TABLE II

HYDROXY-THIO ACIDS

Acid	Neut. Equiv. Calcd.	Neut. Equiv. Found	M.P.
6-Hydroxy-6-(5-hexadecyl-2-thienyl)hexanoic acid[a]	438.7	438.0	84–85
4-Hydroxy-4-(5-hexadecyl-2-thienyl)butyric acid[b]	410.7	410.1	78–79
10-Hydroxy-10-(5-octadecyl-2-thienyl)decanoic acid	522.9	523.1	68–69
10-Hydroxy-10-(5-dodecyl-2-thienyl)decanoic acid	437.7	438.9	31–32[c]

[a] *Anal.* Calcd. for $C_{26}H_{46}O_3S$: C, 71.18; H, 10.57; S, 7.29. Found: C, 71.30; H, 10.41; S, 7.13. [b] Product obtained as lactone which was converted to free acid. [c] Crystallized very slowly.

Desulfurization.[20]

TABLE III

DESULFURIZATION OF DERIVATIVES

Derivative III R	Derivative III n	Product Acid	Product % Yield
n-pentadecyl	4	6-Hydroxyhexacosanoic	63.9
n-pentadecyl	2	4-Hydroxytetracosanoic	68.0
n-heptadecyl	8	10-Hydroxydotriacontanoic	75.0
n-undecyl	8	10-Hydroxyhexacosanoic	74.7

To a suspension of Raney nickel catalyst (dissolved and digested as described by Bilicka and Adkins)[21] in 900 ml. distilled water was added 5 g. 6-hydroxy-6-(5-hexadecyl-2-thienyl)hexanoic acid in 10% sodium carbonate (aqueous). The resultant mixture was stirred at 80 ± 3° for 3 hr., the catalyst was filtered off, the filtrate acidified (hydrochloric acid) and extracted with ether. The spent catalyst was dissolved in 15% hydrochloric acid and the solution extracted with ether. The ether extracts were combined, washed, dried (magnesium sulfate), and the solvent evaporated. Recrystallization of the residue (benzene-ethanol) gave pure 6-hydroxyhexacosanoic acid (63.9%), m.p. 89.5–90.5°.

Anal. Calcd. for $C_{26}H_{52}O_3$: C, 75.66; H, 12.65; OH, 4.12; Neut. Equiv., 412.7. Found: C, 75.53; H, 12.73; OH, 4.03; Neut. Equiv., 412.0.

Desulfurization of 4-hydroxy-4-(5-hexadecyl-2-thienyl)-butyric acid by the above procedure yielded 4-hydroxytetracosanoic acid (68.0%). The pure material, obtained from the lactone, had m.p. 80–82°.

Anal. Calcd. for $C_{24}H_{48}O_3$: OH, 4.42; Neut. Equiv., 384.6. Found: OH, 4.33; Neut. Equiv., 384.1.

In a similar manner, 10-hydroxydotriacontanoic acid was obtained by the desulfurization of 10-hydroxy-10-(5-octadecyl-2-thienyl)decanoic acid. Recrystallization from ethanol at −5° afforded the pure material (75%) of m.p. 81–83°.

Anal. Calcd. for $C_{32}H_{64}O_3$: OH, 3.42; Neut. Equiv., 496.6. Found: OH, 3.38; Neut. Equiv., 496.3.

10-Hydroxyhexacosanoic acid was likewise obtained by the desulfurization of 10-hydroxy-10-(5-dodecyl-2-thienyl)-decanoic acid. The pure product (74.7%), obtained by recrystallization from ethanol, had m.p. 93–95°.

Anal. Calcd. for $C_{26}H_{52}O_3$: OH, 4.12; Neut. Equiv., 412.7. Found: OH, 4.10; Neut. Equiv., 409.3.

The hydroxyl analysis mentioned in each of the above four desulfurizations was carried out according to the general procedure described by Smith and Shriner.[22]

Acknowledgment. The authors are indebted to the Sharples Chemicals Inc. for a generous sample of thiophene.

MILWAUKEE, WIS.

AMES, IOWA

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[20] The weights of all thio-acids used were based on the introduction of 125 g. Raney nickel-aluminum alloy powder, the alloy being present in excess.

[21] H. R. Bilicka and H. Adkins, *Org. Syntheses*, **Coll. Vol. III,** 176 (1955).

[22] Walter T. Smith, Jr. and Ralph L. Shriner, *The Examination of New Organic Compounds*, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 112.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Reactions of Triphenylsilyllithium with Some Halides and Related Compounds of Group V Elements

M. V. GEORGE, BERNARD J. GAJ, AND HENRY GILMAN

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Whereas the reactions of triphenylsilyllithium with phosphorus trichloride, phosphorus tribromide, and phosphorus oxychloride give hexaphenyldisilane as the chief product, the reaction with tributyl phosphate gives *n*-butyltriphenylsilane. Arsenic trichloride, antimony trichloride, and bismuth trichloride give hexaphenyldisilane and the corresponding metals when allowed to react with triphenylsilyllithium. A possible explanation for the high yield of hexaphenyldisilane is given.

In the course of the past few years a study has been carried out in this Laboratory to ascertain the usefulness of triphenylsilyllithium as a synthetic tool for the preparation of various organosilicon compounds. Successful preparations of this reagent in a suitable solvent like tetrahydrofuran, by the lithium cleavage of hexaphenyldisilane[1] and by the direct reaction of chlorotriphenylsilane and lithium[2] have greatly increased the scope of this study.

The object of the present investigation was to study possible approaches to the synthesis of organosilylmetallic compounds containing some

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[1] H. Gilman and G. D. Lichtenwalter, *J. Am. Chem. Soc.*, **80,** 608 (1958).

[2] H. Gilman, D. J. Peterson, and D. Wittenberg, *Chem. & Ind.* (*London*), 1479 (1958). See, also, H. Gilman and T. C. Wu, *J. Org. Chem.*, **18,** 753 (1953).

group V elements of the periodic table, P, As, Sb, and Bi, through the reaction of silyllithium compounds with halides of these elements.

Various instances of the reaction of organolithium compounds with phosphorus halides are reported in the literature. Phenyllithium, for example, reacts with phosphorus trichloride to give 61% of triphenylphosphine.[3] Similarly, reactions of arsenic, antimony, and bismuth trichloride with aryllithium compounds give the desired trisubstituted derivatives of these elements. Recently, Seyferth[4] has prepared tris(trimethylsilylmethyl) compounds of phosphorus, arsenic, antimony, and bismuth by the reaction of trimethylsilylmethylmagnesium chloride with the appropriate group V trichloride in tetrahydrofuran.

$$3\ \mathrm{Me_3SiCH_2MgCl} + \mathrm{M^v\,Cl_3} \longrightarrow (\mathrm{Me_3SiCH_2})_3\mathrm{M^v} + 3\ \mathrm{MgCl_2}\ (\mathrm{M^v} = \mathrm{P, As, Sb, or\ Bi})$$

It seemed of interest to study some of the reactions of triphenylsilyllithium with group V trichlorides under conditions analogous to those of the reactions of organolithium and Grignard reagents, to prepare group V tris(triphenylsilyl) compounds.

The reaction in a 3:1 mole ratio, of triphenylsilyllithium and bismuth trichloride gave 78.8% of hexaphenyldisilane together with small amounts of triphenylsilane (3.4%), triphenylsilanol (7.6%), and hexaphenyldisiloxane (2.1%). Metallic bismuth was isolated in an 81.3% yield. The reaction of triphenylsilyllithium with bismuth trichloride seems to proceed through a route similar to that of the reaction of mercury salts.[5] For example, phenylmercuric bromide on treatment with triphenylsilyllithium gives mostly tetraphenylsilane (73%) and metallic mercury. The high yield of tetraphenylsilane in this reaction was explained on the basis of an unstable silicon-mercury intermediate. Similarly, reactions of mercury(II) chloride and of diphenylmercury with triphenylsilyllithium[5] gave products which could be explained satisfactorily only on the basis of such an unstable silicon-mercury intermediate. Bismuth trichloride may be reacting likewise with triphenylsilyllithium to give an unstable silicon-bismuth intermediate which decomposes to give hexaphenyldisilane and metallic bismuth.

$$(\mathrm{C_6H_5})_3\mathrm{SiLi} + \mathrm{C_6H_5HgBr} \longrightarrow [(\mathrm{C_6H_5})_3\mathrm{SiHgC_6H_5}] + \mathrm{LiBr}$$

$$[(\mathrm{C_6H_5})_3\mathrm{SiHgC_6H_5}] \longrightarrow (\mathrm{C_6H_5})_4\mathrm{Si} + \mathrm{Hg}$$

$$(\mathrm{C_6H_5})_3\mathrm{SiLi} + \mathrm{BiCl_3} \longrightarrow [(\mathrm{C_6H_5})_3\mathrm{SiBiCl_2}] + \mathrm{LiCl}$$

$$[(\mathrm{C_6H_5})_3\mathrm{SiBiCl_2}] \longrightarrow (\mathrm{C_6H_5})_3\mathrm{SiCl} + [\mathrm{BiCl}]$$

$$(\mathrm{C_6H_5})_3\mathrm{SiCl} + (\mathrm{C_6H_5})_3\mathrm{SiLi} \longrightarrow (\mathrm{C_6H_5})_3\mathrm{SiSi}(\mathrm{C_6H_5})_3 + \mathrm{LiCl}$$

$$3\ [\mathrm{BiCl}] \longrightarrow \mathrm{BiCl_3} + 2\ \mathrm{Bi}$$

Another possibility is the formation of an unstable bis- or tris(triphenylsilyl)bismuth intermediate, which could decompose to give hexaphenyldisilane and bismuth.

$$3\ (\mathrm{C_6H_5})_3\mathrm{SiLi} + \mathrm{BiCl_3} \longrightarrow [((\mathrm{C_6H_5})_3\mathrm{Si})_3\mathrm{Bi}] + 3\ \mathrm{LiCl}$$

$$2\ [((\mathrm{C_6H_5})_3\mathrm{Si})_3\mathrm{Bi}] \longrightarrow 3\ (\mathrm{C_6H_5})_3\mathrm{SiSi}(\mathrm{C_6H_5})_3 + 2\ \mathrm{Bi}$$

When triphenylsilyllithium was treated with antimony trichloride, 50.1% of hexaphenyldisilane, 21.1% of triphenylsilanol, 6.2% of hexaphenyldisiloxane and 5.1% of triphenylsilane were isolated. A nearly quantitative amount (90.5%) of metallic antimony was obtained from this reaction. Similarly, from the reactions of arsenic trichloride, phosphorus trichloride and phosphorus tribromide with triphenylsilyllithium, 44%, 68.1%, and 80.5% of hexaphenyldisilane, respectively, were isolated. Smaller amounts of other products like triphenylsilanol and hexaphenyldisiloxane were also obtained from these runs. It is interesting to note that a substance like phosphorus oxychloride gives a nearly quantitative yield (90%) of hexaphenyldisilane and it appears that this reaction also proceeds through a route similar to those of the phosphorus trichloride and phosphorus tribromide reactions. As in the case of the bismuth trichloride reaction, the products formed in these experiments could be satisfactorily explained on the basis of transient silicon-antimony, silicon-arsenic, and silicon-phosphorus intermediates.

It is also conceivable that a halogen-metal interconversion reaction may be involved, particularly in the case of the more nonmetallic members of the series, and this mechanism should not be ignored. Although at least one compound containing the Si—P bond has been reported,[6] namely trimethylsilyldiphenylphosphine, no details of the preparation or work-up were given, so that no conclusions can be drawn as to the stability of such compounds to cleavage by reactive species such as triphenylsilyllithium. It is the opinion of the authors that such compounds would be cleaved readily under the conditions used in this investigation. This aspect is presently under investigation at this laboratory.

In order to study the reaction of a phosphate ester with a silyllithium compound, a reaction was carried out using a 1:1 mole ratio of tri-*n*-butyl phosphate and triphenylsilyllithium. From this run an 83.5% yield of *n*-butyltriphenylsilane was isolated. It would appear that triphenylsilyllithium is effecting a cleavage of one of the butyl groups from the phosphate ester. This reaction is analogous to the reaction of an organolithium or Grignard reagent with a sulfate ester like methyl sulfate. The applicability of this reaction as a general alkylation procedure is under investigation.

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(3) E. M. Mikhailov, N. F. Kucherova, *Doklady Akad. Nauk S.S.S.R.*, **74**, 501 (1950).

(4) D. Seyferth, *J. Am. Chem. Soc.*, **80**, 1336 (1958).

(5) M. V. George, G. D. Lichtenwalter, and H. Gilman, *J. Am. Chem. Soc.*, **81**, 978 (1959).

(6) W. Kuchen and H. Buchwald, *Angew. Chem.*, **69**, 307 (1957).

EXPERIMENTAL

All melting points are uncorrected. Reactions were carried out under an atmosphere of dry, oxygen-free[7] nitrogen. Tetrahydrofuran, boiling at 65–66°, was freed from peroxides and moisture before use by refluxing over sodium, followed by distillation from lithium aluminum hydride. The halides and esters were anhydrous samples. Triphenylsilyllithium solutions were prepared in tetrahydrofuran by the cleavage of hexaphenyldisilane using lithium according to reported procedure.[1]

Triphenylsilyllithium and phosphorus trichloride. A solution of 0.09 mole of triphenylsilyllithium in 150 ml. of tetrahydrofuran was added, during 1.5 hr. to 4.6 g. (0.03 mole) of phosphorus trichloride, dissolved in 100 ml. of dry diethyl ether. The mixture was kept cooled in a bath of Dry Ice and acetone (−70°) during addition; the solution turned yellow at first and later brown. Color Test I[8] was negative when the addition was complete. The mixture was warmed to room temperature and the solvent was removed by distillation. The residue was successively extracted with 400 ml. of petroleum ether (b.p. 60–70°) and 600 ml. of benzene in a Soxhlet apparatus. The residue left in the Soxhlet thimble (17.6 g.) was then treated with hot tetralin to give 11.3 g. of hexaphenyldisilane, m.p. and mixed m.p. 362–364°. The tetralin-insoluble portion (4.9 g.) contained lithium chloride and a water-insoluble orange residue which gave a qualitative test for phosphorus.

The solvent from the petroleum ether extract was removed to give a solid with a wide melting range (145–200°) from which 1.7 g. (6.1%) of triphenylsilanol was isolated as the soluble fraction on treatment with methanol. It melted at 151–153° and did not depress the melting point of an authentic sample of triphenylsilanol. The methanol-insoluble fraction was mixed with the benzene extract of the original mixture and worked up.

The benzene extract when concentrated, deposited 6.8 g. of hexaphenyldisilane, m.p. and mixed m.p. 360–362°. Solvent from the mother liquor was removed and the residue was chromatographed on alumina. Elution of the column with chloroform gave 1.05 g. (2.0%) of hexaphenyldisiloxane, m.p. and mixed m.p. 226–228°. Further elution with methanol gave 0.85 g. (3.0%) of triphenylsilanol, which melted at 152–154° after crystallization from cyclohexane and did not depress the melting point of an authentic sample. The total yield of hexaphenyldisilane from various fractions was 18.2 g. (68.1%), and of triphenylsilanol, 2.6 g. (9.1%).

Triphenylsilyllithium and phosphorus tribromide. A solution of 0.06 mole of triphenylsilyllithium in 130 ml. of tetrahydrofuran was cooled to −50° in a Dry Ice–acetone bath. To this solution was added 5.4 g. (0.02 mole) of phosphorus tribromide dissolved in 50 ml. of tetrahydrofuran. When the addition was complete, the mixture gave a negative Color Test I. The solvent from the reaction mixture was removed by distillation under nitrogen and the residue was extracted with 400 ml. of benzene. The clear, amber-colored benzene extract was concentrated to about 300 ml. and filtered hot to deposit 3.7 g. of lithium bromide, identified by qualitative tests. Further concentration of the filtrate gave 2.1 g. of hexaphenyldisilane, m.p. 358–361°, identified by mixed melting point determination, and 1.6 g. (9.7%) of triphenylsilanol, m.p. 151–153° (mixed m.p.).

The original benzene-insoluble residue was extracted with hot tetralin to give 10.5 g. of hexaphenyldisilane, m.p. 362–364° (mixed m.p.). The total yield of hexaphenyldisilane was 80.5%. The tetralin insoluble portion contained lithium bromide and an orange-red solid (0.4 g.) which when dissolved in nitric acid gave a yellow precipitate with ammonium molybdate solution.

In a second run using the same quantities of reactants and solvent but with reverse addition, the products isolated were 12.7 g. (81.5%) of hexaphenyldisilane and 1.0 g. (6.0%) of triphenylsilanol, identified by mixed melting point determinations with authentic samples. In addition, 3.12 g. of lithium bromide and 0.45 g. of a residue which gave a positive test for phosphorus, were obtained.

Triphenylsilyllithium and phosphorus oxychloride. A solution of triphenylsilyllithium (0.09 mole, 103.5 ml.) was added, during one hour to 4.6 g. (0.03 mole) of phosphorus oxychloride dissolved in 25 ml. of tetrahydrofuran. The reaction was exothermic and the mixture became canary-yellow during the addition. The reaction mixture turned brown when all the triphenylsilyllithium had been added. Color Test I was negative. Tetrahydrofuran was removed from the mixture by distillation; the residue was treated with a mixture of 200 ml. of dry ether and 200 ml. of sodium-dried petroleum ether (b.p. 60–70°), and filtered under nitrogen. The filtrate was distilled to give a small amount of viscous material, which on treatment with cyclohexane gave 0.5 g. of an insoluble residue. It melted at 363–365° after crystallization from hot benzene and did not depress the melting point of an authentic sample of hexaphenyldisilane. The cyclohexane-soluble portion was chromatographed on alumina. Elution with carbon tetrachloride gave 0.2 g. (0.8%) of hexaphenyldisiloxane, m.p. and mixed m.p. 226–228°. Further elution with methanol gave 0.5 g. (2.0%) of triphenylsilanol, which melted at 152–153° after crystallization from cyclohexane, and did not depress the melting point of an authentic sample.

The residue obtained after treatment with the petroleum ether–ether mixture was hydrolyzed with water; a pronounced odor of phosphine was noticed. The mixture was filtered and the water-insoluble portion gave 21.0 g. (90.0%) of hexaphenyldisilane, m.p. and mixed m.p. 365–366°. The aqueous layer was worked up by extraction with ether, but no product could be isolated.

Triphenylsilyllithium and tri-n-butyl phosphate. To 23.0 g. (0.09 mole) of tri-*n*-butyl phosphate was added 0.09 mole of a solution of triphenylsilyllithium in 150 ml. of tetrahydrofuran, during one hour. Color Test I was negative at the end of the addition and the mixture was hydrolyzed by adding a half-saturated solution of ammonium chloride. It was extracted with ether and dried over anhydrous sodium sulfate. Partial evaporation of the solvent from the ether extract precipitated out a small quantity of hexaphenyldisilane (0.27 g., 1.2%) which melted at 360–362° and did not depress the melting point of an authentic sample. Complete removal of the solvent gave a residue which was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave 23.7 g. (83.5%) of *n*-butyltriphenylsilane, m.p. 78–85°. Crystallization from methanol raised the melting point to 85–87°. The melting point was not depressed when the compound was admixed with an authentic sample of *n*-butyltriphenylsilane. Elution of the alumina column with benzene gave 0.3 g. (1.3%) of hexaphenyldisiloxane, m.p. and mixed m.p. 225–227°; and elution with methanol gave 1.2 g. (4.6%) of triphenylsilanol, which melted at 153–155° after crystallization from cyclohexane. No depression in melting point was observed when mixed with an authentic sample.

Triphenylsilyllithium and arsenic trichloride. To a solution of 5.4 g. (0.03 mole) of arsenic trichloride in 50 ml. of tetrahydrofuran was added 0.09 mole of a tetrahydrofuran solution of triphenylsilyllithium (150 ml.), during one hour. The reaction was strongly exothermic and the rate of addition was controlled to regulate the temperature. When the addition was complete the mixture gave a negative Color Test I and it was then hydrolyzed by adding water. The insoluble residue (11.8 g.) was extracted with hot tetralin to give 10.0 g. of hexaphenyldisilane, m.p. and mixed m.p. 362–364°. The tetralin insoluble portion was a black solid (1.8 g.) which was identified as metallic arsenic by qualitative tests. A portion of this residue was dissolved in con-

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[7] L. J. Brady, *Anal. Chem.*, **20**, 1034 (1948).

[8] H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

centrated nitric acid. The addition of ammonium molybdate solution followed by warming of the mixture gave a yellow precipitate, indicating the presence of arsenic.

The aqueous layer of the hydrolyzed reaction mixture was extracted with ether and removal of the solvent from the ether extract after drying over sodium sulfate, gave a residue which was successively extracted with petroleum ether (b.p. 60–70°), methanol and hot benzene. The methanol extract gave 5.7 g. of triphenylsilanol, which melted at 151–153°, after crystallization from cyclohexane. A mixed melting point with an authentic sample was not depressed.

From the benzene extract, 0.3 g. of hexaphenyldisilane, m.p. and mixed m.p. 360–362° and 0.25 g. of hexaphenyldisiloxane, m.p. and mixed m.p. 224–226°, were isolated by fractional crystallization.

The petroleum ether extract was chromatographed on alumina. Elution with the same solvent gave 3.1 g. (13.2%) of triphenylsilane, identified by a comparison of the infrared spectrum in carbon tetrachloride with that of an authentic sample. The characteristic Si-H absorption band was observed at 2105 cm.$^{-1}$. Elution of the column with carbon tetrachloride gave 0.97 g. of hexaphenyldisiloxane, m.p. and mixed m.p. 224–226°. The column was finally eluted with methanol to give 1.1 g. of triphenylsilanol, m.p. and mixed m.p. 152–153°. The total yield of hexaphenyldisilane was 10.0 g. (44%), of triphenylsilanol was 6.8 g. (13.3%), and that of hexaphenyldisiloxane was 1.3 g. (5.1%).

Triphenylsilyllithium and antimony trichloride. A solution of 0.06 mole (140 ml.) of triphenylsilyllithium was slowly added to 4.6 g. (0.02 mole) of antimony trichloride dissolved in 25 ml. of tetrahydrofuran, during one hour at room temperature. Color Test I was negative after all the triphenylsilyllithium had been added. The mixture was hydrolyzed by adding water, the insoluble residue was removed by filtration and the aqueous layer was extracted with ether. The brown residue was extracted with hot tetralin to give 7.8 g. (50.1%) of hexaphenyldisilane, m.p. and mixed m.p. 364–365°. The tetralin-insoluble portion (2.2 g., 90.5%) was identified as metallic antimony by qualitative tests.

The ether extract was dried over sodium sulfate and removal of the solvent gave a viscous liquid, which was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave 0.8 g. (5.1%) of triphenylsilane, identified by a comparison of the infrared spectrum with that of an authentic sample. Elution with benzene gave 1.0 g. (6.2%) of hexaphenyldisiloxane, m.p. and mixed m.p. 227–228°; and final elution of the column with methanol resulted in the isolation of 3.5 g. (21.1%) of triphenylsilanol, m.p. and mixed m.p. 154–155°.

Triphenylsilyllithium and bismuth trichloride. Addition of 0.09 mole (103.5 ml.) of triphenylsilyllithium to 9.5 g. (0.03 mole) of bismuth trichloride (dissolved in 50 ml. of tetrahydrofuran) was carried out, at room temperature, during 1 hr. The reaction was exothermic to give a black mixture and Color Test I was negative at the end of the addition. The mixture was hydrolyzed with water. The insoluble residue on extraction with tetralin gave 18.4 g. (78.8%) of hexaphenyldisilane, m.p. and mixed m.p. 365–366°, and 5.1 g. (81.3%) of metallic bismuth, identified by qualitative tests. The aqueous layer obtained after hydrolysis was extracted with ether and work-up as in the previous case by chromatography, gave 0.8 g. (3.4%) of triphenylsilane, 0.5 g. (2.1%) of hexaphenyldisiloxane and 1.9 g. (7.6%) of triphenylsilanol. These compounds were characterized by mixed melting point determinations with authentic samples.

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AMES, IOWA

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT OF THE KOPPERS CO., INC.]

Reductions with Dialkylaluminum Hydrides

ALFRED E. G. MILLER, JEAN W. BISS, AND LOUIS H. SCHWARTZMAN

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Dialkylaluminum hydrides, such as diisobutylaluminum hydride and diethylaluminum hydride, effectively reduced cyclohexanone to cyclohexanol, benzoic acid to benzyl alcohol, benzonitrile to benzaldehyde, *n*-butyl caproate to *n*-butanol and *n*-hexanol, methyl benzoate to benzyl alcohol and diethyl fumarate to *trans*-2-butene-1,4-diol. No selectivity in reduction of the acetylenic bond of 2-butyne-1,4-diol was obtained but some selectivity was found with 1-ethynylcyclohexanol. The stoichiometries involved in the reductions with dialkylaluminum hydrides are very similar to those observed with lithium aluminum hydride.

Dialkylaluminum hydrides, *i.e.*, diisobutylaluminum hydride, are effective reducing agents and are similar to lithium aluminum hydride in their reactivities. The dialkylaluminum hydrides are liquids and are conveniently handled under nitrogen. Although the equivalent reducing weight of lithium aluminum hydride is lower than that of the dialkylaluminum hydrides, the latter appear to be more selective in certain reactions. Moreover, the ease of preparation and the relatively low cost of the dialkylaluminum hydrides offer certain advantages over lithium aluminum hydride.

The reduction of cyclohexanone with diisobutylaluminum hydride in a 1:1 mole ratio gave 83% yields of cyclohexanol.

Meerwein[1] reported that triethylaluminum and triethylboron could be used to reduce aldehydes,

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[1] H. Meerwein, G. Hinz, H. Majert, and H. Sonke, *J. Prakt. Chem.*, **147**, 226 (1937).