reagents, phenylmagnesium bromide reacted with triphenylgermane to afford a 7.3% yield of 4-hydroxybutyltriphenylgermane; but *n*-butylmagnesium bromide did not appear to react, as no products attributable to metalation could be isolated.

Structure proof of 4-hydroxybutyltriphenylgermane. *p*-Toluenesulfonyl chloride (2.5 g., 0.013 mole) was added in three portions over a period of 5 min. to 4.0 g. (0.0106 mole) of 4-hydroxybutyltriphenylgermane dissolved in 10 ml. of dry pyridine, maintained at *ca.* 20°. The reaction mixture was stirred for 1 hr., cooled to 10–15°, and then poured upon crushed ice containing 20 ml. of concd. hydrochloric acid. Ether was added and the organic layer was separated. After drying with anhydrous sodium sulfate, the solvent was evaporated. The resulting white solid was treated with 100 ml. of dry ether and added as a suspension to 1.25 g. (0.033 mole) of lithium aluminum hydride in 30 ml. of ether. This mixture was heated at reflux for 20 hr. and subsequently poured upon crushed ice. The reaction products were worked up in the usual manner and chromatographed over alumina to give 2.99 g. (78.3%) of *n*-butyltriphenylgermane, m.p. 84–86°, identified by mixed melting point and by comparison of the infrared spectra; and 0.52 g. (13%) of recovered 4-hydroxybutyltriphenylgermane.

Reaction of triphenylgermyllithium with refluxing tetrahydrofuran. A tetrahydrofuran solution of triphenylgermyllithium, prepared from 9.12 g. (0.015 mole) of hexaphenyldigermane and 1 g. of lithium in 100 ml. of tetrahydrofuran, was freed of excess lithium by filtration and heated at gentle reflux for 5 days. Color Test I[7] remained positive. Hydrolysis was effected by pouring upon crushed ice, and the solid subsequently filtered. This material was recrystallized from benzene to give 0.96 g. (10.5%) of hexaphenyldigermane, m.p. 344–347°.

The organic layer was worked up and the products chromatographed. Employing the usual techniques, there were obtained 1.03 g. (11.3%) of triphenylgermane, m.p. 45–47°; an additional 0.13 g. (1.4%) of hexaphenyldigermane, m.p. 342–345°; 2.58 g. (22.8%) of 4-hydroxybutyltriphenylgermane, m.p. 101–104°; and 0.97 g. (10.1%) of triphenylgermanol, m.p. 131–134°.

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Preparation and Reactions of Some *n*-Amylated Boranes[1]

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In the course of investigating certain boron-nitrogen bonded materials some *n*-amylated boranes have been prepared. Di-*n*-amylchloroborane was obtained by the reaction of trichloroborane with the commercially available tri-*n*-amylborane[2] according to the method of McCusker and coworkers[3] in 87% yield. The interaction of stoichiometric amounts of di-*n*-amylchloroborane and di-*n*-amylamine afforded the amineborane, which was thermally decomposed to release hydrogen chloride and to form tetra-*n*-amylaminoborane. On treatment of the aminoborane with trichloroborane, di-*n*-amylchloroborane was reconstituted along with lesser amount of di-*n*-amylamino dichloroborane. However, as dialkylchloroboranes tend to disproportionate, the resultant yields were not satisfactory. Di-*n*-amylaminodichloroborane has also been obtained by treating trichloroborane with di-*n*-amylamine.

Alcoholysis of di-*n*-amylchloroborane with methanol afforded di-*n*-amylmethoxyborane. Careful hydrolysis of the methoxyborane or the chloroborane in a nitrogen atmosphere did not yield pure di-*n*-amylhydroxyborane but instead gave disproportionation products contaminated with that material; hydrolysis in open air afforded mainly *n*-amyldihydroxyborane, which was isolated in a high state of purity and in good yield. The latter compound easily eliminates the elements of water to yield B-tri-*n*-amylboroxine. The boroxine reacts with trichloroborane in the usual manner[4] to reconstitute *n*-amyldichloroborane.

EXPERIMENTAL[5]

Di-n-amylchloroborane. One hundred grams (0.445 mole) of tri-*n*-amylborane and 26.1 g. (0.224 mole) of trichloroborane were mixed with vigorous stirring. The mixture was distilled rapidly and the fraction boiling from 180–220° collected. The major portion of the product distilled at 204–216°. Redistillation *in vacuo* through a column afforded 107 g. (87%) of di-*n*-amylchloroborane, b.p. 79–81°/10mm.

Anal. Calcd.: B, 5.7. Found B, 5.8.

Tetra-n-amylaminoborane. A solution of 22.1 g. (0.114 mole) of di-*n*-amylchloroborane in 100 cc. of dry benzene was added with stirring to a solution of 18.5 g (0.117 mole) of di-*n*-amylamine in 500 cc. of benzene. The resultant exothermic reaction produced a white precipitate, which dissolved on refluxing with the release of hydrogen chloride. The mixture was refluxed for several hours until the evolution of hydrogen chloride had almost ceased; the resultant solution was filtered and the solvent removed by evaporation. The residue was distilled *in vacuo* affording 24 g. (69%) of tetra-*n*-amylaminoborane, b.p. 124°/8 mm.

Anal. Calcd. for $(C_5H_{11})_2N—B(C_5H_{11})$: C, 77.6; H, 14.3; B, 3.5; N, 4.5; mol. wt. 309.4. Found: C, 75.4; H, 14.1; B, 4.1; N, 4.3; mol. wt. 317.

Di-n-amylamino-dichloroborane. A solution of 15.7 g. (0.1 mole) of di-*n*-amylamine in 100 cc. of toluene was added with stirring to a solution of 12.9 g. (0.11 mole) trichloroborane in 300 cc. of toluene. The mixture was refluxed for 10 hr. and the solvent stripped. Distillation of the residue

(1) Supported by the Office of Ordnance Research, U. S. Army.

(2) Anderson Chemical Company, Weston, Mich.

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(5) Analyses by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y.

afforded 20 g. (84%) of di-*n*-amylaminodichloroborane, b.p. 121°/10 mm.

Anal. Calcd. for $(C_5H_{11})_2N—BCl_2$: C, 50.4; H, 9.3; B, 4.55; N, 5.9; Cl, 29.85. Found: C, 50.6; H, 9.2; B, 4.4; N, 5.9; Cl, 29.5. The reaction of this product with *n*-amyl Grignard reagent[6] resulted in the formation of the tetra-alkylated aminoborane, identical with the one described above.

Di-n-amylmethoxyborane. In a dry nitrogen atmosphere, 18.9 g. (0.1 mole) of di-*n*-amylchloroborane was added with stirring to 125 cc. of pure anhydrous methanol. The reaction mixture was slowly concentrated at room temperature *in vacuo* and the residue distilled, yielding 14.5 g. (78%) of di-*n*-amylmethoxyborane, b.p. 114–116°/8 mm.

Anal. Calcd. for $(C_5H_{11})_2BOCH_3$: C, 71.7; H, 13.7; B, 5.9. Found: C, 73.9; H, 13.7; B, 6.1.

n-Amyldihydroxyborane. Water was added dropwise to 9.2 g. (0.05 mole) of di-*n*-amylmethoxyborane in a beaker. The resultant exothermic reaction afforded 5.4 g. (93%) of white crystals of *n*-amyldihydroxyborane,[7] m.p. after recrystallization from ligroin, 92–93°. The elementary analysis corresponded to the dihydroxyborane. However, molecular weight determinations (cryoscopically in benzene) gave a value of 295, indicating the existence of a dehydrated trimeric product (calcd. for $(C_5H_{11}BO)_3$: 293.9) and illustrating the ready dehydration of an alkyldihydroxyborane.

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Synthesis and Properties of Isomeric Menthyl Phosphates.[1] Organophosphorus Compounds. III[2]

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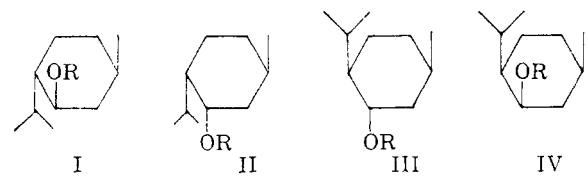
The synthesis of menthyl dihydrogen phosphate (Ib) has been reported by Milobedzki and Janczak[3] by phosphorylating (−)-menthol with phosphorus oxychloride. The same phosphate was also isolated from a reaction mixture of (−)-menthol and phosphorus pentachloride.[4] However the other isomeric menthyl phosphates have not yet been synthesized. We have synthesized the isomeric menthyl phosphates by an unequivocal method to obtain the reference compounds for the study of terpene biosynthesis. Here the syntheses and some of the properties of the phosphates are described.

Isomeric menthols employed as the starting compounds were (−)-menthol (I), (+)-neomenthol (II), (+)-isomenthol (III), and (+)-neoisomenthol (IV), and the phosphorylating agent was tetra-(*p*-nitrophenyl)pyrophosphate which was prepared by the reaction of bis(*p*-tolyl)carbodiimide with two equivalents of bis(*p*-nitrophenyl)phosphate in dioxane as described by Khorana.[5,6] Tetra(*p*-nitrophenyl)pyrophosphate was allowed to react with I, II, III, and IV in dioxane. After a reaction for approximately forty hours at room temperature, the bis(*p*-nitrophenyl)phosphates of the isomeric menthols (Ia, IIa, IIIa, and IVa) were obtained in fair yields. Among these isomeric menthyl bis(*p*-nitrophenyl)phosphates, neo- (IIa) and neoisomenthyl bis(*p*-nitrophenyl)phosphate (IVa) were unstable in polar solvents—*i.e.* they liberated bis(*p*-nitrophenyl)phosphate group on leaving the methanol solution at room temperature.



I II III IV

I, II, III, and IV. R = H.
Ia, IIa, IIIa, and IVa. R = $—PO(OC_6H_4NO_2)_2$.
Ib, IIb, IIIb, and IVb. R = $—PO_3H_2$.
Ic. R = $—PO(OC_6H_4NO_2)OH$.

On the hydrogenation over Adams' platinum catalyst, Ia, IIa, IIIa and IVa were hydrogenolyzed to the corresponding menthyl dihydrogen phosphates, (Ib), (IIb), (IIIb), and (IVb), liberating cyclohexylamine as the hydrochloride. In this case, the addition of hydrochloric acid was necessary for smooth absorption of fourteen moles of hydrogen. If the acid was not added, the absorption of hydrogen ceased at ten moles. The necessity for the addition of acid was also pointed out by Mofatt and Khorana,[5] but the isolation of cyclohexylamine salt was not described. The role of acid may be the detoxication of toxic free amine by converting it to nontoxic ammonium ion as observed in the hydrogenation of aromatic amines.[7]

The hydrolysis of Ia with 1*N* sodium hydroxide in dioxane solution yielded menthyl mono(*p*-nitrophenyl)phosphate (Ic), liberating quantitatively one of the two *p*-nitrophenyl groups which could be determined spectrophotometrically. The solubilities of isomeric dihydrogen phosphates in water, either in the free state or as the salts, were low. Melting points of the phosphates are summarized in Table I.

(1) Presented at the 153th meeting of the Kansai Section of the Agricultural Chemical Society of Japan, Kyoto, October 18, 1958.

(2) For a previous paper in this series, see T. Hashizume, K. Fujimoto, H. Unuma, K. Takinami, and K. Morimoto, *Bull. Inst. Chem. Res. Kyoto Univ.*, **38**, 70 (1960).

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