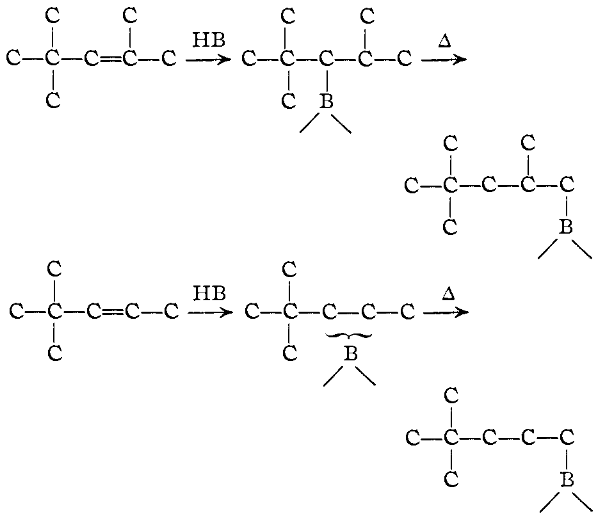
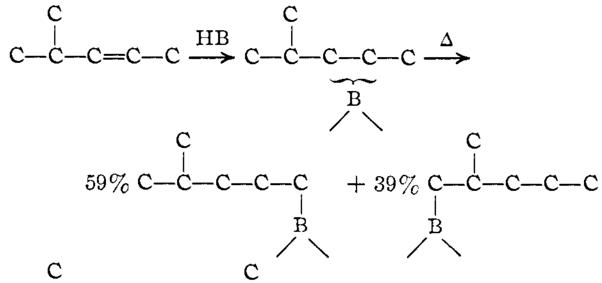
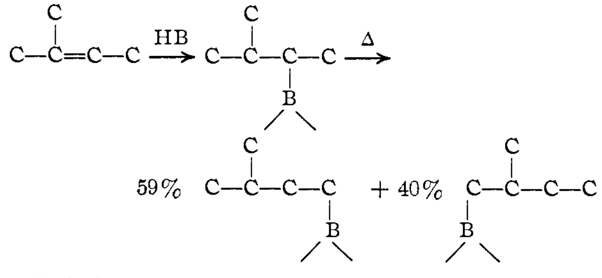


In both cases migration of the boron atom occurs only in one direction to the 1-position. No evidence of migration past the double branch was observed.[3] On the other hand, the hydroboration products from both 4-methyl-2-pentene and 2-methyl-2-butene exhibit migration of the boron atom to both ends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

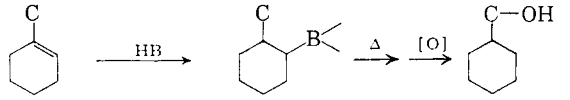
Thus, the initial hydroboration product from 4-methyl-2-pentene yielded 57% 4-methyl-2-pentanol and 43% 2-methyl-3-pentanol, whereas the isomerized product yielded 59% 4-methyl-1-pentanol, 2% 4-methyl-2-pentanol, and 39% 2-methyl-1-pentanol. Likewise, the hydroboration products from 3-methyl-1-butene, 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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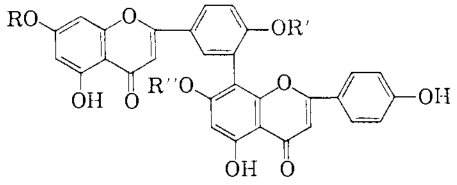
RECEIVED FEBRUARY 1, 1960

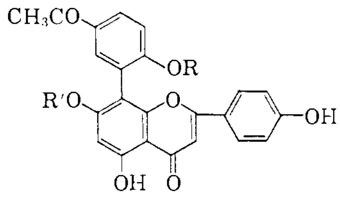
THE STRUCTURE OF SOTETSUFLAVONE

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) $R = H, R' = CH_3, R'' = H$
(III) $R = R' = CH_3, R'' = H$
(IV) $R = R' = H, R'' = CH_3$



(II) $R = CH_3, R' = H$
(IX) $R = H, R' = CH_3$

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

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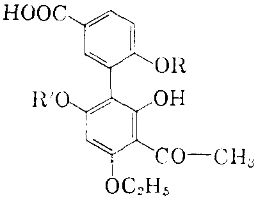
[3] The hydroboration of *trans*-di-*t*-butylethylene and the behavior of the reaction product under isomerization conditions has been examined by T. J. Logan and T. J. Flautt of The Procter and Gamble Co. Their results will be published shortly.

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

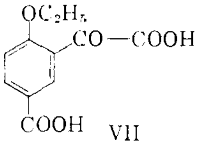
[2] T. Kariyone and T. Sawada, *Yakugaku Zasshi*, **78**, 1016 (1958).

[3] N. Kawauo, *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).

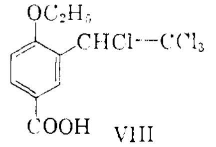
hinokiflavone,[4] sotetsuflavone pentaethyl ether produces 2,4-diethoxy-6-hydroxyacetophenone, *p*-ethoxybenzoic acid, and a phenolic acid (V), m.p. 257–258° (found: C, 63.89; H, 6.02. Calcd. for $C_{20}H_{22}O_7$: C, 64.16; H, 5.92). V is not identical, by admixture, with a formerly reported acid (VI)[3], m.p. 258–259°, similarly obtained from sciadopitysin triethyl ether, and gives a monoketodicarboxylic acid (VII), m.p. 248–249° (dec.) (found: C, 55.79; H, 4.25. Calcd. for $C_{11}H_{10}O_6$: C, 55.46; H, 4.23) on oxidation with alkaline potassium permanganate solution. VII was identified with a synthetic sample, which was newly prepared by the mild oxidation of a condensation product (VIII),[5] through admixtures of itself and of its 2,4-dinitrophenylhydrazone, $C_{17}H_{14}O_9N_4$, m.p. 239–241°.



V. $R = C_2H_5, R' = CH_3$
VI. $R = CH_3, R' = C_2H_5$



VII



VIII

This degradative evidence leads to the assignment of structure IV for sotetsuflavone. Therefore, a ketoflavone obtained by the hydrolysis of sotetsuflavone must be represented by formula (IX) instead of II.

We thank Dr. Kariyone for his encouragement throughout this work, which was carried out with the financial support of a Grant-in-Aid for Scientific Research from the Ministry of Education (Japan).

[4] N. Kawano and Y. Fukui, THIS JOURNAL, **81**, 6331 (1959).

[5] N. Kawano and H. Miura, *Yakugaku Zasshi*, **79**, 1469 (1959).

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RECEIVED DECEMBER 15, 1959

ASSOCIATION OF POLYMERS THAT REQUIRES ACTIVATION ENERGY[1]

Sir:

It is known that some groups, if present in polymeric molecules, may cause their reversible association in solution. Hydrogen bonding,[2] dipole interactions[3] or formation of clusters in polymeric salts[4] are responsible for these phenomena. For example, polystyrene endowed with the ——COO^-, Na^+ or ——CH_2O^-, Na^+ end groups associates in THF solution, while presence of the ——$CH(Ph)^-Na^+$ end-groups does not produce any detectable association.[5] These associations proceed very rapidly, in a second or two the system approaches closely the state of equilibrium if the viscosity of the solution is not too high.

A polystyrene endowed with the ——$CH(Ph)^-$, Li^+ end-groups has been prepared recently by polymerizing styrene in THF with lithium naphthalene. The initially fluid solution becomes gradually more and more viscous and a gel is formed after a day or two if the concentration is sufficiently high. The following experiment proved that this phenomenon is not due to a slow polymerization. A THF solution of polystyrene polymerized by lithium naphthalene was divided into three portions. By addition of water the organolithium compound was destroyed in the first portion shortly after its preparation, and at that time the solution was quite fluid. The second portion was kept at room temperature for 16 hours and then, when it was viscous, water was added. Finally, the last portion was kept for 40 hours and it was very viscous when the organolithium compound was destroyed by addition of water. After precipitation of the respective polymers it was shown that the polymerization was completed in each portion, and the intrinsic viscosities of the resulting polymers were identical, $[\eta] = 0.130$ in units g./100 cc.

The slowness of the association is astonishing and suggests that the process requires activation energy. This indeed seems to be the case. A solution of polystyrene polymerized by lithium naphthalene was divided into two portions. One was stored at −80°, while the second was introduced into a viscosimeter (a falling weight type). The time of falling slowly increased, being initially 9 sec., then 20 sec. after 12 hours, 40 sec. after 24 hours, and eventually 250 sec. after 48 hours. At that time the solution was very viscous, while the stored solution still remained fluid in spite of its low temperature. On the third day the stored solution was brought up to room temperature and then introduced into the same viscosimeter. Its initial viscosity corresponded again to 9 sec., and over a period of two days the viscosity increased to about 250 sec., the rate of increase being similar to that observed previously.

An explanation of this phenomenon is proposed. The polymeric ends might exist in 2 forms, *e.g.*, as covalent C–Li bonds and as ion pairs. Since each form represents a stable configuration, transformation of one form into the other must require activation energy. If the initially formed bond does not associate while the other does, then the observed association would show an apparent activation energy. This explanation is supported by another observation, namely, deepening of the color of the solution (from a bright red to a dark brown) with increase in the viscosity. Thus, the solution kept at −80° remained bright red and fluid; the color changed only after it was brought to room temperature and then left for two days. Alternatively it is possible that the activation energy is required for the reaction $2 —— \text{-}C^-, Li^+ \rightarrow \{——C, Li, C——\}^-, Li^+$, and it is hoped that future experiments will permit distinction between these alternatives.

[1] Research supported by Quartermaster Contract DA19-129-QM-1297, and by the National Science Foundation, G 5914.

[2] Q. A. Trementozzi, R. F. Steiner and P. Doty, THIS JOURNAL, **74**, 2070 (1952).

[3] E. F. Evans and H. M. Spurlin, *ibid.*, **72**, 4750 (1950).

[4] C. R. Singleterry, *J. Amer. Oil Chem. Soc.*, **32**, 446 (1955).

[5] H. Brody, D. H. Richards and M. Szwarc, *Chem. Industry (London)*, 1473 (1958).