mother liquor after the removal of 0.8 g. of solid melting at 150–200°, resulted in 0.12 g. of colorless crystals melting at 163–167°. The infrared spectra of this slightly impure product and of hexaphenyldisilazane (the latter prepared by reaction of triphenylsilane with sodium in liquid ammonia[7]) are nearly identical, and a mixed melting point was not depressed.

Reaction of hexaphenyldisilane with chromic acid. Chromic acid solution was prepared by dissolving 5.0 g. of chromium trioxide in 5 ml. of water followed by the addition of 10 ml. of glacial acetic acid. This solution was added to 3.0 g. of hexaphenyldisilane, and the mixture was heated at 80–90° for 2 hr. with occasional shaking. The resulting dark green mixture was diluted with 100 ml. of water. Solid sodium carbonate was added to neutralize the reaction product until the addition of a small amount did not cause evolution of gases. Following filtration of the neutralized mixture there was obtained 2.7 g. (90%) of impure hexaphenyldisilane melting at 356–360°. It was boiled with petroleum ether (b.p. 60–70°) and filtered hot to separate 2.5 g. (83%) of purified hexaphenyldisilane. Only a trace of brown solid remained from the distillation of the filtrate.

In a second experiment, twice the amount of chromic acid was used, and the reaction mixture was refluxed for 48 hr. In this run, only a 48% yield of hexaphenyldisilane could be recovered. The aqueous solution was extracted with ether, from which a sirupy residue was obtained. Purification of this residue was unsuccessful.

Attempted reactions of hexaphenyldisilane with other oxidizing agents, and lithium aluminum hydride. Hexaphenyldisilane was treated with 30% hydrogen peroxide in refluxing glacial acetic acid for 24 hr. with no sign of reaction. It was also treated separately in refluxing solvent for 48 hr. with selenium dioxide in dioxane, nitric acid in water, periodic acid in benzene, and lead tetraacetate in acetic acid. In all cases no cleavage was observed while more than 90% of the unchanged disilane was recovered. Practically quantitative recoveries of hexaphenyldisilane were also obtained after it had been treated separately for 48 hr. with potassium permanganate in acetone, nitric oxide in ether, or lithium aluminum hydride in refluxing ether.

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Organoboron Compounds. VII. Alkylarylborinates

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Ethanolamine has proved to be a very useful reagent for the isolation and characterization of diarylborinic acids.[2] It reacts readily with the borinic acids, even in the presence of water, to yield air stable, sharp melting esters. As the boronic acids (also the boronate esters) and triarylborines do not behave in this manner, the borinates can be separated readily from reaction mixtures containing the three types of substances.

We now find that these techniques involving ethanolamine also provide a convenient means for isolating derivatives of the alkylarylboron-oxygen compounds. The preparation of three representative compounds, aminoethyl benzylphenylborinate (Ia), aminoethyl butylphenylborinate (Ib), and aminoethyl 1-methylheptylphenylborinate (Ic), are described in this note. In all cases the alkyl-boron bond was formed by reaction of the appropriate Grignard reagent with dibutyl benzeneboronate (II). Following hydrolysis the aminoethyl esters were precipitated by addition of ethanolamine. These esters are lower-melting and more soluble in

I II

I (a) R = $C_6H_5CH_2-$
(b) R = C_4H_9-
(c) R = $C_6H_{13}-C(CH_3)(H)-$

organic solvents than the previously described diarylborinates. The benzyl and butyl derivatives (Ia,b) have stood in vials in air over a year without change; however, the 1-methylheptyl derivative (Ic) is less stable. After a period of several months this compound melted over a range of several degrees at a lower temperature and a strong odor of octanol was noticed. All of the aminoethyl esters hydrolyzed very rapidly in dilute hydrochloric acid to give air sensitive substances (no doubt the free borinic acids since the aminoethyl esters could be regenerated by extraction of the acid with ether and reprecipitation with ethanolamine; however, crystalline borinic acids could not be obtained).

EXPERIMENTAL

Aminoethyl benzylphenylborinate. Benzylmagnesium bromide (55 cc. of 1.81*M* ether solution) was added over a period of 1 hr. to a stirred solution of 23.4 g. (0.1 mole) of dibutyl benzeneboronate in 175 cc. of ether. The initial temperature of the reaction mixture was −70°; after an hour of stirring the mixture was allowed to warm to room temperature and then hydrolyzed with dilute hydrochloric acid. The ether layer was then separated and to it was added 15 cc. of ethanolamine in 15 cc. of methanol. Up to this point a

(1) National Science Foundation Fellow, 1954.

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nitrogen atmosphere had been maintained; thereafter, the reaction products were handled in air without special precautions. The ether layer was mixed with 150 cc. of water and the ether removed at reduced pressure. A white precipitate of aminoethyl ester separated as the ether distilled. This material, after drying in a vacuum desiccator melted at 128–135° and weighed 19.9 g. (83%). The first crystallization from toluene gave a 96% recovery of ester melting at 139.5–141°, and the second recrystallization an 80% recovery of ester (over-all yield of purified material, 64%), m.p. 141–142°; neutralization equivalent, determined by titration with standard hydrochloric acid, 242; calcd. for $C_{15}H_{13}BON$, 239.

To prove the presence of the benzyl group in the molecule a 0.539-g. sample of the ester was oxidized with 2.5 g. of potassium permanganate in 50 cc. of water made alkaline with potassium hydroxide. After the initial exothermic reaction, an additional 2.5 g. of permanganate was added and the mixture warmed on a steam bath for 15 min. It was then cooled, decolorized with ethylene glycol, acidified, cleared of manganese dioxide with sodium hydrogen sulfite, and extracted with ether. The mixture of acids isolated from the ether was separated by sublimation to give benzoic acid (sublimate) m.p. 121–122°, 0.217 g. (80%); and benzeneboronic acid (residue) as the oxide, m.p. (193–197°), 0.079 g. (29%).

In another degradation 1.00 g. of ester was shaken with 3*N* hydrochloric acid and ether for several seconds to effect hydrolysis. The ether layer was evaporated on a steam bath to leave an oil which was warmed with 10 cc. of 5% potassium hydroxide solution. Air was passed through the solution for an hour then the mixture separated into neutral and organic acid products. From the acid portion was obtained 0.358 g. (70%) of benzeneboronic acid (m.p. 222–223°), proving the presence of a phenyl-boron linkage in the aminoethyl ester; and from the neutral fraction was isolated, following treatment with 3,5-dinitrobenzoyl chloride, 0.08 g. of benzyl 3,5-dinitrobenzoate, m.p. 111–113° (undepressed on mixture with an authentic sample).

Aminoethyl butylphenylborinate. By the procedure described for the benzyl compound 13.8 g. (71%) of aminoethyl butylphenylborinate m.p. 104–107°, was obtained from 0.103 mole of dibutyl benzeneboronate and 0.103 mole of *n*-butylmagnesium bromide. One recrystallization from toluene-hexane raised the melting point to 106–107° (12.2 g., 60% yield), and a subsequent recrystallization raised the melting point to 108–108.5°. As expected, aromatic C—H absorption was weak in the infrared whereas aliphatic C—H absorption was strong.

Anal. Calcd. for $C_{12}H_{20}BON$; C, 70.26; H, 9.83; N, 6.83; neut. equiv., 205. Found: C, 69.97; H, 9.42; N, 7.18; neut. equiv., 206 (C, H, and N analyses by H. Beck).

Mercuric chloride in ethanol cleaved 1.241 g. of the aminoethyl ester in ethanol to give 1.8 g. (95%) of phenylmercuric chloride. In another experiment, 0.92 g. of ester was hydrolyzed with hydrochloric acid, the reaction products taken up in ether and the ether evaporated. Sufficient oxidation had occurred that 0.2 g. (37%) of benzeneboronic acid could be isolated from the residue.

Aminoethyl 1-methylheptylphenylborinate. By the above procedure 23.5 g. of crude ester, m.p. 85–92°, was isolated from a reaction of 0.090 mole of dibutyl benzeneboronate with 0.090 mole of 1-methylheptylmagnesium bromide. Recrystallization from hexane that contained a small amount of benzene yielded 12.83 g. (55%) of the aminoethyl ester, m.p. 93–95°, neut. equiv. 258; calcd. for $C_{16}H_{28}BON$, 261. Acid hydrolysis of the aminoethyl ester in the presence of air yielded, as in the case of the butylphenylborinate, benzeneboronic acid, 0.153 g. (64%). The ease of oxidation of this mixed borinic acid points up the value of ethanolamine as a tool for working with this class of compounds.

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Acetylation of Amides with Ketene

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Although it has been demonstrated by several workers that amides can be acetylated with ketene, the number of such examples is rather limited. Rice and co-workers[1] prepared *N*-phenyldiacetamide by passing ketene into acetanilide at 140°. They suggested that *N*-acetylbenzamide was formed similarly from benzamide at 180° but that it decomposed into benzonitrile as the reaction progressed. Later, Padgham and Polya[2] isolated *N*-acetylbenzamide and diacetamide by passing ketene into molten benzamide and acetamide, respectively. The use of sulfuric acid as a catalyst in the formation of *N*-phenyldiacetamide from ketene and molten acetanilide was reported by Smirnova[3] and others.

In this present study seven amides, namely: acrylamide, methacrylamide, cyanoacetamide, *p*-toluamide, formamide, acetamide, and benzamide, have been successfully acetylated by ketene. Of these, the first four were treated with ketene for the first time. These reactions were carried out in a suitable solvent and in some cases in the presence of catalytic amounts of sulfuric acid. When sulfuric acid was used it was necessary to wash it from the reaction mixture as soon as possible after the reaction was completed. Continued contact with the catalyst in most instances caused decomposition of the acetylated product with a proportional decrease in yield. Monoacetyl derivatives were formed with the exception that formamide yielded *N*-formyldiacetamide. This triacylated ammonia is crystalline, a fact of interest in connection with Smirnova's[3] statement that triacetylammonia is a liquid. *N*-Acetylacrylamide and *N*-acetylmethacrylamide, prepared in the present study, are two additional new compounds reported for the first time, and their melting points are recorded. The melting point of cyanoacetamide is also recorded, as well as that of *N*-formyldiacetamide. The carbon, hydrogen, and nitrogen content of the latter is also reported in support of its identity.

EXPERIMENTAL

The ketene used was generated by the pyrolysis of acetone using the lamp previously described.[4] The amides were each individually placed in the gas absorption apparatus designed

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