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Abstract

Full Text

Chemistry

S. V. Zavgorodnii and I. A. Nasyr

Cycloalkylation of Monoalkylbenzenes with Cyclohexene

(Presented by Academician A. V. Topchiev, March 21, 1962)

Cyclohexylalkylbenzenes are of interest as possible model hydrocarbons and as intermediates in the synthesis of various derivatives of aromatic hydrocarbons. Recently it has been shown that some cyclohexylalkylbenzenes are oxidized comparatively readily by atmospheric oxygen to hydroperoxides, and the latter are effective initiators of the emulsion copolymerization of divinyl with styrene ([1],[2]). In the present work, results are reported on the cycloalkylation of toluene, ethylbenzene, and *n*-propylbenzene with cyclohexene in the presence of a catalyst, the molecular compound of boron fluoride with orthophosphoric acid. The reaction was studied at various molar ratios of the reactants and catalyst over the temperature range from 0 to 80°.

It was established that, in the cycloalkylation of the indicated hydrocarbons with cyclohexene in the presence of $BF_3 \cdot H_3PO_4$ at molar ratios equal to 1-5 : 1 : 0.1-0.4, mainly one cyclohexyl radical enters the benzene nucleus, and monocyclohexylalkylbenzenes are obtained, representing a mixture of ortho and para isomers with predominance of the latter. In the products of cycloalkylation of *n*-propylbenzene, *m*-cyclohexyl-*n*-propylbenzene was also found in small amounts. The yield of monocyclohexylalkylbenzenes is greatly affected by the molar ratios of the reactants. With an increase in the relative amounts of alkylbenzenes to cyclohexene from 1 to 5 moles, under otherwise identical conditions, the yield of monocyclohexylalkylbenzenes usually increases, as is seen from Fig. 1. At these ratios of reactants, in the case of cycloalkylation of *n*-propylbenzene, along with mono- compounds, dicyclohexyl-*n*-propylbenzenes are also formed in considerable amounts. Their yield at ratios of *n*-propylbenzene of 1, 3, and 5 to 1 mole of cyclohexene decreases and amounts, respectively, to 19.6, 14.2, and 11.1% of theory. In the reaction of toluene and ethylbenzene at the above-indicated molar ratios, the yields of dicyclohexylalkylbenzenes amount to 3-5% of theory. The ease of cycloalkylation decreases from toluene to ethylbenzene and *n*-propylbenzene. The optimum conditions for the cycloalkylation of toluene, under which monocyclohexyltoluenes are formed in 91% yield, are molar ratios of toluene, cyclohexene, and catalyst equal to 5 : 1 : 0.3 and a temperature of 20°. Monocyclohexylethylbenzenes with a maximum yield of 90% are obtained at molar ratios of reactants and catalyst equal to 3 : 1 : 0.3 (or 5 : 1 : 0.4) and a

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Fig. 1 and Fig. 2: graphs

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temperature of 60°. Monocyclohexyl-*n*-propylbenzenes with a maximum yield of 87% of theory are obtained at a temperature of 60° and molar ratios of reactants and catalyst equal to 3 : 1 : 0.3. The yield of dicyclohexyl-*n*-propylbenzenes under these conditions is 8.6% of theory.

When alkylbenzenes, cyclohexene, and catalyst are used in molar ratios of 0.5 : 1 : 0.3, with toluene and ethylbenzene, as well as with *n*-propylbenzene, cyclohexylalkylbenzenes are obtained in significant yield. Their yields decrease regularly from toluene to ethylbenzene and *n*-propylbenzene, whereas the yields of monocyclohexylalkylbenzenes increase.

The effect of temperature on the reaction within the range 20–80° does not show so clearly expressed a regularity as does the effect of the molar ratios of the reactants. In the cycloalkylation of toluene, the yields of monocyclohexyltoluenes decrease as the temperature is raised from 20 to 80°. In the reaction of ethylbenzene, the yields of monocyclohexylethylbenzenes increase up to 60°, and with a further increase in temperature to 80° they decrease. For *n*-propylbenzene, the yields of monocyclohexyl-*n*-propylbenzenes increase up to 40°, and at a higher temperature decrease. This effect of temperature on the reaction, for molar ratios of reactants and catalyst equal to 3 : 1 : 0.3, is presented in Fig. 2. The yields of dicyclohexylalkylbenzenes are almost independent of temperature within the indicated limits at these ratios of reactants. Thus, for example, the yields of dicyclohexyl-*n*-propylbenzenes at 20, 40, 60, and 80° are, respectively, 14.2, 14.6, 15.5, and 16.1% of theory.

Fig. 1. Effect of the molar ratios of alkylbenzenes and cyclohexene on the cycloalkylation of toluene (1), ethylbenzene (2), and *n*-propylbenzene (3) (temperature 20°, amount of catalyst 0.3 mole per 1 mole of cyclohexene)

Fig. 2. Effect of temperature on the cycloalkylation of toluene (1), ethylbenzene (2), and *n*-propylbenzene (3) (molar ratios of alkylbenzenes, cyclohexene, and catalyst 3 : 1 : 0.3)

The amount of catalyst within the range 0.2–0.4 mole per 1 mole of cyclohexene does not exert a sharp influence on the overall composition of the alkylate or on the yield of monocyclohexylalkylbenzenes. The use of $BF_3 \cdot H_3PO_4$ in an amount of 0.1 mole in the reaction of toluene and ethylbenzene very strongly lowers the yield of cycloalkylation products and has almost no effect on the reaction with *n*-propylbenzene. 0.05 mole of catalyst per 1 mole of cyclohexene practically does not catalyze the cycloalkylation of toluene, as is evident from Fig. 3.

As can be seen from Fig. 4, slower addition of cyclohexene within the range 1–6 g/g-mole · h to the mixture of alkylbenzenes and catalyst usually increases the yield of cycloalkylation products, especially noticeably in the reaction with *n*-propylbenzene. The time of additional stirring of the reaction mixture after addition of the calculated amounts of cyclohexene, within the range 1–8 h, in the reaction of toluene and ethylbenzene has almost no effect on the yield or composition of the alkylate. In the cycloalkylation of *n*-propylbenzene, with an increase in the time of additional stirring from 4 to 8 h, the yields of monocyclohexyl-*n*-propylbenzenes decrease from 76 to 66%, while the yields of dicyclohexyl-*n*-propylbenzenes increase from 14 to 20% of theory.

Toluene and ethylbenzene were used in the work in the form of freshly distilled commercial preparations. *n*-Propylbenzene was synthesized by Fittig' s method from bromobenzene and propyl bromide; cyclohexene was obtained from cyclohexanol by dehydration with sulfuric acid (^{3}); the catalyst was prepared by saturating 88% orthophosphoric acid with boron trifluoride. The cycloalkylation reaction was carried out, as previously (^{4}), by adding cyclohexene

to the mixture of alkylbenzene and catalyst with vigorous stirring and at the specified temperature. After the appropriate treatment, the alkylate was subjected to repeated fractionation. The mono- and dicyclohexylalkylbenzenes thus isolated were oxidized with 25% nitric acid. It was established that monocyclohexylalkylbenzenes, on prolonged heating under gentle reflux with an excess of 25% nitric acid, are converted into phthalic and cyclohexylbenzoic acids. On

[Figure 3 and Figure 4 graphs]

Fig. 3. Effect of the amount of catalyst on the cycloalkylation of toluene (1), ethylbenzene (2), and *n*-propylbenzene (3) (molar ratios of alkylbenzenes and cyclohexene 3 : 1, temperature 20°)

Fig. 4. Effect of the time of addition of cyclohexene to the alkylbenzene and catalyst on the rate of cycloalkylation of toluene (1), ethylbenzene (2), and *n*-propylbenzene (3) (molar ratios of alkylbenzenes, cyclohexene, and catalyst 3 : 1 : 0.3, temperature 20°)

oxidation of cyclohexylethylbenzenes, *p*-ethylbenzoic acid was also isolated. The acids obtained were characterized by conversion into the corresponding methyl esters of phthalic and cyclohexylbenzoic acids. Dicyclohexylalkylbenzenes could not be oxidized to the corresponding acids under similar conditions.

Below we give the characteristics only of the principal reaction products. *p*-Cyclohexyltoluene is a colorless liquid. B.p. 101°/4 mm, d_4^{20} 0.9380, n_D^{20} 1.5244, MR_D 56.88; calculated 56.43. On oxidation with dilute (25%) HNO_3, terephthalic and *p*-cyclohexylbenzoic acids were obtained, which were characterized by conversion into the corresponding methyl esters.

p-Cyclohexylethylbenzene has b.p. 108–109°/4 mm, d_4^{20} 0.9291, n_D^{20} 1.5204, MR_D 61.65; calculated 61.05. On prolonged heating with 25% HNO_3, it is converted into terephthalic and *p*-cyclohexylbenzoic acids. In the oxidation products, *p*-ethylbenzoic acid was also detected in small amounts.

p-Cyclohexyl-*n*-propylbenzene has b.p. 119-120°/4 mm, d_4^{20} 0.9216, n_D^{20} 1.5160, MR_D 66.31; calculated 65.67. It is oxidized by 25% HNO_3 to terephthalic and *p*-cyclohexylbenzoic acids.

Kyiv Polytechnic Institute
Institute of Organic Chemistry
Academy of Sciences of the Ukrainian SSR

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