

moles of cyanide from hydrolysis of benzoyl cyanide and pyruvonnitrile. A spectrophotometric study of the decomposition of II<sup>14</sup> in the presence of various concentrations of cyanide (Figure 1) indicates that cleavage is catalyzed by cyanide. This catalysis is especially demonstrated by an experiment in which  $4 \times 10^{-4}$  mole of potassium cyanide was added to  $4 \times 10^{-2}$  mole of II. At 6 hr, when the experiment was stopped, 1 equiv of cyanide had induced the decomposition of nearly 20 molecular equiv of II. Very slow decomposition occurs in the absence of cyanide.

It is possible to inhibit the decomposition of II by adding 2-phenylglyoxylamide as a cyanide scavenger (cyanohydrin formation). Most pronounced effects are noticed when *excess* 2-phenylglyoxylamide is added to solutions containing small amounts of cyanide (Figure 1, curve E). Leveling-off effects in rate of decomposition of II such as illustrated in Figure 1 may be at least partly explained by the cyanohydrin formation.

### Experimental Section

**Reaction of 1-Phenyl-1,2,3-butanetrione 2-Oxime (II) with Potassium Cyanide.**—A solution of 14.3 g (0.22 mole) of potassium cyanide in 100 ml of distilled water was added dropwise during a 1-hr period to a stirred and cooled solution of 19.0 g (0.1 mole) of II in 100 ml of methanol. The temperature was maintained at 10–20° throughout the reaction and work-up. After 1 hr the clear, yellow solution was slowly acidified (pH 2) with 40% sulfuric acid; a heavy, white precipitate resulted. Products were obtained by either method described below.

**Method 1.**—The entire reaction mixture was extracted with three 150-ml portions of ether. The ether extracts were dried with anhydrous sodium sulfate and the ether was evaporated. The residue was 20.5 g of light yellow, waxy solid. Repeated washing with benzene gave 8.5 g of white solid, mp 91–92°.

**Method 2.**—The acidified reaction mixture was first extracted with three 150-ml portions of benzene; the benzene extract was separately investigated. The aqueous residue was next extracted with ether. The ether extract was dried with sodium sulfate and the ether was removed *in vacuo* to give 13.9 g of light yellow solid. Washing with benzene left 8.5 g of white crystals, mp 91–92° (48.2% of theoretical for 2-hydroxy-2-cyano-2-phenylacetamide); recrystallization from ether–petroleum ether (bp 30–60°) (1:1) gave mp 91.5–93°. The infrared spectrum was identical with that of the product isolated by method 1, and with that published<sup>15</sup> for 2-cyano-2-hydroxy-2-phenylacetamide. The nmr spectrum (measured in acetone-*d*<sub>6</sub> and D<sub>2</sub>O with TMS as an internal standard) showed a multiplet at  $\delta = 7.4$ –7.8 ppm (five aromatic H) and a singlet at  $\delta = 4.0$  ppm (three exchangeable H).

*Anal.* Calcd for C<sub>9</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>: C, 70.57; H, 5.92. Found: C, 70.4; H, 5.9.

A mixture of benzoic acid, methyl benzoate, and II was recovered from the benzene solution. These products were separated on the basis of solubility in aqueous sodium bicarbonate and sodium hydroxide. Benzoic acid and unreacted II were each recrystallized from hot water and identified by melting point and infrared spectra. Methyl benzoate was distilled under reduced pressure (24 mm) and identified by odor, infrared spectrum (identical with Sadtler Spectrum No. 1052)<sup>16</sup> and elemental analysis.

The following yields, calculated for the purified products, are minimum yields because of separation difficulties: 2-hydroxy-2-cyano-2-phenylacetamide, 8.5 g (48.3%); benzoic acid, 2.3 g (18.8%); methyl benzoate, 0.5 g (3.6%); unreacted II 3.0 g (15.8%).

(14) The decomposition of II was followed spectrophotometrically by the decrease in the absorbance at 405 m $\mu$ . This is a shoulder in the absorption spectrum of II for which a linear relationship between optical density and concentration, in the range under study, was demonstrated.

(15) A. Nenz, L. Marangoni, E. Gallinella, and A. Iliceto, *Chem. Ind. (Milan)*, **46**, 509 (1964).

(16) Published by Sadtler Research Laboratories, Philadelphia, Pa.

**2-Acetoxy-2-cyano-2-phenylacetamide (IV).**—The cyanohydrin of 2-phenylglyoxylamide was prepared by reaction with potassium cyanide, using the reaction conditions described for the II-cyanide reaction. Acetylation of the cyanohydrin with acetic anhydride and pyridine gave IV in good yield as white crystals (from benzene), mp 163–164°. The structure was confirmed by infrared and nmr spectra.

*Anal.* Calcd for C<sub>11</sub>H<sub>10</sub>N<sub>2</sub>O<sub>3</sub>: C, 60.55; H, 4.62. Found: C, 60.06; H, 4.6.

**Catalysis of Decomposition of II by Cyanide.**—Experiments were performed with  $4 \times 10^{-2}$  M solutions of II in borate buffer ( $2.6 \times 10^{-2}$  M tetraborate, adjusted to pH 9.4 with potassium hydroxide). Potassium cyanide concentrations were  $4 \times 10^{-2}$  M,  $4 \times 10^{-3}$  M,  $4 \times 10^{-4}$  M, and zero. The solutions were kept in glass-stoppered flasks in a 50° bath. Samples were removed at timed intervals for the measurement of the absorption at 405 m $\mu$ , using a Beckman DK-2A spectrophotometer. Experimental data are illustrated in Figure 1. A linear relationship was demonstrated between concentration of II (up to at least  $10^{-2}$  M) and absorbance.

**Inhibition of the II-Cyanide Reaction by 2-Phenylglyoxylamide.**—After 150 min at 50°, a solution  $4 \times 10^{-2}$  M in II and  $4 \times 10^{-4}$  M in potassium cyanide was made  $4 \times 10^{-2}$  M in benzoylformamide. The disappearance of the 405-m $\mu$  absorbance was followed concurrently for the solutions with and without 2-phenylglyoxylamide. At these relative concentrations, the decomposition of II was almost completely halted.

In another experiment 2-phenylglyoxylamide was added to a solution of II and potassium cyanide to give a solution  $4 \times 10^{-2}$  M in each of the three reagents. The 2-phenylglyoxylamide was added at the beginning of the experiment. With equivalent amounts of II, potassium cyanide, and benzoylformamide the rate of decomposition of II was only slightly decreased (Figure 1, curves D, E).

**Registry No.**—II, 6797-44-0; III, 7616-87-7; IV, 7616-88-8.

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## Organoboron Compounds. XX. Trineopentylborane from the Neopentyl Grignard Reagent<sup>1</sup>

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Trineopentylborane, [(CH<sub>3</sub>)<sub>3</sub>CCH<sub>2</sub>]<sub>3</sub>B, previously unknown, is of considerable interest in mechanistic studies of organoboron chemistry because it is the simplest trialkylborane which is sterically crowded and restrained, cannot be made by hydroboration, and cannot participate in any reaction where direct elimination of olefin is mechanistically involved.<sup>1</sup> Thus the facile formation of intermediate BH species *via* elimination is not expected in trineopentylborane reactions. Furthermore, since the reaction of *t*-

(1) Previous paper: F. M. Rossi, P. A. McCusker, and G. F. Hennion, *J. Org. Chem.*, **32**, 450 (1967).

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butylmagnesium chloride with boron fluoride produces *t*-butyldiisobutylborane,<sup>3</sup> obviously with rearrangement of two alkyl groups, the corresponding reaction of the neopentyl Grignard reagent was considered worthy of study. Interest was stimulated also by the fact that all attempts to prepare sterically crowded tri-*t*-butylborane in this laboratory have failed, regardless of the method tried.<sup>4</sup>

In the early stages of this investigation many attempts to prepare neopentylmagnesium chloride by the ordinary method<sup>5</sup> surprisingly failed, both in ether and in tetrahydrofuran. The apparent reaction of the chloride with magnesium turnings could be sustained only as long as an active halide, such as methyl iodide or ethyl bromide, was added also. Recourse was therefore made to the massive entrainment method of Pearson,<sup>6</sup> using 1 equiv of ethylene dibromide with ether as the solvent and this technique was successful in every experiment.

The reaction of the Grignard reagent with boron fluoride etherate then consistently gave trineopentylborane in 50–60% yields. The structure of this compound was proved by the facts (a) that oxidation with alkaline hydrogen peroxide gave neopentyl alcohol (no other alcohols) identified by glpc, and (b) that the pmr spectrum had two singlets, one at 1.04 and the other at 1.46 ppm below TMS. Based on the relative areas of 4.5 to 1, the 1.04 peak is assigned to the methyl protons and the 1.46 peak to the methylene protons.

Trineopentylborane proved to be stable to distillation, even at atmospheric pressure [bp 227° (747 mm)]; distillates showed no evidence of decomposition or isomerization. Unlike other primary trialkylboranes, it does not react with boron chloride<sup>7</sup> up to 175° (no RBCl<sub>2</sub> or R<sub>2</sub>BCl detected). The failure of this reaction suggests that BH species may be required for the process as suggested by Koster's observation<sup>8</sup> that diborane acts as a catalyst for the reaction of boron chloride with trialkylboranes.

Studies of the behavior of trineopentylborane when heated with other trialkylboranes (alkyl group redistribution reactions) will be reported in a later paper.

#### Experimental Section

**Neopentyl chloride**, purchased from K & K Laboratories, Plainview, N. Y., was distilled through a spinning-band column: bp 83.0–83.2°; *n*<sub>D</sub><sup>20</sup> 1.4041; *d*<sub>4</sub><sup>20</sup> 0.8654; glpc pure. Ethylene dibromide was dried over calcium chloride and distilled before use.

**Neopentyl Grignard Reagent**.—A mixture of 51 g (2.1 g-atoms) of magnesium turnings, 500 ml of anhydrous ether, and 106 g (1 mole) of neopentyl chloride was stirred under dry nitrogen and a solution of 186 g (1 mole) of ethylene dibromide in 500 ml of ether was then added dropwise over a period of 17 hr. The entire mixture was then boiled with stirring for an additional 3

hr. Additional ether (total 500 ml) was added periodically to maintain fluidity.

**Trineopentylborane**.—Boron fluoride etherate (46 g, 0.32 mole) was added dropwise to the Grignard reagent with stirring under dry nitrogen (exothermic reaction). The reaction mixture was stirred for an additional 2 hr and cooled, and 620 ml of cold water was added. The upper ethereal layer was removed by siphoning under nitrogen pressure and the lower layer was washed twice with ether in the same manner. The combined ethereal solution was dried over calcium chloride and distilled. The fraction with bp 50–52.6° (0.5–0.6 mm) was retained (55% yield). Redistillation gave pure product: bp 67.5° (1.4 mm), 164° at (143 mm), 227° (747 mm); *n*<sub>D</sub><sup>20</sup> 1.4356; *d*<sub>4</sub><sup>20</sup> 0.7634.

*Anal.* Calcd for C<sub>15</sub>H<sub>33</sub>B: B, 4.83; MR<sub>D</sub>, 76.5. Found: B, 4.82, 4.83; MR<sub>D</sub>, 76.6.

**Registry No.**—[(CH<sub>3</sub>)<sub>3</sub>CCH<sub>2</sub>]<sub>3</sub>B, 7687-73-2.

### The Course of the Mannich Reaction with Methyl Isobutyl Ketone. Preparation of 2-Isopropyl-1-butenone-3

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Having need of 2-isopropyl-1-butenone-3 (1) for use in synthesis, we ran the Mannich condensation of methyl isobutyl ketone (2) with formaldehyde and diethylamine hydrochloride, a reaction which is reported<sup>2</sup> to afford 3-(*N,N*-diethylaminomethyl)-4-methylpentanone-2 (3), a precursor or functional equivalent of 1. This Mannich reaction has, in fact, recently been described<sup>3</sup> as a high-yield (94.5%), commercial-scale source of 1.

When this reaction was run in our laboratory, however, there was obtained in 63% yield a product, bp 70–82° (3.5 mm), whose nmr spectrum displayed *no* acetyl methyl singlet. This material was converted to its hydrochloride (89%) and distilled to afford a vinyl ketone (34%) whose nmr spectrum also showed *no* acetyl methyl singlet and had a vinyl proton region essentially identical with that of methyl vinyl ketone. These properties clearly indicated that this Mannich product contained virtually *no* 3, but was instead Mannich base 4, resulting from condensation at the methyl group of 2. The identity of the vinyl ketone obtained was confirmed as 5-methyl-1-hexenone-3 (5), a readily polymerized substance which formed a 2,4-dinitrophenylhydrazone with mp 104–106.5°. Several repetitions of the procedure afforded identical results; *no* nmr acetyl methyl singlet ascribable to 3 was detected.<sup>4</sup>

The Mannich reaction of 2 was also run with dimethylamine hydrochloride and the same nmr results

(1) (a) Alfred P. Sloan Foundation Research Fellow. (b) Recipient of support under the terms of an institutional research training grant from the U. S. Public Health Service, summer 1966.

(2) R. Heilmann, G. de Gaudemaris, and P. Arnaud, *Compt. Rend.*, **234**, 1177 (1952).

(3) M. I. Farberov and G. S. Mironov, *Dokl. Akad. Nauk SSSR*, **148**, 1095 (1963); *cf. Chem. Abstr.*, **59**, 5062 (1963).

(4) Possibly the composition of the products obtained by previous investigators differed from that reported here. However, insufficient information is given in either ref 2 or 3 to come to any conclusion about this possibility, and *no* reasons are given in these articles for the structural assignments made.

(3) (a) G. F. Hennion, P. A. McCusker, and A. J. Rutkowski, *J. Am. Chem. Soc.*, **80**, 617 (1958); (b) G. F. Hennion, P. A. McCusker, and J. V. Marra, *ibid.*, **81**, 1768 (1959).

(4) Despite many literature references to tri-*t*-butylborane, this compound remains unknown to this date. Our studies lead to the conclusion that workers who alleged making or using this compound actually had either triisobutyl- or *t*-butyldiisobutylborane.<sup>3b</sup>

(5) F. C. Whitmore, *et al.*, *J. Am. Chem. Soc.*, **61**, 1585 (1939); **64**, 1239 (1942).

(6) D. E. Pearson, D. Cowan, and J. D. Beckler, *J. Org. Chem.*, **24**, 504 (1959).

(7) P. A. McCusker, G. F. Hennion, and E. C. Ashby, *J. Am. Chem. Soc.*, **79**, 5192 (1957).

(8) R. Koster, *Angew. Chem.*, **73**, 66 (1961).