Russian Journal of Applied Chemistry, Vol. 77, No. 7, 2004, pp. 1130–1135. Translated from Zhurnal Prikladnoi Khimii, Vol. 77, No. 7, 2004, pp. 1144–1149. Original Russian Text Copyright © 2004 by Sadykov, Samokhina, Petrov, Paramonov, Dzhemilev.

= CATALYSIS =

Transformations of Cyclohexane under the Action of *in situ* Generated Aluminum Halides

R. A. Sadykov, M. G. Samokhina, P. N. Petrov, E. A. Paramonov, and U. M. Dzhemilev

Institute of Petrochemistry and Catalysis, Academy of Sciences of Bashkortostan Republic and Ufa Scientific Center, Russian Academy of Sciences, Ufa, Bashkortostan, Russia Bashkir Republican Ecological Center, Ufa, Bashkortostan, Russia

Received January 9, 2004

Abstract—Transformations of inert cyclohexane into dimethyldecalins under mild conditions in the presence of a simple catalytic system consisting of aluminum metal and halomethanes were studied.

The catalytic activation of C–H bonds in cyclic and acyclic alkanes with transition metal complexes or electrophilic agents such as Friedel–Crafts catalysts is a promising field of research. As a rule, the catalysts used for activating hydrocarbons are aprotic Lewis acids based on salts of transition and maingroup metals in combination with active additives.

Superelectrophilic complexes $RCOX \cdot 2AIX_3$ and $CX_4 \cdot 2AIX_3$ (X = Cl, Br) are the most effective in transformations of saturated hydrocarbons under mild conditions [1-3]. It was shown recently [4] that the reaction system consisting of an organoaluminum compound (OAC) and halomethane in the presence of catalytic amounts of transition metal complexes exhibits similar activity toward cycloalkanes. The activity of this system was tentatively explained by generation of AlCl₃ in the reaction of OAC with halomethane, catalyzed with a transition metal, which is followed by formation of a superelectrophilic complex with the starting halomethane, similar to $CX_4 \cdot 2AIX_3$. If this is true, then it will be possible to generate a similar complex in situ using a simpler and more available agent, aluminum metal [5]:

$$2Al + 6CCl_4 \rightarrow 2AlCl_3 + 3C_2Cl_6.$$
(1)

This work is the first study of chemical transformations of cyclohexane under the action of aluminum halides generated *in situ* by the reaction of halomethanes (CCl₄, CHCl₃, CHBr₃, CH₂Cl₂, CH₂Br₂) with aluminum metal preliminarily activated with iodine or AlR₃.

The choice of cyclohexane as investigation object was governed by the large body of data available on the effect of aluminum halides in combination with various promoters on cyclohexane.

Pure anhydrous AlCl₃ is virtually inert toward cyclohexane [6]. However, in the presence of water [6], HCl, and acetyl chloride [7] AlCl₃ effects isomerization of cyclohexane into methylcyclopentane. The reaction of cyclohexane with cyclohexyl bromide [8] in the presence of AlCl₃ yields a mixture of dimethyldecalins. A similar mixture of dimethyldecalins is formed by dimerization of methylcyclopentane, effect by the reaction system $AlCl_3 + t$ -BuCl in the HCl [9]. Dimethyldecalins were detected in the reaction of chlorocamphor with AlBr₃ in cyclohexane [9]. Heating of cyclohexane with AlCl₃ and HCl in an autoclave for 1 day to 140-150°C results not only in isomerization into methylcyclopentane but also in formation of dicyclohexyl and di(methylcyclopentyl) [10]. At 180°C, methylcyclopentane, 1,3-dimethylcyclohexane, dicyclohexyl, and di(methylcyclopentyl) $C_{12}H_{22}$ were detected together with a small amount of isobutane [11]. Formation of dimethyldecalins was also reported in [12]. Transformation of cyclohexane into alkyladamantanes was noted in [13].

Under the action of superelectrophilic systems $RCOX \cdot 2AlBr_3$ [2] and $CH_nX_{4-n} \cdot AlX_3$ (X = Cl, Br) [3], cyclohexane transforms into dimethyldecalins at room temperature or 40°C with 22 and 10% yield based on cyclohexane, respectively. With excess cyclohexane, dimethyldecalins are formed selectively in low yields.

Aluminum metal was activated by a common procedure by heating under argon in the presence of several iodine crystals until iodine sublimed virtually completely and was removed from the reaction vessel. In some cases, to accelerate the start of the reaction of aluminum with halomethane, a small amount (~0.1 ml) of *i*-Bu₃Al and Et₃Al was added to the reaction mixture.

TRANSFORMATIONS OF CYCLOHEXANE

Run no.	CX_nH_{4-n}	C_6H_{12} : CX_nH_{4-n} : Al	C ₆ H ₁₂ con- version, %	Product yield,** mol %		
				alkylcyclohexanes	dimethyldecalin	tricyclanes
1	CCl ₄	100 : 22 : 8	20	_	27	_
2	CCl_4	100:32:20	62	4	47	13
3	CCl_4	100:45:28	74	13	49	25
4	CCl_4	100:45:28	80	19	40	28
5	CCl_4	100 : 160 : 23	56	4	46	21
6	CHCl ₃	100 : 34 : 25	48	6	35	13
7	CHCl ₃	100 : 54 : 27	51	6	38	11
8	CHCl ₃	100 : 100 : 49	47	4	50	14
9	CHCl ₃	100 : 108 : 30	52	4	23	9
10	CHBr ₃	100 : 74 : 31	49	9	48	13
11	CH_2Br_2	100:154:40	21	29	33	_
12	CH_2I_2	100 : 80 : 31	42	14	17	_
13	BuĈl	100 : 57 : 27	47	24	22	13

Yields of major products of cyclohexane transformations under the action of the reaction system Al-halomethane*

* Some other products (see text for details) were detected in insignificant amounts.

** Yield based on converted cyclohexane.

Transformations of the hydrocarbon start simultaneously with the onset of the reaction of aluminum with halomethane. The exothermic reaction is accompanied by the release of HCl and tarring. The major chlorinated reaction products in the case of CCl_4 are $CHCl_3$ and CH_2Cl_2 . In contrast to the reaction of Al with CCl_4 without a solvent, in which the yield of hexachloroethane is virtually quantitative, in the presence of the hydrocarbon the yield of C_2Cl_6 is low. Among other chlorinated prodcts, trace amounts of tetrachloroethylene and tetrachloroethane were detected.

According to GLC and GC/MS, the major products of cyclohexane transformation are isomeric dimethyldecalins (see table). The figure shows as example the



Chromatogram of a mixture of products obtained in run no. 4 (see table) and their identification. (*I*) Intensity and (τ) retention time. (*I*) Methylene chloride, (*2*) methylcyclopentane, (*3*) cyclohexane, (*4*) alkylcyclohexanes, (*5*) perchloroethylene, (*6*) decalin, (*7*) hexachloroethane, (*8*) methyldecalin, (*9*) methyl-substituted adamantanes, (*10*) isomeric dimethyldecalins, (*11*) trimethyldecalins, (*12*, *13*) tricyclanes with $[M]^+$ 192, and (*14*) tricyclanes with $[M]^+$ 248.

RUSSIAN JOURNAL OF APPLIED CHEMISTRY Vol. 77 No. 7 2004

chromatogram of a mixture of products obtained in run no. 4 (see table). The mass spectrum of each isomer contains a fairly strong molecular peak ([M]⁺ 166) and the same set of fragment peaks characteristic of dimethyldecalins (*m*/*z* 151, 137, 124, 123, 110, 109, 96, 82, etc.), corresponding to elimination of alkyl radicals [14] from CH₃ to C₆H₁₂ from the moleclar ion. The isomeric mixture mainly consists of the most thermodynamically stable [15] E3, E8-dimethyl-transbicyclo[4.4.0]decane and E3,E9-dimethyl-trans-bicyclo[4.4.0]decane. The structures of these isomers were determined from the ¹³C NMR spectra by comparison with the reference data [16] after isolation of the group of compounds corresponding to M 166 from the product mixture by preparative chromatography. As seen from the chromatogram (see figure), other isomers of dimethyldecalin are also present.

Among other products, we detected alkyl-substituted cyclohexanes whose total yields are also given in the table. For example, in run no. 4 we detected methylcyclohexane ($[M]^+$ 98, 2.5%), dimethyl- ($[M]^+$ 112, 4%), trimethyl- ($[M]^+$ 126, 2.4%), tetramethyl-($[M]^+$ 140, 5.8%), ethyl- ($[M]^+$ 112, traces), methyl-ethyl- ($[M]^+$ 126, 0.15%), and dimethylethylcyclohexanes ($[M]^+$ 140, 1.5%). Also, in the same experiment we detected methylcyclopentane ($[M]^+$ 84, 5%), decalin ($[M]^+$ 138, 0.3%), methyldecalin ($[M]^+$ 152, 1.3%), and trimethyldecalin ($[M]^+$ 180, 5.5%). These compounds were identified by GC/MS. The mass spectra obtained by us coincided with the reference data (NBS library) to 90–96%.

In the mixture of products, we also detected small amounts of methyl-substituted adamantanes: dimethyladamantane ($[M]^+$ 164, 0.5%), trimethyladamantane ($[M]^+$ 178, 1.4%), and tetramethyladamantane ($[M]^+$ 192, 1,1%). The assignment was based on comparison with published data [17].

Peaks 12 and 13 in the chromatogram (see figure) correspond to hydrocarbons with $[M]^+$ 192 and 206, respectively. Group of peaks 14 mainly belongs to hydrocarbons with $[M]^+$ 248. The mass spectra of compounds giving the strongest chromatographic peaks in this group are characterized by the base peak at m/z 233 $[M^+ - CH_3]$ and medium-intensity peaks at m/z 177, 163, 123, and 109. Some of them contain ions with m/z 219 $[M^+ - C_2H_5]$. The products of oxidative dimerization of cyclohexane formed under the action of the superelectrophilic complex [3] $CBr_4 \cdot 2AlBr_3$ contain hydrocarbons with $[M]^+$ 248 giving similar mass spectra. Apparently, in our case these compounds can also be identified as alkylated tricyclanes

 $C_{18}H_{32}$ with methyl and, possibly, ethyl substituents. In addition, compounds with molecular weights of 206, 220, 234, and 262 were identified in trace amounts:



where R = Me, Et; n = 1, 2, 3, 4.

The relative yields of all the heavy products are listed in the table.

As in [2], in experiments with excess cyclohexane alkylcyclohexanes and tricyclanes are not formed, and the reaction products contain dimethyldecalins and methylcyclopentane. As the content of halomethane and aluminum in the starting mixture is increased, the content of methylcyclopentane in the reaction products decreases simultaneously with an increase in the content of dimethyldecalin, alkylcyclohexanes, and tricyclanes. Analysis of the reaction products in various steps showed a similar dependence of the product concentrations on the reaction time. The content of methylcyclopentane grows in the initial steps and then decreases. This fact indicates that cyclohexane first isomerizes into methylcyclopentane, transforming then into dimethyldecalin and other products. This result is consistent with the available data [6, 7] on equilibrium isomerization of cyclohexane into methylcyclopentane under the action of AlCl3 with additions of various promoters and on dimerization of methylcyclopentane under the action of AlCl₃ and *t*-BuCl [9].

Cyclohexane is successfully involved in transformations also on replacement of CCl_4 by other halomethanes. Data obtained with chloroform, bromoform, methylene bromide, methylene iodide, and butyl chloride are given in the table.

It should be noted that the order of adding reagents [successively (see table, run no. 4), with CCl_4 added to activated Al first and cyclohexane added after the reaction completion, or simultaneously (run no. 3)] have no noticeable effect on the yield of the major products.

As it is difficult to isolate $AlCl_3$ from the reaction mixture and determine its content, we determined the residual content of active aluminum in the reaction mixture after the reaction completion. We found that, after activation of Al with iodine, the amount of Al^{3+} did not exceed 0.5% of the initial amount; after treatment with CCl_4 , it was ~42%, and after the reaction with cyclohexane, ~64%. Carbon tetrachloride was taken in 3 : 1 ratio relative to Al. A noticeable increase in the Al³⁺ content in the presence of cyclohexane can be accounted for as follows. In the reaction of Al with CCl₄ in the absence of the hydrocarbon, the main reaction products are C_2Cl_6 and AlCl₃ in the complex with CCl₄, and also tars. On adding cyclohexane, the complex AlCl₄⁻ CCl₃⁺ reacts with the hydrocarbon to form CHCl₃ and cyclohexyl carbocation. Chloroform subsequently reacts with a new portion of Al to give AlCl₃. AlCl₃ effects transformations of cyclohexane. Thus, AlCl₃ is formed not only in the initial step of the reaction, but also directly in the course of transformations of the hydrocarbon.

It should be noted that oxidative dimerization of cyclohexane to dimethyldecalin under the action of the system $Al-CCl_4$ occurs selectively when cyclohexane is in excess.

Our results and published data suggest the following reaction mechanism. In the first step, aluminum metal reacts with CCl_4 to give $AlCl_3$ which forms the complex $AlCl_4 \cdot CCl_3^+$ with the starting halomethane:

$$AlCl_3 + CCl_4 \rightarrow AlCl_4^- \cdot CCl_3^+.$$
 (2)

Then formation of dimethyldecalins follows the known scheme [9] according to which CCl_3^+ abstracts the hydride ion from a cyclohexane molecule to give cyclohexyl cation and chloroform. Cyclohexyl carbenium ion isomerizes into more stable methylcyclopentyl carbenium ion:

$$\operatorname{CCl}_{3}^{+} \cdot \operatorname{AlCl}_{4}^{-} + \overset{H}{\longrightarrow} \overset{H}{\longrightarrow} \overset{H}{\longrightarrow} \cdot \operatorname{AlCl}_{4}^{-} + \operatorname{CHCl}_{3}, (3)$$

$$\overset{H}{\longrightarrow} \cdot \operatorname{AlCl}_{4}^{-} \longrightarrow \overset{\downarrow}{\longrightarrow} \cdot \operatorname{AlCl}_{4}^{-}. \qquad (4)$$

The latter transfers the charge to the cyclohexane molecule to give methylcyclopentane:

$$\begin{array}{c} \stackrel{\downarrow^{+}}{\longrightarrow} \cdot \operatorname{AlCl}_{4}^{-} + \bigoplus_{H} \longrightarrow \bigwedge_{+} \stackrel{H}{\longrightarrow} \cdot \operatorname{AlCl}_{4}^{-} \dots & (5)
\end{array}$$

Alternatively, proton abstraction yields methylcyclopentene, AlCl₃, and HCl (HCl evolution is indeed observed in the course of the reaction):

RUSSIAN JOURNAL OF APPLIED CHEMISTRY Vol. 77 No. 7 2004

$$\bigwedge^{\downarrow} \cdot_{\text{AlCl}_{4}^{-}} \longrightarrow \bigwedge^{\downarrow} + \text{HCl} + \text{AlCl}_{3}. \quad (6)$$

Addition of the olefin to methylcyclopentyl carbenium ion yields dicycloalkylcarbenium ion, whose rearrangement yields thermodynamically stable dimethyldecalinium ion. The subsequent charge transfer from the cyclohexane molecule to the dimethyldecalinium ion results in formation of dimethyldecalin and generation of cyclohexyl cation:



According to [3], the activity of the complex $CCl_4 \cdot 2AlBr_3$ toward cyclohexane is noticeably higher than that of the complex $CCl_4 \cdot 2AlCl_3$. In our case, the complex based on *in situ* generated $AlCl_3$ shows high activity, comparable with that of the superelectrophilic complex $CCl_4 \cdot 2AlBr_3$ which is today one of the most effective initiators of alkane activation under mild conditions, along with the system $RCOX \cdot 2AlBr_3$.

EXPERIMENTAL

 CCl_4 , $CHCl_3$, $CHBr_3$, CH_2Br_2 , CH_2I_2 , *t*-BuBr, and cyclohexane (chemically pure grade) were dried and distilled from P₂O₅. Aluminum (chemically pure grade) was used as powder. For comparison, we tested preliminarily ground granulated aluminum (analytically pure grade) and aluminum wire. The results were identical. The ¹³C NMR spectra were recorded on a JEOL-FX90Q spectrometer. The products were analyzed on a Chrom-5 chromatograph with a capillary column (25 m, SE-30). The GC/MS analysis was performed on a VG TRIO 1000 device (the United King-

dom). We used a JZW Scientific DB-5 capillary column (60 m \times 0.25 mm \times 0.2 μm) (the Unted States) in the linear heating mode and the NBS library of mass spectra (the United States) containing 75000 mass spectra.

To perform the reaction of cyclohexane with the system Al-CCl₄, a 50-ml glass reactor was charged under Ar with 0.348 g (13 g-at) of Al and several crystals of iodine. The mixture was heated on an alcohol burner until the iodine completely sublimed and was removed from the reactor. The reactor was placed on a magnetic stirrer, and 7 ml (65 mmol) of cyclohexane and 2 ml (19 mmol) of CCl_4 were added. Stirring was continued at room temperature for 2 h. The reaction was accompanied by HCl evolution. After reaction completion, two layers formed: a transparent upper layer and a dark brown viscous lower layer containing aluminum chloride and residual aluminum metal. The upper layer was separated and filtered through Al₂O₃. Determination of the bromine number showed the absence of unsaturated bonds in the products. A GLC analysis of the resulting transparent liquid revealed the presence of dimethyldecalins (39%) nd unchanged cyclohexane (19.6%). The products giving a group of peaks with $[M]^+$ 166 (GC/MS) were isolated by preparative chromatography. Their ¹³C NMR analysis showed that the samples contained 45% E3,E8-dimethyl-trans-bicyclo-[4.4.0]decane, 41% E3,E9-dimethyl-trans-bicyclo-[4.4.0]decane, four unidentified isomers of dimethyldecalin with $[M]^+$ 166 (2–3% each), and five other isomers with $[M]^+$ 166 (0.2–0.3% each).

E3,E8-Dimethyl-*trans*-bicyclo[4.4.0]decane. ¹³C NMR spectrum (CDCl₃), δ , ppm (in parentheses are published data [16]): C¹, C², C⁶, C⁷ 43.0, (43.0); C³, C⁸ 33.1 (33.1); C⁴, C⁹ 35.6 (35.6); C⁵, C¹⁰ 34.3 (34.2); C³ CH₃, C⁸ CH₃ 22.8 (22.8); [M]⁺ 166.

E3,E9-Dimethyl-*trans*-bicyclo[4.4.0]decane. ¹³C NMR spectrum: C¹, C², C¹⁰ 43.3 (43.3); C³, C⁹ 33.1 (33.1); C⁴, C⁸ 35.7 (35.7); C⁵, C⁷ 34.0 (34.0); C⁶ 42.9 (42.9); C³ CH₃, C⁹ CH₃ 22.9 (22.8); [M]⁺ 166.

Mass spectra. Methylcyclopentane. Experiment: *rt* [retention time (min)] 5.98; m/z (I_{rel} , %): 84 [M]⁺ (17), 69 (59), 57 (5), 56 (100), 55 (28), 42 (24), 41 (51); published data [18]: 84 [M]⁺ (16), 69 (32), 57 (5), 56 (100), 55 (26), 42 (28), 41 (64).

Methylcyclohexane. Experiment: *rt* 8.13; 98 $[M]^+$ (51), 84 (7), 83 (100), 82 (18), 70 (20), 69 (20), 67 (5), 56 (21), 55 (59), 42 (19), 41 (31); published data [18]: 98 $[M]^+$ (41), 84 (7), 83 (100), 82 (17), 70 (20), 69 (21), 67 (4), 56 (28), 55 (83), 42 (30), 41 (46).

Ethylcyclohexane. Experiment: *rt* 11.85; 112 $[M]^+$ (25), 84 (7), 83 (100), 82 (47), 69 (7), 67 (13), 57 (1), 56 (10), 55 (77), 42 (8), 41 (33); published data [18]: 112 $[M]^+$ (19), 84 (6), 83 (100), 82 (41), 69 (9), 67 (11), 57 (5), 56 (12), 55 (75), 42 (8), 41 (34).

Dimethylcyclohexane. Experiment: *rt* 9.83; 112 $[M]^+$ (29), 97 (100), 84 (2), 83 (5), 70 (8), 69 (17), 56 (15), 55 (63), 43 (6), 41 (19); published data [18] (1,3-dimethylcyclohexane): 112 $[M]^+$ (28), 97 (100), 84 (3), 83 (5), 70 (10), 69 (19), 56 (21), 55 (88), 43 (9), 41 (27).

Methylethylcyclohexane. Experiment: *rt* 14.03; 126 $[M]^+$ (19), 111 (2), 97 (100), 96 (14), 83 (2), 81 (7), 70 (3), 69 (19), 56 (9), 55 (86), 43 (7), 41 (21); published data [18] (*cis*-1-methyl-3-ethylcyclohexane): 126 $[M]^+$ (15), 111 (2), 97 (100), 96 (14), 83 (2), 81 (5), 70 (3), 69 (20), 56 (10), 55 (91), 43 (8), 41 (23).

Trimethylcyclohexane. Experiment: *rt* 11.75; 126 $[M]^+$ (26), 111 (97), 97 (3), 84 (2), 83 (4), 70 (10), 69 (100), 56 (12), 55 (51), 43 (8), 42 (9), 41 (26); published data [18] (*cis,cis*-1,3-trimethylcyclohexane): 126 $[M]^+$ (23), 111 (95), 97 (2), 84 (2), 83 (4), 70 (10), 69 (100), 56 (12), 55 (56), 43 (10), 42 (5), 41 (30).

Tetramethylcyclohexane. Experiment: *rt* 14.82; 140 $[M]^+$ (2), 125 (100), 97 (1), 84 (7), 83 (40), 70 (12), 69 (99), 57 (14), 56 (9), 55 (33), 43 (12), 41 (26); published data [18] (1,1,3,5-tetramethylcyclohexane): 125 (92), 97 (3), 84 (7), 83 (53), 70 (6), 69 (100), 57 (15), 56 (11), 55 (34), 43 (13), 41 (27).

Decalin. Experiment: *rt* 21.55; 138 $[M]^+$ (99), 110 (9), 108 (18), 96 (71), 95 (60), 82 (71), 81 (61), 69 (41), 68 (87), 67 (100), 55 (34), 41 (51); published data [18] (*trans*-decalin): 138 $[M]^+$ (100), 110 (7), 109 (17), 96 (58), 95 (63), 82 (60), 81 (54), 69 (45), 68 (91), 67 (91), 55 (41), 41 (82).

Trimethyldecalin. Experiment: *rt* 29.25; 180 $[M]^+$ (74), 165 (98), 138 (3), 137 (4), 123 (15), 109 (94), 95 (100), 83 (34), 82 (18), 81 (67), 69 (30), 67 (37), 55 (55); published data [18] (3,4,8-trimethyldecalin): 180 $[M]^+$ (74), 165 (97), 138 (5), 137 (6), 123 (21), 109 (94), 95 (100), 83 (40), 82 (21), 81 (70), 69 (30), 67 (39), 55 (68).

Dimethyladamantane. Experiment: *rt* 24.30; 164 [M]⁺ (10), 150 (13), 149 (100), 107 (18), 95 (6), 93 (31), 91 (9), 81 (7), 79 (9), 77 (7), 67 (6), 55 (6); published data [17] (1,4-dimethyladamantane): 164 [M]⁺ (14), 150 (13), 149 (100), 107 (18), 95 (11), 93 (35), 91 (11), 81 (17), 79 (16), 77 (11), 67 (13), 55 (14).

Trimethyladamantane. Experiment: rt 24.67; 178

 $[M]^+$ (8), 164 (13), 163 (100), 150 (1), 149 (2), 135 (3), 121 (8), 107 (48), 93 (10), 91 (9), 79 (7), 77 (6), 55 (8); published data [17] (1,3,5-trimethyladamantane): 178 $[M]^+$ (8), 164 (12), 163 (100), 150 (11), 121 (16), 107 (62), 93 (17), 91 (12), 81 (8), 79 (10), 77 (8), 67 (6), 55 (8).

Tetramethyladamantane. Experiment: *rt* 24.80; 192 $[M]^+$ (5), 178 (14), 177 (100), 163 (2), 135 (3), 121 (42), 107 (13), 95 (6), 93 (5), 91 (7), 81 (3), 79 (5), 77 (5), 67 (4), 55 (9); published data [17] (1,3,5,6-tetramethyladamantane): 192 $[M]^+$ (7), 178 (16), 177 (100), 163 (4), 135 (5), 121 (37), 107 (25), 95 (9), 93 (8), 91 (10), 81 (6), 79 (7), 77 (6), 67 (6), 55 (13).

Tricyclane (see figure, peak *12*). Experiment: *rt* 35.59; 192 [M]⁺ (100), 177 (62), 151 (33), 149 (22), 135 (27), 121 (22), 109 (20), 107 (16), 95 (85), 93 (25), 81 (49), 79 (29), 77 (13), 67 (35), 55 (24).

Tricyclane (see figure, peak *13*). Experiment: *rt* 37.32; 206 $[M]^+$ (100), 191 (70), 165 (15), 149 (18), 135 (44), 121 (19), 109 (61), 107 (17), 95 (72), 91 (16), 81 (43), 79 (26), 67 (34), 55 (33).

To determine active aluminum, a three-necked flask was charged under Ar with 100 mg of Al. Several crystals of iodine were added, and the flask was heated until the iodine completely sublimed and was removed from the vessel. To the resulting activated Al, 50 ml of distilled water was added, and the mixture was analyzed according to [19].

Two three-necked flasks were charged under Ar with 100 mg of Al each. After actvation with iodine, the reaction with 2 ml of CCl_4 was performed in both flasks, and then the reaction with 5 ml of cyclohexane was performed in one of them. After the reaction completion, the resulting mixtures were hydrolyzed with 50 ml of water. The subsequent analysis was performed similarly.

CONCLUSION

The readily available reaction system consisting of activated aluminum metal and halomethane efficiently induces chemical transformations of cyclohexane at $20-60^{\circ}$ C and atmospheric pressure. The major product is an equilibrium mixture of dimethyldecalin isomers; methyl-substituted cyclohexanes and tricyclic compounds are formed in smaller amounts.

- 1. Akhrem, I.S. and Orlinkov, A.V., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1998, no. 5, pp. 771–794.
- Akhrem, I.S., Orlinkov, A.V., Mysov, E.I., and Volpin, M.E., *Tetrahedron Lett.*, 1981, vol. 22, no. 39, pp. 3891–3894.
- 3. Akhrem, I.S., Churilova, I.M., and Vitt, S.V., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2001, no. 1, pp. 78–84.
- Sadykov, R.A., Samokhina, M.G., and Dzhemilev, U.M., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2001, no. 7, pp. 1262–1265.
- Furman, A.A. and Rabovskii, B.G., Osnovy khimii i tekhnologii bezvodnykh khloridov (Fundamentals of Chemistry and Technology of Anhydrous Chlorides), Moscow: Khimiya, 1970.
- Nenitescu, C.D., *Chimie generala*, Bucharest: Technic, 1963.
- Zelinsky, N.D. and Tarasova, E.M., *Lieb. Ann.*, 1934, no. 508, pp. 115–118.
- Doering, W.E. and Schoenewaldt, E.F., J. Am. Chem. Soc., 1951, vol. 73, no. 11, pp. 4578–4580.
- Conn, W.K. and Schneider, A., J. Am. Chem. Soc., 1954, vol. 76, pp. 4578–4580.
- 10. Komarewsky, V.I. and Ipatieff, V.N., J. Am. Chem. Soc., 1934, vol. 56, no. 9, pp. 1926–1928.
- 11. Zelinskii, N.D. and Arbuzov, Yu.A., *Dokl. Akad. Nauk SSSR*, 1941, vol. 30, no. 8, pp. 717–717.
- 12. Thoret-Bauchet, J.P., Mortreux, A., and Petit, F., *J. Mol. Catal.*, 1993, vol. 83, pp. 323–327.
- Gavrilov, B.T., Luksha, V.G., Slobodin, Ya.M., and Kovyazin, V.E., *Zh. Org. Khim.*, 1975, no. 11, pp. 597–600.
- 14. Brodskii, E.S., Lukashenko, I.M., Musaev, I.A., *et al.*, *Neftekhimiya*, 1976, vol. 16, no. 1, pp. 13–15.
- 15. Berman, S.S., Stukanova, L.N., and Petrov, A.A., *Nef-tekhimiya*, 1970, vol. 10, no. 5, pp. 635–641.
- Whitesell, J.K. and Minton, M.A., Stereochemical Analysis of Alicyclic Compounds by ¹³C NMR Spectroscopy, London: Chapman and Hall, 1987.
- 17. Polyakova, A.A., Khramova, E.V., Bagrii, E.I., et al., Neftekhimiya, 1973, vol. 13, no. 1, pp. 9–16.
- Petrov, A.A., Golovkina, L.S., and Rusinova, G.V., Mass-spektry neftyanykh uglevodorodov (Mass Spectra of Petroleum Hydrocarbons), Moscow: Nedra, 1975.
- 19. Charlot, G., Les methods de la chimie analytique. Analyse quantitative minerale, Paris: Masson, 1961, 4th ed.