Organic Chemistry

Unusually facile transformations of cyclopentane into cyclohexanes, decalins, and adamantanes

I. S. Akhrem, S. V. Vitt, I. M. Churilova, and A. V. Orlinkov*

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: cmoc@ineos.ac.ru

Cyclopentane is converted into a mixture of cyclohexanes, decalins, and adamantanes (and isomeric cycloalkanes) in overall yields of 18—31% (w/w) under the action of superelectrophilic complex $CBr_4 \cdot 2AlBr_3$ either in CH_2X_2 (X = Br, Cl) or without a solvent at 20 °C.

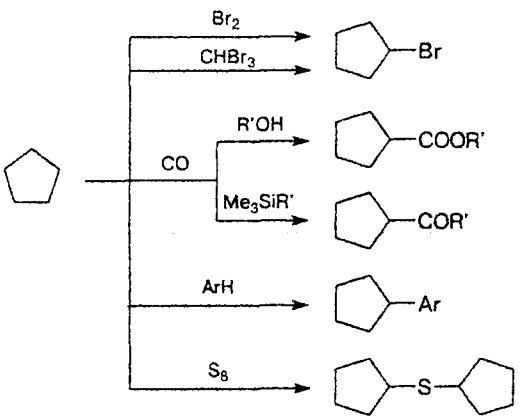
Key words: cyclopentane, cyclohexanes, decalins, adamantanes, tricyclanes, superelectrophilic complex $CBr_4 \cdot 2AlBr_3$, cyclooligomerization, GLC—MS analysis.

Previously we reported that in the presence of superelectrophilic complexes based on polyhalomethanes and aluminum bromide,[1] cyclopentane is converted into the functionalization products[2] shown in Scheme 1.

In this study, we describe the transformations of cyclopentane into mono- and polycyclic hydrocarbons.

The reactions of cyclopentane with the superelectrophilic complex $CBr_4 \cdot 2AlBr_3$ (E) were carried out without a solvent or in solutions in CH_2X_2 (X = Cl, Br) at 20 °C at a $[C_5H_{10}] : [E]$ molar ratio of 10 or 5 over a period of 0.5—2 h. Study of the volatile reaction products by GLC—MS showed that alkylcyclohexanes, decalins, and adamantanes are the major products of the transformations of cyclopentane. Simultaneously, small amounts of cyclopentyl bromide (3%), traces of cyclohexyl bromide and methylcyclopentyl bromide, and some other products are formed. The reactions are accompanied by exhaustive reduction of CBr_4 to $CHBr_3$.

Scheme 1



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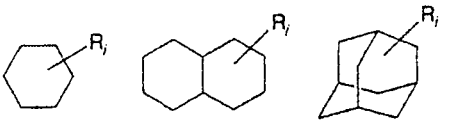
Determination of the reaction products by GLC—MS analysis. Semiquantitative group analysis of hydrocarbons

Analysis of the reaction mixtures using high-performance capillary columns and both flame ionization and mass spectral detection showed that the number of chromatographic peaks (at a level exceeding 0.1% of the overall ionic current) is 50 to 150.

The product structures were determined and the mixture components were assigned to saturated or unsaturated mono-, bi-, tricyclic compounds, *etc.* based on the fairly substantiated assumptions that the molecular ions of cyclanes should be rather stable and that their spectra should contain characteristic ions of the $[M - Me]^+$, $[M - Et]^+$, *etc.* types, which confirm the validity of the selection of molecular ions. The well-known regularities of fragmentation of mono-, bi-, and tricyclic compounds were also taken into account.[3] In all cases, the mass spectra of the products were compared with the mass spectra in the standard libraries, NBS 75K and Wiley 138.

Due to limitations of library identification, the spectra were directly interpreted in all cases; to increase the reliability of the group assignment, the reconstruction of ionic currents was carried out. It became possible to distinguish groups of isomers with close retention parameters and to follow the general trend in the distribution of the homologs by their retention values. Examples illustrating the distribution of the molecular ions of hydrocarbons with various numbers of rings are given in Figs. 1—4.

The GLC—MS data indicate that 80—90% of the products of the transformation of cyclopentane at 20 °C are three types of hydrocarbons, namely monocyclanes C_nH_{2n} with $n = 7—10$ (**I**), bicyclanes C_nH_{2n-2} with $n = 10—16$ (decalins, **II**), and tricyclanes C_nH_{2n-4} with $n = 10—21$ (adamantanes, **III**).



I **II** **III**

R_i are one or several alkyl radicals

In addition to the above-mentioned products, cyclic hydrocarbons of the general formula C_nH_{2n-6} (**IV**) are produced; they form molecular ions with m/z 232, 246, 260, 274, and 288.

The hydrocarbons C_nH_{2n} were identified as methylated cyclohexanes (type **I**) relying on the high degree of similarity (91—97%) of the spectra of the compounds under study with the spectra of methylcyclohexanes, available from the libraries. The formation of *trans*-decalin (type **II**) was proved by the fact that the mass spectra and the retention time coincide with those of an authentic sample of *trans*-decalin. The facts that *trans*-decalin is the major (75%) or the only $C_{10}H_{18}$ hydrocarbon and that the mass spectra of its homologs $C_{11}H_{20}$ and $C_{12}H_{22}$ are close to the library spectra of methyldecalins provide grounds for considering decalins as the main components of the C_nH_{2n-2} hydrocarbon products (type **II**). Analysis of the mass spectra of the C_nH_{2n-4} hydrocarbons formed in the reactions and the known data on the thermodynamic stability of the adamantane polyhedron indicates that the main bulk of

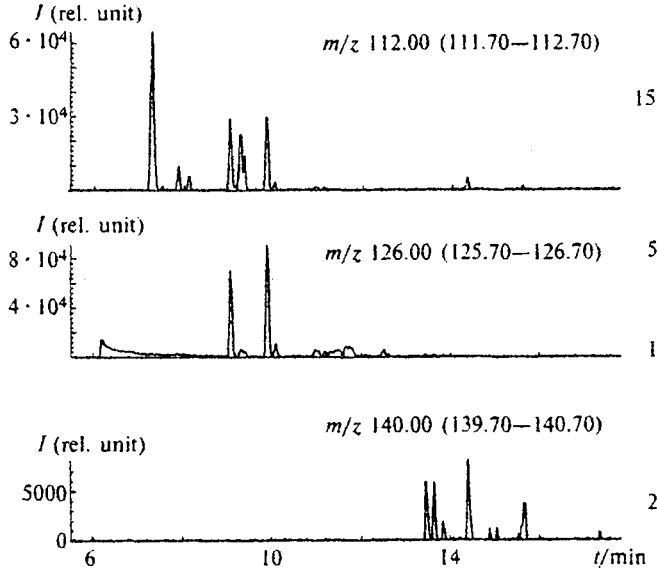


Fig. 1. Distributions of the molecular ions of cyclohexanes **I**.

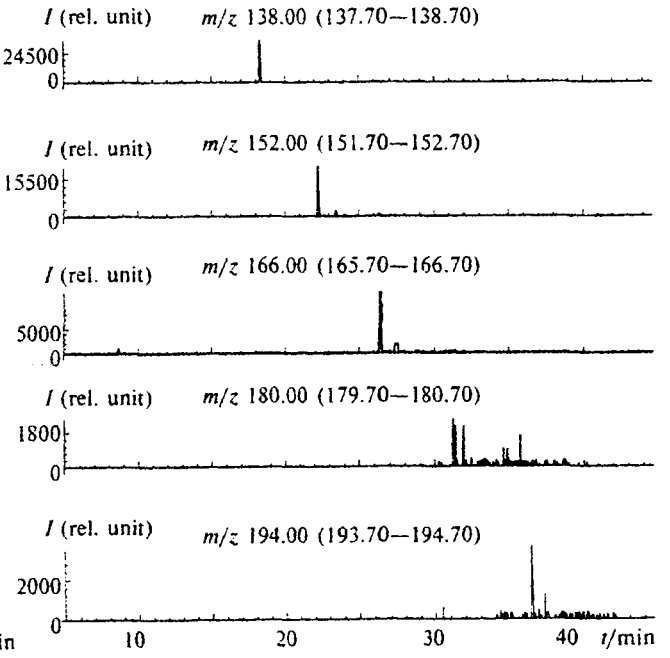


Fig. 2. Distributions of the molecular ions of bicyclanes **II**.

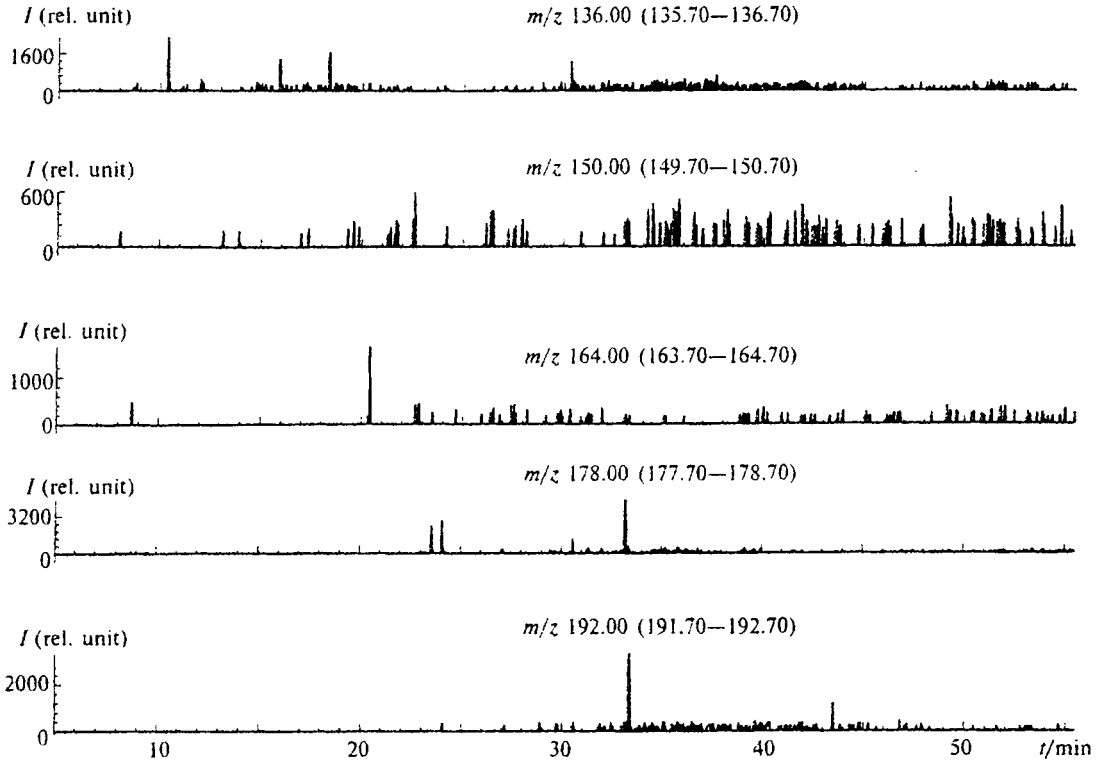


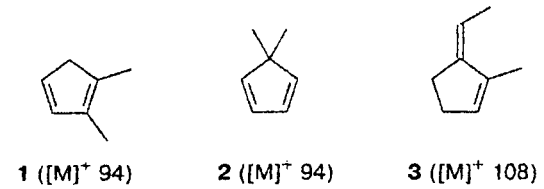
Fig. 3. Distributions of the molecular ions of tricyclanes **III**.

C_nH_{2n-4} hydrocarbons are adamantanes. However, formation of small amounts of nonadamantane tricyclanes having the same molecular and fragment ions as adamantanes also cannot be ruled out.[4]

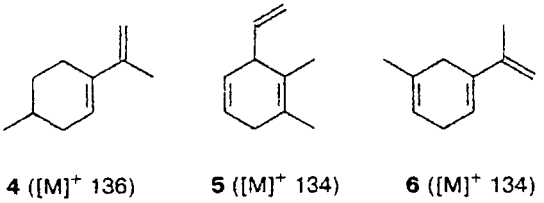
The conclusion that cyclohexanes, decalins, and adamantanes is the major products of the transformation of cyclopentane is consistent with the known data on the thermodynamic stability of these types of hydrocarbons and on their formation from saturated hydrocarbons on treatment with electrophilic reagents at elevated temperatures.[5]

In addition to saturated cyclanes of types **I**—**III**, we detected small amounts of unsaturated cyclic hydrocarbons C_nH_{2n-4} (C_7—C_{10}); for some of these compounds, library search gives the cyclopentadiene (**1**—**3**) and cyclohexadiene (**4**) structures, presented below, with a degree of similarity of 81—91%. The mass spectra of the C_nH_{2n-6} hydrocarbons ($C_{10}H_{14}$, *m/z* 134 $[M]^+$; $C_{11}H_{16}$, *m/z* 148 $[M]^+$), which are also produced in minor amounts, are close to the spectra of cyclohexadienes with an exocyclic double bond, for example, hydrocarbons **5** and **6** (the degree of similarity is 90%), rather than to the spectra of isomeric alkylbenzenes.

In the "heavier" (having longer retention times) zone of the reaction mixture, we found a homologous series of hydrocarbons that have the same molecular formula, C_nH_{2n-6}, as hydrocarbons **5** and **6** (n = 16—21) but exhibit a fundamentally different fragmentation pattern. The mass spectra of hydrocarbons of this group (type **IV**) contain some fragment ions typical of tricyclanes of the adamantane type. However, unlike adamantanes, whose molecular ions are prone to split off alkyl groups, in the case of type **IV** hydrocarbons, both alkyl and alkenyl groups are eliminated. Therefore, we suggest that hydrocarbons of this series are either alkylalkenyltricyclanes (adamantanes) or cycloalkyladamantanes. The fraction of hydrocarbons of type **IV** in the reaction products varies from 2 to 12%.



1 ($[M]^+$ 94) **2** ($[M]^+$ 94) **3** ($[M]^+$ 108)



4 ($[M]^+$ 136) **5** ($[M]^+$ 134) **6** ($[M]^+$ 134)

The total yield of cyclic products was determined by GLC using an internal standard (undecane) without taking into account a calibrating coefficient. The ratios

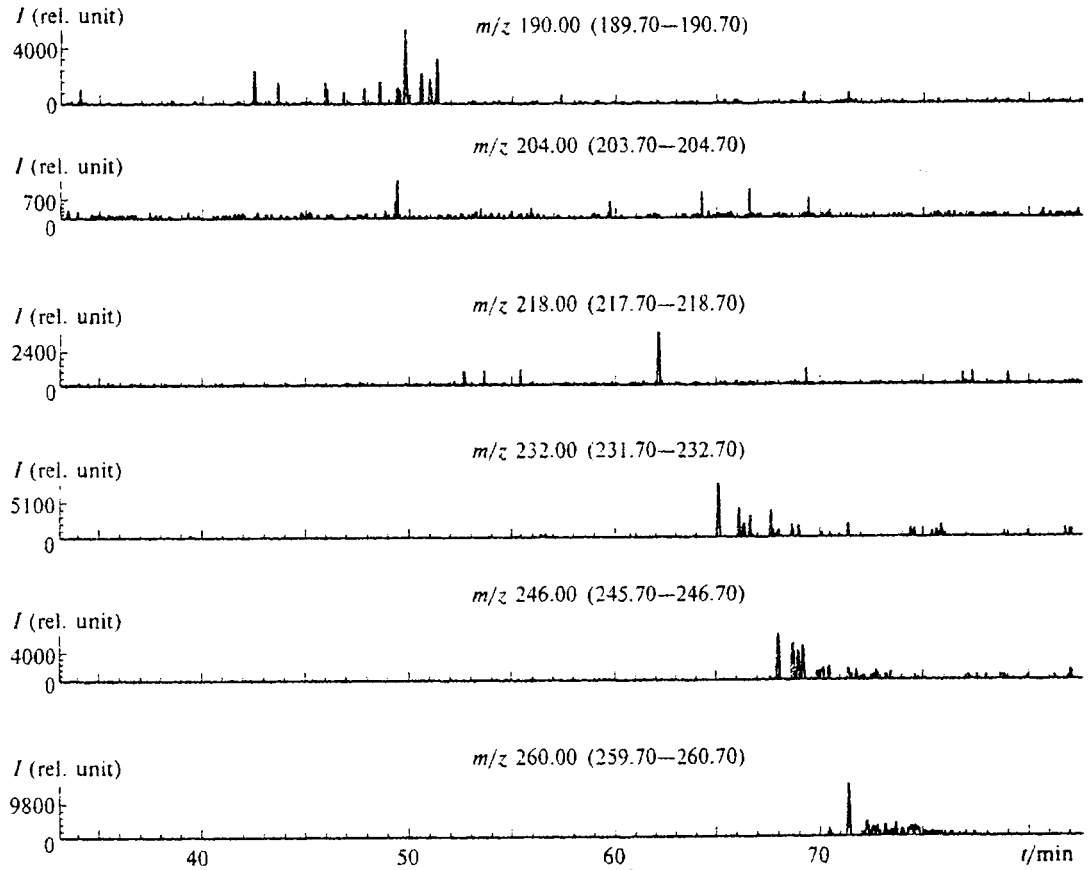


Fig. 4. Distributions of the molecular ions of the C_nH_{2n-6} cyclanes (**IV**).

of various classes of hydrocarbons as functions of the reaction conditions were found by TIC (total ionic current) GLC—MS analysis under standard conditions of chromatography and scanning, also without a calibrating coefficient.

Data on the relative concentrations of hydrocarbons found by integration of GLC and GLC—MS chromatograms differed, on the average, by 10—20% in either direction. The substances present in nonresolved chromatographic areas (nonresolved peaks) were included in the quantitative determination list only if the structure of the major component of a nonresolved peak was beyond doubt. The total concentration of substances not included in any group due to the difficulty in the interpretation of the spectrum or obviously nonindividual character of the corresponding mass spectrum did not exceed 10% of the total amount.

Results and Discussion

The total yield of cyclic hydrocarbons **I**—**IV** formed on treatment of cyclopentane with $CBr_4 \cdot 2AlBr_3$ at 20 °C in CH_2Br_2 or without a solvent is 18—31% (w/w) based on the weight of cyclopentane equivalent to the weight of the superelectrophile taken in the reaction and determined from the ratio N/m, where N is the weight of the starting cyclopentane and m is the $[C_5H_{10}] : [E]$ molar ratio. The total yield of the higher cyclanes in the reaction carried out in CH_2Cl_2 is lower, apparently due to the fast halogen exchange between CH_2Cl_2 and $AlBr_3$, resulting in the transformation of the latter into less reactive $AlCl_3$. The qualitative composition of the reaction products at 20 °C (Table 1) is rather close. However, the product ratio depends on the reaction conditions.

It can be seen from Table 1 that, as the weight of the superelectrophilic complex and the reaction duration increase (from entry *1* to entry *3*), the amount of monocyclic compounds decreases 2.1-fold and that of higher cyclic hydrocarbons increases 4.4-fold. The ratio of bicyclanes to tricyclanes changes insignificantly. The reaction carried out without a solvent not only gives products in a higher total yield but also results in a much greater weight ratio of monocyclanes to higher cyclic C_nH_{2n-6} hydrocarbons; 100 : 1 (see Table 1, entry *4*) instead of 12 : 1 (entry *1*).

The distribution of the resulting hydrocarbons over the number of C atoms shows a clear tendency for predominance of C_9, C_{12}, C_{14}, C_{17}, and C_{21} compounds, whereas C_{11}, C_{13}, C_{15}, and C_{19} species correspond to minima on the distribution plot (Fig. 5).

Table 1. Total yields and ratios of higher cyclanes in the products of transformation of cyclopentane under the action of the superelectrophile $CBr_4 \cdot 2AlBr_3$ (E) at 20 °C[a]

Entry	$[C_5H_{10}] : [E]$ molar ratio	t/h	Total yield of cyclanes I—IV (% (w/w))[b]	Contents of cyclanes I—IV in the mixture of hydrocarbon products (% (w/w))[c]			
				I	II	III	IV
1	10	0.5	18	31	40	27	2.5
2	5	0.5	31	25	42	24	9
3	5	2.0	27	15	47	26	12
4	10	1.0	22	41	39	19	0.41
5[d]	5	0.5	11	—	—	—	—

[a] Entries *1—3* were carried out in CH_2Br_2, entry *4* was performed without a solvent, and entry *5* was performed in CH_2Cl_2 ([E] = 2 mmol per mL of the solvent).
[b] The yields determined by GLC are expressed in % (w/w) based on the weight of cyclopentane equimolar to the superelectrophile taken, *i.e.*, based on N/m, where N is the weight of the initial cyclopentane sample used in the reaction, $m = [C_5H_{10}] : [E]$.
[c] The distribution of cycloalkanes was determined based on the intensity of the ionic current.
[d] The content of cycloalkanes was not determined.

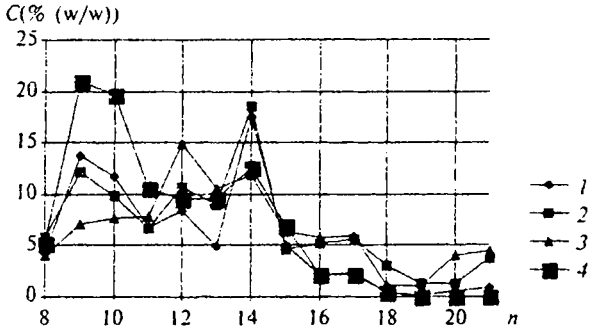
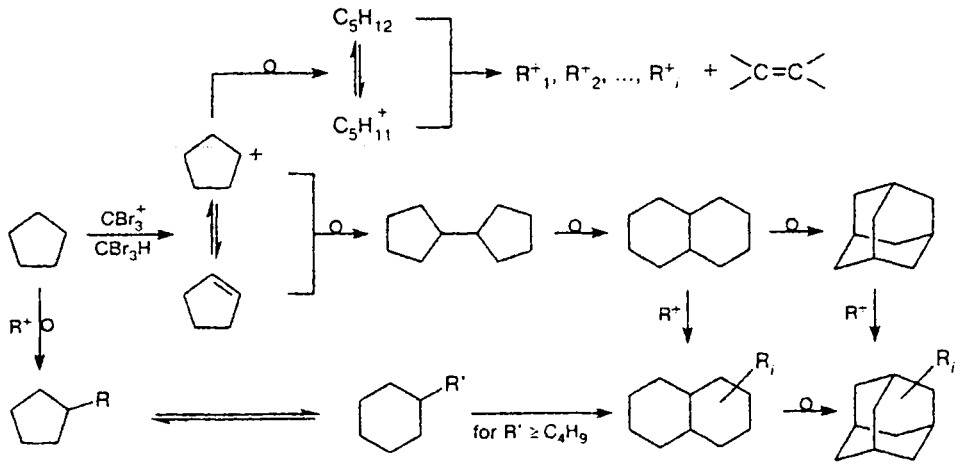


Fig. 5. Contents of cyclanes (C) in the hydrocarbon mixture *vs* the number of C atoms (n) in entries *1—4*.

It can be assumed that the first step of the transformations in question (as in the reactions given in Scheme 1) is abstraction of a hydride ion from the cyclopentane molecule to give a cyclopentyl cation. This process is accompanied by reduction of the tribromomethyl cation. In fact, CBr_4 is entirely consumed during the reaction. Having added the Br^- anion, the cyclopentyl cation is converted into cyclopentyl bromide. Yet another pathway of transformation of the cyclopentyl cation includes the attack of cyclopentene, equilibrated with it, and apparently gives rise to dicyclopentyl and then to decalin and adamantane, which should also be accompanied by the reduction of CBr_4. In addition to the processes involving the formation of C—C bonds, opening of the cyclopentane ring occurs; this yields pentyl cations in equilibrium with pentenes. Thus, cyclopentane also acts as a hydrogen acceptor in oxidative cyclooligomerization of cyclopentane. The pentyl cations and pentenes start a series of alkyl cations and olefins, which alkylate cyclic compounds. The observed products are, apparently, the result of a set of numerous reactions involving formation and cleavage of the C—C bonds. The driving force of these reactions is the formation of the thermodynamically most stable hydrocarbons (Scheme 2).

Scheme 2



Previously,[6] it has been reported that alkyladamantanes are formed, in addition to slight amounts of decalins and C_7—C_9 alkylcyclohexanes, on heating dicyclopentyl with $AlBr_3$—Bu^tBr at 160 °C for 10 h ($RH : AlBr_3 : Bu^tBr = 1 : 1 : 0.3$). Under similar conditions, cyclopentane also gives alkyladamantanes.[7] Syntheses of decalincarboxylic acids by carbonylation of cyclopentanol in H_3PO_4 (125 °C, CO pressure 100 atm)[8] or carbonylation of cyclopentene in H_2SO_4 (CO pressure 80 atm) or on treatment with HCOOH (under atmospheric pressure)[9] have been reported. Apparently, these reactions involve the cyclopentyl cation and cyclopentene. Opening of the cyclopentane ring under the action of FSO_3H—SbF_5 and HF—SbF_5 at −10 °C to give a *tert*-pentyl cation has been described previously.[10] The considerable interest in the transformations of saturated hydrocarbons into alkylated bicyclic compounds and adamantanes, which are parent compounds for the preparation of valuable biologically active products, polymers, and compounds important for industry, has stimulated the search for active systems initiating these transformations. To the best of our knowledge, we were the first to perform transformations of this type under so mild conditions.

Experimental

GLC—MS analysis was carried out on an AEI MS-1073 instrument (a 50-m long DB-5 quartz capillary column with an inner diameter of 0.32 mm, layer thickness 0.5 μm, programmed temperature variation from 50 to 280 °C at a rate of 2 deg min^{-1}, EI, ionization potential 70 eV, ion source temperature 220 °C; scanning rate 1 mass decade s^{-1}). Computer processing of the signal was carried out using software developed by MS-service (Moscow).

Quantitative analysis of the reaction mixtures was carried out by gas chromatography on a Finnigan 9001 chromatograph with a flame ionization detector (a 30-m long DB-5.625 quartz capillary column with an inner diameter of 0.3 mm, helium as the carrier gas, programmed temperature variation from 50 to 200 °C at a rate of 8 deg min^{-1} and from 200 to 310 °C at a rate of 12 deg min^{-1}.

General procedure. Anhydrous $AlBr_3$ (2 mmol), CBr_4 (1 mmol), and 0.5 mL of a solvent (CH_2Br_2 or CH_2Cl_2) were placed in a round-bottom flask equipped with a magnetic stirrer and a Dewar reflux condenser, the mixture was stirred until the superelectrophilic complex dissolved, and cyclopentane (5 or 10 mmol) was added. The mixture was stirred at 20 °C for the period of time indicated in Table 1 and poured into water, the products were extracted with ether, and the organic layer was washed with water to neutral reaction and dried with Na_2SO_4. According to GLC, the reaction of cyclopentane (0.36 g, 5 mmol) with $CBr_4 \cdot 2AlBr_3$ (1 mmol) in 1 mL of CH_2Br_2 for 2 h (entry *3*) gave 0.02 g of higher cycloalkanes (27% (w/w) with respect to the amount of cyclopentane equimolar to the superelectrophile taken).

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