CATALYTIC DEHYDROCYCLIZATION OF 2-OCTYLNAPHTHALENE


M. V. Lomonosov Moscow State University
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In the course of the investigation of the dehydrocyclization of 2-hexylnaphthalene it was found that the process proceeds not only at a carbon atom of the naphthalene nucleus, but also at a carbon atom of the alkyl group itself with formation of 2-phenylnaphthalene [1]. An analogous reaction is observed for alkylbenzenes, which are converted under dehydrocyclization conditions into hydrocarbons of the biphenyl series [2]. Our further observations showed that with increase in the number of carbon atoms in the alkyl group of the alkynaphthalene, cyclization with formation of phenylnaphthalene homologs becomes still more noteworthy. The cyclization products obtained from 2-octyl-naphthalene (I) over an alumina - chromium oxide catalyst (20% Cr2O3) at 450°C to an extent of about 50% consisted of products of cyclization at the naphthalene nucleus: phenanthrene (II) and a little anthracene (III). The remaining amount consisted of 11H-benzo[a]fluorene (IV), 11H-benzo[b]fluorene (V), chrysene (VI), and benz[a]anthracene (VII), probably formed from 2-o-ethylphenylnaphthalene (VIII), an intermediate product in the cyclization of 2-octynaphthalene at a carbon atom of the alkyl group. To confirm this view we specially synthesized the 2-(2-methyl-
cyclohexenyl)- and 2-(2-ethylcyclohexenyl)-naphthalenes (IX) and (X) and subjected them to dehydrocyclization in presence of an alumina – chromium oxide catalyst at 450°. From the products of their catalytic transformations we succeeded in isolating 11H-benzo[a]fluorene (IV) and 11H-benzo[b]fluorene (V) from (IX) and 11-methyl-11H-benzo[a]fluorene (XI), 11H-benzo[a]fluorene (IV), and chrysene (VI) from (X). In addition, in the products of the transformations of 2-(2-ethylcyclohexenyl)naphthalene we detected benzo[a]anthracene spectroscopically.

Benzo[a]anthracene, found in the dehydrocyclization catalyzates from 2-octynaphthalene, could be formed both from 2-octylnaphthalene (VIII) and also as a result of the dehydrocyclization of 1-butynaphthalene (XII). We were unable to detect products of the cyclization of butylphenanthrene (XIII), i.e., benzo[c]phenanthrene (XIV), ethylpyrene (XV), and pyrene itself. We cannot exclude the possibility that they are formed, but they are very difficult to find in such a complex mixture of condensed hydrocarbons as that obtained in the dehydrocyclization of 2-octynaphthalene. Moreover, these must be very small in amount because of the low strength of the bond between the alkyl substituent and the quaternary carbon atom of phenanthrene under dehydrocyclization conditions [1]. Hence, the dehydrocyclization of 2-octynaphthalene can be presented diagrammatically as follows:

With increase in the length of the alkyl chain in the alkynaphthalene the total yield of cyclization products falls and the cracking of the side chain becomes more marked. As a result of the dehydrocyclization of 2-octynaphthalene over an alumina – chromium oxide catalyst at 450° with a space velocity of 0.4 h⁻¹ we obtained 37.8% of cyclization products, whereas under analogous conditions from 2-butylnaphthalene we obtained 55.8% of phenanthrene [3]. The main cracking products were methyl-, ethyl-, and propyl-naphthalenes. The naphthalene content of the catalyzate was 1.3-2.5%.

**EXPERIMENTAL**

2-Octynaphthalene (I). This was synthesized by the reduction of heptyl 2-naphthyl ketone by a modification of Kizhner's method [4]. The ketone itself was prepared by reaction between naphthalene and octanoyl chloride in presence of aluminum chloride in a nitrobenzene medium [5]. The yield was 75-78%; b.p. 243-245° (5 mm); m.p. 54.5-55°; semicarbazone, m.p. 130-131°. The literature [6] gives: m.p. 56°; semicarbazone, m.p. 135°. 2-Octynaphthalene had: b.p. 173-175° (3 mm); nD²⁰ 1.5513; d₄ 0.9360; MR 81.84. C₁₉H₁₄. Calculated: MR 82.59. The exaltation of the molecular refraction was 3.25, which is in accord with data in the literature for 2-alkynaphthalenes [5]. Ultraviolet spectrum (in methanol)[λmax, μμ (log ε)]: 275 (3.66), 304 (2.64), 319 (2.32). The literature [7] gives: b.p. 344° (760 mm); nD 30 1.5511; d₄ 0.9390.