. of benzene. After the exothermic reaction had subsided, the mixture was refluxed for 30 minutes and then distilled under reduced pressure to obtain the sulfide, a pale yellow oil, b.p. 214° (1 mm.), $n^{25}\text{D}$ 1.5005.

Anal. Calcd. for $C_{15}H_{27}O_6PS$: C, 49.16; H, 7.42. Found: C, 48.89; H, 7.41.

Bis-(2-cyanoethyl)-phenylphosphine Oxide.—To a solution of 8.0 g. (0.037 mole) of bis-(2-cyanoethyl)-phenylphosphine in 20 ml. of acetic acid, preheated to 60°, was added dropwise during one hour 4.2 g. (0.037 mole) of 30% hydrogen peroxide solution. The heat of the reaction maintained the temperature between 60 and 70° during the addition. The reaction mixture then was heated at 75° for 15 minutes, treated with Darco, and heated at 100° for an additional 15 minutes. Filter aid was added, and the mixture was filtered. Evaporation of the solvent under reduced pressure gave a white crystalline solid. Recrystallization from isopropyl alcohol provided 7.8 g. (91%) of bis-(2-cyanoethyl)-phenylphosphine oxide, m.p. 108–109°.

Anal. Calcd. for $C_{12}H_{13}N_2OP$: C, 62.07; H, 5.64; P, 13.34. Found: C, 61.92; H, 5.53; P, 13.55.

Bis-(2-carboxyethyl)-phenylphosphine Oxide.—Bis-(2-cyanoethyl)-phenylphosphine oxide (5.6 g., 0.024 mole) was added to Claisen alkali, made by adding 16 ml. of methanol to a cool solution of 5.4 g. (0.096 mole) of potassium hydroxide in 4 ml. of water. The reaction mixture was heated under reflux for 5.5 hours. It was then neutralized with dilute hydrochloric acid and concentrated under reduced pressure to obtain 5.8 g. (90%) of bis-(2-carboxyethyl)-phenylphosphine oxide, m.p. 201–204°. Recrystallization from methanol provided an analytical sample, m.p. 199–202°.

Anal. Calcd. for $C_{12}H_{15}O_5P$: C, 53.34; H, 5.60; P, 11.46. Found: C, 53.01; H, 5.82; P, 11.15.

Methyltris-(2-cyanoethyl)-phosphonium Iodide.—A mixture of 1.0 g. of tris-(2-cyanoethyl)-phosphine and 1.0 g. of methyl iodide was warmed on the steam-bath for 15 minutes. The product was washed onto a filter with ethanol and recrystallized twice from acetonitrile to obtain the iodide, m.p. 238–239°.

Anal. Calcd. for $C_{10}H_{15}IN_3P$: C, 35.83; H, 4.51. Found: C, 35.56; H, 4.63.

Allyltris-(2-cyanoethyl)-phosphonium Chloride.—A solution of 10.0 g. (0.052 mole) of tris-(2-cyanoethyl)-phosphine and 4.0 g. (0.052 mole) of allyl chloride in 25 ml. of dimethylformamide was heated under reflux for 3 hours. The solvent was evaporated under reduced pressure to give an oil which crystallized on treatment with acetone. The white solid was dissolved in acetic acid, and the solution was diluted with 3 volumes of acetone. While standing at 0° overnight the solution deposited white crystals, which after drying at 80° *in vacuo* melted at 135–136°.

Anal. Calcd. for $C_{12}H_{17}ClN_3P$: Cl, 13.14; P, 11.48. Found: Cl, 13.27; P, 11.28.

An aqueous solution of the chloride when treated with sodium picrate solution deposited a yellow solid, which after recrystallization from a mixture of ethanol and acetone melted at 126–127°.

Anal. Calcd. for $C_{18}H_{19}N_6O_7P$: C, 46.75; H, 4.14. Found: C, 46.56; H, 4.31.

2,4-Dichlorobenzyltris-(2-cyanoethyl)-phosphonium Iodide.—A solution of 5.0 g. (0.026 mole) of tris-(2-cyanoethyl)-phosphine and 5.0 g. (0.026 mole) of 2,4-dichlorobenzyl chloride in 25 ml. of dimethylformamide was heated under reflux for 2 hours, cooled and poured into 100 ml. of ether. The resulting oil was dissolved in water and treated with saturated potassium iodide solution. The crystalline iodide was collected and recrystallized from water to obtain 5.0 g. of white plates, m.p. 176–177°.

Anal. Calcd. for $C_{16}H_{17}Cl_2IN_3P$: I, 26.43. Found: I, 26.70.

Hydroxymethyltris-(2-cyanoethyl)-phosphonium Chloride.—To a solution of 19.3 g. (0.1 mole) of tris-(2-cyanoethyl)-phosphine in 25 ml. of concentrated hydrochloric acid was added portionwise with stirring 8.9 g. (0.11 mole) of 37% aqueous formaldehyde solution. The temperature rose to 50° during the addition. The solution was allowed to stand an additional 15 minutes and then was evaporated to dryness. The residue was recrystallized from acetic acid and dried at 80° *in vacuo* to obtain the product, m.p. 149–151°.

Anal. Calcd. for $C_{10}H_{15}ClN_3OP$: C, 46.24; H, 5.82; P, 11.92; N, 16.18. Found: C, 46.35; H, 6.03; P, 12.03; N, 16.11.

The product was soluble in water, but when an aqueous solution was treated with 5% sodium hydroxide solution the starting phosphine separated.

STAMFORD, CONN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Some Reactions of Silyllithium Compounds with Epoxides

BY HENRY GILMAN, DAN AOKI AND DIETMAR WITTENBERG

RECEIVED SEPTEMBER 19, 1958

The addition of silylmetallic compounds to ethylene oxide, propylene oxide, cyclohexene oxide and styrene oxide has been found to give good yields of β-silylcarbinols. Some dehydration reactions of these carbinols have been studied. The reaction of triphenylsilyllithium with epibromohydrin and with epichlorohydrin was investigated.

A variety of silyl-substituted carbinols has been prepared recently using silylmetallic reagents. Triphenylsilyllithium (I) and methyldiphenylsilyllithium have been found to cleave tetrahydrofuran with the formation of 4-silyl-substituted butanols.[1,2] Similarly, I reacted with trimethylene oxide to form 3-(triphenylsilyl)-propanol.[2] Various α-silylcarbinols have been prepared from the reaction of silyllithium or silylpotassium compounds with aliphatic aldehydes,[3,4] aliphatic ketones,[5,6] and with acid chlorides.[4]

---

(1) D. Wittenberg and H. Gilman, THIS JOURNAL, **80**, 2677 (1958).

(2) D. Wittenberg, D. Aoki and H. Gilman, *ibid.*, **80**, 5933 (1958).

(3) H. Gilman and T. C. Wu, *ibid.*, **76**, 2502 (1954).

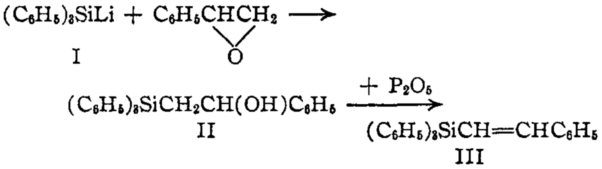
(4) D. Wittenberg and H. Gilman, *ibid.*, **80**, 4529 (1958); also, unpublished studies by D. J. Peterson.

(5) A. G. Brook, *ibid.*, **80**, 1886 (1958).

(6) H. Gilman and G. D. Lichtenwalter, *ibid.*, **80**, 2680 (1958).

In an extension of these studies, the reaction of silyllithium compounds with various epoxides has now been investigated. Whereas Grignard reagents in many reactions with epoxides yield a mixture of two or more isomers,[7] organolithium compounds have been found to react more selectively, generally giving rise to good yields of β-substituted carbinols.[8] Similarly, triphenylgermyllithium has been reported recently to add to certain epoxides.[9]

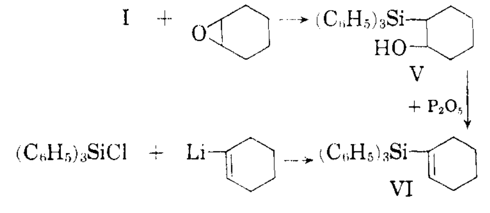
When triphenylsilyllithium (I) was allowed to react with ethylene oxide and with propylene oxide, 2-(triphenylsilyl)-ethanol and 1-(triphenylsilyl)-propan-2-ol were isolated in 85.5 and 69.2% yields, respectively. From the reaction of I with styrene oxide, a 56.5% yield of 1-phenyl-2-(triphenylsilyl)-ethanol (II) was obtained. The structure of II was confirmed by dehydration with phosphorus pentoxide, which yielded triphenyl-β-styrylsilane (III). Similarly, methyldiphenylsilyllithium (IV)[10] added to styrene oxide to give a 47.8% yield of 1-phenyl-2-(methyldiphenylsilyl)ethanol.



$$\underset{\text{I}}{(C_6H_5)_3SiLi} + C_6H_5\underset{\diagdown O \diagup}{CHCH_2} \longrightarrow$$

$$\underset{\text{II}}{(C_6H_5)_3SiCH_2CH(OH)C_6H_5} \xrightarrow{+ P_2O_5} \underset{\text{III}}{(C_6H_5)_3SiCH{=}CHC_6H_5}$$

Whereas cyclohexanol and low yields of 2-alkylcyclohexanols were obtained from the reaction of cyclohexene oxide and *n*-propyl- or *n*-butyllithium, methyllithium had been found to give high yields of 2-methylcyclohexanol.[11] The silyllithium reagents I and IV produced the expected 2-(triphenylsilyl)-cyclohexanol (V) and 2-(methyldiphenylsilyl)-cyclohexanol in 68.6 and 72% yields, respectively.



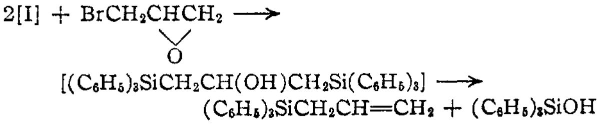
V

VI

Dehydration of compound V with phosphorus pentoxide gave a 33.5% yield of 1-cyclohexenyltriphenylsilane (VI). The structure of VI was established by an independent synthesis from chlorotriphenylsilane and 1-cyclohexenyllithium, the latter prepared[12] from 1-chlorocyclohexene and lithium.

The dehydration reactions of II and V with phosphorus pentoxide produced the desired olefins only in low yield; triphenylsilanol and hexaphenyldisiloxane also were isolated. The reaction may involve a cleavage of a carbon–silicon bond of the olefin by the action of phosphoric acid.[13] On the other hand, related cleavage reactions of 2-chloro-substituted silanes have been explained by the β-silicon effect.[14]

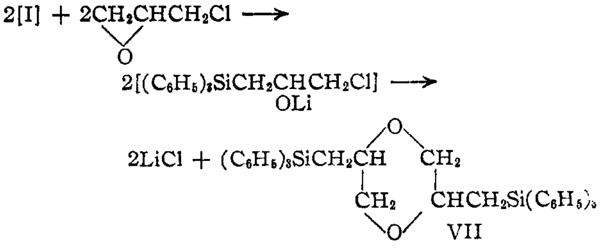
The reaction of aryllithium compounds with epichlorohydrin has been used as a convenient synthesis of arylpropylene chlorohydrins.[15] A similar course of reaction was expected when triphenylsilyllithium was allowed to react with epibromohydrin and with epichlorohydrin. However, hexaphenyldisilane resulted in a 68.6% yield when compound I was treated with epibromohydrin, the reaction apparently involving a halogen–metal interconversion[16] followed by coupling of the resulting bromotriphenylsilane with an excess of I. In addition, small amounts of allyltriphenylsilane and triphenylsilanol were obtained, possibly formed according to the equation



$$2[\text{I}] + BrCH_2\underset{\diagdown O \diagup}{CHCH_2} \longrightarrow$$

$$[(C_6H_5)_3SiCH_2CH(OH)CH_2Si(C_6H_5)_3] \longrightarrow (C_6H_5)_3SiCH_2CH{=}CH_2 + (C_6H_5)_3SiOH$$

No halogen–metal interconversion took place when Compound I was allowed to react with epichlorohydrin, as indicated by the absence of hexaphenyldisilane in the reaction mixture. In addition to allyltriphenylsilane, a compound was isolated, the analysis of which suggested a formula $C_{21}H_{20}OSi$, as might have been expected for 3-(triphenylsilyl)-propylene oxide. Attempts to reduce the compound with lithium aluminum hydride were unsuccessful, thereby excluding this possible structure. Molecular weight determinations indicated that the compound is a dimer and it might possibly have the structure of 2,5-bis-(triphenylsilylmethyl)-1,4-dioxane (VII).



$$2[\text{I}] + 2\underset{\diagdown O \diagup}{CH_2CHCH_2Cl} \longrightarrow$$

$$2[(C_6H_5)_3SiCH_2\underset{OLi}{CH}CH_2Cl] \longrightarrow$$

VII

Experimental[17]

2-(Triphenylsilyl)-ethanol.—A solution of 0.050 mole of triphenylsilyllithium in tetrahydrofuran[10] was placed in a

---

[7] For a detailed discussion see the excellent review articles of N. G. Gaylord and E. I. Becker, *Chem. Revs.*, **49**, 413 (1951); S. Winstein and R. B. Henderson in Chapter I (pp. 1–60), Vol. I of Elderfield's "Heterocyclic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950; M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice–Hall, Inc., New York, N. Y., 1954.

[8] S. J. Cristol, J. R. Douglas and J. S. Meek, THIS JOURNAL, **73**, 816 (1951).

[9] H. Gilman, C. W. Gerow and M. B. Hughes, *J. Org. Chem.*, **23**, in press (1958).

[10] H. Gilman and G. D. Lichtenwalter, THIS JOURNAL, **80**, 608 (1958).

[11] R. L. Letsinger, J. C. Traynham and E. Bobko, *ibid.*, **74**, 399 (1952).

[12] E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 2014 (1950).

[13] For cleavage studies of tetrasubstituted silanes, see R. H. Meen and H. Gilman, *J. Org. Chem.*, **20**, 73 (1955), and references given in that paper.

[14] L. H. Sommer, D. L. Bailey and F. C. Whitmore, THIS JOURNAL, **70**, 2869 (1948); see also A. G. Brook, *Chemistry in Can.*, **43** Sept. (1955), for a very good review.

[15] H. Gilman, B. Hofferth and J. B. Honeycutt, THIS JOURNAL, **74**, 1594 (1952).

[16] For halogen–metal interconversion reactions involving silylmetallic compounds, see A. G. Brook, H. Gilman and L. S. Miller, *ibid.*, **75**, 4759 (1953); A. G. Brook and S. Wolfe, *ibid.*, **79**, 1431 (1957); D. Wittenberg and H. Gilman, *ibid.*, **80**, 2677 (1958).

[17] Melting points and boiling points are uncorrected. Reactions involving organometallic compounds were carried out in an atmosphere

three-necked flask, equipped with Dry Ice condenser, stirrer and tubes for the entry and exit of nitrogen. During continuous stirring, the nitrogen was replaced by a stream of dry ethylene oxide which was passed over the surface of the solution. After 5 min. a color change was observed and Color Test I[18] was found to be negative. The work-up by hydrolysis, addition of some ether, extraction with water, drying of the organic layer with sodium sulfate, and removal of the solvents gave oily crystals, which were recrystallized from cyclohexane to yield 13.0 g. (85.5%) of 2-(triphenylsilyl)-ethanol, m.p. 97–98.5°. A second recrystallization from the same solvent raised the melting point to 99–100°.

Anal. Calcd. for $C_{20}H_{20}OSi$: Si, 9.22. Found: Si, 9.25, 9.11.

1-(Triphenylsilyl)-propan-2-ol.—A solution of 0.1 mole of triphenylsilyllithium in tetrahydrofuran was added dropwise over a period of 10 min. to 5.8 g. (0.1 mole) of propylene oxide. During the addition, the flask was cooled with Dry Ice–acetone. Color Test I[18] was negative immediately after the addition. The work-up in the manner described in the first experiment gave 22.0 g. (69.2%) of 2-(triphenylsilyl)-propan-2-ol, m.p. 86–88° (after recrystallization from petroleum ether, b.p. 60–70°).

Anal. Calcd. for $C_{21}H_{22}OSi$: Si, 8.82. Found: Si, 8.75, 8.89.

1-Phenyl-2-(triphenylsilyl)-ethanol.—A solution of 0.067 mole of triphenylsilyllithium in tetrahydrofuran was added slowly to 9.5 g. (0.079 mole) of styrene oxide. During the addition, the flask was cooled with ice. The work-up gave a solid material, which was recrystallized from ethanol to yield 14.36 g. (56.5%) of 1-phenyl-2-(triphenylsilyl)-ethanol, m.p. 129–130.5°. Recrystallization from the same solvent raised the melting point to 130–131°.

Anal. Calcd. for $C_{26}H_{24}OSi$: Si, 7.38. Found: Si, 7.26, 7.18.

In a second experiment, the reverse addition was employed. A solution of 10.5 g. (0.088 mole) of styrene oxide in 20 ml. of tetrahydrofuran was added slowly to 0.08 mole of triphenylsilyllithium in the same solvent. The work-up gave 8.75 g. (28.4%) of 1-phenyl-2-(triphenylsilyl)-ethanol, m.p. 127–129°. Two recrystallizations from ethanol raised the melting point to 131–133°.

Dehydration of 1-Phenyl-2-(triphenylsilyl)-ethanol with Phosphorus Pentoxide.—A mixture of 2.0 g. (0.005 mole) of 1-phenyl-2-(triphenylsilyl)-ethanol and 2.0 g. (0.014 mole) of phosphorus pentoxide in 50 ml. of benzene was stirred at reflux temperature for 1 hr. The benzene layer was extracted with concd. ammonium chloride solution. The dried organic layer, subsequent to evaporation of the solvent, gave a solid residue which was chromatographed on alumina. Two products were obtained: 0.40 g. (30.5%) of triphenylsilanol, and 0.43 g. (23%) of triphenyl-β-styrylsilane, m.p. 143–145°, identified by a mixed melting point with an authentic sample[19] and by infrared spectra.

1-Phenyl-2-(methyldiphenylsilyl)-ethanol.—A solution of 0.04 mole of methyldiphenylsilyllithium[10] in tetrahydrofuran was added slowly to 4.5 g. (0.04 mole) of styrene oxide. The work-up in the manner described in the first experiment gave an oil, which was distilled at reduced pressure to yield 6.1 g. (47.8%) of 1-phenyl-2-(methyldiphenylsilyl)-ethanol, b.p. 192–193° (0.03 mm.), n^{20}_D 1.6012.

Anal. Calcd. for $C_{21}H_{22}OSi$: Si, 8.82; MR_D, 100.31. Found: Si, 8.75, 8.71; MR_D, 99.84.

2-(Triphenylsilyl)-cyclohexanol.—The addition of 0.08 mole of triphenylsilyllithium in tetrahydrofuran to 9.8 g. (0.10 mole) of cyclohexene oxide, and then the usual work-up, gave a solid residue which was recrystallized from ethanol. There was obtained 19.7 g. (68.6%) of 2-(triphenylsilyl)-cyclohexanol, m.p. 142–145°.

Anal. Calcd. for $C_{24}H_{26}OSi$: Si, 7.83. Found: Si, 7.79, 7.78.

2-(Methyldiphenylsilyl)-cyclohexanol.—A solution of 0.04 mole of methyldiphenylsilyllithium was added slowly to 4.0 g. (0.04 mole) of cyclohexene oxide. The work-up gave a solid material, which was recrystallized from ethanol. The yield of 2-(methyldiphenylsilyl)-cyclohexanol, m.p. 115–117°, was 8.39 g. (72%).

Anal. Calcd. for $C_{19}H_{24}OSi$: Si, 9.48. Found: Si, 9.47, 9.43.

1-Cyclohexenyltriphenylsilane. A. From 1-Cyclohexenyllithium and Chlorotriphenylsilane.—1-Cyclohexenyllithium was prepared by a slight modification of the method described by Braude and Coles.[12] A solution of 13.55 g. (0.117 mole) of freshly distilled 1-chlorocyclohexene[12] in 150 ml. of ether was added dropwise with continuous stirring to 1.68 g. (0.24 mole) of finely cut lithium wire. The reaction started immediately; Color Test I was positive. After stirring for 6 hr. at room temperature, the metal was completely coated with lithium chloride. An additional 1.68 g. (0.24 mole) of lithium wire was added and stirring continued overnight. Titration of an aliquot indicated an 86% yield of 1-cyclohexenyllithium.

A solution of 0.1 mole of 1-cyclohexenyllithium in ether was placed in a flask and 29.4 g. (0.1 mole) of chlorotriphenylsilane was added at once. The reaction was exothermic. After 30 min. of stirring, Color Test I was negative. Subsequent to hydrolysis, 14.05 g. of a solid, m.p. 165–168°, was separated by filtration. From the organic layer, an additional 10.7 g. of a solid, m.p. 167–169°, was isolated, *i.e.*, a total yield of 72.7% of 1-cyclohexenyltriphenylsilane. Recrystallization from petroleum ether (b.p. 60–70°) raised the melting point to 171–174°.

Anal. Calcd. for $C_{24}H_{24}Si$: Si, 8.26. Found: Si, 8.21, 8.12.

B. By Dehydration of 2-(Triphenylsilyl)-cyclohexanol with Phosphorus Pentoxide.—A mixture of 2.0 g. (0.0056 mole) of 2-(triphenylsilyl)-cyclohexanol and 2.0 g. (0.014 mole) of phosphorus pentoxide in 50 ml. of benzene was stirred at reflux temperature for 1 hr. The benzene solution was extracted with concd. ammonium chloride solution. The dried organic layer, after removal of the solvent, gave a solid residue which was chromatographed on alumina. Two products were isolated: 0.02 g. (1.3%) of hexaphenyldisiloxane, m.p. 225–227°, and 0.55 g. (33.5%) of 1-cyclohexenyltriphenylsilane, m.p. 162–163°. The compound gave no melting point depression when admixed with an authentic sample, prepared from 1-cyclohexenyllithium and chlorotriphenylsilane. The infrared spectra were superimposable.

Reaction of Triphenylsilyllithium with Epibromohydrin.—Epibromohydrin (6.85 g., 0.050 mole) was added dropwise to a solution of 0.050 mole of triphenylsilyllithium in tetrahydrofuran. The reaction was exothermic and Color Test I was negative immediately after the addition. Subsequent to hydrolysis, 9.42 g. (72.6%) of hexaphenyldisilane, m.p. 355–358°, was separated by filtration. Work-up of the organic layer yielded a small amount of oily residue which was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave 0.13 g. (1%) of allyltriphenylsilane, m.p. 86–89°, identified by a mixed melting point determination with an authentic sample[20] and infrared spectra.

In a second experiment, the reverse addition was employed, *i.e.*, addition of triphenylsilyllithium to epibromohydrin. During the reaction the flask was cooled in a Dry Ice–acetone-bath. The work-up gave a 68.6% yield of hexaphenyldisilane, in addition to 4.4% of triphenylsilanol.

Reaction of Triphenylsilyllithium with Epichlorohydrin.—A solution of 0.050 mole of triphenylsilyllithium in tetrahydrofuran was added dropwise to 4.62 g. (0.050 mole) of epichlorohydrin. The reaction was exothermic and Color Test I was negative immediately after the addition. Work-up by hydrolysis, addition of some ether, drying of the organic layer with sodium sulfate, followed by removal of the solvent, left an oily residue which subsequently was chromatographed on alumina. Three compounds were isolated: 1.2 g. (8%) of allyltriphenylsilane, m.p. 85–88°, identified by a mixed melting point determination with an authentic sample; 1.1 g. (8%) of triphenylsilanol, identified by mixed melting point and by infrared spectra; and 2.95 g. (19%) of a compound (possibly 2,5-bis-(triphenylsilylmethyl)-1,4-dioxane), m.p. 144–145.5°.

Anal. Calcd. for $C_{42}H_{40}O_2Si_2$: Si, 8.88; mol. wt., 633.0. Found: Si, 8.68, 8.71; mol. wt., 623.5 (Rast).

---

of dry, oxygen-free nitrogen. Silicon analyses were carried out according to the procedure of H. Gilman, B. Hofferth, H. W. Melvin, Jr., and G. E. Dunn, THIS JOURNAL, **72**, 5767 (1950).

[18] H. Gilman and F. Schulze, *ibid.*, **47**, 2002 (1925).

[19] H. Gilman and J. F. Nobis, *ibid.*, **72**, 2629 (1950).

[20] Unpublished studies of T. Soddy; see, H. Gilman and E. A. Zuech, *ibid.*, **79**, 4560 (1957).

The compound was unaffected by lithium aluminum hydride in tetrahydrofuran at room temperature. After one hour of refluxing in the same solvent with a large excess of lithium aluminum hydride, 50% of the starting material was recovered unchanged. No 1-(triphenylsilyl)-propan-2-ol was detected.

Acknowledgment.—This research was supported in part 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. Infrared analyses were obtained through the courtesy of the Institute for Atomic Research, Iowa State College. Special thanks are due to Dr. V. A. Fassel, Mr. R. Kniseley and Miss M. Powers for the spectra.

AMES, IOWA

[JOINT COMMUNICATION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, AND THE SHELL DEVELOPMENT CO.]

Boron Fluoride–Alcohol Alkylations I. Benzene and the Amyl Alcohols[1]

BY A. STREITWIESER, JR., D. P. STEVENSON AND W. D. SCHAEFFER[2]

RECEIVED AUGUST 12, 1958

The alkylation of benzene with alcohols and boron fluoride has been carried out with all eight amyl alcohols. Primary alcohols require several hours at 60°; secondary alcohols react within minutes at 0°; *t*-amyl alcohol gave no alkylation products at 0°. Rearrangements are general. 2-Pentanol and 3-pentanol gave identical product mixtures containing 65% 2-phenylpentane, 25% 3-phenylpentane and apparently about 10% of *t*-amylbenzene. Neopentyl alcohol gave pure *t*-amylbenzene.

Although a number of investigations of the alkylation of aromatic compounds with boron fluoride and alcohols[3] and ethers[4] have been reported, many questions remain regarding the preparative usefulness of the reaction, the extent of the rearrangements which may occur, and the mechanism of the reaction. The reaction conditions used are often more severe than necessary; in many cases polyalkylbenzenes formed a substantial proportion of the products. Rearrangements are known to occur; *e.g.*, *n*-propyl alcohol gives isopropylbenzene and *n*-butyl alcohol gives *sec*-butylbenzene; however, there is some confusion about how prevalent or extensive these rearrangements may be. Toussaint and Hennion[3d] report that "alkylation apparently occurs without carbon skeleton rearrangement." The results of Hennion and Pieronik[3i] were presented with the implication that the boron fluoride alkylation of chlorobenzene with 2-pentanol yields 2-*p*-chlorophenylpentane and 3-pentanol yields 3-*p*-chlorophenylpentane, etc., although Burwell, *et al.*,[4i] found that 2-methoxypentane with boron fluoride and benzene yields a mixture of 75% of 2-phenylpentane and 25% of 3-phenylpentane. In preparation for experiments designed to examine the mechanism of the reaction between aromatic hydrocarbons and alcohols and boron fluoride, we studied the behavior of all of the eight isomeric amyl alcohols in this reaction.

In the present work alkylations were run with a large excess of benzene to minimize the production of dialkylated products. Generally, 10–20 g. of alcohol in 100 g. of benzene was saturated with boron fluoride and maintained at an appropriate temperature. With secondary alcohols reaction takes place rapidly at 0°; primary alcohols require several hours at 60°. Promoters such as phosphorus pentoxide and sulfuric acid which have been used frequently in such alkylations were not used in our experiments to avoid any complicating factors which they may introduce. Small amounts of water, however, were present in some cases; water is known to be a potent promoter.[5]

In agreement with previous workers[3b] we found that *n*-propyl alcohol and *n*-butyl alcohol give good yields of isopropyl- and *sec*-butylbenzene, respectively. Ethanol does not react under similar conditions.[3b,3d] The amyl alcohols generally give mixtures of monoalkylated products (Table I) which were analyzed by mass spectral and infrared spectral techniques. The mass spectra of primary alkylbenzenes have a prominent peak due to $C_7H_8^+$. The absence of this peak in all of the alkylation products demonstrated the complete absence of 1-phenylpentane, 1-phenyl-2-methylbutane, 1-phenyl-3-methylbutane and 1-phenyl-2,2-

---

(1) Presented in part at the 128th Meeting of the American Chemical Society, Minneapolis, Minn., Sept. 11, 1955. This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

(2) General Electric Fellow, 1955–1956.

(3) (a) F. J. Sowa, G. F. Hennion and J. A. Nieuwland, THIS JOURNAL, **57**, 709 (1935); (b) J. F. McKenna and F. J. Sowa, *ibid.*, **59**, 470 (1937); (c) **60**, 124 (1938); (d) N. F. Toussaint and G. F. Hennion, *ibid.*, **62**, 1145 (1940); (e) C. C. Price and M. Lund, *ibid.*, **62**, 3105 (1940); (f) C. E. Welsh and G. F. Hennion, *ibid.*, **63**, 2603 (1941); (g) R. L. Burwell, Jr., and S. Archer, *ibid.*, **64**, 1032 (1942); (h) D. Nightingale, H. D. Radford and O. G. Shanholtzer, *ibid.*, **64**, 1662 (1942); (i) G. F. Hennion and V. R. Pieronik, *ibid.*, **64**, 2751 (1942); (j) G. F. Hennion and L. A. Auspos, *ibid.*, **65**, 1603 (1943); (k) D. Nightingale and J. R. Jones, *ibid.*, **66**, 154 (1944); (l) G. Vermillion and M. A. Hill, *ibid.*, **67**, 2209 (1945); (m) G. F. Hennion and N. F. Toussaint, U. S. Patent 2,390,835 (1946); (n) W. N. Axe, U. S. Patent 2,403,963 (1946); (o) G. B. Bachman and H. M. Hellman, THIS JOURNAL, **70**, 1772 (1948); (p) A. V. Topchiev, G. M. Egorova and R. S. Aizinson, *Doklady Akad. Nauk, S.S.S.R.*, **74**, 295 (1950); *C. A.*, **45**, 3825 (1951); (q) I. Romadane and T. I. Rendel, *J. Gen. Chem., U.S.S.R.*, **26**, 215 (1956) (Engl. transl.); (r) I. Romadane, J. Pelcere and O. Vitola, *Latvijas PSR Zinatnu Akad. Vestis*, No. 4, 143 (1957); *C. A.*, **52**, 10025 (1958).

(4) (a) F. J. Sowa, H. D. Hinton and J. A. Nieuwland, THIS JOURNAL, **54**, 2019 (1932); (b) G. F. Hennion, H. D. Hinton and J. A. Nieuwland, *ibid.*, **55**, 2857 (1933); (c) F. J. Sowa, H. D. Hinton and J. A. Nieuwland, *ibid.*, **55**, 3402 (1933); (d) M. J. O'Connor and F. J. Sowa, *ibid.*, **60**, 125 (1938); (e) A. J. Kolka and R. R. Vogt, *ibid.*, **61**, 1463 (1939); (f) W. J. Monacelli and G. F. Hennion, *ibid.*, **63**, 1722 (1941); (g) R. L. Burwell, Jr., and L. M. Elkin, *ibid.*, **73**, 502 (1951); (h) R. L. Burwell, Jr., L. M. Elkin and A. D. Shields, *ibid.*, **74**, 4567 (1952), (i) **74**, 4570 (1952).

(5) A. Streitwieser, Jr., W. D. Schaeffer and S. Andreades, *ibid.*, **81**, 1113 (1959).