Chemistry

S. V. Zavgorodnii

1962

SovietRxiv

Abstract

Full Text

Chemistry

S. V. Zavgorodnii

Alkylation of 1,1,3-Trimethyl-3-phenylindane with Olefins in the Presence of the Catalyst $BF_3 \cdot H_3PO_4$

(Presented by Academician A. V. Topchiev, November 13, 1961)

In the production of phenol and acetone from cumene, considerable amounts of α-methylstyrene are formed; it contains small quantities of phenol that is difficult to separate, and therefore it has not yet been used by the synthetic-rubber industry and is a production waste. Such α-methylstyrene, in the presence of H_2SO_4, $BF_3 \cdot O(C_2H_5)_2$, or $BF_3 \cdot H_3PO_4$, is readily dimerized to 1,1,3-trimethyl-3-phenylindane (I), which is a very stable compound, distilling at 308–309° C at atmospheric pressure without noticeable decomposition. Its chloro derivatives have found application in the manufacture of dielectrics and insulators, and the hydrogenation products (1,1,3-trimethyl-3-cyclohexylindane and 1,1,3-trimethyl-3-cyclohexylhydrindane) are good plasticizers for polystyrene rubbers. It was of interest to introduce one more alkyl group into trimethylphenylindane and to study some properties of such hydrocarbons. For this purpose we carried out the alkylation of 1,1,3-trimethyl-3-phenylindane with propylene, isobutylene, and cyclohexene in the presence of the catalyst $BF_3 \cdot H_3PO_4$. It was established that in all cases the principal reaction products are 1,1,3-trimethyl-x-alkyl-3-phenylindanes. In the alkylation of I with propylene, the most favorable conditions, under which 1,1,3-trimethyl-x-propyl-3-phenylindane (II) is obtained in a yield of 51% of theory, are molar ratios of I, propylene, and $BF_3 \cdot H_3PO_4$ equal to 5 : 1 : 0.3, a temperature of 52–55°, and a propylene feed rate of 1 l/hr. Decreasing the molar ratios of the reagents and increasing the temperature lower the yield of II.

Alkylation of I with isobutylene is accompanied by considerable polymerization of the olefin. The most favorable reaction conditions, under which 1,1,3-trimethyl-x-tert-butyl-3-phenylindane (III) is obtained in 43% yield, are molar ratios of I, isobutylene, and $BF_3 \cdot H_3PO_4$ equal to 2 : 1 : 0.3, a temperature of 52–55°, and a time of 10 hr. Increasing the molar ratios of the reagents to 4 : 1 or decreasing them to 1 : 1, as well as lowering the reaction temperature to 20°, leads to a decrease in the yield of the principal product. Raising the temperature to 70° has no substantial effect on the yield of III. The reaction of cyclohexene with I in the presence of $BF_3 \cdot H_3PO_4$, in contrast to isobutylene, is not accompanied by noticeable polymerization of the cycloolefin and leads to the formation of 1,1,3-trimethyl-x-cyclohexyl-3-phenylindane (IV) with a maximum yield of 45% of theory at molar ratios of I, cyclohexene, and $BF_3 \cdot H_3PO_4$ equal to $3 : 1 : 0.3$, a temperature of 52–55°, and a time of 10 hr. As in the case of isobutylene, increasing or decreasing the molar ratios of the reagents lowers the yield of IV. A temperature within the range 50–70° has no great influence on the reaction.

Hydrocarbons II, III, and IV are viscous colorless liquids, distilling at atmospheric pressure; with atmospheric oxygen, in the presence of manganese resinate and soda or calcium hydroxide, they are oxidized to the corresponding hydroperoxides. Studies of the infrared spectra and absorption spectra* established that the alkyl group of the synthesized hydrocarbo-

is in the benzene ring of the indane, and compounds II, III, and IV correspond to the following structure:

[structural formula]

$$R = \text{iso-}C_3H_7,\ \text{tert-}C_4H_9,\ C_6H_{11}$$

Experimental Part*

The starting hydrocarbon I was obtained by dimerization of α-methylstyrene in the presence of $BF_3 \cdot H_3PO_4$. The reaction was carried out in a three-necked flask equipped with a mechanical stirrer, thermometer, and gas-inlet tube or dropping funnel. Anhydrous orthophosphoric acid was placed in the reactor flask and saturated with boron fluoride. Then I was added to the catalyst, and the olefin was introduced into the mixture at the specified temperature with vigorous stirring. After addition of the calculated amounts of olefin, the mixture was stirred for a definite time at the temperature of the experiment, worked up in the usual manner, and distilled.

Alkylation of I with propylene. For each experiment, 0.3 or 0.5 mole of I and the corresponding amounts of propylene and $BF_3 \cdot H_3PO_4$ were taken. Additional stirring of the reaction mixture after addition of the calculated amounts of propylene was continued in all cases for 2 hours. The most characteristic experiments are summarized in Table 1.

Table 1

Alkylation of 1,1,3-trimethyl-3-phenylindane with propylene

---

* The spectroscopic studies were carried out by M. V. Shishkina in the laboratory of the Institute of Petrochemical Synthesis, Academy of Sciences of the USSR, headed by Prof. M. M. Kusakov.

Experiment No.	Molar ratios of trimethylphenylindane, propylene, and $BF_3 \cdot H_3PO_4$	Rate of propylene introduction, L/h	Reaction duration, h	Temp., °C $±$2°	1,1,3-Trimethyl-x-isopropyl-3-phenylindane fraction, boiling at 325–335°, % of theory
1	5 : 1 : 0.3	0.5	4.5	52	51
2	4 : 1 : 0.3	0.5	6	52	47
3	3 : 1 : 0.2	1	4.5	52	23
4	3 : 1 : 0.3	1	3.5	52	41
5	3 : 1 : 0.3	1.5	3	70	25
6	3 : 1 : 0.4	1	3.5	52	31
7	3 : 1 : 0.4	1.5	4	70	22
8	3 : 1 : 0.5	1.5	3	70	17
9	2 : 1 : 0.3	1	6	52	32

1,1,3-Trimethyl-*x*-isopropyl-3-phenylindane (II) (the fraction given in Table 1, redistilled after preliminary treatment with conc. H_2SO_4) is a colorless, odorless, very viscous liquid which, upon standing for 2 years in a sealed ampoule, changed neither in consistency nor in color. B.p. 329-331° at atmospheric pressure and 152.5-153.5° at 3 mm; d_4^{20} 0.9754, n_D^{20} 1.5520, MR_D found 90.58; calculated 90.08. Molecular weight found 282.8, 280.0; for $C_{21}H_{26}$, calculated 278.2.

Hydrocarbon II readily undergoes autoxidation with atmospheric oxygen at 110° to hydroperoxide. As in the case of alkylaromatic hydrocarbons, here too there is initially a rapid accumulation of hydroperoxide, but near the maximum the oxidation rate decreases; decomposition of the hydroperoxide probably begins to predominate over the rate of its formation, and the concentration of hydroperoxide in the solution rapidly decreases; with prolonged passage of air the hydroperoxide disappears completely. Autoxidation of II proceeds especially intensively with attainment of the maximum concentration of hydrohydroperoxide in the reaction mass to 60.8% in the presence of manganese resinate, soda, and caustic soda, as is seen from the curves in Fig. 1. In the presence of manganese resinate and caustic soda, autoxidation proceeds somewhat more slowly, but more uniformly, with formation of a hydroperoxide concentration in the solution of 58.7% in 32 h. In the presence of manganese

---

* V. M. Perelygin, G. G. Shcheglova, and V. S. Pokachalova participated in carrying out the experiments.

Fig. 1 and Fig. 2: graphs of hydroperoxide concentration versus time

Figure 1: Fig. 1 and Fig. 2: graphs of hydroperoxide concentration versus time

resinate and soda, autoxidation of II proceeds still more slowly. The maximum hydroperoxide concentration is reached in 17 h and is 41.6%. Autoxidation of II proceeds smoothly and uniformly in the presence of manganese resinate and calcium hydroxide, but at a relatively low rate (the maximum hydroperoxide concentration in the solution is reached in 27 h and is 35%).

Fig. 1. Autoxidation of 1,1,3-trimethyl-*x*-isopropyl-3-phenylindane at 110° in the presence of manganese resinate (10 mg/mol) and alkaline additives (0.5 g/mol): caustic soda (1), sodium ethoxide (2), soda (3), and calcium hydroxide (4).

Fig. 2. Autoxidation of 1,1,3-trimethyl-*x*-tert-butyl-3-phenylindane (1, 2) and 1,1,3-trimethyl-*x*-cyclohexyl-3-phenylindane (3, 4) at 110° in the presence of manganese resinate (15 mg/mol) and additives (1 g/mol): soda (1, 3) and calcium hydroxide (2, 4).

Alkylation of I with Isobutylene

The reaction was carried out analogously to that described for propylene. For each experiment, 0.25 mole of isobutylene and the corresponding amounts of I and $BF_3 \cdot H_3PO_4$ were taken. The time of addition of isobutylene in all experiments was 2 h; the time of additional stirring of the reaction mixture after introduction of the calculated amounts of isobutylene was 8 h. The influence on the reaction of the ratios of reactants and catalyst, as well as of temperature, is evident from the data summarized in Table 2.

Table 2

Alkylation of 1,1,3-trimethyl-3-phenylindane with isobutylene

No. of experiments	Molar ratios of trimethylphenylindane, isobutylene, and $BF_3 \cdot H_3PO_4$	Temp., °C $±$2°	1,1,3-Trimethyl-*x*-tert-butyl-3-phenylindane fraction boiling at 325-335°, % of theory	Isobutylene polymers boiling at 106-306°, g
1	4 : 1 : 0.3	70	20.2	12.7
2	3 : 1 : 0.3	20	10.1	10.4
3	3 : 1 : 0.3	52	30.0	9.0
4	3 : 1 : 0.3	70	30.8	7.4
5	3 : 1 : 0.4	20	13.0	13.2

No. of experiments	Molar ratios of trimethylphenylindane, isobutylene, and $BF_3 \cdot H_3PO_4$	Temp., °C $±$2°	1,1,3-Trimethyl-*x*-tert-butyl-3-phenylindane fraction boiling at 325–335°, % of theory	Isobutylene polymers boiling at 106–306°, g
6	3 : 1 : 0.6	20	12.0	8.0
7	3 : 1 : 0.6	52	23.3	8.0
8	2 : 1 : 0.3	52	43.3	7.6
9	2 : 1 : 0.4	52	28.7	11.0
10	1 : 1 : 0.3	52	19.9	10.0

1,1,3-Trimethyl-*x*-tert-butyl-3-phenylindane (III) (a fraction redistilled after treatment with conc. H_2SO_4, given in Table 2) is a viscous colorless liquid. B.p. 331–333° (uncorr.), d_4^{20} 0.9776, n_D^{20} 1.5487, MR_D found 94.80; calculated 94.39. Molecular weight found 291.1, 289.0; $C_{22}H_{28}$, calculated 292.4.

Hydrocarbon III undergoes autoxidation by atmospheric oxygen at 110° in the presence of manganese resinate and alkaline additives only with great difficulty, as is evident from the curves presented in Fig. 2. The maximum concentration of hydroperoxide in the solution does not exceed 4.5% under the best conditions.

Cycloalkylation of I with cyclohexene. For each experiment, 0.25 mole of cyclohexene and the corresponding amounts of I and $BF_3 \cdot H_3PO_4$ were taken. In all experiments the time of addition of cyclohexene was 2 hours, and the time of additional stirring of the reaction mixture was 8 hours. The influence on the reaction of the molar ratios of the reagents and catalyst, as well as of temperature within the range 52–70°, is seen from the data given in Table 3.

Table 3

Cycloalkylation of 1,1,3-trimethyl-3-phenylindane with cyclohexene

No. of experiments	Molar ratios of trimethylphenylindane, cyclohexene, and $BF_3 \cdot H_3PO_4$	Temp., °C $±$2°	1,1,3-Trimethyl-*x*-cyclohexyl-3-phenylindane fraction boiling above 350°, % of theory
1	7 : 1 : 0.3	70	23.1
2	4 : 1 : 0.3	70	23.5
3	4 : 1 : 0.3	52	23.4
4	3 : 1 : 0.2	52	29.9
5	3 : 1 : 0.3	52	44.6

No. of experiments	Molar ratios of trimethylphenylindane, cyclohexene, and $BF_3 \cdot H_3PO_4$	Temp., °C $±$2°	1,1,3-Trimethyl-*x*-cyclohexyl-3-phenylindane fraction boiling above 350°, % of theory
6	3 : 1 : 0.3	70	43.2
7	3 : 1 : 0.3	90	34.1
8	3 : 1 : 0.6	52	27.9
9	3 : 1 : 0.6	70	29.9
10	2 : 1 : 0.3	52	26.1
11	2 : 1 : 0.6	52	35.3
12	2 : 1 : 0.6	70	39.3
13	1 : 1 : 0.3	52	23.9
14	1 : 1 : 0.3	70	24.2

1,1,3-Trimethyl-*x*-cyclohexyl-3-phenylindane (IV), isolated by repeated distillation of the fraction boiling above 350°, is a very viscous, almost colorless and odorless liquid. At atmospheric pressure it distills without noticeable decomposition. B.p. 373-378° at 760 mm (uncorr.), 214–219° at 4 mm, d_4^{20} 1.0147, n_D^{20} 1.5602, MR_D found 101.20; calculated 101.43. Molecular weight found 316.1, 317.6; $C_{24}H_{30}$, calculated 318.5.

Hydrocarbon IV undergoes autoxidation by atmospheric oxygen in the presence of manganese resinate and alkaline additives more readily than III, as is evident from Fig. 2. The maximum concentration of hydroperoxide in the reaction mass in the presence of manganese resinate and soda is 12.5%.

Kiev Polytechnic Institute

Received
13 XI 1961

REFERENCES

1. S. V. Zavgorodnii, B. A. Zaitsev, D. P. Elchinov, ZhOKh, **30**, 2196 (1960).
2. V. T. Renne, L. A. Morozov et al., *Izv. vyssh. uch. zav.*, Energetika, No. 2, 51 (1960).

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