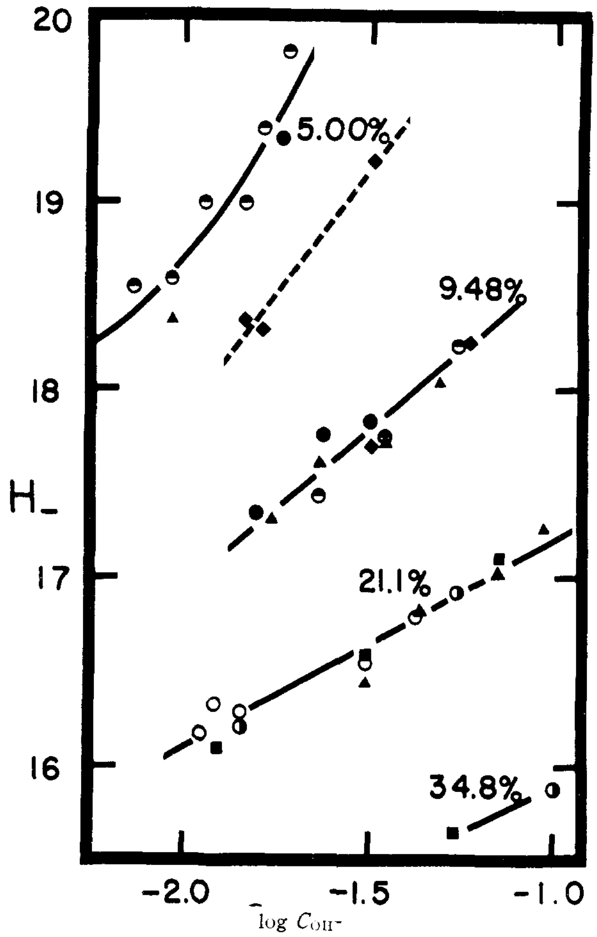

Fig. 1.—H_- function.

was estimated from vapor pressure measurements on sulfolane–water solutions to be about a factor of about 10. Very probably, the remaining factor of 10^5 enters largely *via* the activity coefficient of the hydroxide ion. Alkali metal hydroxides are insoluble in sulfolane and one can get hydroxide ion into solution only by using a large, polarizable cation. Analogous factors seem responsible for the high basicity of potassium *t*-butoxide in dimethyl sulfoxide,[5] a solvent similar to sulfolane in many ways.

TABLE I

ACIDITY CONSTANTS OF WEAK ACIDS

Indicator acid[d]	This research[a]	Aqueous hydrazine[3]	Aqueous ethylenediamine[4]
p-Nitrobenzyl cyanide[c]	(13.45)[b]	13.43	13.45
6-Bromo-2,4-dinitroaniline	13.71		
3-Nitrocarbazole		14.16	15.10
○ 2,4-Dinitroaniline	15.34		15.80
■ 4-Nitrodiphenylamine	15.76	15.43	
◑ 4,4′-Dinitrodiphenylmethane[c]	15.82	15.90	
▲ 4-Chloro-2-nitroaniline	17.21		
● 2-Nitrofluorene[c]	17.59		
⊖ *p*-Nitroaniline	18.47		
● 9-Phenylfluorene[c]	18.49		

[a] Estimated precision in pK_a is about 0.1 [b] Assumed. [c] Because of the rapid oxidation of the conjugate base, measurements required complete exclusion of oxygen. [d] Symbols at left refer to Fig. 1.

Similarly, a 0.01 *M* solution of sulfuric acid in sulfolane is much more acidic than the corresponding aqueous solution.

With 21 and 35 mole % water (Fig. 1), plots of H_- *vs.* log C_{OH^-} are linear with unit slope. However, the slope steadily increases as water content is lowered, apparently because of strong solvation of hydroxide ion by water molecules. If each hydroxide ion removes four water molecules, the slopes are reasonable. In agreement with this, at concentrations of hydroxide ion lower than shown in Fig. 1, the slope decreases considerably in the 5 mole % solution.

The anomalous behavior of 2-nitrofluorene in the 5 mole % solution may have one of two origins: One may no longer have a good H_- function at the lowest water concentration, or 2-nitrofluorene may not be a simple proton acid. The observed color change may result from addition of OH^- to the fluorene ring as, indeed, must happen with *m*-dinitrobenzene for which one may measure an apparent pK_a of 16.8.[4]

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(5) D. J. Cram, J. L. Mateos, F. Hauck, A. Langemann, K. R. Kopecky, W. D. Nielsen and J. Allinger, THIS JOURNAL, **81**, 5774 (1959).

(6) Monsanto Fellow, 1957–1958. National Science Foundation Pre-Doctoral Fellow, 1958–1959.

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ISOMERIZATION OF ORGANOBORANES DERIVED FROM BRANCHED-CHAIN AND RING OLEFINS—FURTHER EVIDENCE FOR THE ELIMINATION-ADDITION MECHANISM OF ISOMERIZATION

Sir:

The isomerization of organoboranes[1] occurs with remarkable ease under hydroboration conditions.[2] This facile shift of the boron atom down the *n*-alkane chain, from an internal position to the terminal position, makes possible the simple conversion of internal olefins into *n*-alkyl derivatives. In order to determine the full scope of this reaction, it was important to establish whether the boron atom can be shifted past an alkyl branch, or from a naphthene ring into a side-chain.

Hydroboration of 2,4,4-trimethyl-2-pentene at 25°, then oxidation with alkaline hydrogen peroxide, gives 99% 2,4,4-trimethyl-3-pentanol, with only 1% of the tertiary alcohol, 2,4,4-trimethyl-2-pentanol (vapor phase chromatography analysis). However, if the initial hydroboration product is heated for one hour at 160° (refluxing diglyme), the reaction product is essentially pure 2,4,4-trimethyl-1-pentanol. Similarly, 4,4-dimethyl-2-pentene yields 57% of 4,4-dimethyl-2-pentanol and 43% of 4,4-dimethyl-3-pentanol. After the isomerization treatment, the product is 96% 4,4-dimethyl-1-pentanol.

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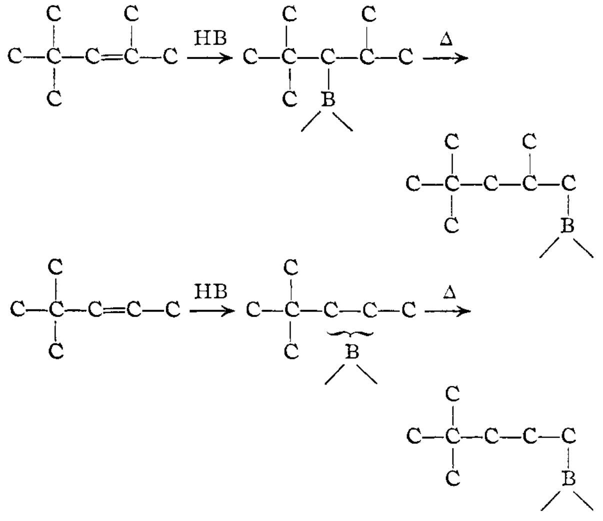
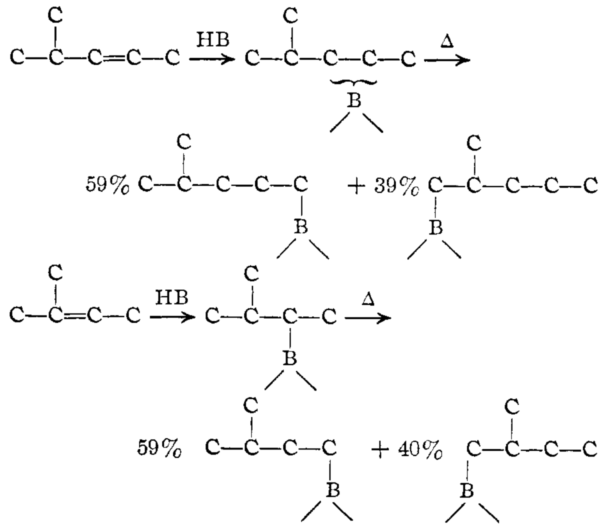
(1) G. F. Hennion, P. A. McCusker, E. C. Ashby and A. J. Rutkowski, THIS JOURNAL, **79**, 5190 (1957).

(2) H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1136 (1957); H. C. Brown and B. C. Subba Rao, THIS JOURNAL, **81**, 6434 (1959).



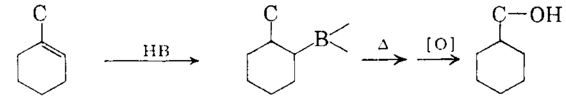
In both cases migration of the boron atom occurs only in one direction to the 1-position. No evidence of migration past the double branch was observed.[3] On the other hand, the hydroboration products from both 4-methyl-2-pentene and 2-methyl-2-butene exhibit migration of the boron atom to both ends of the carbon chain.

Thus, the initial hydroboration product from 4-methyl-2-pentene yielded 57% 4-methyl-2-pentanol and 43% 2-methyl-3-pentanol, whereas the isomerized product yielded 59% 4-methyl-1-pentanol, 2% 4-methyl-2-pentanol, and 39% 2-methyl-1-pentanol. Likewise, the hydroboration products from 3-methyl-1-butene, 2-methyl-2-butene, and 2-methyl-1-butene, isomerized for four hours at 160°, yielded essentially identical oxidation products: 59% 3-methyl-1-butanol, 1% 3-methyl-2-butanol, traces of 2-methyl-2-butanol, and 40% of 2-methyl-1-butanol.



It is important that the boron atom favors the less hindered terminal position, in spite of the statistical factor favoring the two methyl groups of the iso grouping.

Finally, the hydroboration product from 1-methylcyclohexene, after six hours at 160°, yields 50% of cyclohexylmethanol.



From these results, several conclusions are apparent: (1) Under these isomerization conditions the boron atom will move past a single branch. (2) Under isomerization conditions the boron atom is equilibrated among all possible positions in the molecule and tends to accumulate at the least hindered position. (3) The boron atom can be transferred from the ring position of a naphthene to the side chain.

These results should greatly extend the applicability of the hydroboration reaction in synthetic chemistry. The observations are consistent with the elimination–addition mechanism proposed for the isomerization reaction.[2]

We continue to explore the full scope of the hydroboration and isomerization reactions.

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RECEIVED FEBRUARY 1, 1960

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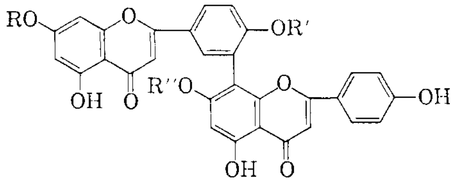
[3] The hydroboration of *trans*-di-*t*-butylethylene and the behavior of the reaction product under isomerization conditions has been examined by T. J. Logan and T. J. Flautt of The Procter and Gamble Co. Their results will be published shortly.

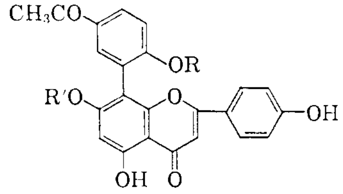
THE STRUCTURE OF SOTETSUFLAVONE

Sir:

Baker, Ollis and Robinson recently have proposed[1] the structure (I) for sotetsuflavone on the basis of the statement by Kariyone and Sawada[2] that a degradation product was similar and perhaps identical with a ketoflavone (II) obtained similarly from ginkgetin (III). However, this reported identity is not compatible with recent experimental observations, and we wish to report that sotetsuflavone must have the structure (IV).



(I) R = H, R′ = $\mathrm{CH_3}$, R″ = H
(III) R = R′ = $\mathrm{CH_3}$, R″ = H
(IV) R = R′ = H, R″ = $\mathrm{CH_3}$



(II) R = $\mathrm{CH_3}$, R′ = H
(IX) R = H, R′ = $\mathrm{CH_3}$

When treated with methanolic barium hydroxide by the same procedure as for sciadopitysin[3] and

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[1] W. Baker, W. D. Ollis and K. W. Robinson, *Proc. Chem. Soc.*, 269 (1959).

[2] T. Kariyone and T. Sawada, *Yakugaku Zasshi*, **78**, 1016 (1958).

[3] N. Kawano, *Chemistry & Industry*, 368, 852 (1959); T. Kariyone, N. Kawano and H. Miura, *Yakugaku Zasshi*, **79**, 1182 (1959); N. Kawano, *Chem. Pharm. Bull.* (Tokyo), **7**, 821 (1959).