

heat would cause the reaction. Comparison of Runs 4 and 5 indicates that there is no substantial difference in reactions containing catalyst and those not containing catalyst at this temperature (230°), although no silane gas was noted in the noncatalyzed reaction. At the lower temperature of Runs 2 and 3, the platinum definitely seems to act as a catalyst. Comparison of Runs 2, 4, and 7 shows that *increased temperature will cause disproportionation of diphenylsilane in the absence of any added catalyst.*

The fact that such disproportionations occur should be of interest in view of current research with regard to the addition reactions of silicon hydride compounds; these important side reactions may be caused by certain catalysts or take place in the absence of any added catalyst.

It would be interesting to consider whether many other substances may redistribute in the absence of added catalyst, provided that their decomposition temperatures are not too low.

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### Stereoselectivity in the Carbanion-Catalyzed Isomerization of 1-Butene<sup>1</sup>

Sir:

The double bond isomerization of alkenes and cyclenes in the presence of a sodium catalyst has been reported recently,<sup>2-4</sup> and it was observed<sup>3a,b</sup> that this is a reversible reaction leading to an equilibrium mixture.

It was suggested that the double bond migration occurs through a chain mechanism involving a carbanion attack on an allylic hydrogen. In order

(1) Paper XII of the series "Base Catalyzed Reactions of Hydrocarbons." For paper XI see M. Kolobielski and H. Pines, *J. Am. Chem. Soc.*, **79**, 5820 (1957).

(2) H. Pines, J. A. Vesely, and V. N. Ipatieff, *J. Am. Chem. Soc.*, **77**, 347 (1955).

(3) H. Pines and H. E. Eschinazi, *J. Am. Chem. Soc.*, (a) **77**, 6314 (1955); (b) **78**, 1178 (1956); (c) **78**, 5950 (1956).

(4) A. A. Morton and E. J. Lanpher, *J. Org. Chem.*, **20**, 839 (1955).

to elucidate further the mechanism of double bond migration a kinetic study of the carbanion-catalyzed isomerization of alkenes was undertaken.

The present communication deals with the isomerization of 1-butene to 2-butenes in the temperature range of 37–195° using as catalysts sodium-anthracene, sodium-alumina, and lithium-alumina.

It was found that the initial products obtained from the isomerization of 1-butene over a sodium-anthracene catalyst are kinetically controlled and that the less stable *cis*-2-butene is produced at a higher rate than the *trans* isomer. The initial ratio of the *cis/trans* isomers decreases with increasing temperature, as indicated in Table I.

TABLE I  
RESULTS OBTAINED FROM THE ISOMERIZATION OF 1-BUTENE<sup>a</sup>

Time, Min.	Butene %			<i>cis/trans</i> <sup>a</sup>
	1-	2- <i>trans</i>	2- <i>cis</i>	
Temperature 145°				
10	95.9	1.4	2.7	2.0
40	86.6	4.5	8.9	2.0
70	71.5	9.6	18.9	2.0
160	20.0	30.9	49.1	1.6
Temperature 195°				
10	87.4	5.7	6.9	1.20
25	74.5	11.8	13.7	1.16
45	55.5	21.4	23.1	1.1
65	39.9	31.0	29.1	0.94
105	22.3	46.5	31.2	0.67
145	18.1	50.4	31.5	0.63
245	14.7	54.4	30.9	0.57
Calcd. <sup>b</sup>	12.6	58.3	29.1	0.50

<sup>a</sup> The reaction was carried out in a 450-ml. capacity rotating autoclave charged with 5 g. of 1-butene, about 1 g. of sodium and 0.4 g. of anthracene. <sup>b</sup> Calculated from the thermodynamic data.<sup>6</sup>

When the sodium is dispersed on powdered alumina<sup>5</sup> it is possible to carry out the isomeriza-

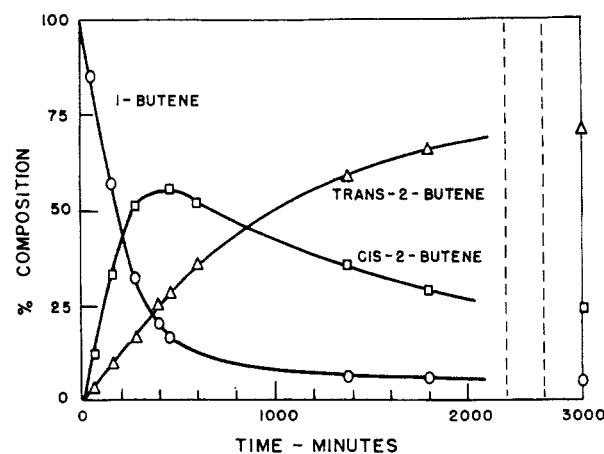


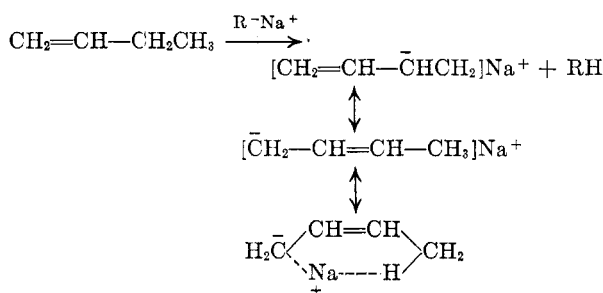
Fig. 1. Isomerization of 1-Butene. The reaction was made in a 450 ml. autoclave at 37° using 20 g. of 8% sodium on alumina and 16 g. of 1-butene

(5) S. E. Voltz, *J. Phys. Chem.*, **61**, 756 (1957).

tion at much lower temperatures. It appears from the results which are presented in Fig. 1 that initially both *cis*- and *trans*-2-butene are produced at nearly constant rates, the ratio of the *cis/trans* isomers being about 15 times greater than that of the thermodynamic equilibrium mixture.<sup>6</sup> This fast double bond migration is accompanied by a much slower *cis-trans* isomerization. After 50 hr. of contact the composition of the 2-butene corresponded to the calculated equilibrium mixture.

A similar but less pronounced selectivity was noticed when lithium-alumina was used as a catalyst.

This stereoselective isomerization of 1-butene has not been reported previously. The preferred formation of the less stable *cis*-2-butene in the carbanion-catalyzed reactions can be explained by postulating the participation in the transition state of a cyclic structure:



An independent study in this laboratory demonstrated that aluminas showing only weak or no acidic properties can stereoselectively isomerize at 350° 1-butene to form preferentially the less stable *cis*-2-butene. Stereoselective reactions were also observed in the catalytic dehydration of 1- and 2-butanol and 2- and 3-pentanol.

The analysis of the butenes was performed by vapor phase chromatography using a 16-ft. column of tricresyl phosphate on firebrick as the stationary phase and helium as the carrier gas. The absence of isobutylene was established by using a 12-ft. column of silver nitrate-glycol on firebrick.

In the kinetic experiments, 0.5 ml. samples were withdrawn from the reaction vessel with a syringe and charged directly into the chromatograph.

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(6) J. E. Kilpatrick, E. J. Prosen, K. S. Pitzer, and F. D. Rossini, *J. Research Natl. Bur. Stand.*, **36**, 559 (1946).

## Scyllitol Diborate

Sir:

The borate esters of the inositol isomers have been reported to exist as tridentate complexes.<sup>1</sup> Scyllitol, the all *trans* isomer of inositol, in its all equatorial conformation cannot form a tridentate complex and hence forms no borate derivative under mild conditions.<sup>1</sup> Theoretically, however, the all-axial conformation of scyllitol could form a double tridentate complex with borate (Fig. 1). In support of

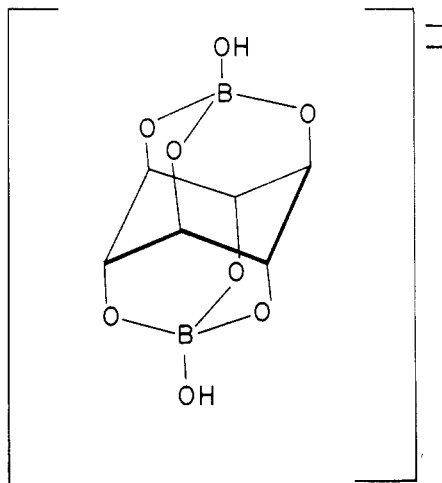


FIGURE 1

this hypothesis, scyllitol diborate has now been isolated.

The reduction of scyllo-myo-inosose with sodium borohydride has been reported to yield a mixture of 32% scyllitol and 45% myo-inositol.<sup>2</sup> During the course of this reduction, we observed that a white solid began to precipitate from the reaction mixture after a few hours. Precipitation ceased after 24–36 hours and this precipitate was collected, washed twice with small quantities of water and dried *in vacuo*. Starting with 1 gram of inosose, a yield of 0.9 gram of precipitate was obtained.

The material (I) isolated in this manner was distinguished from scyllitol, myo-inositol, and scyllo-myo inosose by paper chromatography using phenol saturated with water or acetone-water (85/15) as solvents and visualizing the spots with silver nitrate.<sup>3</sup> Upon paper ionophoresis in 0.125*M* sodium borate, compound I was observed to migrate twice as fast as myo-inositol which has been postulated to form a monoborate of the tridentate type under these conditions. Scyllitol, in this borate ionophoresis shows no migration.<sup>1</sup>

I is nonreducing in the Fehling or Park-Johnson

(1) S. J. Angyal and D. J. McHugh, *J. Chem. Soc.*, 1433 (1957).

(2) D. Raymond, *Helv. Chim. Acta*, **40**, 492 (1957).

(3) E. F. L. J. Anet, and T. M. Reynolds, *Nature*, **174**, 930 (1954).