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1958

SovietRxiv

Abstract

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CHEMISTRY

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REDUCTION OF MONOOLEFINIC HYDROCARBONS WITH SODIUM IN LIQUID AMMONIA IN THE PRESENCE OF tert-BUTYL ALCOHOL

The reduction of an isolated carbon-carbon double bond by alkali metals in liquid ammonia, as has already been reported earlier (^{1}), apparently proceeds by an ionic scheme:

$$> C = C < +2\bar{e} \to> C\bar{e} - C\bar{e} < \qquad \text{(a)}$$

$$> C\bar{e} - C\bar{e} < 2H^+ \to> CH - CH < \qquad \text{(b)}$$

$$2\bar{e} + 2H^+ \to H^2 \qquad \text{(c)}$$

The overall rate of the reduction reaction is determined by the ratio of the rates of two competing reactions: the reaction of addition of hydrogen to the double bond of the olefin ((a) and (b)) and the reaction of liberation of free hydrogen (c). The rates of these reactions, in turn, depend on the structure of the olefin, the nature of the metal, and the acidity of the protolytic agent.

In the preceding work (^{1}) we studied the influence on the rate of reduction of the nature of the metal in the series Li, Na, K and of the acidity of the alcohol, using methyl and ethyl alcohols as examples. α-Monoolefinic hydrocarbons can be reduced by Na, K, and Li in liquid ammonia in the presence of methyl and ethyl alcohols, but hydrocarbons with a double bond removed from the end of the chain are not reduced under these conditions. Apparently, the action of two electron-donating alkyl groups at the double bond greatly hinders the formation of the carbanion, i.e., lowers the rate of reaction (a), as a result of which the relative rate of the side reaction of formation of hydrogen from electrons and protons increases (reaction (c)).

Therefore it seemed of interest to carry out the reduction of monoolefins with different positions of the double bonds in the presence of a weaker source of protons than methyl or ethyl alcohols and thereby to decrease the rate of the side reaction. As such a weaker protolite we chose tert-butyl alcohol, whose acidity, according to McEwen (^{2}), is 10 times lower than that of ethyl alcohol. Sodium served as the reducing metal.

Table 1

Hydrocarbon	Percent reduction, Na + NH_3 + CH_3OH	Percent reduction, Na + NH_3 + C_2H_5OH	Percent reduction, Na + NH_3 + tert.-C_4H_9OH
Pentene-1	43	45	72
Hexene-1	40	42	60
Heptene-1	38	41	42
Octene-1	20	29	32
Nonene-1	6	20	16
Decene-1	4	8	8

The following monoolefins of normal structure were subjected to reduction: pentene-1, hexene-1, heptene-1, octene-1, nonene-1, decene-1, pentene-2, a mixture of hexene-2 and hexene-3, heptene-3, octene-2. The greater part of the α-monoolefinic hydrocarbons studied is reduced by sodium in liquid ammonia in the presence of tert-butyl ···

alcohol faster than under analogous conditions in the presence of methyl or ethyl alcohols, as is evident from the data in Table 1.

β- and γ-monoolefins under the same conditions are reduced to a very slight extent, but with certain changes in the reduction procedure the reaction already proceeds at an appreciable rate: pentene-2 is reduced by 12%, a mixture of hexenes by 11%, heptene-3 by 9%, octene-2 by 5%.

Thus, decreasing the relative rate of formation of free hydrogen by using a weaker protolytic agent makes it possible to carry out the reduction even of hydrocarbons as inert toward reduction under these conditions as β- and γ-monoolefins.

It is characteristic that the rates of reduction of β- and γ-olefins of different molecular weight differ little from one another, in contrast to α-olefins, for which the dependence between the rate of reduction and molecular weight is rather sharply expressed. In addition, the reduction reaction proceeds at approximately the same rates for β-olefins and γ-olefins, i.e., the position of the double bond within the olefin chain has little effect on the results of reduction.

The data obtained serve as further confirmation of the ionic scheme for the reduction of an isolated double bond by metals in liquid ammonia.

Experimental Part

The methods for synthesizing monoolefins have been described by us earlier (^{1}). Pentene-2 (b.p. 36.6–36.8°/760 mm, n_D^{20} 1.3810, d_4^{20} 0.6502) was prepared by reducing piperylene with sodium in liquid ammonia in the presence of methyl alcohol; a mixture of hexene-2 and hexene-3 (b.p. 67.5–68.0°/760 mm, n_D^{20} 1.3930, d_4^{20} 0.6785) was obtained by catalytic hydrogenation of dipropenyl over palladium. The constants of the α-monoolefins correspond to the most reliable literature data (^{3}). The constants of the β- and γ-olefins correspond to mixtures of their cis- and trans-isomers. The bromine numbers of all the monoolefins studied are close to the theoretically calculated values.

Properties of the monoolefins studied. Pentene-1: b.p. 30.0°/760 mm, n_D^{20} 1.3718, d_4^{20} 0.6411; hexene-1: b.p. 63.2°/760 mm, n_D^{20} 1.3876, d_4^{20} 0.6735; heptene-1: b.p. 93.7°/760 mm, n_D^{20} 1.3995, d_4^{20} 0.6965; heptene-3: b.p. 95.7–95.8°/760 mm, n_D^{20} 1.4048, d_4^{20} 0.7002; octene-1: b.p. 121.3°/760 mm, n_D^{20} 1.4092, d_4^{20} 0.7155; octene-2: b.p. 124.7-125.2°/760 mm, n_D^{20} 1.4140, d_4^{20} 0.7215; nonene-1: b.p. 146.6°/760 mm, n_D^{20} 1.4158, d_4^{20} 0.7292; decene-1: b.p. 170.7°/760 mm, n_D^{20} 1.4215, d_4^{20} 0.7410.

Table 2

Hydrocarbon	n_D^{20}	Bromine number	H_2, mol. %, added to H\C=C/$^{\mathrm{R}}$H/ \H	H_2, mol. %, evolved in free state
Pentene-1	1.3615	63.5	72	33
Hexene-1	1.3799	76.0	60	30
Heptene-1	1.3947	95.2	42	21
Octene-1	1.4052	97.2	32	20
Nonene-1	1.4143	105.8	17	25
Decene-1	1.4208	106.0	8	32

Reduction of α-monoolefins. The reduction of α-monoolefins and investigation of the reaction products were carried out by us according to method A, described earlier (^{1}). For 0.1 gram-mole of hydrocarbon, 0.2 gram-atom of sodium and 0.25 gram-mole of tert-butyl alcohol were taken for the reaction. The reaction time was 3 hours. The results of the experiments are given in Table 2. As is evident from these data, in the presence of tert-butyl alcohol the reaction of evolution of free hydrogen proceeds rather slowly—during the experiment 20–30% of hydrogen is evolved.

hydrogen from the theoretical value; the rate of reduction of the α-monoolefins changes markedly with a change in the molecular weight of the olefin.

Reduction of β- and γ-monoolefins. The reduction of pentene-2, a mixture of hexene-2 and hexene-3, heptene-3, and octene-2 was carried out under the same conditions as for the α-monoolefins. The change in bromine numbers was insignificant in this case. In the following experiments, 0.32 g-at. of sodium and 0.4 mol of alcohol were taken per 0.08 g-mol of hydrocarbon. The concentration of sodium in liquid ammonia remained the same as before: 0.32 g-at. of sodium was dissolved in 250 ml of liquid ammonia. The results obtained are given in Table 3.

Table 3

Hydrocarbon	n_D^{22}	Bromine number	H_2, mol. %, added to R\C = C/R, H/ \H	H_2, mol. %, liberated in the free state
Pentene-2	1.3801	201.5	12	40
Hexene-2 + hexene-3	1.3914	170.1	11	31
Heptene-3	1.4032	148.3	1	28
Octene-2	1.4133	135.7	5	25

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named after M. V. Lomonosov

Received
17 VII 1957

CITED LITERATURE

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