tion of sodium hydroxide, followed by 50 cc. of 30% hydrogen peroxide. The reaction mixture was extracted with ether, the ether extract washed four times with water to remove diglyme, dried and distilled. There was obtained 18.2 g. (80% yield) of 2-(*p*-anisyl)-ethanol, b.p. 138–140° at 10 mm., m.p. 27–28°. Gas chromatographic analysis indicated a purity of at least 98%.

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BIS-3-METHYL-2-BUTYLBORANE AS A SELECTIVE REAGENT FOR THE COMPETITIVE HYDROBORATION OF OLEFINS AND DIENES

Sir:

Bis-3-methyl-2-butylborane, readily prepared by the hydroboration of 2-methyl-2-butene, exhibits a high selectivity for the less hindered of the two carbon atoms of a double bond.[1] This observation suggested that this reagent might exhibit a marked selectivity for olefins of varying structural types and prompted an examination of the relative rates of reaction of this reagent with a series of representative olefins.

The reactivity of olefins toward bis-3-methyl-2-butylborane decreases in the order: 1-hexene ≥ 3-methyl-1-butene > 2-methyl-1-butene > *cis*-2-hexene ≥ cyclopentene > *trans*-2-hexene > *trans*-4-methyl-2-pentene > cyclohexene > 1-methylcyclopentene > 2-methyl-2-butene ≥ 1-methylcyclohexene ≥ 2,3-dimethyl-2-butene.

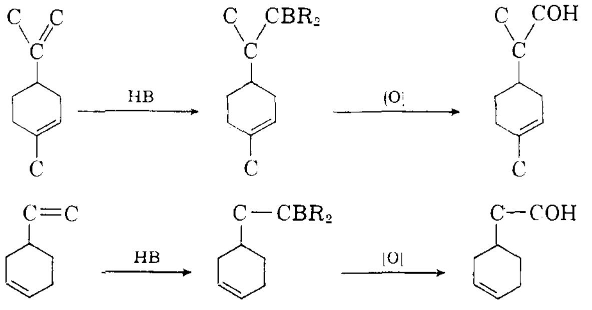
In many instances these differences in reactivity are quite large, suggesting the utility of the reagent for the selective hydroboration of a more reactive olefin in a mixture of two or more olefins. This possibility was tested by treating synthetic mixtures of two olefins in diglyme at 0° with a slight excess of the reagent, following the course of the reaction by gas chromatographic analysis for residual olefin.

In this way 1-pentene was essentially quantitatively removed from 2-pentene, and 2,4,4-trimethyl-1-pentene was removed from 2,4,4-trimethyl-2-pentene. Similarly, 1-pentene was selectively reacted in the presence of 2-methyl-1-pentene, and 1-hexene was quantitatively removed from cyclohexene. An equimolar mixture of cyclopentene and cyclohexene yielded a product which consisted of 95% cyclohexene.

Even more remarkable is the large difference in reactivity exhibited by *cis–trans* isomers, permitting the selective removal of the more reactive *cis* isomer from the *trans*. Treatment of a commercial sample of 2-pentene, 18% *cis*- and 82% *trans*-, with the reagent yielded *trans*-2-pentene in a purity of at least 97%.

It was demonstrated previously that the hydroboration of acetylenes makes available the *cis* olefin in a state of high purity.[2] Consequently, hydroboration now provides a synthetic route to the preparation of both *cis* and *trans* olefinic isomers in high purity.

Previously, we had attempted the selective hydroboration of *d*-limonene with diborane, without success.[3] However, the new reagent permitted a clean reaction involving the selective hydroboration of the exocyclic double bond in both *d*-limonene and 4-vinylcyclohexene.



The reagent, bis-3-methyl-2-butylborane, should be exceedingly helpful for the selective hydroboration of many terpenes and steroids.[4] A representative procedure is given.

To 0.165 mole of bis-3-methyl-2-butylborane, freshly prepared in diglyme,[1] was added (at 0°) 20.4 g. of a *d*-limonene (0.15 mole, $n^{20}_{\rm D}$ 1.4730, $[\alpha]^{25}_{\rm D}$ +125°) over a period of five minutes. After three hours at room temperature, the reaction mixture was oxidized with alkaline hydrogen peroxide in the usual manner. There was obtained 18.3 g. (79% yield) of primary terpineol, b.p. 115–116° at 10 mm., $n^{20}_{\rm D}$ 1.4855, $[\alpha]^{25}_{\rm D}$ +99° (*c*, 4.2 in benzene), m.p. 3,5-dinitrobenzoate 91–92°.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 78.05; H, 11.96.

In the same way 16.2 g. of 4-vinylcyclohexene was converted into 13.7 g. (72% yield) of 2-(4-cyclohexenyl)-ethanol, b.p. 86–87° at 6 mm., $n^{20}_{\rm D}$ 1.4834, m.p. 3,5-dinitrobenzoate 66–67°.

Anal. Calcd. for $C_8H_{14}O$: C, 76.13; H, 11.18. Found: C, 76.72, H, 11.30.

The selective hydroboration of the exocyclic double bond was confirmed by hydrogenation of the product over platinum oxide to 2-cyclohexylethanol, b.p. 77–78° at 4 mm., $n^{20}_{\rm D}$ 1.4651, m.p. 3,5-dinitrobenzoate, 71–72°.[5]

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[1] H. C. Brown and G. Zweifel, THIS JOURNAL, **82**, 3222 (1960).

[2] H. C. Brown and G. Zweifel, *ibid.*, **81**, 1512 (1959).

[3] Similar unsuccessful results were realized by R. Dulou and Y. Chrétien-Bessière, *Bull. soc. chim. France*, **9**, 1362 (1959).

[4] The utility of other substituted boranes for such selective hydroborations is under investigation by Dr. A. Moerikofer.

[5] G. S. Hiers and R. Adams, THIS JOURNAL, **48**, 2385 (1926) report b.p. 87–89° at 6 mm., $n^{25}_{\rm D}$ 1.4636; J. J. Bost, R. E. Kepner and A. D. Webb, *J. Org. Chem.*, **22**, 51 (1957), report m.p. 3,5-dinitrobenzoate, 70.0–70.5°.

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LOSS OF RADIOACTIVITY FROM OROTATE-7-C^{14} ON ALUMINUM PLANCHETS[1]

Sir:

During August, 1959, in experiments involving the chromatography of orotate-7-C^{14} [2] on Dowex-1

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[1] This work was supported in part by a grant (C-646) from the National Cancer Institute, NIH, USPHS.

[2] Orotate 7-C^{14} was obtained from New England Nuclear Corp.