CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR N. I. SHUIKIN, L. A. ERIVANSKAYA

1960

SovietRxiv

Abstract

Full Text

CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR N. I. SHUIKIN,
L. A. ERIVANSKAYA
and YAN AI-SI

CATALYTIC DEHYDROCYCLIZATION OF β-*n*-BUTYLNAPHTHALENE

In the development of the first studies in the field of catalytic dehydrocyclization of alkanes over oxide catalysts, a number of authors showed that not only free alkane molecules are involved in the cyclization reaction, but also side chains of a benzene nucleus with a number of carbon atoms not less than four. First, B. L. Moldavskii and co-workers (^{1}), and then S. S. Nametkin, M. I. Khotimskaya, and L. M. Rozenberg (^{2}), observed the formation of naphthalene while investigating the transformations of *n*-butylbenzene over dehydrogenating catalysts. As a result of the dehydrocyclization of isoamylbenzene, S. R. Sergienko (^{3}) obtained β-methylnaphthalene. Recently one of us showed that higher alkanes of normal structure, for example hexane, heptane, and octadecane, under certain conditions also undergo dehydrocyclization with the formation of condensed systems—naphthalene, phenanthrene, benzanthracene, and chrysene (^{4,5}).

In the present work we have carried out the dehydrocyclization of β-*n*-butylnaphthalene to phenanthrene and anthracene. A detailed investigation of the composition of the resulting catalyzates showed that, under the conditions adopted by us, cyclization proceeds at the carbon atom of the naphthalene nucleus α to the butyl group, with predominant formation of phenanthrene:

$$\text{-}n\text{-butylnaphthalene} \xrightarrow[450\text{–}500^\circ]{Al_2O_3+Cr_2O_3} \begin{pmatrix} \text{phenanthrene} & (70\text{–}80\%) \\ \text{anthracene} & (1.5\text{–}2.0\%) \end{pmatrix} + 3H_2$$

The dehydrocyclization experiments were carried out in a conventional flow-type apparatus in a hydrogen atmosphere at 400, 450, 500, and 550° and with a volumetric hydrocarbon feed rate from 0.1 to 1.0 hr^{-1} in the presence of an alumina-chromia catalyst containing 20% chromium oxide. The catalyst was prepared by the joint precipitation of aluminum and chromium hydroxides from molar solutions of their nitrate salts with an excess of ammonia solution. The formed and dried catalyst at 120° was treated with hydrogen in the catalytic tube before the experiments, with gradual elevation of the temperature to 500°. After each experiment the catalyst was regenerated in the usual manner by successive oxidation with air and treatment with hydrogen. The starting β-*n*-butylnaphthalene was obtained by the Friedel-Crafts reaction as a result of the interaction of naphthalene and butyric acid chloride in nitrobenzene medium in the presence of aluminum chloride (^{6}), followed by reduction of the resulting *n*-propyl-β-naphthyl ketone by a modified Kishner-Wolff method (^{7}). Pure β-*n*-butylnaphthalene had the following properties: b.p. 136-137°/7 mm, n_D^{20} 1.5780, d_4^{20} 0.9669. Literature data (^{6}): b.p. 292°/760 mm, n_D^{20} 1.5776, d_4^{20} 0.966.

The results of the dehydrocyclization experiments are presented in Table 1.

Table 1

Results of experiments on the dehydrocyclization of β-*n*-butylnaphthalene in the presence of an alumina-chromium catalyst

Experiment no.	T, °C	Space velocity, h^{-1}	β-*n*-butylnaphthalene passed, g	Catalyst composition: total, g	Catalyst composition: total, wt. %	Catalyst composition: liquid part, wt. %	Catalyst composition: phenanthrene, wt. %	Catalyst composition: anthracene, wt. %	Gaseous reaction products at n.t.p., l
1	452	0.12	22.3	17.1	76.7	4.2	92.4	2.6	6.1
2	450	0.21	23.2	17.6	76.0	12.3	82.6	–	7.0
3	450	0.20	22.9	17.5	76.3	12.3	82.6	–	7.0
4	451	0.38	22.9	18.1	78.9	43.9	55.8	–	4.2
5	452	0.60	23.2	19.1	82.2	49.0	50.0	–	not determined
6	448	1.0	22.2	20.4	92.0	85.8	14.2	–	2.0
7	400	0.38	23.2	19.5	84.4	85.5	13.3	–	not determined
8	500	0.38	23.2	19.1	82.5	5.0	93.4	1.6	5.3
9	550	0.38	23.2	17.9	79.1	5.0	94.1	0.8	6.2

The content of cyclization products in the catalysts from experiments carried out at a space velocity of 0.38 h^{-1} was 13.3% at 400°, 55.8% at 450°, and 95% at 500 and 550°. The catalyst obtained at 450° and a space velocity of 0.1 h^{-1} likewise consisted of 95% cyclization products. Increasing the space velocity tenfold at the same temperature led to a decrease in the content of cyclization products in the catalyst to 14.2%. The cyclization products consisted predominantly of phenanthrene. Anthracene in an amount from 1 to 3% was isolated from the catalysts of experiments carried out at 500 and 550° and a space velocity of 0.38 h^{-1}, and at 450° and a space velocity of 0.1 h^{-1}. In the remaining experiments, anthracene was detected only in trace amounts, by the formation of a band with blue fluorescence in ultraviolet light during chromatography of the cyclization products on alumina.

The catalysts were analyzed as follows. The liquid part of the catalyst was separated from the solid by filtration and distilled in vacuum; the crystalline residue obtained in this process was added to the solid part of the catalyst. The crystalline part of the catalyst was treated with ether in the cold. After removal of the ether, "crude" phenanthrene remained in the flask (m.p. 96–98°), containing as an impurity a small amount of anthracene, which is poorly soluble in ether. Further purification of the phenanthrene was carried out by passing its solution in hexane through a column of alumina and subsequently washing with a mixture of hexane and benzene (1:1). Control was effected by viewing the column under a quartz lamp. After purification, the phenanthrene melted at 99.5–100°. The ether-insoluble part of the catalyst was anthracene with m.p. 216–216.5° (after chromatography on alumina). The liquid part of the catalyst from each experiment was combined and fractionated on a vacuum column. As analysis showed, it consisted chiefly of unchanged β-n-butylnaphthalene. As a result of fractionation of 32.0 g of the combined liquid portion of the catalysts from experiments 1–6, carried out at 450°, 19.2 g of the starting hydrocarbon was isolated (b.p. 115–116°/3 mm, n_D^{20} 1.5782, d_4^{20} 0.9670), 0.65 g (0.6% of the butylnaphthalene passed) of naphthalene (as a sublimate), and 4.2 g (3.8%) of fractions boiling below β-n-butylnaphthalene: 2.1 g with b.p. 119–121°/10 mm, n_D^{20} 1.6012, d_4^{20} 0.9873, and 2.1 g with b.p. 121–141°/10 mm, n^{20} 1.5892. These fractions apparently consisted of lower alkylnaphthalenes formed as a result of cracking of β-n-butylnaphthalene. The gaseous reaction products formed in the experiments carried out at 450° contained, in addition to hydrogen, a certain amount of pro-

cracking products: 0.5–0.9% unsaturated and 6–7% saturated hydrocarbons. Thus, cracking under the conditions we adopted, as these data show, does not play a substantial role.

The work has shown that β-n-butylnaphthalene, in the presence of an alumina-chromia catalyst, readily undergoes dehydrocyclization predominantly at the α-carbon atom, with formation of phenanthrene. The yields of phenanthrene at 450° and a space velocity for passage of butylnaphthalene of 0.1 h^{-1}, and also at 500° and a space velocity of 0.4 h^{-1}, reach 70–80% of the theoretical value. The yields of anthracene under these conditions do not exceed 1.5–2%.

At present the work is being continued in the direction of studying the dehydrocyclization of other β-, as well as α-alkyl derivatives of naphthalene.

Moscow State University
named after M. V. Lomonosov

Received
29 IV 1960

CITED LITERATURE

1. B. L. Moldavskii, G. D. Kamusher, M. V. Kobylskaya, ZhOKh, **7**, 169 (1937).

2. S. S. Nametkin, M. I. Khotimskaya, L. M. Rozenberg, Izv. AN SSSR, OTN, 1947, No. 7, 795.

3. S. R. Sergienko, DAN, **27**, 960 (1940).

4. N. I. Shuykin, N. G. Bekauri, DAN, **126**, 103 (1959).

5. N. I. Shuykin, N. G. Bekauri, T. S. Shakarashvili, Izv. AN SSSR, OKhN, 1959, 110.

6. A. S. Bailey, G. B. Pikering, J. C. Smith, J. Inst. Petrol., **35**, 103 (1949).

7. Huang-Minlon, J. Am. Chem. Soc., **68**, 2487 (1946).

Note: Figure translations are in progress. See original paper for figures.