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Abstract

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Thermal Alkylation of Cyclohexane with Olefins under Pressure

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The alkylation of aromatic, normal, and isoparaffinic hydrocarbons with olefins has been the subject of many investigations. This route for the synthesis of isoparaffinic and alkyl aromatic hydrocarbons has found broad industrial application. In contrast to this, the alkylation of the important class of cycloparaffinic hydrocarbons has remained almost entirely unstudied up to the present time.

Pines and Ipatieff (1) investigated the alkylation of methylcyclopentane in the presence of 100% H_2SO_4 and HF with butylenes, isobutylene, pentene-1, and other olefins. The process proceeded in a very complex manner, and products of direct addition of olefins were not obtained. The presence of an alkylation process could be inferred only by taking into account possible intermediate reactions —the isomerization of the dialkylcyclopentane formed into dialkylcyclohexane and the migration of alkyl groups. Mamedaliev with Kuliev (2) and Mamedova (3) alkylated methyl-, ethyl-, and isopropylcyclohexanes with propylene and butylene in the presence of H_2SO_4. In this case substituted cyclohexanes with side alkyl groups corresponding to the olefin used were isolated. However, unsubstituted cyclohexane and cyclopentane were not alkylated under these conditions, and monoalkylcyclanes could not be obtained in this way.

In the present work, the direct alkylation of cyclohexane with ethylene, propylene, and isobutylene at elevated temperatures and pressures has been carried out for the first time. The principal reaction products were isolated and characterized, and the influence of a number of factors on the course of the process was studied.

Experimental Part

The experiments were carried out in a flow-type apparatus similar to that described earlier (4). The pressure in the reactor was produced by the reacting mixture, which was fed from a mixer by means of a liquid pump. Into a reactor of 120 ml volume were charged 50 ml of $Ca_3(PO_4)_2$ and 70 ml of porcelain chips, or 120 ml of pieces of quartz. The cyclohexane had: b.p. 80.3°, $n_D^{20.5}$ 1.4266 and d_4^{20} 0.7752. The catalysts obtained were fractionated on a high-efficiency column. Homogeneous fractions from several experiments were combined and

Fig. 1. Fractionation curve of the alkylate from experiment No. 3

Figure 1: Fig. 1. Fractionation curve of the alkylate from experiment No. 3

subjected to investigation. Removal of unsaturated impurities and isolation of aromatic hydrocarbons were carried out by chromatography on silica gel. The structure of the alkylcyclohexanes obtained was determined by converting them, by dehydrogenation over a Pt/C catalyst (20% Pt) at 300°, into the corresponding aromatic hydrocarbons and by oxidizing the latter to acids.

Alkylation with ethylene. In experiments at pressures of 200 and 450 atm (450°), the ethylene taken into the reaction was absorbed completely, and at 100 atm—by 90%. After removal of cyclohexane from the alkylate, the following fractions were isolated: I—monoethylcyclohexane (b.p. 129-131°), II—diethylcyclohexane (b.p. 170-185°) and a higher-boiling residue, Fig. 1. After removal of the unsaturated compounds from 30 ml of fraction I, 27 ml of product was obtained with n_D^{20} 1.4323 and d_4^{20} 0.7857. According to (5), for ethylcyclohexane: b.p. 131.78°, n_D^{20} 1.4378, d_4^{20} 0.7879. After its dehydrogenation and subsequent chromatography, ethylbenzene was isolated with n_D^{20} 1.4957, d_4^{20} 0.8660. According to (5), for ethylbenzene n_D^{20} 1.4959, d_4^{20} 0.8670. Oxidation by Ullmann gave benzoic acid with m.p. 122.5°.

After removal of the unsaturated compounds (28%) from fraction II, it distilled completely at 172-175° and had n_D^{20} 1.4415, d_4^{20} 0.8013. These properties are close to those of isomeric diethylcyclohexanes. After dehydrogenation and subsequent chromatography, a narrow fraction of hydrocarbons (80%) was isolated from the catalyzate, with b.p. 178-180°/740 mm, n_D^{20} 1.4918, d_4^{20} 0.8613. These properties correspond to isomers of diethylbenzene (5). On the chromatogram of the diethylbenzene obtained (with dibutyl sebacate as the carrier), two peaks were found. Diethylbenzene was oxidized according to (6) into a mixture of phthalic acids, from which, taking advantage of their different solubility in hot water (7), the individual acids were isolated: *o*-phthalic, iso-phthalic, and terephthalic—in weight ratios of 1 : 1.6 : 8. Sublimation of the *o*-isomer gave needle-shaped crystals of the anhydride.

Fig. 1. Fractionation curve of the alkylate from experiment No. 3

Under the optimum conditions (experiment 3), of the 253 g of cyclohexane charged into the reaction, 212 g was recovered. In addition to the fractions of mono- and diethylcyclohexane, constituting the main part of the alkylate (50 and 20%, respectively), a small amount (3.2%) of low-boiling products (b.p. up to 75°) from cracking and dimerization of the olefin, which we did not investigate, was also isolated. The remaining part of the alkylate consists of intermediate fractions (85-125° and 135-170°) and a high-boiling residue. The residue, 75% of which was distributed between the fractions: b.p. 185-220°, n_D^{20} 1.4570, d_4^{20} 0.8262 and b.p. 220-250°, n_D^{20} 1.4640, d_4^{20} 0.8393, apparently represents a mixture of polyethylcyclohexanes. In experiment 3 of Table 1, 11% of unsaturated hydrocarbons was present, most of which belonged to the intermediate—

Table 1

No.	Pressure, atm	Cyclohexane: ethylene, mol	Rate of passage of the mixture, ml/min	Alkylate yield based on ethylene taken, %	Monoethylcyclohexane fraction, wt. %	Diethylcyclohexane fraction, wt. %	Residue, wt. %
1	100	3.0	1.6	89	34	14	26
2	200	3.0	0.3*	225	46	–	–
3	200	3.9	1.5	240	51	20	20
4	450	3.0	0.5	230	50	–	–
5	200	1.2	1.7	150	34	16	32
6	200**	2.0	0.6	176	28	9	44
7	200	2.1	3.3	220	27	16	38
8	200	4.4	3.4	230	41	20	26

* Experiment 1-6 were carried out with $Ca_3(PO_4)_2$; 7 and 8 in the presence of quartz.
** At 400°.

fractions and the residue. The monoethylcyclohexane fraction contained 3.4%, and the diethylcyclohexane fraction 13%, of unsaturated hydrocarbons, the nature of which was not studied.

From Table 1 it is seen (the experiments were carried out at 450°) that, with an increase in the concentration of ethylene in the initial mixture, the yield of monoethylcyclohexane decreased, while the yield of the higher-boiling residue increased. A similar effect is exerted by a decrease in the space velocity of passage of the mixture.

Table 2

Run Nos.	Temp., °C	Pressure, atm	Cyclohexane: olefin, mol.	Space velocity of passage of the mixture, h^{-1}	Degree of conversion of olefin, %	Alkylate yield based on olefin taken, %	Content in the alkylate, wt.%: monoalkylcyclohexane fraction	Content in the alkylate, wt.%: residue
Alkylation with propylene								
9	450	200	2,8	1,60	32	96	28	51
10	450	200	3,7	1,45	30	93	44	45
11	500	450	3,0	1,20	70	206	31	56
12	500	450	5,0	1,45	70	180	53	34
Alkylation with isobutylene								
13	450	200	1,9	1,17	–	85	39	35
14	450	450	3,0	1,19	–	180	44	38
15	450	450	2,7	1,31	31	150	42	38

Alkylation with propylene. A propylene-propane fraction containing 13% propane was used. From Table 2 it is seen that, at 200 atm, the degree of conversion of propylene (30%) and the yield of alkylate (93–96%) are considerably lower than with ethylene. At 450 atm and 500° the degree of conversion of propylene and the yield of alkylate increased. From the alkylates, by distillation, there were isolated: a low-boiling fraction of cracking products, fraction II with b.p. 150–157°, and a residue. After removal of unsaturated compounds (5%), fraction II had: n_D^{20} 1,4370, d_4^{20} 0,7929. According to (5), for *n*-propylcyclohexane: b.p. 156,72°, n_D^{20} 1,4370, d_4^{20} 0,7936. After dehydrogenation over Pt/C, by distillation and chromatography there was isolated a product (48%) with b.p. 158,2–158,5°, n_D^{20} 1,4903, d_4^{20} 0,8612. According to (5), for *n*-propylbenzene: b.p. 159,22°, n_D^{20} 1,4920, d_4^{20} 0,8620. From the residue, by distillation and chromatography on silica gel, there was isolated a hydrocarbon with b.p. 209–211°/739 mm, n_D^{20} 1,4481, d_4^{20} 0,8102, the weight of which amounted to approximately 30% of the weight of the residue. These properties are close to the properties of di-*n*-propylcyclohexane. According to (8), for the 1,2-isomer: b.p. 214,7–215°, n_D^{20} 1,4510, d_4^{20} 0,8188, and for the 1,4-isomer: trans—b.p. 220°, n_D^{20} 1,4440, d_4^{20}

0,8030; cis—b.p. 221°, n_D^{20} 1,4480, d_4^{20} 0,8138 (9).

From a comparison of the results of experiments 9 and 11 on quartz and 10 and 12 on $Ca_3(PO_4)_2$, it is seen that, in the presence of phosphate, the content of monopropylcyclohexane in the alkylate is higher, and that of di- and polysubstituted products lower.

Experiments with isobutylene were carried out in the presence of quartz. The degree of conversion of isobutylene was lower than that of propylene. From the alkylate, by distillation, a fraction with b.p. 168–183° was isolated. After removal of unsaturated compounds (bromine number 11–12) and distillation, a hydrocarbon (57%) with b.p. 171–172°/742 mm, n_D^{20} 1,4393, d_4^{20} 0,7942, was obtained from it. According to (5), for isobutylcyclohexane the b.p. is 171,32°, n_D^{20} 1,4386, d_4^{20} 0,7952.

Table 3 gives the constants of hydrocarbons of normal and iso structure, taken from (5) and obtained by us. From Table 3 it is seen that the constants of the propylbenzene obtained are close to the constants of the hydrocarbon with normal

Table 3

Hydrocarbons	B.p., °C	d_4^{20}	n_D^{20}
Cyclohexyl-CH_2-CH_2-CH_3	156.72	0.7936	1.4370
Cyclohexyl-$CH(CH_3)_2$	154.56	0.8022	1.4409
Cyclohexyl-C_3H_7, obtained by us	155–156	0.7929	1.4370
Phenyl-CH_2-CH_2-CH_3	159.22	0.8620	1.4920
Phenyl-$CH(CH_3)_2$	152.39	0.8618	1.4915
Phenyl-C_3H_7, obtained by us	158.2–158.5	0.8612	1.4903
Cyclohexyl bearing two propyl groups, $(CH_2CH_2CH_3)_2$	214.7–215.0	0.8188	1.4510
Dipropylcyclohexane, trans-	220	0.8030	1.4440
Dipropylcyclohexane, cis-	221	0.8138	1.4480

Hydrocarbons	B.p., °C	d_4^{20}	n_D^{20}
Cyclohexyl-$(C_3H_7)_2$, obtained by us	209-211 (739 mm)	0.8102	1.4481
Cyclohexyl-CH_2-$CH(CH_3)$-CH_3	171.32	0.7952	1.4386
Cyclohexyl-$C(CH_3)_3$	171.59	0.8127	1.4469
Cyclohexyl-C_4H_9, obtained by us	171-172 (742 mm)	0.7942	1.4393

side chain. The constants of the butylcyclohexane obtained are close to the constants of isobutylcyclohexane. Thus, in both cases, cyclohexane apparently adds to the terminal unsaturated C atom of the olefin:

$$C_6H_{12} + CH_2{=}CH{-}CH_3 \longrightarrow C_6H_{11}{-}CH_2{-}CH_2{-}CH_3$$

$$C_6H_{12} + CH_2{=}C(CH_3){-}CH_3 \longrightarrow C_6H_{11}{-}CH_2{-}CH(CH_3){-}CH_3$$

In contrast, in the acid alkylation of methylcyclohexane with propylene, methylisopropylcyclohexane was obtained (^{3}), i.e., cyclane adds to the middle unsaturated C atom of the olefin:

$$CH_3{-}C_6H_{11} + CH_2{=}CH{-}CH_3 \longrightarrow CH_3{-}CH(CH_3){-}C_6H_{11}$$

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