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Abstract

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REDUCTION OF DIENE HYDROCARBONS WITH A CONJUGATED SYSTEM OF DOUBLE BONDS BY HYDROGEN "AT THE MOMENT OF LIBERATION"

Hydrogen "at the moment of liberation" is capable of adding to diene hydrocarbons not only in the 1,4-position, but also in the 1,2- or 3,4-position (1–6). The order of addition depends on the structure of the diene: an increase in the number of alkyl groups at the terminal 1st and 4th carbon atoms of the conjugated system favors the addition of hydrogen in the 1,2- and 3,4-positions, while the presence of alkyl groups at the 2nd and 3rd atoms of the conjugated system favors addition in the 1,4-position. Thus isoprene and diisopropenyl (2,3-dimethylbutadiene-1,3) add hydrogen "at the moment of liberation" almost exclusively in the 1,4-position, whereas diisocrotyl (2,5-dimethylhexadiene-2,4) and 2-methylhexadiene-2,4 add it predominantly in the 1,2- and 3,4-positions.

In reduction with a solution of sodium in liquid ammonia (1–4) or with calcium hexammine (5–6), metal amides are formed simultaneously with the addition of hydrogen at the double bond:

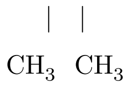
$$> C = C < +2Na + 2NH_3 \rightarrow > CH - HC < +2NaNH_2,$$

$$> C = C < +Ca(NH_3)_6 \rightarrow > CH - HC < +Ca(NH_2)_2 + 4NH_3.$$

As has recently been established, amides are capable of catalyzing the migration of double bonds in mono- and diolefin hydrocarbons (7–10). In this connection one may expect that, under certain conditions, the structure of the monoolefins formed upon addition of one molecule of hydrogen to dienes will depend not only on the structure of the starting diene, but also on the secondary isomerization reaction under the influence of the metal amide being formed.

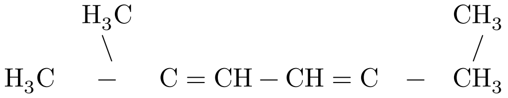
In order to assess the role of this possible secondary reaction, we carried out the reduction of diisopropenyl

$$\mathrm{CH_2 - CH - CH = CH_2}$$



$$\begin{array}{cc} | & | \\ CH_3 & CH_3 \end{array}$$

and diisocrotyl



$$\begin{array}{ccccc} & H_3C & & & CH_3 \\ & \backslash & & & / \\ H_3C & - & C=CH-CH=C & - & CH_3 \end{array}$$

which differ most sharply in the arrangement of methyl groups relative to the four carbon atoms of the butadiene grouping, under conditions excluding the isomerizing action of the metal amide. For this purpose, as reducing agent we used a solution of sodium in liquid ammonia with the addition of ethyl alcohol. As was shown earlier ([11]), in the partial reduction of heptene-1 and octene-1 the double bond does not migrate under these conditions.

In addition, the reduction of diisopropenyl with calcium hexammine and of diisocrotyl with sodium in liquid ammonia was carried out (under the same conditions as in the experiment with alcohol). The latter reaction had already been studied by Levina and co-workers ([2]), though under somewhat different conditions (at higher sodium concentrations and with a longer duration of the experiment).

The data obtained in the present work on the reduction of the hydrocarbons indicated above, as well as those already reported in the literature, are given in Table 1.

Table 1

Composition of the reduction products, wt. %

Starting diene	Monoolefin	Direction of reaction	Reducing agent, $Ca(NH_3)_6$	Reducing agent, $Na+NH_3$	Reducing agent, $Na+NH_3+C_2H_5OH$
Diisopropenyl (2,3-dimethylbutadiene-1,3)	2,3-dimethylbutene-1	1,2	9	2	4
Diisopropenyl (2,3-dimethylbutadiene-1,3)	2,3-dimethylbutene-2	1,4	91*	98^(3)	96*
Diisocrotyl (2,3-dimethylhexadiene-2,4)	2,5-dimethylhexene-2	1,2	77	84	71

Starting diene	Monoolefin	Direction of reaction	Reducing agent, $Ca(NH_3)_6$	Reducing agent, $Na+NH_3$	Reducing agent, $Na+NH_3+C_2H_5OH$
Diisocrotyl (2,3-dimethylhexadiene-2,4)	2,5-dimethylhexene-3	1,4	23^(5)	16*	29*

* Data obtained in the present work.

According to these data, upon reduction by all the hydrogen sources studied “at the moment of liberation,” diisopropenyl adds it almost exclusively in the 1,4 position. The reduction of diisocrotyl proceeds less selectively, although hydrogen is added predominantly in the 1,2 position.

Comparison of the data obtained for calcium hexammoniate and for a solution of sodium in liquid ammonia—systems capable of causing migration of double bonds in monoolefins—with the data obtained for sodium and alcohol in liquid ammonia shows that, although the secondary isomerization reaction somewhat changes the results of the primary reduction reaction, it does not distort them, and that, consequently, the regularities reported in the works of Levina and Kazanskii et al. concerning the influence of the structure of dienes on the direction of their reduction remain valid.

Experimental Part

Reduction with sodium in liquid ammonia was carried out in a three-necked half-liter flask placed in a thermostat and equipped with a stirrer, a dropping funnel, and tubes for the introduction and removal of ammonia. To 250 ml of liquefied ammonia, with vigorous stirring, 0.4 g-atom of sodium was added, and then the diene (0.2 mole) was added dropwise at −33°. After all the diene had been added, stirring was continued for another 2 hours at the same temperature; then 100 ml of dry ether was added to the flask, and the reaction mixture was left until the ammonia evaporated. On the following day it was treated with water; the ether layer was separated, washed with water, and dried over $CaCl_2$.

Reduction with sodium and ethyl alcohol in liquid ammonia was carried out in the apparatus described above; to 0.4 g-atom of sodium in 250 ml of liquefied ammonia was added a mixture of 0.2 mole of diene and 0.8 mole of absolute ethyl alcohol. Stirring of the mixture was continued until it became decolorized, but for no longer than 2 hours; further treatment was as described above.

Reduction with calcium hexammoniate was carried out by the procedure described earlier (5-12). The molar ratio Ca : diene was 4 : 1.

Investigation of the reaction products was carried out by distillation on an 80 theoretical-plate column and by determining the properties of the fractions obtained.

Reduction of Diisopropenyl

Diisopropenyl, obtained by dehydration of 2,3-dimethylbutanediol-2,3^(13), had b.p. 67.5°/760 mm, n_D^{20} 1.4395, d_4^{20} 0.7276, MR_D 29.67, found for $C_8H_{10}(F_2)$ 28.97; ΣMR_D 0.70.

I. 75.4 g of diisopropenyl were reduced with calcium hexaammine. 57 g of a mixture of hydrocarbons was obtained, from which, after boiling with maleic anhydride, 39.4 g of a mixture of olefins was isolated. The result of distillation of the mixture is presented in Table 2 and in Fig. 1.

Table 2

Fraction no.	B.p., °C*	Yield, wt. %	n_D^{20}	d_4^{20}
1	55.7–56.2	6.4	1.3892	0.6756
2	56.2–72.7	4.5	1.4055	0.7000
3	72.7–73.2	23.5	1.4139	0.7107
4	73.2	61.0	1.4144	0.7110

* The boiling temperatures in Tables 2–7 are given for a pressure of 760 mm Hg.

The data of the distillation curve and a comparison of the properties of the fractions with the properties of olefins that can be obtained by reduction of diisopropenyl (Table 3) show that the reaction products contain about 9% 2,3-dimethylbutene-1 and 91% 2,3-dimethylbutene-2.

II. 51 g of the diene were reduced with sodium and alcohol in liquid ammonia; 24.9 g of reduction products was obtained. The characteristics of the fractions obtained on distillation are given in Table 4, the distillation curve in Fig. 1.

In this case the principal reaction product is 2,3-dimethylbutene-2 with a small admixture of 2,3-dimethylbutene-1, the content of which, according to the distillation curve, does not exceed 4%.

Table 3

Olefin	B.p., °C	n_D^{20}	d_4^{20}	Source
2,3-Dimethylbutene-1	55.67	1.3904	0.6779	(14)
2,3-Dimethylbutene-2	73.21	1.4122	0.7080	(14)

Fig. 1. Distillation curves of products of reduction of diisopropenyl: 1—calcium hexaammine; 2—sodium and alcohol in liquid ammonia

Figure 1: Fig. 1. Distillation curves of products of reduction of diisopropenyl: 1—calcium hexaammine; 2—sodium and alcohol in liquid ammonia

Fig. 2. Distillation curves of products of reduction of diisocrotyl: 1—sodium in liquid ammonia; 2—sodium and alcohol in liquid ammonia

Figure 2: Fig. 2. Distillation curves of products of reduction of diisocrotyl: 1—sodium in liquid ammonia; 2—sodium and alcohol in liquid ammonia

Reduction of diisocrotyl

Diisocrotyl was obtained by isomerization of diisobutenyl in the presence of calcium amide; b.p. 134.4°/760 mm; n_D^{20} 1.4780; d_4^{20} 0.7627; MR_D 40.82, calculated for C_8H_{14} (F_2) 38.21, increment MR_D 2.61.

Fig. 1. Distillation curves of products of reduction of diisopropenyl: 1—calcium hexaammine; 2—sodium and alcohol in liquid ammonia.

Fig. 2. Distillation curves of products of reduction of diisocrotyl: 1—sodium in liquid ammonia; 2—sodium and alcohol in liquid ammonia.

I. 44.8 g of diisocrotyl were reduced with sodium in liquid ammonia; 38.7 g of a mixture of hydrocarbons was obtained. The distillation curve is given in Fig. 2; the characteristics of the fractions obtained on distillation are presented in Table 5.

Comparison of the properties of the obtained fractions with the properties of octenes that can be formed upon reduction of diisocrotyl (Table 6) shows that fraction 1 corresponds to 2,5-dimethylhexene-3, fraction 3 to 2,5-dimethylhexene-2, and the residue in the flask to unreacted diisocrotyl.

Table 4

Fraction No.	B.p., °C	Yield, wt. %	n_D^{20}	d_4^{20}
1	56.7–60.3	1.4	1.3894	–
2	60.3–73.3	7.3	1.4068	–
3	73.3	63.2	1.4122	0.7089
Residue	–	18.1	1.4165	–

Table 5

Fraction No.	B.p., °C	Yield, wt. %	n_D^{20}	d_4^{20}
1	101.5–102.3	7.0	1.4020	0.7008
2	102.3–114.0	12.4	1.4090	0.7109

Fraction No.	B.p., °C	Yield, wt. %	n_D^{20}	d_4^{20}
3	114.0	63.3	1.4150	0.7187
Residue	–	15.0	1.4718	0.7694

Calculation of the composition of the monoolefinic portion of the reduction products from the distillation curve and Table 6 leads to the following ratios: 2,5-dimethylhexene-3, 16%; 2,5-dimethylhexene-2, 84%.

Table 6

Olefins	B.p., °C	n_D^{20}	d_4^{20}	Source
2,5-Dimethylhexene-2	112.2	1.4140	0.720	(14)
2,5-Dimethylhexene-3 (mixture of cis and trans)	102	1.406	0.710	(14)
2,5-Dimethylhexene-3 (mixture of cis and trans)	103.5	1.4100	0.7122	(15)
2,5-Dimethylhexene-3 (mixture of cis and trans)	99.7–99.9	1.4040	0.7015	(16)

II. 66 g of diene was reduced with sodium and alcohol in liquid ammonia; 54.4 g was obtained. The distillation curve is given in Fig. 2, and the characteristics of the fractions in Table 7.

Table 7

Fraction No.	B.p., °C	Yield, wt. %	n_D^{20}	d_4^{20}	Fraction No.	B.p., °C	Yield, wt. %	n_D^{20}	d_4^{20}
1	96.5–101.5	7.5	1.4020	0.7063	5	113.0–134.4	4.9	1.4648	0.7597
2	101.5	12.7	1.4045	0.6998	6	134.4	16.8	1.4780	0.7628
3	101.5–113.0	6.4	1.4125	0.7142	Residue	–	7.0	1.4780	–

Fraction No.	B.p., °C	Yield, wt. %	n_D^{20}	d_4^{20}	Fraction No.	B.p., °C	Yield, wt. %	n_D^{20}	d_4^{20}
4	113.0	43.6	1.4155	0.7189					

Fractions 1 and 2 correspond to 2,5-dimethylhexene-3, fraction 4 to 2,5-dimethylhexene-2, and fraction 6 and the residue to unreacted diene. Calculation of the composition of the monoolefinic portion shows that it contains 2,5-dimethylhexene-3, 29%, and 2,5-dimethylhexene-2, 71%.

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