ISSN 1070-4272, Russian Journal of Applied Chemistry, 2008, Vol. 81, No. 12, pp. 2137–2140. © Pleiades Publishing, Ltd., 2008.
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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Polycondensation of Naphthalene and Its Alkyl Derivatives

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Received May 23, 2008

Abstract—Polycondensation of naphthalene and its alkyl derivatives (stripping oil, 2,5-dimethylnaphthalene) in the presence of aluminum halides was performed. Under the action of an ultrasonic field on a benzene solution of naphthalene in the presence of the catalyst, intermolecular condensation and benzene addition are observed.

DOI: 10.1134/S1070427208120185

The formation of tarry by-products from aromatic hydrocarbons at elevated temperatures and in the course of alkylation in the presence of catalysts has been described in the literature [1, 2]. In some cases, tars can act as target products, rather than as contaminating components. In particular, this occurs in preparation of a binder for composite anodes in aluminum production. It seemed appropriate to examine the possibility of transformation of naphthalene and its alkyl derivatives into more complex products under the influence of catalysts and to evaluate the degree of conversion. To accelerate the condensation, we used ultrasonic activation instead of prolonged heating. Aluminum halides were tested as catalysts. It should be noted that the effect of ultrasound on fused aromatic hydrocarbons is poorly understood. It has been reported [3] that, under cavitation treatment, naphthalene undergoes cleavage with the formation of the simplest gaseous compounds.

EXPERIMENTAL

Liquid stripping oil was prepared by distillation of coal tar pitch; its boiling point is about 300°C. An ultrasonic source (UZDN-2T device, nominal power 400 W, generator working frequency 22 kHz) was immersed in a vessel with stripping oil containing 10% $AlBr_3$. In the process, the temperature of the mixture increased to 200°C. After keeping for 30 min and cooling to room temperature, the mixture solidified. To remove aluminum bromide, the mixture was poured over with water and boiled, after which it was extracted with benzene. After removing the solvent, we obtained a viscous tar. The results of its analysis by gas chromatography–mass spectrometry (GC/MS) are listed in Table 1.

Table 1. Composition of stripping oil before and after ultrasonic treatment in the presence of 10% $AlBr_3$, 0.5 h

Compound	Retention time, min	Content, %	
		before treatment	after treatment
1,2,3,4-Tetrahydro-naphthalene	9.461		5.6
Naphthalene	9.885	18.7	3.6
Isoquinoline	10.757	3.7	
Quinoline	11.149	1.0	
5-Methylquinoline	12.505	1.0	
1-Methylnaphthalene	11.680	16.1	4.2
2-Methylnaphthalene	11.935	7.5	5.2
2-Ethylnaphthalene	12.855	7.1	19.5
1-Ethylnaphthalene	13.040	2.5	
1,5-Dimethylnaphthalene	13.207	3.3	
1,3-Dimethylnaphthalene	13.418	2.7	
2,7-Dimethylnaphthalene	13.452	1.8	
2,3-Dimethylnaphthalene	13.674	1.0	
1,4-Dimethylnaphthalene	13.885	0.5	
1,4,5-Trimethylnaphthalene	14.491	0.2	
2,3,6-Trimethylnaphthalene	14.852	0.2	
1,4,6-Trimethylnaphthalene	15.089	0.1	
Fluorene	15.52	2.0	8.4
3-Ethylbiphenyl	19.51		8.9
Dibenzofuran	14.764	11.5	28.4
Acenaphthylene	13.832	8.5	
Acenaphthene	14.297	7.7	
Benz[*a*]pyrene	26.684		1.6
Perylene	28.353	Σ 97.6	0.1

We found that heating of naphthalene for 0.5 h at 180°C in the presence of 10% aluminum chloride does

Table 2. Composition of the reaction mixture obtained after ultrasonic treatment of a benzene solution of naphthalene in the presence of 10% $AlBr_3$ (air flow 200 ml min^{-1}, 60°C, 0.5 h)

Compound	MW	Yield, %
Naphthalene	128	7.7
2-Phenylacetic acid	136	18.7
Hexadecanoic acid	230	0.8
Oleic acid	284	0.7
1,4-Diphenylbutane	210	0.8
1-Phenylnaphthalene	204	4.6
1,2-Dihydro-1-phenylnaphthalene	206	0.7
1,2,3,4-Tetrahydro-1-phenylnaphthalene	208	4.7
2-Phenylnaphthalene	204	8.9
1,7-Diphenylnaphthalene	280	1.0
$1,2^1$ -Binaphthyl	254	1.5
$2,2^1$ -Binaphthyl	254	5.3
Phenanthrene	178	0.4
9,10-Diphenylphenanthrene	312	0.5
Perylene	252	0.2
$1^1,2^1,3^1,4^1$ -Tetrahydro-$1,2^1$-binaphthyl	258	2.1
9,10-Dihydrobenz[1^1, 2^1]-anthracene	278	0.5
Benz[*j*]fluoranthene	252	0.1
Benz[*k*]fluoranthene	252	0.3
Tetrahydro[*k*]fluoranthene	256	0.7
Benz[*e*]pyrene	252	0.1
Benz[*a*]pyrene	252	2.4
Tetrahydrobenz[*a*]pyrene	258	0.1
Octahydrobenz[*a*]pyrene	260	0.3

not chromatographically detectable changes. Therefore, we performed a combined cavitation-catalytic treatment of naphthalene. The procedure was as follows.

A glass beaker was charged with 1 g of naphthalene and 20 ml of benzene, after which 0.1 g of $AlBr_3$ was added. A plate-type emitter was immersed, and the UZDN-2T device was switched on. The temperature increased in the course of the treatment from 20 to 60°C. In the process, the mixture was bubbled with air for 30 min at a rate of 200 ml min^{-1}. After the treatment completion, water was added, the mixture was shaken, the aqueous solution was separated, and the tar precipitated on the beaker walls was washed out with benzene and acetone. The organic solutions were combined, dried over $CaCl_2$, filtered, and vacuum-evaporated. The yield was quantitative. To evaluate the contribution from benzene condensation to the tar formation, we subjected a solution of aluminum bromide in benzene to ultrasonic treatment. No significant amount of tar was formed upon 30-min treatment. The results of GC/MS analysis of the tar are listed in Table 2.

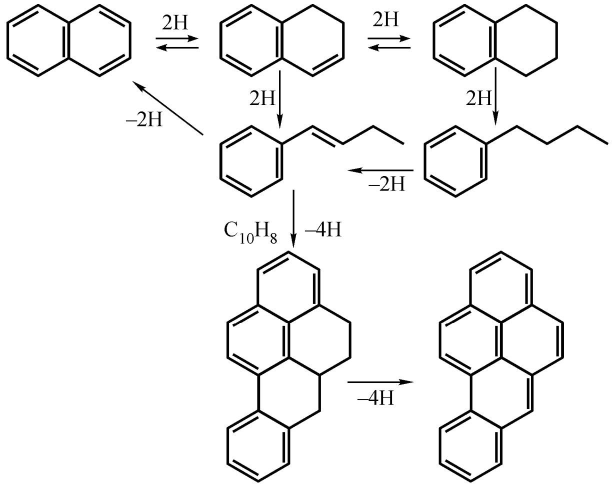
The tar composition was determined on an HP 6890A gas chromatograph equipped with an HP 5972A mass-selective detector, using NIST CSD database (275000 compounds). We used an HP-5MS quartz column, 30 m long, 0.25 mm i.d., coated with a 0.3-μm layer of 5% diphenyl–95% dimethylsiloxane copolymer.

Conditions of GC/MS analysis: initial column temperature 70°C, 4 min; linear heating at a rate of 100 deg min^{-1}; final temperature 300°C, 5 min; vaporizer temperature 280°C; sample volume 1 μl. The mass spectra were recorded with electron impact ionization (70 eV). The scanning rate was 1 scan per second, and the scanning range, 40–600 amu.

The organic compounds were identified by comparison of the experimental mass spectra with those from the NIST CSD database using the ChemStation standard system for GC/MS data processing. Polycyclic aromatic hydrocarbons (PAHs) were analyzed in the mode of selective detection of individual ions, with identification by characteristic ions and retention times, using solutions of reference substances.

According to the chromatogram, the stripping oil contained (%) naphthalene 18.7, alkylated naphthalenes 45, dibenzofuran 11.5, acenaphthene 7.6, and fluorene about 2. High-boiling carcinogenic compounds were absent (Table 1).

After the cavitation treatment, the oil composition changed considerably: The amount of naphthalene and methylnaphthalenes decreased, and di- and trimethylnaphthalenes virtually disappeared. At the same time, the amount of 2-ethylnaphthalene and dibenzofuran increased, which suggests their relative inertness under the experimental conditions. The appearance of benz[*a*]pyrene in the reaction mixture points to the occurrence of polycondensation. Apparently, benz[*a*]pyrene is



Scheme 1.

formed by a sequence of reactions involving naphthalene (Scheme 1).

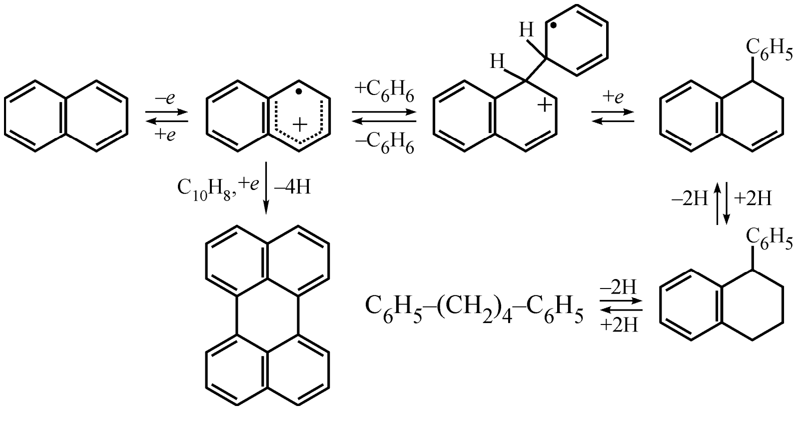
According to Scheme 1, for the formation of benz[*a*]pyrene to be formed, naphthalene should add a fragment consisting of phenyl residue and a radical with four carbon atoms. Such a fragment can be formed after hydrogenation of naphthalene to dihydronaphthalene or tetralin. The ring opening in these compounds will lead to formation of fragments required for "assembling" benz[*a*]pyrene.

If the naphthalene transformation follows this pattern, its polycondensation should lead to formation of tetrahydrobenz[*a*]pyrene and benz[*a*]pyrene. According to the chromatogram, the naphthalene tar contains more than 50 substances. The major components identified using the database on polycyclic compounds are listed in Table 2.

Indeed, heating of a benzene solution of naphthalene in the presence of $AlBr_3$ at 60°C for 0.5 h under the action of cavitation leads to formation, along with other substances, of benz[*a*]pyrene and its hydrogenated analogs: tetrahydro- and octahydrobenz[*a*]pyrenes. The occurrence of this reaction pathway is also confirmed by the detection of 1,4-diphenylbutane among reaction products.

At the same time, it should be noted that methylated naphthalenes losing methyl substituents under the conditions of acid catalysis can also be precursors of benz[*a*]pyrene. To evaluate the possibility of this route, we heated 2,5-dimethylnaphthalene with 10% aluminum chloride at 180°C for 0.5 h. By liquid chromatography, we detected among reaction products acenaphthene, 2-methylnaphthalene, benz[a]pyrene, and dibenz[*a*,*h*]anthracene (40.5, 28.1, 5.8, and 1.8%, respectively).

Along with undergoing disproportionation and condensation, naphthalene also reacts with benzene to form 1- and 2-phenylnaphthalenes, 1,2- and 1,7-diphenylnaphthalenes, and their hydrogenation products. Also, naphthalene undergoes self-condensation to form dinaphthyl and perylene. The formation of the above products can be described by Scheme 2 involving radical cations. According to Scheme 2, the reaction mixture should also contain dihydro- and tetrahydro-1-phenylnaphthalenes, which were, indeed, detected (Table 2). The formation of carboxylic acids (2-phenylacetic, hexadecanoic, oleic) is attributable to the presence of air in the reaction medium.



Scheme 2.

CONCLUSIONS

(1) Naphthalene and its methyl derivatives transform in the course of acid catalysis of the polycondensation into a complex mixture of products, some of which are carcinogenic (e.g., benz[*a*]pyrene).

(2) Ultrasonic treatment of a solution of naphthalene in benzene in the presence of aluminum halides leads to considerable tarring and formation of numerous high-molecular-weight polyaromatic derivatives.

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