

The *sym*-trinitrobenzene derivative, showed m.p. 157–159°.

*Anal.* Calcd. for  $C_{34}H_{30}(C_6H_3N_3O_6)_2$ : C, 63.88; H, 4.20; N, 9.72. Found: C, 63.58; H, 4.16; N, 9.72.

Concentration of the benzene filtrates gave the lower melting form, m.p. 198–200°, of 3,4-bis-(2-phenanthryl)-hexane (XV).

*Anal.* Calcd. for  $C_{34}H_{30}$ : C, 93.10; H, 6.89; mol. wt., 438. Found: C, 92.80; H, 6.80; mol. wt. (Rast's method), 428.

**Reaction of  $\alpha$ -(2-Phenanthryl)-*n*-propyl Bromide with Cuprous Cyanide and Pyridine.**—A mixture of XIV (1.0 g.), cuprous cyanide (600 mg.) and pyridine (5 ml.) was heated at 160° for 24 hours. The reaction mixture was poured into dilute ammonium hydroxide and an ethereal extract of the resulting organic material was washed repeatedly with am-

monium hydroxide solution until the aqueous layer did not develop a blue color. After being washed with dilute hydrochloric acid and then with water, the ether solution was dried over calcium chloride. Evaporation of the solvent gave a gummy material which, after several crystallizations from ethanol, gave 250 mg. of the unsaturated hydrocarbon XVI, m.p. 101–102°.

*Anal.* Calcd. for  $C_{34}H_{28}$ : C, 93.53; H, 6.47. Found: C, 93.83; H, 6.38.

**Bromination of XVI.**—A solution of bromine in carbon tetrachloride was added to 200 mg. of XVI dissolved in absolute ethanol, until a pale yellow color persisted. The mixture was allowed to stand for 8 hours. Concentration of the solution gave a solid which, after three crystallizations from ethanol, gave the pure tetrabromide, m.p. 145°, yield 60 mg.

*Anal.* Calcd. for  $C_{34}H_{26}Br_4$ : C, 54.14; H, 3.47. Found: C, 54.36; H, 3.73.

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## COMMUNICATIONS TO THE EDITOR

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### BIS-3-METHYL-2-BUTYLBORANE AS A SELECTIVE REAGENT FOR THE REDUCTION OF REPRESENTATIVE FUNCTIONAL GROUPS

Sir:

Bis-3-methyl-2-butyloborane is a highly selective reagent for the hydroboration of olefins and dienes.<sup>1</sup> We now report that this reagent exhibits remarkable selectivity in its reducing action toward representative functional groups, permitting selective reductions not otherwise feasible.

The groups listed are reduced at 0° in 0.5 *M* solution in tetrahydrofuran (products in parentheses): aldehydes and ketones (alcohols), unhindered olefins and acetylenes (organoboranes),  $\gamma$ -lactones (hydroxyaldehydes) and *N,N*-dimethylamides (aldehydes). Nitrobenzene and nitriles react only slowly under these conditions.

These groups react to evolve hydrogen, but do not undergo reduction: alcohols, phenols, carboxylic acids, amides, and sulfonic acids. No reaction occurs under these conditions with esters, acid chlorides, acid anhydrides, azobenzene, sulfones and sulfonyl chlorides.

The failure of bis-3-methyl-2-butyloborane to reduce carboxylic acids is unexpected in view of the very fast reaction with diborane.<sup>2</sup> It makes possible both selective reductions and hydroborations in the presence of unprotected carboxylic acid groups, as illustrated by the following conversion of 10-undecenoic acid to 11-hydroxyundecanoic acid.

Undecenoic acid, 25 mmoles, was treated with a solution of 50 mmoles of bis-3-methyl-2-butyloborane<sup>1</sup> in tetrahydrofuran at 0°. Hydrogen (24 mmoles) was rapidly evolved. After 30 minutes, the reaction mixture was treated with alkaline hydrogen peroxide and the product was recrystallized from water. There was obtained 20.6 mmoles, 82% yield, of 11-hydroxyundecanoic acid, m.p. 68–69°.<sup>3</sup>

(1) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **82**, 3222 (1960).

(2) H. C. Brown and B. C. Subba Rao, *ibid.*, **82**, 681 (1960).

(3) P. Chuit and J. Hausser, *Helv. Chim. Acta*, **12**, 463 (1929), report m.p. 70–70.5°.

$\gamma$ -Lactones react with one mole of the reagent, even when the latter is in excess. That the product is the hydroxyaldehyde was confirmed by demonstrating the reduction of  $\gamma$ -butyrolactone to  $\omega$ -hydroxybutyraldehyde (73% yield of 2,4-dinitrophenylhydrazone, m.p. 198–199°). A representative procedure is given.

$\gamma$ -Valerolactone, 50 mmoles, was treated with 0.5 *M* reagent for about 15 hours at 25°, followed by oxidation with alkaline (pH 8) hydrogen peroxide at 0°.  $\gamma$ -Hydroxyvaleraldehyde, b.p. 60–61° at 9 mm.,<sup>4</sup> was isolated, 38 mmoles, 76% yield.

The reaction of the reagent with these lactones is more rapid than its reaction with typical ketones. Consequently, it should be possible to achieve the selective reduction of such lactones in the presence of ketone, carboxylic acid or ester groups.

We continue to explore the full applicability of this versatile reagent.

**Acknowledgment.**—This study was made possible by a grant from the American Cyanamid Company. This support is gratefully acknowledged.

(4) B. Helferich, *Ber.*, **52**, 1123 (1919), reports b.p. 63–65° at 10 mm.

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### HYDROBORATION AS A CONVENIENT PROCEDURE FOR THE ASYMMETRIC SYNTHESIS OF ALCOHOLS OF HIGH OPTICAL PURITY

Sir:

We wish to report a new asymmetric synthesis which permits the conversion of olefins into optically active alcohols with optical purities in the neighborhood of 90%.

We previously observed that the hydroboration of hindered olefins proceeds rapidly to the dialkylborane stage and these compounds exhibit a remarkable selectivity for the hydroboration of olefins