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Abstract

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ALKYLATION OF CYCLOPARAFFINS

In a previously published communication we presented data on the alkylation of petroleum methylcyclohexane with propylene in the presence of sulfuric acid (1). It was noted that the secondary carbon atom of methylcyclohexane is readily alkylated and that the tertiary carbon atom is indifferent to the reaction under conditions of sulfuric-acid alkylation.

For the purpose of a detailed study of this reaction, an investigation was undertaken of the alkylation of five- and six-membered cyclanes, namely cyclopentane, cyclohexane, methylcyclohexane, ethylcyclohexane, isopropylcyclohexane, and tert-butylcyclohexane.

In addition to the practical significance of such a study, which consists in developing a convenient method for the synthesis of alkylcyclanes, it will make it possible to elucidate certain theoretical questions of organic chemistry—such as the order of orientation in the alicyclic series, the influence of ring saturation on the reactivity of cyclic compounds, the effect of the degree of nucleophilicity of side alkyl groups on the rate of substitution in the ring, etc.

Experimental Part

The initial six-membered cyclanes were obtained by hydrogenation of the corresponding aromatic hydrocarbons over a nickel-kieselguhr catalyst at atmospheric pressure and a temperature of 180–200°. Cyclopentane was obtained by hydrogenation of cyclopentadiene in a rotating autoclave at room temperature, under a hydrogen pressure of 60–70 atm., over Raney nickel.

After appropriate purification, the hydrogenation products were distilled on a precision rectification column, with isolation of chemically pure cyclanes. The constants of the cyclanes obtained are given in Table 1.

Table 1

Hydrocarbons	d_4^{20} found	d_4^{20} lit.	n_D^{20} found	n_D^{20} lit.	Aniline point found	Aniline point lit.
Cyclohexane	0.7784	0.7786	1.4266	1.4262	31.0°	31.0
Methylcyclohexane	0.7695	0.7694	1.4232	1.4231	41.0	41.0

Hydrocarbons	d_4^{20} found	d_4^{20} lit.	n_D^{20} found	n_D^{20} lit.	Aniline point found	Aniline point lit.
Ethylcyclohexane	0.7881	0.7879	1.4332	1.4330	44.5	43.8
Isopropylcyclohexane	0.8120	0.8122	1.4466	1.4408	49.5	48.9
tert-Butylcyclohexane	0.8130	0.8127	1.4500	1.4499	54.0	53.6
Cyclopentane	0.7456	0.7454	1.4168	1.4066	17.0	16.6

As alkylating agents there were used a propylene-propane fraction of pyrolysis gases containing 75.5 wt.% propylene, as well as propylene and butylene obtained by dehydration of the corresponding alcohols over aluminum oxide. Alkylation was carried out in the apparatus whose scheme was given in communication (1).

To establish the optimum conditions, experiments were carried out at temperatures from 0 to 60° with different values of the gas flow rate, the concentration of sulfuric acid, and the molar ratio of the reacting components. The present communication gives the results of several characteristic experiments carried out in the presence of 98% sulfuric acid, with a molar ratio of cyclane to olefin of 1 : 1, at temperatures of 0, 30–35, and 60° and an olefin feed rate of 3.8–4 l/hr.

The experimental data are summarized in Table 3 (at 0°), Table 4 (at 30–35°), and Table 5 (at 60°).

To establish the structure of the compounds corresponding to the products of interaction of 1 mole of cyclane with 1 mole of olefin, the latter were subjected to dehydrogenation catalysis according to N. D. Zelinskii over a Pt catalyst at a temperature of 300–310°. The aromatic hydrocarbons obtained by dehydrogenation were oxidized with an alkaline solution of potassium permanganate to the corresponding phthalic acids. Analysis of the phthalic acids showed that the bulk of the compounds (75–80%) consists of para isomers.

As a result of the investigation carried out, it was possible to synthesize certain alkyl-substituted cyclanes that had not previously been obtained and to determine their physical constants (Table 2).

Table 2

Compounds	b.p., °C	n_D^{20}	d_4^{20}	Mol. weight	Aniline point
Ethylisopropylcyclohexane	190–194	1.4430	0.8035	153.5	63.5
Ethyl-*tert*-butylcyclohexane	206–219	1.4450	0.8058	168.0	70.0

Compounds	b.p., °C	n_D^{20}	d_4^{20}	Mol. weight	Aniline point
Methyl-*tert*-butylcyclohexane	184–190	1.4405	0.7968	154.0	65.0
Isopropyl-*tert*-butylcyclohexane	212–217	1.4459	0.8088	178.5	73.0

The experimental data show that, among the representatives of six-membered cycloparaffins studied, substituted cyclanes—methylcyclohexane, ethylcyclohexane, and isopropylcyclohexane—were readily alkylated with olefins, forming the corresponding alkyl derivatives.

Table 3

Hydrocarbons*	Cyclopentane	Cyclohexane	Methylcyclohexane	Ethylcyclohexane	Isopropylcyclohexane	*tert*-Butylcyclohexane
Catalyst						
Yield with respect to initial cyclane, wt. %	93	94	103.7	106.9	103.0	98.8
d_4^{20}	0.7470	0.7820	0.7755	0.7899	0.7965	0.8090
n_D^{20}	1.4102	1.4310	1.4256	1.4342	1.4375	1.4448
Iodine number	0.0	0.0	0.0	0.0	0.0	0.0
Sulfurizability	1.0	2.8	2.0	1.5	0.5	3.0
Mol. weight	74	88.7	108.0	116.5	123.5	138
Aniline point	17.5	34.5	48	49.2	58	57

Hydrocarbons*	Cyclopentane	Cyclohexane	Methylcyclohexane	Ethylcyclohexane	Isopropylcyclohexane	*tert*-Butylcyclohexane
Content of components in the catalyzate, wt. %						
Initial cyclane	92.1	86.48	84.13	84.79	77.74	89.04
Monoalkylcyclane	–	–	6.65	6.39	7.3	–
Residue	4.5	9.7	7.56	7.52	13.46	10.36
Losses	3.4	1.85	1.66	1.3	1.5	1.6

Note. Monoalkylcyclane corresponds to the product formed as a result of the interaction of 1 mole of cyclane with 1 mole of olefin. Experimental conditions: ratio of cyclane to olefin = 1 : 1, acid concentration 98%, temperature 0°.

* With propylene.

The optimum reaction temperature is 30–35°, which corresponds to the maximum yield of alkylation products.

As can be seen from Table 4, under optimum experimental conditions the catalyzates consist of unreacted cyclanes (50–60%), products of direct alkylation of the initial cyclanes (20–30%), and residues consisting mainly of polyalkylcyclanes (14.18%). Thus, in the alkylation of methylcyclohexane, ethylcyclohexane, isopropylcyclo—

Table 4

	Cyclopentane	Cyclohexane	Methylcyclohexane	Methylcyclohexane	Ethylcyclohexane	Ethylcyclohexane	Isopropylcyclohexane	Isopropylcyclohexane	tert-Butylcyclohexane
Hydrocarbons*	a	a	a	b	a	b	a	b	a
Catalyzate									

Hydrocarbons*	Cyclopentane	Cyclohexane	Methylcyclohexane	Methylcyclohexane	Ethylcyclohexane	Ethylcyclohexane	Isopropylcyclohexane	Isopropylcyclohexane	tert-Butylcyclohexane
	a	a	a	b	a	b	a	b	a
Yield based on initial cyclane, wt. %	67.85	90	116.3	109.5	110.9	109.5	110.5	108.2	97.7
d_4^{20}	0.7475	0.7838	0.7909	0.7784	0.7956	0.7882	0.7970	0.7844	0.8065
n_D^{20}	1.4108	1.4318	1.4340	1.4301	1.4373	1.4358	1.4400	1.4335	1.4451
Iodine number	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Sulfonatability	1.5	4.0	1.2	1.5	1.0	1.0	1.5	1.5	3.5
Mol. wt.	75	93.5	115.5	128.6	129.5	123.5	139	128	135
Aniline point	17.5	34.5	52.5	56	56.5	61.5	60.5	64	55
Content of components in the catalyzate, wt. %									
Initial cyclane	90.8	85.0	47.26	56.56	57.25	62.45	62.87	59.78	90.54
Monoalkylcyclane	90.8	–	31.79	26.8	22.26	18.39	20.36	18.63	–
Residue	6.6	14.53	18.27	14.23	18.89	17.26	14.89	18.75	6.66
Losses	2.6	0.5	2.68	2.37	1.6	1.9	0.95	2.84	2.8

Note. Experimental conditions: molar ratio of cyclane to olefin = 1 : 1, sulfuric acid concentration 98%, temperature 30–35°.

* a —with propylene, b —with butylene.

Table 5

Hydrocarbons	Cyclopentane*	Cyclohexane	Methylcyclohexane	Ethylcyclohexane	Isopropylcyclohexane	tert-Butylcyclohexane
Catalyzate						
Yield based on initial cyclane, wt. %	60.6	84.2	92.6	94	97.2	92.0
d_4^{20}	0.7468	0.7892	0.7815	0.7920	0.7935	0.8070
n_D^{20}	1.4100	1.4342	1.4315	1.4352	1.4345	1.4475
Iodine number	0.5	0.0	0.0	0.0	0.0	0.0
Sulfonatability	1.0	4.5	1.5	1.0	1.0	3.5
Mol. wt.	72.5	92	109.5	118.8	130	138
Aniline point	17.5	34	51.5	55.5	58	56
Content of components in the catalyzate, wt. %						
Initial cyclane	90.5	87.75	66.3	76.93	73.36	93.16
Monoalkylcyclane	–	–	15.68	9.7	9.4	–
Residue	6.0	10.68	16.52	11.47	17.24	6.64
Losses	3.5	11.55	1.5	1.8	–	3.4

Note. Experimental conditions: molar ratio of cyclane to olefin = 1 : 1, acid concentration 98%, temperature 60°.

* With propylene.

hexane with olefins under optimal conditions—about 60–70% of the cyclane that has entered into the reaction is converted into the primary products of their alkylation.

Alkylation of cyclohexane with propylene did not lead to positive results. The ability of alkylcyclohexanes to enter into an alkylation reaction with olefins in the presence of sulfuric acid, and the absence of this ability in the unsubstituted cyclane—cyclohexane—can be explained by the nucleophilicity of the alkyl groups. The latter, disturbing the symmetry of the electron distribution of the ring, cause a shift of electrons toward the nucleus and impart to the ring carbon atoms an additional fractional electric charge. The positively charged carbonium ions formed as a result of the interaction of olefins with sulfuric acid enter much more readily into reaction with ring carbon atoms that have an additional negative charge acquired by them owing to the shift of electrons under the influence of the electron-repelling alkyl groups.

Among the substituted cyclohexane hydrocarbons, which readily enter into interaction reactions with olefins, tert-butylcyclohexane is an exception. In the presence of sulfuric acid, under the conditions studied, it was not alkylated by olefins. The absence of the ability of tert-butylcyclohexane to undergo the alkylation reaction may be explained by a quantitative characteristic of the nucleophilicity of the CH_3-, C_2H_5-, $(CH_3)_2CH$-, and $(CH_3)_3C$- groups, as well as by steric hindrance.

Alkylation of cyclopentane with propylene in the presence of sulfuric acid also does not occur under the conditions studied.

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1. Yu. G. Mamedaliev, A. Kuliev, DAN, **88**, No. 3 (1953).

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