Organic Chemistry

Oxidative transformations of cyclohexane, methylcyclopentane, and pentane on treatment with superelectrophiles based on polyhalomethane and aluminum halides

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Cyclohexane and methylcyclopentane dimerize into dimethyldecalins on treatment with superelectrophilic systems containing polyhalomethanes (CBr_4, CCl_4, $CHCl_3$) and aluminum halides ($AlBr_3$, $AlCl_3$). At 20 °C, the yields of $C_{12}H_{22}$ hydrocarbons reach 140 mol.% based on the superelectrophile. Under the action of $CBr_4 \cdot 2AlBr_3$ at 20 °C in CH_2Br_2 or without a solvent, *n*-pentane is converted predominantly into lower alkanes (mainly, isopentane). In addition, higher branched C_8—C_{12} alkanes, small amounts of alkylated cyclohexanes, cycloalkenes, dienes, and alkylbenzenes are formed in a total yield of 20—23 % (w/w) based on pentane.

Key words: cyclohexane, methylcyclopentane, *n*-pentane, dimethyldecalins, superelectrophiles, polyhalomethanes, complexes of aluminum halides, oxidative transformations of saturated hydrocarbons, mass spectra.

Transformations of saturated hydrocarbons (isomerization, cracking, oligomerization, cyclization, dehydrogenation, dehydrocyclization, aromatization, *etc.*) play an important role in industrial processes.[1] As a continuation of our studies dealing with the transformations of alkanes and cycloalkanes initiated by superelectrophilic complexes containing polyhalomethanes in combination with aluminum halides,[2,3] we studied the action of these systems on cyclohexane, methylcyclopentane, and *n*-pentane.

Contrary to the publication in which cyclohexane and methylcyclopentane were reported to remain unchanged in the presence of 20—30% (w/w) of $AlCl_3$ at 120—150 °C,[4] it was shown that these cycloalkanes dimerize on treatment with aluminum halide-based systems to give a mixture of dimethyldecalins.[5—7] The formation of the product of cyclohexane dimerization was first observed[5] when it was made to react with cyclohexyl bromide in the presence of $AlCl_3$. Later, the hydrocarbon $C_{12}H_{22}$ was detected upon the reaction of chlorocamphor with $AlBr_3$ in cyclohexane.[6] "Self-alkylation" (dimerization) of methylcyclopentane on treatment with Bu^tCl and $AlCl_3$ has been observed in a study,[7] in which the reactions mentioned above[5—7] were demonstrated to afford the same product, 2,6-dimethyldecalin. Other examples of cyclohexane and methylcyclopentane dimerization have also been reported.[8—11]

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 78—84, January, 2001.

Superelectrophiles based on polyhalomethanes could prove to be efficient initiators of the transformations of cycloalkanes into dimethyldecalins, which are precursors of adamantanes. The possibility of direct adamantization or aromatization of C_6 cycloalkanes under the action of the superelectrophiles in question could not be ruled out either. The transformations of saturated hydrocarbons (including cyclohexane) into adamantanes[8—12] and into aromatic compounds under rigorous conditions are well known.[13] For example, heating of 10 g of cyclohexane with 41 g of $AlBr_3$ for 69 h at 110 °C gave rise to 1.9 g of a mixture of dimethyladamantanes.[12]

Another investigation object, pentane, presented interest from several standpoints. On the one hand, the previously observed transformations of cyclopentane[3] under the action of these superelectrophiles undoubtedly include opening of the five-membered ring. Therefore, certain similarity between the products of transformations of cyclic and aliphatic C_5 hydrocarbons should be expected. On the other hand, since C_5—C_{18} *n*-alkanes are converted into isoalkanes and oligomers with qualitatively similar compositions under the action of superelectrophiles based on polyhalomethanes,[2] one could suggest that the reactions observed for pentane would also be probable for its higher homologs. The adamantization of alkanes requires much energy.[13]

$$C_nH_{2n+2} \longrightarrow C_nH_{2n-4} + 3\ H_2 - Q$$

More extensive oxidation of alkanes to aromatic hydrocarbons is even a more endothermic process,[13] unfavorable even at 500 °C.

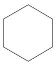
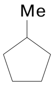
$$C_nH_{2n+2} \longrightarrow C_nH_{2n-6} + 4\ H_2 - Q$$

Nevertheless, high-temperature catalytic transformations of alkanes to aromatic hydrocarbons (aromatization or catalytic reforming) are well known and implemented on an industrial scale.[1d,14] In terms of the ability to form aromatic compounds, hydrocarbons of various classes are arranged in the sequence[1d] cyclohexenes > cyclohexanes > cyclopentanes > alkenes > alkanes. Heating dodecane and squalane with excess $AlBr_3$ at 110—130 °C for 2—5 days[12b] yields small amounts of alkyladamantanes. On heating solid saturated hydrocarbons with aluminum chloride at 210—220 °C for 40 h, a mixture containing 4 to 46% (w/w) of aromatic hydrocarbons was formed. The use of anhydrous aluminum chloride decreases the yields of aromatic hydrocarbons to 2—6 %.[15]

The reactions of hydrocarbons with systems containing polyhalomethanes (CBr_4, CCl_4, $CHCl_3$) in combination with aluminum halides ($AlBr_3$, $AlCl_3$) were carried out in a solution in CH_2X_2 (X = Cl, Br) or without a solvent at 20—60 °C for 0.5—48 h. The structures of products were studied by GC/MS.

On treatment with electrophilic systems $CBr_4 \cdot nAlBr_3$, $CCl_4 \cdot nAlCl_3$, $CHCl_3 \cdot nAlCl_3$ (E, n = 2 or 3) at 20 °C, cyclohexane and methylcyclopentane undergo oxidative dimerization to give isomeric dimethyldecalins (DMD) and, perhaps, their isomers. The reactions were performed without a solvent at the reactant molar ratio [RH] : [E] = (10—20) : 1. Although the reaction mixture is heterogeneous, the yield of $C_{12}H_{22}$ bicycloalkanes based on the superelectrophile is ~25% over a period of 0.5 h; the yield after 2 days is 100—140% (Table 1). Apart from the $CBr_4 \cdot nAlBr_3$ and $CCl_4 \cdot nAlBr_3$ complexes (n = 2 or 3), more readily available systems, $CCl_4 \cdot 2\ AlCl_3$ and $CHCl_3 \cdot 2\ AlCl_3$, are also active in this reaction. However, in the presence of Al_2Br_6 without CBr_4 or CCl_4, no $C_{12}H_{22}$ hydrocarbons can be found after 1 h at 20 °C.

Table 1. Oxidative dimerization of cyclohexane and methylcyclopentane to dimethyldecalins in the presence of superelectrophiles (E) at 20 °C

Run	E	RH	[RH] : [E]	τ/h	Yield (mol.%) based on E
1	$CBr_4 \cdot 2\ AlBr_3$		10 : 1	0.5	17
2	$CBr_4 \cdot 3\ AlBr_3$		10 : 1	0.5	27
3	$CCl_4 \cdot 3\ AlBr_3$		10 : 1	0.5	25
4	Al_2Br_6		20 : 1	0.5	0
5[a]	$CBr_4 \cdot 2\ AlBr_3$		15 : 1	2	24
6	$CBr_4 \cdot 2\ AlBr_3$		20 : 1	24	106
7	$CBr_4 \cdot 2\ AlBr_3$		20 : 1	48	138
8	$CCl_4 \cdot 3\ AlBr_3$		10 : 1	0.5	24
9	$CHCl_3 \cdot 3\ AlCl_3$		10 : 1	0.5	13
10	$CCl_4 \cdot 2\ AlCl_3$		10 : 1	48	97
11	$5\ CCl_4 \cdot AlBr_3$		17 : 1	4	132
12	$5\ CCl_4 \cdot AlCl_3$		17 : 1	4	36
13[b]	$5\ CCl_4 \cdot AlCl_3$		17 : 1	2	150
14[c]	$5\ CCl_4 \cdot AlCl_3$		17 : 1	2	125

[a] In the presence of CH_2Cl_2. The other experiments were performed without a solvent.

[b] At 40 °C.

[c] At 60 °C.

The products of transformation of cyclohexane and methylcyclopentane are virtually the same. The $C_{12}H_{22}$ hydrocarbons formed in these reactions are represented by a large number of isomers. The first six of them (in the order of increasing retention times) account for 92—95% of the total amount of bicyclanes; the major component characterized by the shortest retention time makes 52—60% of the total mixture of isomers. The ratios of chromatographic peaks in the order of increasing retention times corresponding either to individual $C_{12}H_{22}$ hydrocarbons or to their unseparable mixtures in run 3 (see Table 1) are 3.3 : 1 : 0.5 : 0.3 : 0.3 : 0.2; in runs 5 and 10, these ratios are virtually the same, namely, 4 : 1 : 0.5 : 0.3 : 0.3 : 0.1.

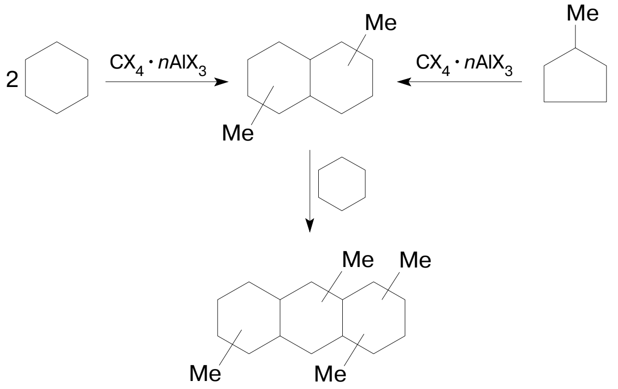
The mass spectrum of each isomer contains a rather intense molecular ion with $[M]^+$ 166 and the same set of peaks of different intensities corresponding to fragment ions typical of DMD (*m/z* 151, 137, 124, 123, 110, 109, 96, 95, 82, *etc.*). These fragment ions are produced upon abstraction of alkyl radicals ranging from CH_3 to C_6H_{11} and olefins from C_3H_6 to C_6H_{12} from the molecular ion.**[16]** The extent of similarity of the observed mass spectra to the spectra reported in standard libraries of mass spectra, NBS 75K and Wiley 138, equals 81—94%.

In our opinion, the major component of the isomer mixture of hydrocarbons with $[M]^+$ 166 having the minimum retention time is a mixture of *cis*,*cis*,*trans*-2,6- and *cis*,*cis*,*trans*-2,7-dimethyldecalins. It has been reported**[16]** that the mass spectra of these two isomers are closely similar to each other; the boiling points of these compounds coincide and the retention times on squalane are equal.**[17]** These compounds are characterized by the shortest retention time among the whole set of geometrical and steric isomers (the only exception is 2,2-DMD; however, its content in the equilibrium mixture of DMD is only 4%).**[17]** It was found that *cis*,*cis*,*trans*-2,6- and *cis*,*cis*,*trans*-2,7-DMD are distinguished by the highest stability among the geometrical and spatial isomers of DMD.**[18]** The composion of the mixture of $C_{12}H_{22}$ bicyclanes formed in these reactions is close to the calculated equilibrium mixture of DMD, 61% of which is a mixture of *cis*,*cis*,*trans*-2,6- and *cis*,*cis*,*trans*-2,7-DMD.**[18]** Previously, we showed**[11]** that 2,6- and 2,7-DMD are the main components of the DMD formed from cyclohexane on treatment with the superelectrophilic complex $AcCl \cdot 2\ AlBr_3$. The high degree of similarity of the mass spectra of the $C_{12}H_{22}$ hydrocarbons under study to the reported DMD, the fact that the component ratio in the resulting mixtures is close to the ratio calculated for an equilibrium DMD mixture, and the enhanced thermodynamic stability of DMD compared to other isomeric bicyclanes provide grounds to believe that at least the main bulk of the $C_{12}H_{22}$ hydrocarbons are DMD. The minor components of these hydrocarbons include 2-ethyldecalin, having the greatest retention index among hydrocarbons with $[M]^+$ 166. The extent of similarity of the mass spectrum of this compound to the mass spectrum of 2-ethyldecalin reported in the Wiley 138 library equals 94%. One of the most intense peaks in its mass spectrum is the peak of an ion with m/z 137 corresponding to the abstraction of the ethyl radical from the molecular ion. Note that the content of 2-ethyldecalin (3%) in the resulting mixture of $C_{12}H_{22}$ hydrocarbons is also close to its content in the equilibrium mixture of DMD.**[18]**

Among other products of transformation of cyclohexane and methylcyclopentane, a hydrocarbon with $[M]^+$ 192 and a series of isomers with a molecular weight of 248 were detected. The mass spectra of hydrocarbons with $[M]^+$ 248 with shorter retention times exhibit a set of fragment ions with close intensities, corresponding to the abstraction of alkyl groups ranging from CH_3 to C_7H_{15} from the molecular ion; the maximum ion has m/z 233 $[M^+ - CH_3]$. Other isomers account for very intense molecular ions. The isomer with $[M]^+$ 248, last in retention time, is responsible for an intense peak with m/z 219, corresponding to the elimination of an ethyl group from the molecular ion. Apparently, hydrocarbons with $[M]^+$ 248 belong to the group of alkylated tricyclanes $C_{18}H_{32}$, both tetramethyl-substituted tricyclanes, present in a predominant amount, and tricyclanes containing ethyl groups. It should be emphasized that oxidative dimerization of cyclohexane and methylcyclopentane in excess cycloalkane proceeds rather selectively giving only traces of trimerization products and other compounds. Conversely, the reaction of cyclohexane with $CBr_4 \cdot 2\ AlBr_3$ in CH_2Br_2 with the molar ratio [RH] : [E] = 5 : 1 results in a low yield of DMD over a period of 30 min. In this case, the reaction mixture contains alkylated cyclohexanes *cyclo*-$C_6H_{11}C_nH_{2n+1}$ (M = 98, 126, 140; n = 1—4), isomeric bromides *cyclo*-$C_6H_{11}Br$, bicyclic alkenes, and dienes ($[M]^+$ 164, 162, 192).

The general scheme of transformations of cyclohexane and methylcyclopentane is presented below.

Scheme 1



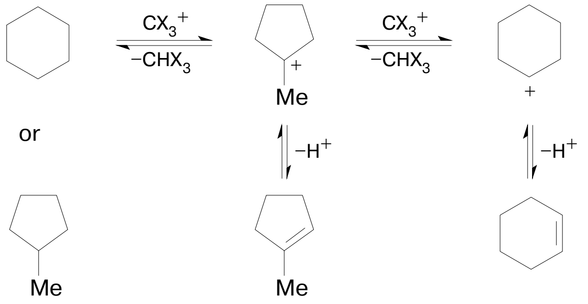
The conjectural mechanism of the observed transformations of C_6 cycloalkanes into bicyclanes $C_{12}H_{22}$ is similar to that proposed previously.**[7—10]** It includes the formation of an active cationic complex (1), generation of the cycloalkylcarbenium ion from cycloalkane (2), addition of the cycloalkylcarbenium ion to the conjugated cycloalkene to give dicycloalkylcarbenium ion (3), rearrangement of this product into thermodynamically stable dimethyldecalinium ion (4), and, finally, the formation of DMD and regeneration of the electrophile (5) (Scheme 2).

Scheme 2

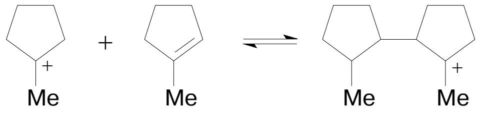
(1) *The formation of the superelectrophilic complex*

$$CX_4 \xrightarrow{AlX_3} CX_3{}^+AlX_4{}^- \xrightarrow{AlX_3} CX_3{}^+Al_2X_7{}^-$$

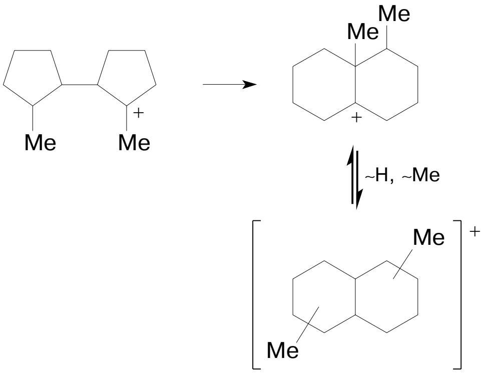
(2) *Generation of the cycloalkylcarbenium ions and conjugated alkenes*



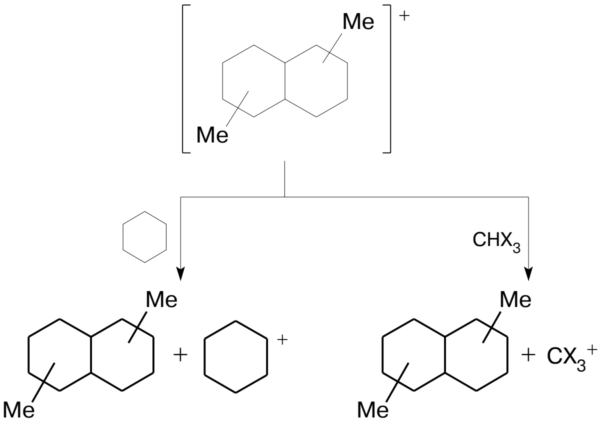
(3) *The formation of the dicycloalkylcarbenium ion*



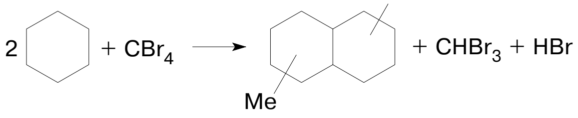
(4) *The formation of the dimethyldecalinium ion*



(5) *The formation of dimethyldecalins and regeneration of electrophilic species*



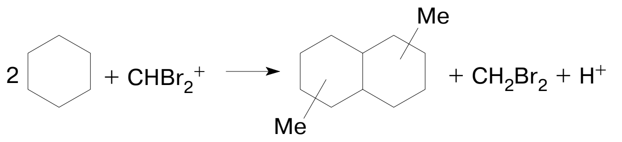
The overall reaction



According to Scheme 2, the formation of one DMD molecule requires two superelectrophile molecules and only one of them can be regenerated. In other words, the maximum possible yield of DMD in the oxidative dimerization reaction should not exceed 100% based on the superelectrophile. The formation of DMD in run 7 (see Table 1) in a yield of more than 100% is due to the fact that CBr_4 reacts with cycloalkane to be reduced to tribromomethane, which is also able (although less efficiently than CBr_3^+) to generate cycloalkylcarbenium ions from cycloalkane in the presence of aluminum halide and thus initiate oxidative dimerization of cyclohexane (Scheme 3).

Scheme 3

$$CHBr_3 \xrightarrow{AlCl_3} CHBr_2^+AlCl_3Br^- \xrightarrow{AlCl_3} CHBr_2^+Al_2Cl_6Br^-$$



Activity of $CHX_3 \cdot 3AlCl_3$ in the dimerization of cyclohexane confirms this conclusion.

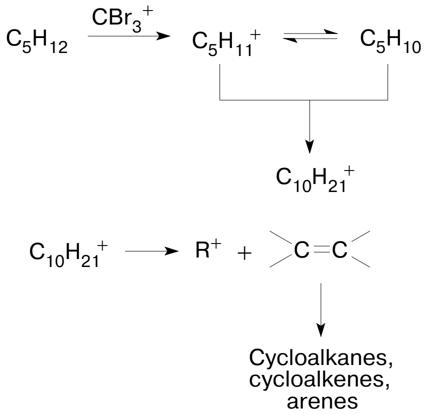
To compare the results obtained here with published data, note that heating of cyclohexane with $AlCl_3$ activated by the products of isooctane cracking at 40—60 °C for 15—20 h gives DMD in 10—15% yields.[8] The HF—BF_3 system promoted by olefins and isoalkanes makes it possible to prepare DMD from cyclohexane in 54% yield at 100 °C over a period of 6 h.[9] Some electrophilic systems are active in this reaction at 20 °C; $Bu^tCl—AlCl_3$,[7] $Cu(Al_2Cl_8)$,[10] and $AcX \cdot 2AlBr_3$[11] are examples. The yields of DMD based on the superelectrophile are 27% after 2 h,[7] 33% after 4 h,[10] and 100% after 1 h.[11]

In conformity with Schemes 2 and 3, dimerization of C_6 cycloalkanes is accompanied by the reduction of initial polyhalomethanes; conversely, aluminum halides function in these reactions as catalysts. We showed that, although systems containing an excess of aluminum halide are more active than equimolar systems, the reactions are not inhibited even by excess CCl_4. The yield of DMD at the $[RH] : [CCl_4] : [AlBr_3] = 17 : 5 : 1$ molar ratio over a period of 4 h at 20 °C is 132% based on $AlBr_3$; in a similar experiment with $AlCl_3$, the yield of DMD is only 36% (see Table 1, runs 11 and 12).

The reactions of methylcyclopentane with the CCl_4—$AlCl_3$ system at 40 and 60 °C afford DMD in 150% and 125% yields, respectively, based on $AlCl_3$ (see Table 1, runs 13, 14). Thus, the catalytic activity of the CCl_4—$AlCl_3$ systems is relatively low. Our attempts to reproduce the results of a publication[10] in which a much higher activity was reported for this system failed.

In this study, we demonstrated that at 20 °C and a $[C_5H_{12}] : [CBr_4 \cdot 2\ AlBr_3]$ molar ratio of 5 or 10, either in CH_2Br_2 or without a solvent, over a period of 30 min to 1 h, pentane undergoes complex oxidative transformations. The light volatile products of these transformations at 20 °C, as has been shown previously,[2a] are lower isoalkanes (C_4—C_6), mainly isopentane. According to GC/MS data obtained in this study, in addition to these isoalkanes, the reaction mixture contained higher branched isoalkanes up to $C_{12}H_{26}$, alkylated cyclohexanes, and unsaturated C_nH_{2n-4} hydrocarbons with m/z 122, 136, 150, 178, and 192. Comparison of the mass spectra of unsaturated hydrocarbons with the spectra presented in the NBS 75K and Wiley 138 libraries of mass spectra allows some of them to be classified as linear branched trienes and some other, as cyclopentadienes (see examples in Fig. 1). It is worth noting that the conversion of pentane also gives slight amounts of C_nH_{2n-6} hydrocarbons, which undoubtedly belong to the series of alkylated benzenes.[19] Table 2 contains the aromatic hydrocarbons formed from pentane at 20 °C and at a $[C_5H_{12}] : [CBr_4 \cdot 2\ AlBr_3]$ molar ratio of 5 : 1 in CH_2Br_2 over a period of 30 min. According to GLC, the total yield of all hydrocarbon products (starting from C_8) is 20—23% (w/w) based on the initial pentane and calculated for a stoichiometric reaction. Thus, *n*-pentane behaves differently from cyclopentane[3] or cyclohexane. When cyclohexane or pentane is treated with an electrophile, alkylation of the conjugate alkene might be the main pathway of transformation of the arising cyclohexyl and pentyl cation.[20] However, due to the different stabilities of *cyclo*-$C_{12}H_{21}^+$ and $C_{10}H_{21}^+$, further transformation pathways are different. The former isomerizes to give the dimethyldecalinium cation, whereas the latter undergoes fragmentation to give a lower alkane and alkene in accordance with the classical scheme. The subsequent transformations of alkenes give rise to cycloalkanes and more unsaturated compounds including aromatic hydrocarbons (Scheme 4).[21]

Scheme 4



Thus, systems containing polyhalomethanes and aluminum halides initiate oxidative dimerization of methylcyclohexane and cyclohexane to DMD in 100—150% yields based on the electrophile. It is significant that not only CBr_4—$AlBr_3$ systems but also markedly more available CCl_4—$AlCl_3$ systems are active in this reaction.

The products of transformation of pentane in the presence of $CBr_4 \cdot 2AlBr_3$ under very mild conditions were found to contain hydrocarbons with different degrees of unsaturation: cyclohexanes, cycloalkenes, cyclo-

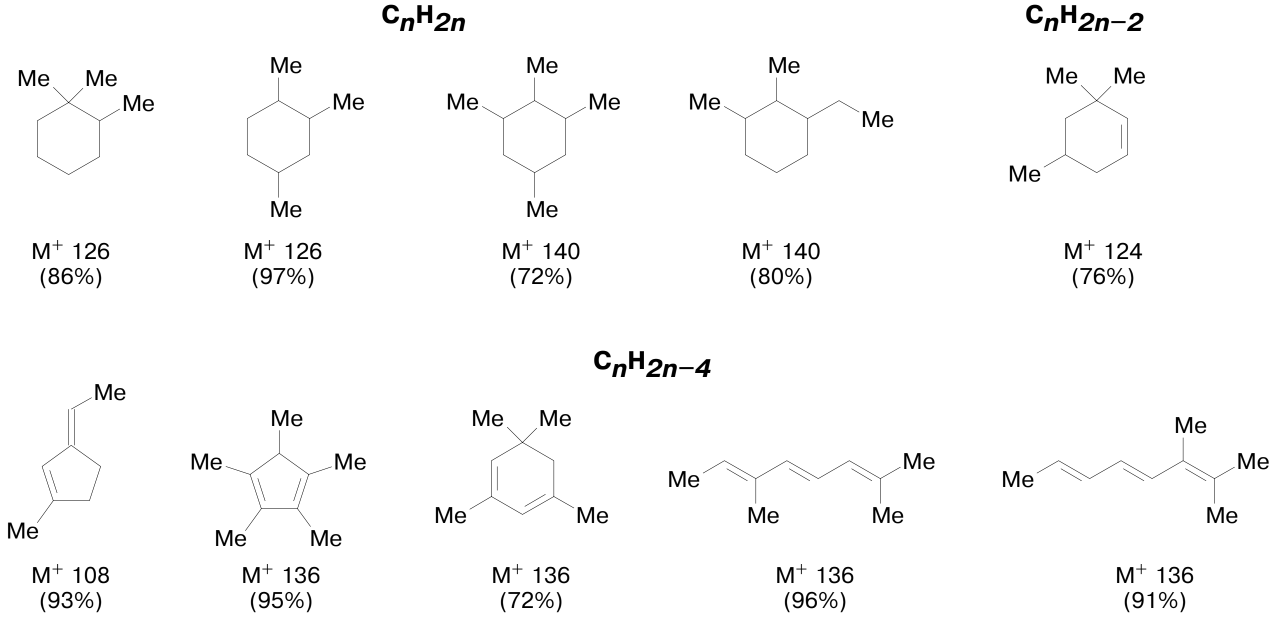
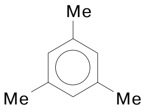
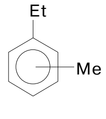
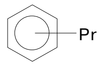
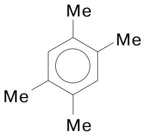
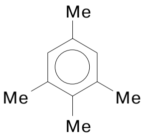
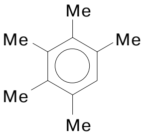
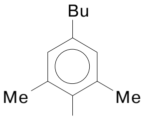
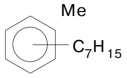
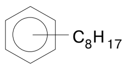


Fig. 1. Cyclic and unsaturated hydrocarbons formed from pentane on treatment with $CBr_4 \cdot AlBr_3$ at 20 °C. The values in parentheses are the extents of similarity of the mass spectra to the mass spectra presented in the NBS 75K and Wiley 138 libraries.

Table 2. Aromatic hydrocarbons in the products of conversion of *n*-pentane in the presence of $CBr_4 \cdot 2\ AlBr_3$ (E) ($[C_5H_{12}]$: [E] = 5 : 1, 20 °C, 30 min)*

Aromatic hydrocarbon	Molecular ion, $[M]^+$	Extent of similarity (%) (for the Wiley 138 library)
	120	94
	120	94
	120	—
	134	91
	134	94
	148	97
	176	83
	176	—
	190	—

* Structures with the most similar mass spectra are presented; in those cases where no data on the extent of similarity are given, we were unable to choose between the isomers, although the fact that the hydrocarbons are aromatic is beyond doubt. The C_3H_7—C_8H_{17} radicals correspond to the overall number of alkyl substituents.

dienes (or linear trienes), and aromatic hydrocarbons. Dehydrocyclization of pentane giving rise to unsaturated hydrocarbons including arenes under so mild conditions has not been reported previously.

Experimental

Saturated hydrocarbons, CCl_4, CBr_4, CH_2Br_2, and anhydrous $AlCl_3$ and $AlBr_3$ (99%) (Aldrich) were used as received; CH_2Cl_2 was refluxed and then distilled from P_2O_5. The reaction mixtures were analyzed by gas chromatography (GC) on a Finnigan 9001 chromatograph with a flame ionization detector (a DB-5.625 30 m×0.3 mm quartz capillary column; helium as the carrier gas) in the linear temperature programming mode. The product yields were determined by GLC with an internal standard (undecane) without a calibration coefficient. GC/MS analysis was performed with a similar capillary column; mass spectra were recorded on an AEI MS 1073 instrument (ionization energy 70 eV).

General procedure. The calculated amounts of anhydrous $AlBr_3$ ($AlCl_3$) and polyhalomethane were placed in a round-bottom flask with a magnetic stirring bar, the required excess of a cycloalkane was added, and the mixture was stirred in the closed flask at the specified temperature for the specified period. The reaction mixture was treated with water and extracted with ether (10 mL × 3), and the organic layer was washed with water to a neutral reaction and dried with Na_2SO_4. The reaction mixture was analyzed by GLC and GC/MS.

Reaction of cyclohexane with the complex $CBr_4 \cdot 2\ AlBr_3$. Carbon tetrabromide (0.81 g, 2.44 mmol) and anhydrous $AlBr_3$ (1.3 g, 4.87 mmol) were mixed in a dry round-bottom flask, and cyclohexane (4.1 g, 48.7 mmol) was added at 20 °C with stirring using a magnetic stirrer. The closed flask with the two-layer reaction mixture was stirred for 48 h at 20 °C.

GC/MS analysis of the reaction mixture (after the standard workup) showed the presence of several isomers with $[M]^+$ 166 and qualitatively similar set of fragment ions differing in intensity. Mass spectrum of the major component with the shortest retention time m/z (I_{rel} (%)): 166 (27), 151 (20), 137 (1), 124 (0.1), 123 (2), 110 (5), 109 (14), 96 (6), 95 (29), 83 (13), 82 (12), 81 (32). The six major $C_{12}H_{22}$ isomers accounted for 92% of the whole sum of isomers; their ratio was 15 : 4 : 2 : 1 : 1 : 0.4. Virtually no other products were formed. The total yield of DMD determined by GLC was 0.56 g (3.4 mmol, 140 mol. % based on $CBr_4 \cdot 2\ AlBr_3$).

Reaction of methylcyclopentane with the complex $CCl_4 \cdot 2\ AlCl_3$. The reaction of anhydrous CCl_4 (0.34 g, 2.21 mmol), anhydrous $AlCl_3$ (0.59 g, 4.42 mmol), and methylcyclopentane (1.87 g, 22.1 mmol) gave, after stirring for 48 h at 20 °C, 0.36 g (2.14 mmol) of a DMD mixture (97 mol.% based on $CCl_4 \cdot 2AlCl_3$). The six major isomers account for 95% of the total mixture of $C_{12}H_{22}$ hydrocarbons. The retention time of the major component is equal to the retention time of the major component formed in the experiment with cyclohexane; however, the fragment ions produced from these two components differ in intensity; in particular, in the present case, the ion with m/z 151 is markedly more intense (perhaps, due to the 2,2-DMD impurity). The ratio of the six major isomers is ~4 : 1 : 0.5 : 0.3 : 0.3 : 0.1. The component with the longest retention time with $[M]^+$ 166, 2-ethyldecalin, is formed in 2% yield. Trace amounts of a hydrocarbon with $[M]^+$ 192 and a large number of isomers with $[M]^+$ 248 were detected.

Reaction of pentane with $CBr_4 \cdot 2\ AlBr_3$. *A.* A mixture of $AlBr_3$ (1.45 g, 5.4 mmol), CBr_4 (0.9 g, 2.7 mmol), and pentane

(1 g, 13.5 mmol) in 1.5 mL of CH_2Br_2 was stirred for 0.5 h at 20 °C. After the usual workup, the total yield of hydrocarbons (according to GLC data) was 0.036 g (20% (w/w) based on pentane equimolar to the superelectrophile introduced in the reaction).

B. In a similar experiment with the same amount of initial compounds, the reaction mixture was treated with water and extracted with 2 mL of CH_2Br_2 and the organic layer was separated. The volatile fraction (b.p. below 100 °C) was distilled *in vacuo* into a trap cooled with liquid nitrogen and analyzed. According to GC/MS (recording of the spectrum started with C_8H_{18}), the volatile fraction contained series of branched aliphatic hydrocarbons C_nH_{2n+2} (n = 8—10, $[M]^+$ 114, 128, 142), cycloalkanes C_nH_{2n} (n = 9, 10; $[M]^+$ 126, 140), and unsaturated hydrocarbons including cycloalkenes C_nH_{2n-2} (n = 9, $[M]^+$ 124, 152) and hydrocarbons C_nH_{2n-4} (n = 8—14, $[M]^+$ 136, 150, 164, 178, 192), which are mainly cyclopentadienes, cyclohexadienes, linear trienes, and aromatic hydrocarbons. Aromatic hydrocarbons account for 12% of the total intensity of the ionic current corresponding to the hydrocarbon products. In addition, compounds with high degrees of unsaturation, C_nH_{2n-8} (n = 17, 18, 20; $[M]^+$ 230, 244, 272), were present; apparently, these were alkylated tetralins or polycyclic compounds. The reaction mixture also contained $CHBr_3$ (the product of reduction of CBr_4) and small amounts of 1,2-dibromoethane and bromides of cyclohexane and bicyclic hydrocarbons.

The reaction of pentane with $CBr_4 \cdot 2AlBr_3$ without a solvent. The reaction of $AlBr_3$ (1.1 g, 4.1 mmol), CBr_4 (0.68 g, 2.06 mmol), and pentane (1.48 g, 20.6 mmol) at 20 °C over a period of 1 h gave, after the usual workup, 0.44 g (23% w/w) of hydrocarbon products, based on pentane equimolar to the amount of the superelectrophilic complex used in the reaction. GC/MS analysis of the reaction mixture showed the presence of alkanes (mainly, branched) C_nH_{2n+2}, where n = 8, 9. The extent of similarity of individual mass spectra of this series of hydrocarbons to the mass spectra reported in the above-mentioned libraries amounts to 60—90%. The mass spectra of the compounds obtained allow them to be classified unambiguously as aliphatic hydrocarbons. The reaction mixture contained isomers of alkylated cycloalkanes C_nH_{2n} (n = 9, $[M]^+$ 126) and unsaturated hydrocarbons C_nH_{2n-2} (n = 9, $[M]^+$ 122) and C_nH_{2n-4} (n = 8—14, $[M]^+$ 122, 136, 150, 164, 178, 192). The mass spectra of some compounds resemble most closely those reported for cyclic dienes (cyclopentadienes and cyclohexadienes); the spectra of other, less numerous compounds correspond more closely to the mass spectra of linear trienes. The products contained aromatic hydrocarbons C_nH_{2n-6} (n = 10, 11; $[M]^+$ 134, 148). Some of the hydrocarbons found in the products of pentane conversion are shown in Fig. 1.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 99-03-33006).

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Received March 24, 2000;
in revised form July 20, 2000