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

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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).

ketones, α,β-unsaturated aldehydes and halogenated aldehydes and ketones to the corresponding alcohols. We view this reaction as a particular case of the *Meerwein-Ponndorf-Verley reduction*[2] in which the alkyl groups act as hydrogen donors to give the corresponding aluminum alkoxide with the evolution of an olefin. However, the exact analogy cannot be drawn since the reduction with triethylaluminum is not reversible.

$$3\ \mathrm{RCHO} + \mathrm{Al(C_2H_5)_3} \longrightarrow \mathrm{Al(OCH_2R)_3} + 3\ \mathrm{C_2H_4}$$

Ziegler[3] repeated Meerwein's work and also noted the use of diisobutylaluminum hydride as a reducing agent but failed to report his experimental results.

Benzoic acid was reduced with diisobutylaluminum hydride to give 72% yields of benzyl alcohol. Gas was evolved upon the addition of the hydride to benzoic acid until one mole of the reducing agent had reacted with three moles of benzoic acid; thereafter, the addition gave no gas. Therefore, the isobutyl groups on the diisobutylaluminum hydride react quantitatively with active hydrogens, but, as we will try to indicate in this paper, these alkyl groups are not involved in the reduction of compounds other than aldehydes and ketones. Moreover, the stoichiometry of the reduction, as based on hydrogen evolved from excess reagent, seems to be six equivalents of hydride per mole of aluminum benzoate. This stoichiometry corresponds to that observed with lithium aluminum hydride.

The reduction of benzonitrile with diisobutylaluminum hydride gave no benzylamine, as such, instead only benzaldehyde and benzalbenzylamine were obtained. Using a 4:1 mole ratio of hydride to nitrile, 68% of benzaldehyde and 31% of benzylamine (based on hydrolysis products) were obtained, whereas a 2:1 mole ratio of hydride to nitrile gave 82% benzaldehyde and 13% benzylamine (based on hydrolysis products). When this reaction was repeated with a 1:1 mole ratio of hydride to nitrile 90% yields of benzaldehyde were obtained with only a trace of benzalbenzylamine. Moreover the gas obtained from the decomposition of the reduction complex consisted of only isobutane with no hydrogen or isobutylene. This indicates that a 1:1 mole ratio of hydride to nitrile is most efficient for reduction to the aldehyde and that the isobutyl groups do not participate in the reduction.

Benzonitrile has been reduced to benzylamine in 72% yield using a 2:1 mole ratio of nitrile to lithium aluminum hydride and in 93% yield with a 1:1 mole ratio.[4] Benzalaniline has been reduced to *N*-benzylaniline in 93% yield with a 4:1 mole ratio of benzalaniline to lithium aluminum hydride.

Friedman[5] reported the reduction of nitriles to aldehydes with lithium aluminum hydride by the very careful addition of one mole of hydride to four moles of nitrile.

Therefore it appears that diisobutylaluminum hydride is a more selective reagent than lithium aluminum hydride in the reduction of nitriles to aldehydes.

n-Butyl caproate was reduced with diisobutylaluminum hydride in varying mole ratios. With a 1:1 mole ratio of hydride to ester very poor yields of 1-hexanol were obtained. This is evidence that the residual alkyl groups on the hydride are not involved in the reduction of esters. Good yields of 1-hexanol were obtained with mole ratios of 3:1 and 4:1 of hydride to ester, but in each case the gases evolved upon decomposition of the complex indicated the proper stoichiometry to be a 2:1 mole ratio of hydride to ester. Therefore, methyl benzoate was reduced with a 2:1 mole ratio of diisobutylaluminum hydride to ester and a 90% yield of benzyl alcohol was obtained. Moreover, the off gas from this experiment contained 4 moles of isobutane and no hydrogen.

Lithium aluminum hydride has been reported[6] to reduce α,β-unsaturated esters to the corresponding α,β-unsaturated alcohols in excellent yields. We were unable to reduce diethyl fumarate to *trans*-2-butene-1,4-diol with lithium aluminum hydride although many different reaction conditions were tried. However, both diisobutylaluminum hydride and diethylaluminum hydride reacted with diethyl fumarate to produce *trans*-2-butene-1,4-diol in 65–70% yields. In each case a 4:1 mole ratio of reducing agent to diester was required. Since the olefin was obtained in good yields and since no gaseous olefin was obtained in the off-gas, it seems apparent that the residual alkyl groups on the hydrides are not involved in the reduction.

Wilke and Mueller[7] reported the reduction of disubstituted acetylenic hydrocarbons, *i.e.*, 3-hexyne, to the corresponding cis olefins with diisobutylaluminum hydride. It has also been shown that[8] lithium aluminum hydride reduced acetylenes to trans olefins in excellent yields if the triple bond is flanked by a propargylic hydroxyl group. Therefore, the reductions of 1-ethynylcyclohexanol and 2-butyne-1,4-diol were tried with diisobutylaluminum hydride. In the case of 2-butyne-1,4-diol the reduction was not selective and a very poor material balance was obtained. The reduction of 2-butyne-1,4-diol with lithium aluminum hydride

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(2) A. L. Wilds, *Org. Reactions*, **II**, 178 (1944).

(3) K. Ziegler, K. Schneider, and J. Schneider, *Angew. Chem.*, **67**, 425 (1955).

(4) R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **70**, 3738 (1948). L. H. Amundsen and L. S. Nelson, *J. Am. Chem. Soc.*, **73**, 242 (1951).

(5) L. Friedman, Abstracts of Papers, 116th Meeting American Chemical Society, September 18–23, 1949, p. 5 M.

(6) C. J. Martin, A. I. Schepartz, and B. F. Daubert, *J. Am. Chem. Soc.*, **79**, 2601 (1948).

(7) J. Wilke and H. Mueller, *Chem. Ber.*, **89**, 444 (1956).

(8) A. B. Bates, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 1854 (1954).

gave *trans*-2-butene-1,4-diol in very poor yields. The reduction of 1-ethynylcyclohexanol with diisobutylaluminum hydride gave a product which contained 48% of 1-vinylcyclohexanol and 52% of unreacted 1-ethynylcyclohexanol.

EXPERIMENTAL

Koppers Co. diisobutylaluminum hydride and diethylaluminum hydride were used in this investigation.

All melting points and boiling points are uncorrected.

Hydrogen numbers were determined by reduction of the compounds in 95% ethanol with 0.1 g. Adams' platinum catalyst at 25° and one atmosphere of hydrogen.

Reduction of cyclohexanone. Cyclohexanone (21.6 g., 0.22 m.) in benzene (28 ml.) was added under nitrogen over 1.5 hr. to a stirred solution of diisobutylaluminum hydride (0.22 m.) in benzene (100 ml.). The temperature rose to 45° during the addition and was maintained at this temperature during an 8-hr. stirring period. The cooled reaction mixture was decomposed by the addition of methanol (22.8 g., 0.71 m.) in 25 ml. benzene followed by the addition of water (12.0 g., 0.66 m.) in 25 ml. methanol. The gas evolved during the decomposition contained isobutane but no isobutylene. The decomposed reaction mixture was filtered and distilled to give 18.3 g. (83% yield) of cyclohexanol; b.p. 82.5–83.0°/40 mm., n_D^{23} 1.4655.

The 3,5-dinitrobenzoate of cyclohexanol was prepared in the usual manner and after recrystallization from aqueous ethanol melted at 111° and gave no melting point depression when admixed with an authentic sample.

Similarly the phenylurethane of cyclohexanol was prepared (m.p. 82° from petroleum ether) and gave no melting point depression when admixed with an authentic sample.

Reduction of benzoic acid. Diisobutylaluminum hydride (0.45 m.) was added under nitrogen over 3 hr. to a stirred mixture of benzoic acid (18.3 g., 0.15 m.) in 200 ml. of benzene. Gas evolution stopped after 0.05 m. of diisobutylaluminum hydride had been added. The reaction temperature rose to 45° and stirring was continued at this temperature for 8 hr. The cooled reaction mixture was decomposed by the addition of methanol (44.8 g., 1.4 m.) in 45 ml. of benzene, followed by water (24.3 g., 1.35 m.) in 25 ml. of methanol. The gas evolved during decomposition contained 0.18 m. hydrogen and 0.69 m. of isobutane. The reaction mixture was filtered and distilled to give 11.7 g. (72% yield) of benzyl alcohol; b.p. 100°/18.5 mm., n_D^{23} 1.5390.

The phenylurethane was prepared in the usual manner and after recrystallization from petroleum ether melted at 77.5° and gave no melting point depression in admixture with an authentic sample of the phenylurethane of benzyl alcohol.

Reduction of benzonitrile. Diisobutylaluminum hydride (0.4 m.) was added under nitrogen over 1.5 hr. to a solution of benzonitrile (10.3 g., 0.1 m.) in 140 ml. of benzene. No gas evolution was observed and the temperature rose to 45°. Stirring was continued at 45° for 8 hr. The cooled reaction mixture was decomposed by the addition of methanol (38.4 g., 1.2 m.) in 45 ml. of benzene followed by water (21.6 g., 1.2 m.) in 50 ml. of methanol. The gas evolved during decomposition contained 0.32 m. hydrogen, 0.60 m. of isobutane and no isobutylene. The solid aluminum salts were filtered and the filtrate was concentrated under reduced pressure. The concentrate was dissolved in ether (300 ml.) and extracted with 5% hydrochloric acid (2 × 100 ml.). The ether layer was dried and distilled to give 3.9 g. (37% yield) of benzaldehyde boiling at 50–60°/5 mm. The 2,4-dinitrophenylhydrazone of benzaldehyde (m.p. 237° from ethanol) was prepared in the usual manner and gave no melting point depression when admixed with an authentic sample.

The acid extract was made alkaline with aqueous sodium hydroxide, the organic amine extracted with ether and dried over anhydrous magnesium sulfate. Distillation of the dry ether solution gave 6.1 g. of product boiling at 168–170°/5 mm.; n_D^{24} 1.5962. Quantitative hydrogenation of this material over a palladium catalyst gave a hydrogen number of 0.98 assuming the compound to be benzalbenzylamine. The hydrogenated product was converted to the benzamide[10] melting at 112.5–113.5° and to the benzenesulfonamide[11] melting at 66–67°.

In a subsequent experiment run under identical conditions benzonitrile (17 g., 0.165 m.) was reduced with diisobutylaluminum hydride (0.33 m.). However, the decomposed reaction mixture was acidified with 300 ml. of 20% sulfuric acid and steam distilled. The steam distillate gave 12.2 g. of benzaldehyde and 4 g. of benzylamine was isolated from the residue by making it alkaline and extracting with ether. The gas evolved during decomposition contained 0.14 m. hydrogen, 0.51 m. of isobutane and no isobutylene.

This experiment was repeated with 22.8 g. (0.22 m.) of benzonitrile and 31.9 g. (0.22 m.) of diisobutylaluminum hydride and a 90% yield (20.9 g.) of benzaldehyde was obtained. Also only a trace of benzalbenzylamine was obtained and the gas evolved (0.44 m.) upon decomposition was entirely isobutane.

Reduction of n-butyl caproate. Diisobutylaluminum hydride (0.33 m.) was added under nitrogen over 2.5 hr. to a stirred solution of *n*-butyl caproate (18.4 g., 0.11 m.) in 150 ml. of benzene. The temperature rose to 45° during the addition and was maintained at this temperature for another 8 hr. The cooled reaction mixture was decomposed by the addition of methanol (32.0 g., 1.0 m.) in benzene (55 ml.) followed by water (18.0 g., 1.0 m.) in methanol (30 ml.). The gas evolved during decomposition contained 0.19 m. of hydrogen, 0.62 m. of isobutane, and no isobutylene. The decomposed reaction mixture was filtered, concentrated, and distilled to give 4.7 g. (58% yield) of 1-butanol boiling at 116°, n_D^{22} 1.3970, and 8.2 g. (73% yield) of 1-hexanol boiling at 155°, n_D^{22} 1.4174.

The α-naphthyl urethane of the 1-hexanol was prepared in the usual manner and after recrystallization from petroleum ether melted at 58.5–59.0°. No mixed melting point depression was observed when admixed with an authentic sample.

This experiment was repeated in petroleum ether and the ester was added to the diisobutylaluminum hydride; 1-hexanol was obtained in 77% yield. With a 1:1 mole ratio of diisobutylaluminum hydride to ester a very poor yield of 1-hexanol was obtained; a 4:1 mole ratio gave 82% yields of 1-hexanol. The gases obtained from decomposition of the reaction mixtures contained very little isobutylene and therefore the isobutyl groups could not be greatly involved in the reductions.

Reduction of methyl benzoate. Diisobutylaluminum hydride (30.6 g., 0.22 m.) was added under nitrogen over 1 hr. to a stirred solution of methyl benzoate (14.6 g., 0.11 m.) in 250 ml. of benzene. The temperature rose to 45° during the addition and was maintained at this temperature for another 2 hr. The product was decomposed in the usual manner to give 0.44 m. of gas which consisted entirely of isobutane with no hydrogen or isobutylene. Distillation of the organic product gave 10.4 g. (90% yield) of benzyl alcohol; b.p. 90–91°/7 mm., n_D^{25} 1.5386.

Reduction of diethyl fumarate. Diisobutylaluminum hydride (0.85 m.) was added under nitrogen over 10 hr. to a stirred solution of diethyl fumarate (34.4 g., 0.2 m.) and benzene (160 ml.). The maximum temperature during the addition was 50°. After standing overnight at room temperature, the reaction mixture was decomposed by the addition of methanol (76.8 g., 2.4 m.) in benzene (150 ml.) followed by water (45 g., 2.5 m.). The gas evolved during the de-

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(10) H. Franzen, *Ber.*, **42**, 2465 (1909) reported a melting point of 112° for dibenzylamine benzamide.

(11) R. L. Shriner and R. C. Fuson, *Identification of Organic Compounds*, p. 194, John Wiley & Sons, New York, 1946, reports the melting point of dibenzylamine benzenesulfonamide to be 68°.

composition contained 0.09 m. of hydrogen, 1.60 m. of isobutane, and 0.06 m. of isobutylene. The reaction mixture was filtered and the aluminum salts were washed several times with methanol. The filtrate was distilled to give 12.3 g. (70% yield) of *trans*-2-butene-1,4-diol boiling at 86–88°/0.5 mm.; n_D^{25} 1.4758.

Bromine (12.2 g., 0.076 m.) was added dropwise over 4 hr. to a stirred mixture of *trans*-2-butene-1,4-diol (6.6 g., 0.075 m.) in chloroform maintained at 5–10°. The product was filtered and recrystallized from chloroform to give 14.2 g. of *meso*-2,3-dibromo-1,4-butanediol[12] melting at 130.0–130.6°.

Anal. Calcd. for $C_4H_8O_2Br_2$: Br, 64.5. Found: Br, 64.5.

Reduction of diethyl fumarate. Diethylaluminum hydride (0.2 m.) was added under nitrogen over 1 hour to a stirred solution of diethyl fumarate (8.6 g., 0.05 m.) in benzene (300 ml.). The temperature rose to 45° during the reaction. After stirring an additional 2 hr., the reaction mixture was decomposed at room temperature by the slow addition of methanol (25.6 g., 0.8 m.) in benzene (55 ml.) followed by water (15 g., 0.8 m.). The gas evolved during the decomposition contained 0.39 m. of ethane and 0.02 m. of ethylene. The decomposed reaction mixture was filtered and the aluminum salts were washed several times with methanol. The filtrates were combined and distilled to give 2.9 g. (66% yield) of *trans*-2-butene-1,4-diol boiling at 86–88°/0.5 mm.; n_D^{25} 1.4752.

Reduction of 2-butyne-1,4-diol with lithium aluminum hydride. 2-Butyne-1,4-diol (43.2 g., 0.5 m.) in tetrahydrofuran (300 ml.) was added dropwise to lithium aluminum hydride (39.0 g., 1.0 m.) in anhydrous ether (1 l.). The reaction mixture was refluxed for 18 hr., cooled, and decomposed by the addition of water (72 g., 4.0 m.). The resulting slurry was filtered, the ether dried and concentrated. Distillation of the residue (6.1 g.) gave 2-butene-1,4-diol (3.3 g., 7.5% yield) boiling at 112–114°/3 mm.

Anal. Calcd. for $C_4H_8O_2$: Hydrogen No., 1.00; Hydroxyl No.,[13] 2.0. Found: Hydrogen No., 1.05; Hydroxyl No., 1.9.

This was confirmed as the *trans* isomer by its infrared spectrum and dibromo derivative (m.p. 129–130°).

Reduction of 2-butyne-1,4-diol with diisobutylaluminum hydride. Diisobutylaluminum hydride (0.2 m.) was added over 4 hr. to a stirred slurry of 2-butyne-1,4-diol (25.8 g., 0.3 m.) in benzene (160 ml.). The volume of gas evolved during this addition indicated that the reaction of the diisobutylaluminum hydride with the hydroxyl groups of 2-butyne-1,4-diol was practically quantitative. After stirring at 45° for 6 hr., a second portion of diisobutylaluminum hydride (0.3 m.) was added over 0.5 hr. The mixture was stirred for 8 hr. at 45° and then was decomposed by the addition of methanol (32.0 g., 1.0 m.) in benzene (35 m.) followed by water (27.0 g., 1.5 m.) in methanol (30 ml.). The reaction mixture was filtered and concentrated under reduced pressure leaving 19.7 g. of solid residue. Recrystallization from ethyl acetate produced unreacted 2-butyne-1,4-diol (15.0 g.) melting at 55–56°.

Reduction of 1-ethynylcyclohexanol. Diisobutylaluminum hydride (0.2 m.) was added under nitrogen to a stirred solution of 1-ethynylcyclohexanol (12.4 g., 0.1 m.) in 150 ml. of benzene over 1.1 hr. The temperature rose to 40° during the addition. The reaction mixture was stirred at 60° for 8 hr., cooled and decomposed by the addition of methanol (19.2 g., 0.6 m.) in benzene (50 ml.) followed by water (10.8 g., 0.6 m.) in methanol (25 ml.). The product was filtered and concentrated to give 9.7 g. of residue which gave a hydrogen number of 1.52 and a methynyl hydrogen number[14] of 0.51. Therefore, this crude product contained 52% of unreacted 1-ethynylcyclohexanol and 48% of 1-vinylcyclohexanol.

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(12) C. Prevost, *Compt. rend.*, **183**, 1292 (1926).

(13) S. Siggia, *Quantitative Organic Analysis via Functional Groups*, p. 9, John Wiley & Sons, New York, 1954.

(14) S. Siggia, *Quantitative Organic Analysis via Functional Groups*, p. 86, John Wiley & Sons, New York, 1954.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, TENNESSEE EASTMAN COMPANY,
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Phosphorus-Containing Derivatives of 2,2-Dimethyl-1,3-propanediol

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A number of phosphorus-containing esters were made from 2,2-dimethyl-1,3-propanediol. Phosphoryl chloride gave a cyclic phosphorochloridate which could be treated with an alcohol or phenol to produce a neutral ester. Phosphonic dichlorides gave cyclic neutral esters directly. When phosphorus trichloride was used, a cyclic bisphosphite was produced; however, when this reaction was carried out in the presence of an alcohol, a cyclic hydrogen phosphite was formed. Treatment of 2,2-dimethyl-1,3-propanediol with diethyl phosphorochloridate gave a neutral bisphosphate which on pyrolysis liberated triethyl phosphate to yield a cyclic neutral ester. In general, these derivatives of 2,2-dimethyl-1,3-propanediol are stable, white, crystalline compounds.

This investigation was undertaken to study the preparation and properties of phosphorus-containing esters derived from 2,2-dimethyl-1,3-propanediol, a derivative of isobutyraldehyde. These esters were made using phosphoryl chloride, phosphonic dichlorides, phosphorus trichloride, and diethyl phosphorochloridate. Treatment of a 1,2- or 1,3-glycol with a phosphorus dihalide or trihalide usually results in the formation of cyclic esters.[1-13]

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(1) A. D. F. Toy (to Victor Chemical Works), U. S. Patent **2,382,622** (1945).

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