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Abstract

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SYNTHESIS OF HYDROCARBONS OF THE INDANE SERIES WITH SIDE CHAINS IN THE FIVE-MEMBERED AND BENZENE RINGS

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In earlier published works, syntheses were described of hydrocarbons of the indane series with substituents in the five-membered (1) or benzene (2) ring. For the synthesis of the former, the reaction proposed by Thiele (3), and somewhat modified by Ruzicka and Peyer (4), was used: condensation of indene with ketones in the presence of an alcoholic solution of potassium hydroxide. The yield of the reaction products—alkyl- and cycloalkylbenzofulvenes, which are intermediate products in the synthesis of alkylindanes—was 24-40%.

In the present communication, syntheses are described of hydrocarbons of the indane series with substituents in the five-membered or six-membered ring, as well as those having substituents in both rings simultaneously.

1-Cyclohexylindane. The starting indene, as a result of fractionation on a column with an efficiency of 12 theoretical plates,* had b.p. 91° at 46 mm; n_D^{20}1.5761; d_4^{20}0.9956, which corresponds to the literature data (5). Cyclohexanone, grade X, after distillation, had b.p. 151—152° at atmospheric pressure and n_D^{20}1.4515.

1-Cyclohexylindane was obtained analogously to 1-cyclopentylindane (2), by condensation of indene (147 g), present in ether solution, with cyclohexanone (62 g), in the presence of a solution of potassium hydroxide (16 g) in methanol (30 ml), with heating and continuous stirring.

Cyclohexanone was added rapidly to the indene, and the alkali solution slowly, dropwise. After all the alkali solution had been added, stirring was continued for another 2 hours. Owing to the instability in air of the diolefinic hydrocarbon formed, the synthesis and the removal of ether from the reaction product were carried out in a stream of nitrogen. Instead of the molar ratio indene–ketone 1 : 1, as used by us in the preceding syntheses (1,2), we introduced them into the reaction in the ratio 2 : 1, respectively. The amount of alcoholic alkali solution was taken for the reaction, as in the preceding syntheses, on the basis of 12 g of potassium hydroxide, dissolved in 28 ml of methanol, per 1 mole of indene (4).

Part of the reaction product was fractionated on a column. The crystalline fraction of cycloalkylbenzofulvene obtained in this way, yellow in color (127—130° at 1 mm), had n_D^{20}1.6159.

Found, %: C 91.88; 91.75; H 8.11; 8.19
$C_{15}H_{16}$. Calculated, %: C 91.78; H 8.22

The yield of the fraction, calculated on the ketone taken into the reaction, was 54%. The remaining part of the product, after removal of ether, was subjected to hydrogenation over a skeletal nickel catalyst at an initial pressure hydrogen pressure of 150 atm and ordinary temperature. As a result of two distillations on a column of the hydrogenated product, a colorless hydrocarbon was isolated, boiling at 121° at 2 mm.

Found, %: C 90.05; 90.01; H 10.04; 10.08
$C_{15}H_{20}$. Calculated, %: C 89.93; H 10.07

Molecular weight: found 200 and 200, calculated 200.
The properties of 1-cyclohexylindane are given in Table 1.

Table 1

Properties of hydrocarbons of the indane series

Hydrocarbon	Boiling temp., °C/mm	Freezing temp. (glass), °C	d_4^{20}	n_D^{20}	Aniline point (max.), °C	MR found	MR calc.
1-Cyclohexylindane $C_{15}H_{20}$	121°/2	−58	0.9917	1.5464	−12	63.99	63.47
1-Isopropylindane $C_{12}H_{16}$	86—87°/4	−65	0.9336	1.5219	−14.8	52.42	51.82
1-Isopropylindane $C_{12}H_{16}$	87—88°/4	−65	0.9350	1.5238	−14.8	52.42	51.82
5-Decylindane $C_{19}H_{30}$	160—161°/4	−65	0.9017	1.5066	11.0	85.23	84.14
1-Isopropyl-5-tert.-butylindane $C_{16}H_{24}$	112—113°/1.5	−35	0.8967	1.5050	18.0	71.56	70.29

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* In all subsequent fractionations the same column was used.

Hydrocarbon	Boiling temp., °C/mm	Freezing temp. (glass), °C	d_4^{20}	n_D^{20}	Aniline point (max.), °C	*MR* found	*MR* calc.
1-Isopropyl-5,7-di-tert.-butylindane $C_{20}H_{30}$	139–140°/1.5	−26	0.8987	1.5090	38.0	90.52	88.76

1-Isopropylindane. 1-Isopropylindane, already described earlier (1), was again obtained in larger quantities with the aim of using it as the starting material for the synthesis of indane hydrocarbons with two alkyl chains. In all, 362 g of indene and 90 g of acetone were introduced into the reaction, corresponding to a molar ratio indene—acetone of 2 : 1. The reaction product was subjected to hydrogenation over a skeletal nickel catalyst at an initial hydrogen pressure of 150 atm and room temperature and was then distilled three times on a column. In this way two hydrocarbon fractions were isolated, boiling within two degrees, having the same composition and possessing different densities and refractive indices (see Table 1).

For the fraction 86–87° at 4 mm, found, %: C 89.92; 89.99; H 10.06; 9.98 and *MR* 52.42.

For the fraction 87–88° at 4 mm, found, %: C 89.92; 89.87; H 10.04; 10.02 and *MR* 52.42.

For $C_{12}H_{16}$, calculated, %: C 89.93; H 10.07 and *MR* 51.82.

The properties of the hydrocarbons are given in Table 1. The study of the two fractions obtained is continuing.

To obtain indane hydrocarbons with alkyl substituents in the benzene ring, as in the preceding cases (2), the alkylation reaction of indane with unsaturated hydrocarbons in the presence of 92% sulfuric acid was employed.

5-Decylindane. The indane needed for the synthesis was obtained by hydrogenating the above-mentioned indene in an autoclave over a skeletal nickel catalyst at an initial hydrogen pressure of 150 atm and room temperature. The indane, distilled twice, had b.p. 173–174° at 751 mm; n_D^{20} 1.5389; d_4^{20} 0.9629, which corresponds to the literature data (6). Decene was obtained from *n*-decyl alcohol (b.p. 109–110° at 9 mm; n_D^{20} 1.4371; d_4^{20} 0.8306), by dehydration at 370° over aluminum oxide. Distilled twice on a column and then over metallic sodium, it had b.p. 172–173° at 745 mm, n_D^{20} 1.4257; d_4^{20} 0.7439.

5-Decylindane was obtained by alkylation of indane with decene in the presence of sulfuric acid. To indane (118 g), with continuous stirring by a mechanical stirrer, decene (70 g) and 92% sulfuric acid (98 g) were added gradually, dropwise. As the reaction products warmed up, they were cooled with ice water. The molar ratio indane—decene—sulfuric acid, in contrast to the preceding syntheses (^{2}), was 2 : 1 : 2. After the necessary amount of olefin had been added, stirring of the mixture was continued for about another 1.5 h. As a result of two distillations on a column of the hydrocarbon obtained, a fraction with b.p. 160–161° at 4 mm was isolated in an amount of 98 g, which corresponds to a yield of decylindane of 76%, based on decene.

The properties of the hydrocarbon obtained are given in Table 1.

Found, %: C 88.34; 88.30; H 11.76; 11.75
$C_{19}H_{30}$. Calculated, %: C 88.29; H 11.71

Mol. wt.: found 259 and 257, calculated 258. Position 5 of the side chain is the most probable in such a synthesis (^{7}).

1-Isopropyl-5-tert-butylindane and 1-isopropyl-5,7-di-tert-butylindane. 1-Isopropyl-5-tert-butylindane was obtained analogously to 5-decylindane, by alkylation of 1-isopropylindane with isobutylene in the presence of 92% sulfuric acid; to 1-isopropylindane (22 g) with b.p. 87–88° at 4 mm; n_D^{20} 1.5238; d_4^{20} 0.9350, with continuous stirring, sulfuric acid (14 g) was added dropwise and isobutylene (4 g) was passed in at a rate of 2–3 l/h. The molar ratio isopropylindane—isobutylene—sulfuric acid was 2 : 1 : 2. After addition of the isobutylene and sulfuric acid, stirring of the mixture was continued for another 1.5 h.

The hydrocarbon layer was treated in the usual manner and distilled twice on a column. A fraction 112–113° at 1.5 mm was thereby isolated.

Found, %: C 88.67; 88.65; H 11.35; 11.25
$C_{16}H_{24}$. Calculated, %: C 88.82; H 11.18

Mol. wt.: found 215 and 216, calculated 216.

The final yield of this hydrocarbon, calculated on isobutylene, was 35%. The properties of the hydrocarbon are given in Table 1. The tert-butyl group must enter indane in position 5, as was shown earlier (^{7}).

From the higher-boiling reaction products a fraction 139–140° at 1.5 mm was isolated. For properties of the hydrocarbon see Table 1.

Found, %: C 88.03; 88.22; H 11.89; 11.82
$C_{20}H_{32}$. Calculated, %: C 88.15; H 11.85

Mol. wt.: found 272 and 272, calculated 272.

In view of the fact that the yield of this fraction was about 3 g, it did not seem possible to subject it to fractionation on a column; however, judging from the data obtained, in the alkylation of 1-isopropylindane with isobutylene, along with the dialkylindane, a small amount of trialkylindane is formed.

The positions of the tert-butyl groups may be considered most probably to be 5,7, since two tert-butyl groups usually do not enter into the ortho position.

All the hydrocarbons described were treated with sulfuric acid under identical conditions in order to obtain comparative data on their sulfonatability. Those of them which were resistant to the action of 98% sulfuric acid were subjected to treatment with 100% sulfuric acid. The most resistant to the action of the acid, as was to be expected, proved to be 1-isopropyl-5,7-di-tert-butylindane. When it was treated with three volumes of 100% sulfuric acid for 30 min, its volume did not change.

1-Isopropyl-5-tert-butylindane, when treated with two volumes of 100% sulfuric acid for 30 min, was sulfonated to the extent of 20%. 1-Isopropylindane, 1-cyclohexylindane, and 5-decylindane were completely sulfonated after 1 h with one volume of 98% sulfuric acid.

1-Cyclohexylindane, 1-isopropyl-5-tert-butylindane, 1-isopropyl-di-tert-butylindane, and 5-decylindane were obtained for the first time.

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