

Hydrogenation of Chlorinated Butadienes

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Hydrogenation of 2-chloro-1,3-butadiene and 2,3-dichloro-1,3-butadiene was investigated. Rhodium black adsorbed on alumina was used as a selective catalyst for hydrogenation of chlorinated alkenes. The hydrogenation of 2-chloro-1,3-butadiene afforded 2-chlorobutane in high yields. The product of hydrogenation of 2,3-dichloro-1,3-butadiene was not the expected mixture of 2,3-dichlorobutanes but isomerization and hydrogenolysis took place in the course of hydrogenation and 2-chlorobutane and 1,2-dichlorobutane predominated in the reaction product.

In the preceding paper [1] we have shown that the most suitable catalyst for hydrogenation of chlorinated alkenes was rhodium black adsorbed on alumina and that the yields of hydrogenated products possessing the same number of chlorine atoms in the molecule as the starting compounds depended on their structure.

With the aim to test the general applicability of rhodium black as a catalyst for hydrogenation of chlorinated alkadienes containing conjugated system of double bonds in the molecule we studied the hydrogenation of 2-chloro- and 2,3-dichloro-1,3-butadienes as the typical representatives of chlorinated butadienes.

Experimental

Materials

The physicochemical constants in the brackets are the reference data from the literature.

2-Chloro-1,3-butadiene (Duslo, Šaľa). n_D^{20} 1.4585 (1.4583 [2]); d_4^{20} 0.9587 (0.9583 [2]).

2,3-Dichloro-1,3-butadiene was prepared by dehydrochlorination of 2,3,4-trichloro-1-butene [3], rectified. n_D^{20} 1.4888 (1.4890 [3]); d_4^{20} 1.1826 (1.1829 [3]). Purity 99.8%, determined chromatographically.

The standards for gas chromatography, hydrogenation apparatus, reaction conditions, and analytical methods were identical with those described in the previous paper [1].

Due to the reactivity of both isomers the reaction mixture was stabilized before hydrogenation by addition of 0.05 weight % of phenothiazine.

Results and Discussion

The results summarized in Table 1 show that hydrogenation of 2-chloro-1,3-butadiene proceeded relatively easily affording high yields of 2-chlorobutane.

Table 1

Hydrogenation of 2-chloro-1,3-butadiene

Time [min]	Composition of hydrogenation product [mole %]		
	<i>n</i> -butane	2-chlorobutane	2-chloro-1,3-butadiene
30	8.0	82.4	9.6
60	8.3	84.5	7.2
90	8.9	91.1	0.0

Table 2

Hydrogenation of 2,3-dichloro-1,3-butadiene

Time [min]	Composition of hydrogenation product [mole %]					
	<i>n</i> -butane	2-chloro- butane	2,3-dichloro- -1,3-butadiene	<i>meso</i> -2,3-di- chlorobutane	<i>D,L</i> -2,3-di- chlorobutane	1,2-dichloro- butane
60	7.6	51.1	20.6	0.0	1.9	18.8
120	7.9	62.3	2.9	0.5	2.5	23.9
180	8.9	63.0	0.0	0.7	3.1	24.3

The hydrogenation of 2,3-dichloro-1,3-butadiene proceeded, however, quite unexpectedly (Table 2). This reaction should afford 2,3-dichlorobutane whose *meso* isomer has b.p. 116°C/760 Torr and the racemic mixture has b.p. 119.5°C/760 Torr [4, 5]. Instead, the main reaction product (when not considering the substances arising from concurrent hydrogenation and hydrogenolysis, *i.e.* 2-chlorobutane and *n*-butane) was 1,2-dichlorobutane.

Comparison of the i.r. and n.m.r. spectra of the starting 2,3-dichloro-1,3-butadiene with the literature data [6–8] proved that the used compound was uniform and did not contain 1,2-dichloro-1,3-butadiene whose n.m.r. spectrum distinctly differed from that of 2,3-dichloro-1,3-butadiene [8].

The formation of substances designated in Table 2 as *meso*-2,3-dichlorobutane and *D,L*-2,3-dichlorobutane in the course of hydrogenation was not directly proved because of the lack of corresponding standards. They were identified only indirectly on the basis of their difference from dichloro- and monochlorobutanes. The boiling points of these compounds estimated from elution parameters on the nonpolar stationary phase were in accordance with the literature data.

On the basis of these experiments it can be stated that rhodium black adsorbed on an insoluble carrier can be used as a catalyst for hydrogenation of both chlorinated alkanes and alkenes, in spite of the fact that in all investigated cases there proceeded also reductive dehalogenation (in the case of hydrogenation of 2,3-dichloro-1,3-butadiene also isomerization) so that the reaction products contained varied mixtures of compounds.

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