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Abstract

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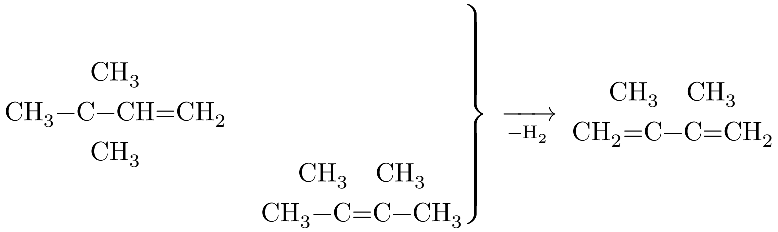
PREPARATION OF 2,3-DIMETHYLBUTADIENE BY A CATALYTIC METHOD

The aim of the present investigation was the synthesis of 2,3-dimethylbutadiene-1,3, which is a potentially valuable starting product for obtaining rubber-like polymers, as well as for a number of syntheses in preparative organic chemistry. The cheapest starting materials for the synthesis of 2,3-dimethylbutadiene-1,3 may be components of the hexane fraction of petroleum-refining products, subjected to conversion into branched hexenes and to subsequent two-stage dehydrogenation. Of particular interest for solving the question of the possibility of using this raw material for the preparation of 2,3-dimethylbutadiene-1,3 is the second stage of the process: dehydrogenation of branched hexenes, in particular tert-butylethylene and tetramethylethylene, to 2,3-dimethylbutadiene-1,3:



$$\left.\begin{array}{l} \mathrm{CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH=CH_2} \\ \qquad\qquad \mathrm{CH_3-\overset{CH_3}{C}=\overset{CH_3}{C}-CH_3} \end{array}\right\} \xrightarrow[-\mathrm{H_2}]{} \mathrm{CH_2=\overset{CH_3}{C}-\overset{CH_3}{C}=CH_2}$$

There are indications in the literature (^{1}) of the possibility of obtaining 2,3-dimethylbutadiene-1,3 from 2,3-dimethylbutane by dehydrogenation of the latter over Al_2O_3 and Cr_2O_3; there is also a patent (^{2}) on the dehydrogenation of neohexane over Al_2O_3/Cr_2O_3 at 426–649° and a pressure of 4 ata to a mixture of hexenes (yield 14–15%), of which 70% was tetramethylethylene.

The dehydrogenation of tert-butylethylene and tetramethylethylene was carried out by us on catalysts used for the industrial conversion of butylene into divinyl. It was established that the first of these hydrocarbons, under dehydrogenation conditions, is not converted into 2,3-dimethylbutadiene-1,3, whereas the dehydrogenation of tetramethylethylene leads to the formation of 2,3-dimethylbutadiene-1,3. Dehydrogenation was carried out at a temperature of 600–675°, a space velocity of 1000–1500–2000 l per 1 l of catalyst per hour, with eightfold dilution with steam, on catalysts K-12, K-18, and K-16. During distillation of the catalyzate, a fraction with b.p. 68–75° was collected, the diene content in which was determined by condensation with maleic anhydride

(3); 2,3-dimethylbutadiene-1,3 was isolated from the fraction with b.p. 68–75° by rectification. The influence of temperature and space velocity on the course of the process was investigated on catalyst K-12. It was established that when the temperature is raised from 600 to 675°, the diene content in the condensate increases, the diene yield remains fairly constant, and gas formation increases. The optimum conditions of the process are: a temperature of 625–650° and a space velocity of about 1500 l per 1 l of catalyst per hour. Under these conditions the diene yield remained fairly constant and was 10–13% based on the material charged and 25–30% based on that which entered into reaction.

hydrocarbon. The results of dehydrogenation on catalyst K-18 did not differ substantially from the results obtained on K-12. On catalyst K-16 the yield of diene was 20–23% based on the hydrocarbon taken and 40–50% based on the hydrocarbon entering into the reaction.

At present we are continuing work on the dehydrogenation of tetramethylethylene, unsymmetrical methylisopropylethylene, and also 2,2- and 2,3-dimethylbutanes.

Experimental Part

tert-Butylethylene, b.p. 40°/760 mm, n_D^{20} 1.3760, d_4^{20} 0.6520, was obtained in 50% yield by pyrolysis of pinacolyl alcohol acetate (4). Tetramethylethylene, b.p. 73°/760 mm, n_D^{20} 1.4122, d_4^{20} 0.7080, was obtained by dehydration of pinacolyl alcohol over $ZnCl_2$ on pumice at 192–200° (5).

Dehydrogenation was carried out in a quartz tube containing 5 ml of catalyst, placed in a tubular electric furnace with an electronic temperature regulator. The temperature was measured with a chromel–alumel thermocouple. Hydrocarbon and water were fed by means of plunger-type metering pumps. The gas was collected in a gasometer; the liquid products and water were condensed in a cooled receiver. The hydrocarbon layer was separated and dried with $CaCl_2$. On its distillation, a fraction with b.p. 68–75° was collected, consisting of tetramethylethylene and diene. 2,3-Dimethylbutadiene-1,3 was identified by an adduct with maleic anhydride—4,5-dimethyl-cis-Δ^4-tetrahydrophthalic anhydride, m.p. 74–76° (from petroleum ether with b.p. 60–80°). The adduct was converted into 4,5-dimethyl-cis-Δ^4-tetrahydrophthalic acid, m.p. 187–192° (from aqueous alcohol) (6). A check of the suitability of the method for determining diene products with maleic anhydride (3) for a mixture of tetramethylethylene and 2,3-dimethylbutadiene-1,3 showed its complete applicability.

Dehydrogenation of tert-butylethylene on K-12 at 625°, space velocity 1580 l per 1 l of catalyst per hour, and dilution with steam 1 : 7.7

Hydrocarbon charged: 45.6 ml (0.353 mole); water: 49.7 ml. Hydrocarbon layer collected: 36 ml (21.7 g); water: 49 ml (2.7 moles). After the experiment the system was purged with nitrogen to displace the remaining gas. Gas collected:

10.25 l (under normal conditions). Distillation of the condensate: fraction I—b.p. 28-40°, 2.5 g; fraction II—b.p. 40-57°, 15.1 g; residue, 0.8 g.

The distillation results show that the catalyzate does not contain a fraction with b.p. 68-75°.

The course of the experiment is presented in Table 1.

Table 1

Time, min	Temperature, °C	Hydrocarbon feed, ml	Water feed, ml	Gas collected, l	Time, min	Temperature, °C	Hydrocarbon feed, ml	Water feed, ml	Gas collected, l
Dehydrogenation of tert-butylethylene	**Dehydrogenation of tert-butylethylene**	**Dehydrogenation of tert-butylethylene**	**Dehydrogenation of tert-butylethylene**	**Dehydrogenation of tert-butylethylene**	**Dehydrogenation of tetramethylethylene**	**Dehydrogenation of tetramethylethylene**	**Dehydrogenation of tetramethylethylene**	**Dehydrogenation of tetramethylethylene**	**Dehydrogenation of tetramethylethylene**
0	625	4.0	–	–	0	630	–	–	–
5	625	4.0	4.25	0.45	5	630	3.4	4.0	0.65
10	625	4.0	4.25	1.25	10	630	3.4	2.8	1.25
15	625	4.0	4.25	2.15	15	630	3.4	3.7	1.80
20	625	4.0	4.25	2.75	20	630	3.4	4.0	2.25
25	625	4.0	4.25	3.65	25	630	4.0	4.0	2.75
30	625	4.0	4.25	4.55	30	630	4.0	4.3	3.25
35	625	4.0	4.25	5.65	35	630	3.7	4.0	3.60
40	625	5.7	4.25	6.95	40	630	3.7	4.0	3.90
45	625	2.8	4.25	7.95	45	630	3.7	7.1	4.20
50	625	4.0	4.25	8.95	50	630	3.7	3.1	4.40
55	625	4.0	4.25	9.65	55	630	3.7	2.3	4.65
60	625	1.4	2.84	10.75	60	630	3.4	4.8	5.0

Dehydrogenation of tetramethylethylene on K-12 at 630°, space velocity 1600 l/l · h and dilution 1 : 7.3. The course of the experiment is given in Table 1. Hydrocarbon, 43.2 ml (0.363 mole), and water, 48 ml (2.6 mole), were fed. Hydrocarbon, 36 ml (25 g), and water, 48 ml, were collected. Gas collected: 6.4 l (under normal conditions). Composition of the gas (without O_2 and N_2): CO_2 5.4%; C_4 unsaturated 9.73%; ethylene 2.39%; H_2 55.5%; saturated 23%; CO 4.04%. Weight of gas: 1.26 g.

Table 2

	600°	600°	612.5°	625°	625°	630°	627.5°	650°	675°
Yield of diene based on hydrocarbon taken, %	4.9	3.5	11.3	11.1	10.4	9.9	11.0	17.3	15.6
Yield of diene based on reacted hydrocarbon, %	11.8	12.8	22.9	29.3	31.8	29.8	30.0	29.5	18.7
Diene content in the catalyzate (fraction b.p. 68–74°), %	7.6	4.4	15.6	15.2	13.0	12.5	16.4	23.8	30.7

On distillation of the condensate, the main fraction (23.6 g) with b.p. 68–74° was collected (2,3-dimethylbutadiene-1,3 content 12.5%). Diene obtained: 2.95 g. Tetramethylethylene entering into reaction: 9.9 g; 20.7 g of it was recovered. The yield of diene based on hydrocarbon taken was 9.9% of theory; the yield of diene based on reacted hydrocarbon was 30.5% of theory. The results of experiments on studying the effect of temperature are given in Table 2.

Table 3

	Space velocity, l/l • h	Space velocity, l/l • h	Space velocity, l/l • h	Space velocity, l/l • h
	1000	1000	1500	2000
Yield of diene based on tetramethylethylene taken, %	10.7	11.7	9.9	8.9
Yield of diene based on reacted tetramethylethylene, %	22.6	20.6	29.8	20.1
				9.3
				24.8

The results of experiments on studying the effect of space velocity at a temperature of 630° are given in Table 3.

Data from comparative experiments on catalysts K-12, K-18, and K-16 are given in Table 4. The experiments were carried out at 630° and a space velocity of 1500 l/l • h.

Table 4

	K-12	K-12	K-18	K-18	K-16	K-16
Yield of diene (theoretical) based on tetramethylethylene taken, %	9.9	8.1	10.7	23.5	23.5	
Yield of diene (theoretical) based on reacted tetramethylethylene, %	29.8	31.0	31.8	49.6	50.8	
Diene content in the catalyzate (fraction b.p. 68–74°), %	12.5	9.6	13.6	30.4	30.0	

Table 5

Fraction	B.p., °C	Amount, ml	Diene content, %
I	34–55	13.6	–
II	61–68.3	4.8	54.6

Fraction	B.p., °C	Amount, ml	Diene content, %
III*	68.3–68.8	22.4	89.5
IV	68.8–70.2	8.6	64.1
V	70.2–71.6	15.0	26.8
VI	71.6–72	10.0	10.2
VII	72–72.8	122.6	–
Residue	–	7.0	–

* According to literature data (^{7}), the b.p. of 2,3-dimethylbutadiene-1,3 is 68.7°.

III. Isolation of 2,3-dimethylbutadiene. 210 ml of condensate (fraction with b.p. 68–74°) was subjected to distillation on a column of 60 theoretical plates. The amounts, boiling temperatures of the fractions obtained, and the content of 2,3-dimethylbutadiene in them are given in Table 5.

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