

cumene and heptane as a solvent. At the end of 20 hours, only the *alpha* product remained (entry 1).

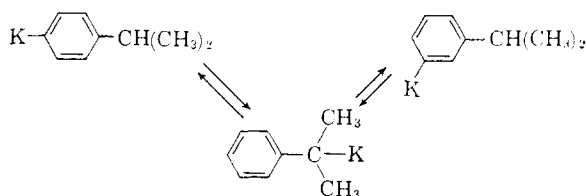
On the other hand, when the reaction was stopped after 4 hours, not only *alpha* product, but *meta* as

TABLE II
REACTION OF HIGHLY PURIFIED *p*-CHLOROCUMENE WITH POTASSIUM

Solvent	Reaction time, hr.	% Isomer distribution		
		Alpha	Meta	Para
1 Cumene	20	100		
2 Cumene	4	60	23	17
3 Heptane ^a	5	56	20	24

^a Contained a two-mole excess of cumene.

well as *para* products were found (entry 2). *Meta* product again appeared when the reaction was carried out in heptane (entry 3). Clearly the data of Table II point to these equilibria in the presence of excess cumene.



With time, the *alpha* isomer predominates because of its greater thermodynamic stability.

These findings provide a different explanation for the anomalous behavior of cumene in the presence of *n*-amylsodium and *n*-amylpotassium than has been presented by earlier workers.^{3,7} According to the new picture, *both* reagents attack the ring of cumene first in a kinetically controlled sequence. The highly energetic *m*- and *p*-isopropylphenylpotassium thus formed equilibrate fairly rapidly to the more thermodynamically stable *alpha* isomer. The less energetic *m*- and *p*-isopropylphenylsodium, however, equilibrate at a negligible rate under the reaction conditions employed.

It is entirely possible that the rapid attainment of equilibrium with *n*-amylpotassium depends, among other things, upon the rate of stirring employed. Bryce-Smith⁸ did not observe this equilibrium even with *p*-tolylpotassium at 20° for 40 days with "occasional shaking."⁸ It seems certain that formation of benzylpotassium should be thermodynamically favored.⁹ It remains for future work to determine why the establishment of these equilibria was so slow in the cases reported by Bryce-Smith.³

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(8) It is recognized that this reagent was prepared from *p*-tolyl-lithium which might well lead to an associated salt as the metalating agent with altered activity and properties. We are presently assessing this possibility as well as the effect of different stirring rates.

(9) H. Gilman, H. A. Pacevitz and O. Baine, *THIS JOURNAL*, **62**, 1514 (1940).

BIS-3-METHYL-2-BUTYLBORANE AS A SELECTIVE REAGENT FOR STERIC CONTROL OF THE DIRECTION OF HYDROBORATION

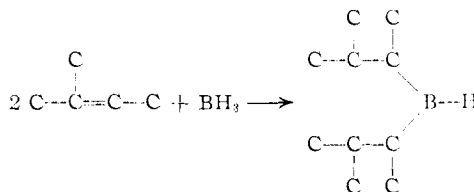
Sir:

The hydroboration of aliphatic terminal olefins proceeds to place the boron atom predominantly in the terminal position. Oxidation of the product provides a convenient route for the anti-Markownikoff hydration of the double bond.¹

A detailed study of directive effects in this reaction² revealed that 1-hexene yields 94% 1-hexanol and 6% of 2-hexanol. Branching of the alkyl group, as in 3-methyl-1-butene and in 3,3-dimethyl-1-butene, does not alter the ratio of attack at the 1- and 2-positions. Similarly, *trans*-isopropylmethylene shows little discrimination between the two possible positions of the double bond: 43% 2-methyl-3-pentanol and 57% 4-methyl-2-pentanol. These results indicate that the direction of addition is determined primarily by electronic factors.

This conclusion is supported by the observation that styrene yields 20% of the α - and 80% of the β -isomer. A *p*-methoxy group changes this to 9% α - and 91% β -, whereas *p*-chloro changes this to 35% α -, 65% β -.

Hydroboration of 2-methyl-2-butene at 0° proceeds to the formation of bis-3-methyl-2-butylborane, even in the presence of excess olefin.



We have observed that this sterically hindered dialkylborane provides a measure of steric control of the hydroboration reaction and permits the synthesis of the less hindered alcohol in greatly improved purities.

Thus, hydroboration of 1-hexene by this reagent, followed by oxidation, yields 1-hexanol in a purity of at least 99%. Similarly, *trans*-isopropylmethylene yields 95% of the less hindered isomer, 4-methyl-2-pentanol. Both styrene and *p*-methoxystyrene yield the corresponding primary alcohols in purities of at least 98-99%.

Bis-3-methyl-2-butylborane is a readily prepared, highly valuable reagent for steric control of the direction of hydroboration.

A mixture of 80 ml. of diglyme, 23.1 g. (0.33 mole) of 2-methyl-2-butene, and 4.8 g. (0.125 mole) of sodium borohydride was cooled (ice bath), flushed with nitrogen, and treated with stirring with 23.6 g. (0.166 mole) of boron trifluoride etherate over a period of 0.5 hour. After standing for an additional hour at 0°, 20.1 g. (0.15 mole) of *p*-methoxystyrene (*n*_D²⁰ 1.5601) was added to the reaction mixture over a period of five minutes. The reaction was permitted to warm up to room temperature (approximately two hours) and then oxidized with alkaline peroxide, 50 cc. of a 3 *N* solu-

(1) H. C. Brown and B. C. Subba Rao, *THIS JOURNAL*, **81**, 6423, 6428 (1959).

(2) H. C. Brown and G. Zweifel, *ibid.*, in press.

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-butyloborane, 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-butyloborane decreases in the order: 1-hexene \geq 3-methyl-1-butene > 2-methyl-1-butene > *cis*-2-hexene \geq cyclopentene > *trans*-2-hexene > *trans*-4-methyl-2-pentene > cyclohexene > 1-methylcyclopentene > 2-methyl-2-butene \geq 1-methylcyclohexene \geq 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.

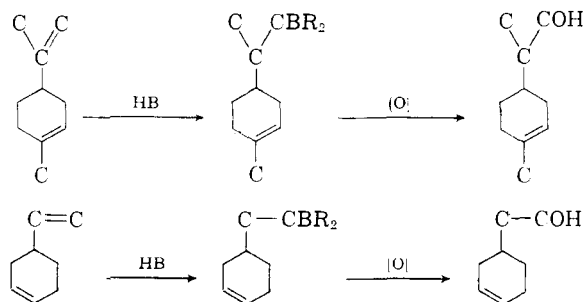
Even more remarkable is the large difference in reactivity exhibited by *cis*-*trans* isomers, permitting the selective removal of the more reactive *cis* isomer from the *trans*. Treatment of a commercial sample of 2-pentene, 18% *cis*- and 82% *trans*-, with the reagent yielded *trans*-2-pentene in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

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

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

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-butyloborane, 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-butyloborane, freshly prepared in diglyme,¹ was added (at 0°) 20.4 g. of a *d*-limonene (0.15 mole, n_D^{20} 1.4730, $[\alpha]_D^{25} +125^\circ$) 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_D^{20} 1.4855, $[\alpha]_D^{25} +99^\circ$ (*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_D^{20} 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_D^{20} 1.4651, m.p. 3,5-dinitrobenzoate, 71–72°.⁵

(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_D^{25} 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-C¹⁴ ON ALUMINUM PLANCHETS¹

Sir:

During August, 1959, in experiments involving the chromatography of orotate-7-C¹⁴ on Dowex-1

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

(2) Orotate 7-C¹⁴ was obtained from New England Nuclear Corp.