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Academician A. V. TOPCHIEV, E. S. POKROVSKAYA, and T. G. STEPANTSEVA

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Abstract

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SYNTHESIS OF ALKYLINDANES

The isolation, in pure form, of hydrocarbons corresponding in boiling point to the kerosene and lubricating-oil fractions of petroleum, and the comprehensive study of their properties, is a necessary preliminary stage in the complex problem of investigating the hydrocarbon composition of these petroleum fractions. Among the aromatic hydrocarbons whose presence is considered possible in the middle petroleum fractions, hydrocarbons of the indane series have as yet been studied quite inadequately.

The literature contains descriptions of individual alkylindanes obtained chiefly by closure of a five-membered ring, but the systematic synthesis and study of these hydrocarbons is still only in its initial stage. Among such systematic investigations one may perhaps cite only the work of Entel' and coauthors (^1), who obtained certain methyl- and dimethylindanes by closure of a five-membered ring and determined, in addition to the usual properties of these hydrocarbons, also their absorption spectra in the infrared and ultraviolet regions.

In order to supplement information on the properties of indane hydrocarbons and to obtain specimens for spectral investigations, we undertook the synthesis of hydrocarbons of this series, primarily alkylindanes with aliphatic substituents in the aromatic ring.

Up to the present time the alkylation reaction of indane in the synthesis of homologs of this hydrocarbon has been used only in a few cases and described in a small number of papers. Thus, Ketz and coauthors carried out the alkylation of indane with ethylene, propylene, and isopropyl alcohol in the presence of $Al_2O_3 \cdot SiO_2$ under pressure and at high temperature (250–300°), obtaining ethylindane, isopropylindane, and condensation products of indane (^2). Butylindane was synthesized by alkylating indane with tert-butyl chloride in the presence of aluminum chloride. However, this work was carried out not for the purpose of studying the properties of the hydrocarbon, but to obtain its nitro derivatives, and the authors give only the boiling and freezing points of tert-butylindane (^3).

The reaction of cyclohexene with indane proceeded very smoothly and in good yield in the presence of aluminum chloride at atmospheric pressure and a temperature of about 5°. Under these conditions mono-, di-, and tricyclohexylindanes were synthesized (^4). Mono- and dicyclopentylindanes were obtained in the same way from indane and cyclopentene (⌢5).

In our work, in order to obtain the starting product, indane, indene was hydrogenated over a skeletal nickel catalyst at room temperature and an initial hydrogen pressure of 150–120 atm. (⌢6). After distillation over metallic sodium, the indane had b.p. 177°, $n_D^{20} = 1.5390$, $d_4^{20} = 0.9640$, which agrees with literature data: b.p. 176.7°, $n_D^{25}1.5355$ and $d_4^{25} = 0.9604$ (⌢1).

Since the alkylation of indane with cycloolefins in the presence of aluminum chloride proceeded smoothly with the formation only of products of za-

substitution in the aromatic nucleus (4,5), this method of synthesis was therefore also applied by us to the preparation of indane homologs with aliphatic side chains.

The alkylation of indane with olefins—propylene, 1-butylene, and trimethylethylene—was carried out in a glass reactor with constant stirring and cooling with ice. The gas was passed through at a rate of 2–4 l/hr; trimethylethylene was added dropwise; aluminum chloride, in an amount of 1/2—1/4 of the weight of the olefin, was added portionwise. The small amount of a layer of the complex of hydrocarbons with aluminum chloride that formed was separated from the main layer of reaction products, which, after the usual work-up, were distilled several times on a 12-theoretical-plate column. The reported yields of reaction products are calculated on the olefin introduced.

Using the method described, from indane and propylene taken in molar ratios of 1 : 0.5 and 1 : 1.5 (with a total amount of indane of 300 g), reaction products were obtained in a yield of $\sim 50\%$ based on propylene; from these, by repeated fractionation, fractions were isolated: one, with b.p. 62°/2 mm, corresponding to isopropylindane $C_{12}H_{16}$ (analysis); the other, with b.p. 83—85°/2 mm, corresponding to diisopropylindane $C_{15}H_{22}$ (analysis). The properties of these hydrocarbons, as well as of all those described below, are given in Table 1. As a result of alkylation with propylene of a broad fraction of monoisopropylindane, with b.p. 228—233°, a solid triisopropylindane $C_{18}H_{28}$ (analysis) and its liquid isomer with b.p. 276—280°, freezing point below −65°, $d_4^{20} = 0.9202$, and $n_D^{20} = 1.5220$, were obtained.

Under analogous conditions, alkylation of indane (total amount 950 g) with an equimolecular amount of 1-butylene was carried out. From the reaction products were isolated sec-butylindane $C_{13}H_{18}$ (analysis), with b.p. 68—69°/2 mm, and di-sec-butylindane $C_{17}H_{26}$ (analysis), with b.p. 121—122°/2 mm.

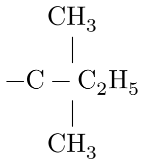
Table 1

Hydrocarbon	B.p., °C/mm Hg	Freezing point, °C	d_4^{20}	n_D^{20}	$\frac{n_F - n_e}{d} 10^4$	Viscosity, cst at 20°	Viscosity, cst at 50°	Viscosity, cst at 100°	Aniline point (max.), °C
Isopropylindane $C_{12}H_{16}$	62/2 230/751	Does not freeze	0.9347	1.5240	164.6	2.9	1.6	0.9	Below −10
Diisopropylindane $C_{15}H_{22}$	83–85/2 255–256/751	−44 Glass	0.9210	1.5183	–	7.6	3.1	1.3	Below −10
Triisopropylindane $C_{18}H_{28}$	108–109/2	45–46	–	–	–	–	–	–	–
sec-Butylindane $C_{13}H_{18}$	68–69/2 245/753	−65 Does not freeze	0.9252	1.5213	157.5	–	–	–	Below −10
Di-sec-butylindane $C_{17}H_{26}$	122–123/2	−50 Glass	0.9068	1.5138	147.4	–	–	–	+0.5
Amylindane* $C_{14}H_{20}$	256–257/744	−56 Glass	0.9355	1.5245	151.4	6.8	2.9	1.3	Below −10
Amylindane** $C_{14}H_{20}$	257–258/744	−55 Glass	0.9350	1.5245	–	–	–	–	–
Amylindane** $C_{14}H_{20}$	81–82/2 255–257/744	−45 Glass	0.9324	1.5230	–	–	–	–	–

* Obtained with $BF_3 \cdot H_3PO_4$ as catalyst.
** Obtained with $AlCl_3$ as catalyst.

For the synthesis of amylindane, trimethylethylene obtained by dehydration of dimethylethylcarbinol was used. The alkylation reaction was carried out at a ratio of reacting substances of 3 : 1, both in the presence of aluminum chloride, starting from 300 g of indane, and with the catalyst $BF_3 \cdot H_3PO_4$ (^{7}), starting from 250 g of indane. In the first case one fraction was isolated in a yield of ~ 20%, and in the second case two fractions of amylindane $C_{14}H_{20}$ (analysis) were isolated in a yield of ~ 40%, differing, however, very little in ···

properties (Table 1). In the first case the high-boiling reaction products contained predominantly products of indane condensation; they did not contain diamylindane. The high-boiling reaction products with $BF_3 \cdot H_3PO_4$ were a resinous mass and were not investigated. Since the alkylation was carried out with trimethylethylene, the side chain of the amyl should have the structure:



$$\begin{array}{c} \mathrm{CH_3} \\ | \\ -\mathrm{C}-\mathrm{C_2H_5} \\ | \\ \mathrm{CH_3} \end{array}$$

Of the hydrocarbons listed in Table 1, only isopropylindane has been described in the literature; it is a mixture of the 4- and 5-isopropylindane isomers, the constants of which[2] almost completely coincide with the properties of the hydrocarbon obtained by us. All the other indane homologs described by us were obtained by us for the first time. The densities and refractive indices of the synthesized hydrocarbons lie within the limits usual for alkylindanes ($d_4^{20} = 0.92$—0.93 and $n_D^{20} = 1.51$—1.52); the aniline points of all the hydrocarbons, except dibutylindane, lie below 0°, which is usual for aromatic hydrocarbons of low molecular weight. The specific dispersion decreases regularly as the number of carbon atoms in the side chains increases.

A. P. Bogomolova took part in the work.

Institute of Petroleum
Academy of Sciences of the USSR

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