Organic Chemistry

Functionalization of saturated hydrocarbons by aprotic superacids
4.* Ionic bromination of ethane and other alkanes and cycloalkanes with molecular bromine in the presence of systems based on polyhalomethanes and AlBr3 under mild conditions

I. S. Akhrem,* A. V. Orlinkov, L. V. Afanas'eva, and M. E. Vol'pin

*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085*

Aprotic organic superacids $CBr_4 \cdot 2AlBr_3$, $CBr_4 \cdot AlBr_3$, $CHBr_3 \cdot 2AlBr_3$, $CCl_4 \cdot 2AlBr_3$, and $C_6F_5CF_3 \cdot 2AlBr_3$ efficiently catalyze the bromination of alkanes and cycloalkanes with Br_2. Ethane is selectively brominated at 55—65 °C to give mostly 1,2-dibromoethane (stoichiometric reaction). Propane, butane, cyclopentane, cyclohexane, and methylcyclopentane react with Br_2 at −40 to −20 °C with good selectivity affording monobromides in high yields (catalytic reactions).

Key words: alkanes, cycloalkanes, ionic bromination; polyhalomethanes, aluminum halides complexes, aprotic superacids.

We have shown previously that polyhalomethanes combined with $AlBr_3$ efficiently initiate transformations of alkanes and cycloalkanes under mild conditions. This permits them to be regarded as aprotic organic superacids.[2] These systems are efficient toward cracking and oligomerization of n-alkanes, isomerization of n-butane and n-pentane into the corresponding isoalkanes; ionic bromination of propane, cyclopentane, and adamantane with $CHBr_3 \cdot AlBr_3$ to give the corresponding monobromides;[2] carbonylation of cyclopentane,[3] methylcyclopentane, and cyclohexane with carbon monoxide,[4] and other processes.

In this work we report on the ionic bromination of alkanes and cycloalkanes with molecular bromine in the presence of the polyhalomethane—$nAlBr_3$ systems.

The ionic bromination of isoalkanes and cycloalkanes with Br_2 in the presence of $AgSbF_6$ was described for the first time by Olah.[5] This reaction involving isobutane yields mostly monobromide, while isopentane is converted predominantly into dibromides. In the case of cyclopentane and cyclohexane, the corresponding monobromides are formed in low yields (5—27 % based on the catalyst). The formation of dibromides has also been observed in the bromination of isoalkanes in the presence of SbF_5 or of the HSO_3F—SbF_5 superacidic system (see Ref. 6). Bromination of isopentane afforded

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* For Part 3, see Ref. 1

Table 1. Ionic bromination of ethane in the presence of $CBr_4 \cdot 2AlBr_3$ at 55—65 °C

Run	$[C_2H_6] : [Br_2] :$ $: [CBr_4 \cdot 2AlBr_3]$	t/h	Yields (mol. %) of products based on Br_2 [on $CBr_4 \cdot 2AlBr_3$]	
			C_2H_5Br	$1,2-C_2H_4Br_2$
1[a]	4.7 : 0 : 1.0	6	[60]	—
2[a]	3.0 : 1.1 : 1.0	6	5.5 [10]	78 [85]
3[a]	5.0 : 1.0 : 1.0	18	5 [10]	104 [104]
4[a]	4.0 : 2.0 : 1.0	6	2.5 [10]	66 [132]
5[a]	12.0 : 4.0 : 1.0	20	Traces	26 [105]
6[b]	7.0 : 1.0 : 1.0	16	11 [22]	69 [69][e]
7[c]	2.0 : 1.0 : 1.0	3	3 [6]	17 [17][f]
8[a]	3.0 : 1.0 : 1.0 $(Al_2Br_6)^d$	6	0	0

[a] The experiments were carried out without a solvent in tubes under an ethane pressure of 45 atm.
[b] In tubes, in CH_2Br_2.
[c] In an atmosphere of ethane.
[d] The reaction was carried out in the presence of the Br_2—Al_2Br_6 system (without CBr_4).
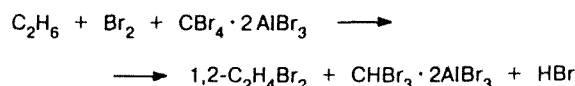[e] 68 % of $CHBr_3$ (based on CBr_4) and 3 % of unreacted CBr_4 were found.
[f] In addition, $1,1,2,2-C_2H_2Br_4$ was formed in a 53 % yield based on Br_2 (27 % based on $CBr_4 \cdot 2AlBr_3$).

1,2-dibromo-2-methylbutane, while bromination of isobutane gave a mixture of isobutyl bromide and 1,2-dibromo-2-methylpropane. A similar mixture was obtained from isooctane, which underwent fragmentation under the reaction conditions. The yields of bromides were not reported in Ref. 6.

The complexes $AcBr \cdot 2AlX_3$ (X = Cl, Br)[7] are known to catalyze efficiently the bromination of the C_4—C_7 n-alkanes, cyclopentane, cyclohexane, and other saturated hydrocarbons, which affords predominantly (or exclusively) monobromides.[8] It was found that $AlBr_3$ in CH_2Br_2 also exhibits an appreciable activity in the bromination of alkanes and cycloalkanes, although its efficiency is substantially lower than that of the $AcBr \cdot 2AlBr_3$ complex (see Ref. 8).

Testing of superacidic systems based on polyhalomethanes as catalysts for the ionic bromination has shown that they exhibit higher activities than the $RCOX \cdot 2AlBr_3$ systems (and, correspondingly, than $AlBr_3$). In addition, reactions occur more selectively, whereas in the presence of the systems based on acyl halides, side carbonyl-containing products are also formed. It is also significant that the use of $CBr_4 \cdot 2AlBr_3$ as the catalyst made it possible to carry out for the first time the ionic bromination of ethane under mild conditions. Ethane reacts with Br_2 at 55—65 °C in the presence of $CBr_4 \cdot 2AlBr_3$ either in CH_2Br_2 or without a solvent* to
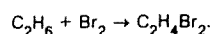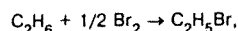
* When $[Br_2] \geq [CBr_4 \cdot 2AlBr_3]$, a homogeneous solution is formed.

give 1,2-dibromoethane as the major product and minor amounts of ethyl bromide.

$$C_2H_6 + Br_2 + CBr_4 \cdot 2AlBr_3 \longrightarrow$$
$$\longrightarrow 1,2-C_2H_4Br_2 + CHBr_3 \cdot 2AlBr_3 + HBr$$

In the stoichiometric reaction ($[CBr_4 \cdot 2AlBr_3]$ = $[Br_2]$) without a solvent, bromine is completely absorbed over a period of 18 h. The overall yield of the products of bromination is 100 % based on the starting Br_2 (Table 1, run 3). This fact indicates that both atoms of a Br_2 molecule are formally involved in the products of bromination.* The reaction carried out under the same conditions for 6 h yields the same bromides with an overall yield of 84 % based on Br_2 (see Table 1, run 2). An increase in the $[Br_2] : [CBr_4 \cdot 2AlBr_3]$ molar ratio leads to a decrease in the efficiency of bromination (see Table 1, runs 4 and 5); when $[Br_2] : [CBr_4 \cdot AlBr_3] = 4 : 1$, the yield of the products based on Br_2 is as low as 26 %. The highest yield of bromination products does not exceed 1.5 moles per mole of CBr_4. The course of the reaction of ethane with Br_2 in CH_2Br_2 is qualitatively similar to that of the reaction without a solvent; however, the [EtBr] : $[C_2H_4Br_2]$ ratio is higher in the former case (see Table 1, runs 6 and 3).

Bromination of ethane also occurs through the action of the $CBr_4 \cdot 2AlBr_3$ superacidic system in the absence of Br_2. Monobromide C_2H_5Br being formed in this case as the only product (see Table 1, run 1). Conversely, the reaction of Br_2 with ethane in the presence of only $AlBr_3$ (instead of $CBr_4 \cdot 2AlBr_3$) under similar conditions does not occur (see Table 1, run 8). It will be shown below that ethane differs markedly in this respect from more active higher alkanes and cycloalkanes, which slowly react with Br_2 in the presence of $AlBr_3$. The reactions of ethane bromination considered above were carried out in tubes (the ethane pressure amounted to ~45 atm). We found that the bromination of ethane with molecular bromine in the presence of $CBr_4 \cdot 2AlBr_3$ can also be performed at an atmospheric pressure of ethane; however, the composition of products differs markedly from that observed in the reactions carried out under an elevated pressure. At an atmospheric pressure of ethane, three products are formed over a period of 3 h, namely, C_2H_5Br, $1,2-C_2H_4Br_2$, and $1,1,2,2-C_2H_2Br_4$ in a molar ratio of 1 : 3 : 5, their overall yield based on Br_2 being 73 % (see Table 1, run 7). The ratio of mono-, di-, and tribromides is very sensitive to experimental conditions; however, the qualitative composition of the products remains invariable.

* The yields of bromination products were calculated according to the following formal equations:

$$C_2H_6 + 1/2 \, Br_2 \rightarrow C_2H_5Br,$$
$$C_2H_6 + Br_2 \rightarrow C_2H_4Br_2.$$

Table 2. Bromination of alkanes and cycloalkanes catalyzed by the polyhalomethane—2AlBr$_3$ superacids

Run	RH	Catalyst (Cat)	[RH] : [Br$_2$] : [Cat]	T/°C	t/h	Product	Yield (mol. %) based on Br$_2$ [on the Cat]
1	C$_3$H$_8$	CBr$_4$ · 2AlBr$_3$	10 : 2 : 1	−20	3	Pr^{i}Br	48 [96]
						C$_3$H$_6$Br$_2$	Traces
2	C$_3$H$_8$	CBr$_4$ · 2AlBr$_3$	10 : 2 : 1	−10	3	Pr^{i}Br	77 [154]
						C$_3$H$_6$Br$_2$	12 [24]
3	C$_3$H$_8$	CBr$_4$ · 2AlBr$_3$	10 : 4 : 1	0	3.5	Pr^{i}Br	18 [74]
						C$_3$H$_6$Br$_2$	17 [70]
						C$_3$H$_5$Br$_3$	36 [96]
4	n-C$_4$H$_{10}$	CBr$_4$ · 2AlBr$_3$	10 : 4 : 1	−20	2	BuBr^a	105 [425]
5	n-C$_4$H$_{10}$	AcBr · 2AlBr$_3$ [6]	10 : 4 : 1	−20	3	BuBr^a	40 [161]
6	n-C$_4$H$_{10}$	Al$_2$Br$_6$	10 : 4 : 1	−20	3	BuBr	24 [96]
7	n-C$_4$H$_{10}$	CBr$_4$ · 2AlBr$_3$	25 : 10 : 1	−20	4	BuBr	37 [370]
8	cyclo-C$_5$H$_{10}$	CBr$_4$ · 2AlBr$_3$	10 : 4 : 1	−20	1	cyclo-C$_5$H$_9$Br	71 [285]
9	cyclo-C$_5$H$_{10}$	CCl$_4$ · 2AlBr$_3$	10 : 4 : 1	−20	0.8	cyclo-C$_5$H$_9$Br	51 [203]
10	cyclo-C$_6$H$_{12}$	CBr$_4$ · 2AlBr$_3$	10 : 4 : 1	−20	1.17	cyclo-C$_6$H$_{11}$Br	75 [301]
11	cyclo-C$_6$H$_{12}$	AcBr · 2AlBr$_3$ [6]	10 : 4 : 1	−20	3	cyclo-C$_6$H$_{11}$Br	75 [300]
12	cyclo-C$_6$H$_{12}$	Al$_2$Br$_6$	10 : 4 : 1	−20	3	cyclo-C$_6$H$_{11}$Br	22 [96]
13	cyclo-C$_6$H$_{12}$	C$_6$F$_5$CF$_3$ · 2AlBr$_3$	10 : 4 : 1	−20	2	cyclo-C$_6$H$_{11}$Br	36 [145]
14	cyclo-C$_6$H$_{12}$	CCl$_4$ · 2AlBr$_3$	10 : 4 : 1	−20	2	cyclo-C$_6$H$_{11}$Br	29 [116]
15	cyclo-C$_6$H$_{12}$	CBr$_4$ · 2AlBr$_3$	25 : 10 : 1	−20	2	cyclo-C$_6$H$_{11}$Br	59 [592]
16	cyclo-C$_6$H$_{12}$	CBr$_4$ · 2AlBr$_3$	10 : 4 : 1	−40	4	cyclo-C$_6$H$_{11}$Br	17 [70]
17	cyclo-C$_5$H$_9$Me	CBr$_4$ · 2AlBr$_3$	10 : 4 : 1	−40	4	cyclo-C$_6$H$_{11}$Br	28 [111]

^{a} A mixture of Me$_3$CBr and (Me(Et)CHBr + Me$_2$CHCH$_2$Br) isomers in a molar ratio of 1.0 : 0.4 in run *4* and 1.00 : 0.85 in run *7*.
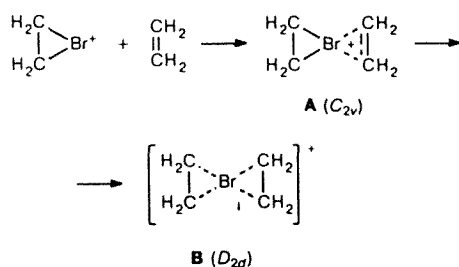
The results obtained can be interpreted in terms of Scheme 1*, according to which the CBr$_3^+$ cation (see Refs. 2 and 10) splits off a hydride ion from ethane to give CHBr$_3$ and an ethyl cation. The latter splits off Br$^-$ from Al$_2$Br$_7^-$ anion or from Br$_2$ molecule, yielding ethyl bromide and Al$_2$Br$_6$ or Br$^+$, respectively.

Path *a* in Scheme 1 is apparently the only reaction route in the absence of Br$_2$. In the presence of Br$_2$, ethylene existing in equilibrium with ethyl cation adds successively Br$^+$ and Br$^-$, thus being converted into 1,2-dibromoethane (path *b*). This reaction is not catalytic, since the Br$_2$—Al$_2$Br$_6$ system does not react with ethane under the conditions studied, and the step of generation

of the ethyl cation from ethane is accompanied by the transformation of the superacidic CBr$_4$ · 2AlBr$_3$ complex into the reduced form CHBr$_3$ · 2AlBr$_3$, which is less active. Furthermore, an increase in the content of Br$_2$ in the system leads to a decrease in its activity. This is probably explained by the fact that equilibrium *c* (see Scheme 1)
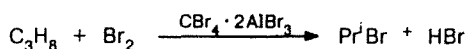
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* The scheme presented is simplified. According to *ab initio* calculations for the model C$_2$H$_4$Br$^+$—C$_2$H$_4$ system, the scheme of the reaction includes the formation of adduct A in which the geometric parameters of the individual components have been changed only slightly. Adduct A is then converted into intermediate B, whose energy is 13 kcal mol^{-1} higher than the energy of A and the geometric parameters differ dramatically from those of the initial components and adduct A.[9]

Scheme 1

shifts to the right and the concentration of the CBr_3^+ cation in the reaction mixture correspondingly decreases.
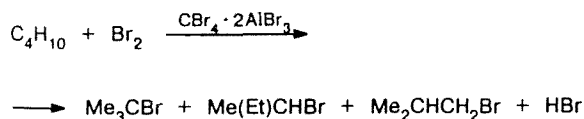
The considerable difference between the compositions of the products formed in the bromination of ethane under atmospheric pressure and under an elevated pressure can be due to its low steady-state concentration in the former case. Therefore, in the case where the reaction is carried out under atmospheric pressure of ethane, further bromination of the initially formed $C_2H_4Br_2$ becomes more pronounced.

Ethane virtually does not undergo bromination at ~20 °C. On the contrary, the more active propane readily reacts with Br_2 even at −20 °C, the bromination occurring selectively and affording Pr^iBr^* (Table 2).

$$C_3H_8 \ + \ Br_2 \ \xrightarrow{\ CBr_4 \cdot 2AlBr_3\ } \ Pr^iBr \ + \ HBr$$

At −10 °C, propane is wholly brominated. However, when the temperature increases, dibromide is formed in addition to the monosubstituted product; the ratio $[Pr^iBr] : [C_3H_6Br_2] = 6 : 1$ at −10 °C (3 h) and 2 : 1 at 0 °C (2 h), *i.e.*, at 0 °C, bromination of propane becomes markedly less selective.

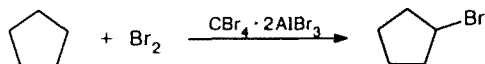*n*-Butane is exhaustively brominated over a period of 2 h at −20 °C to give a mixture of three isomeric monobromides in a $[Bu^tBr] : ([Bu^iBr] + [Bu^sBr])$ ratio of 1.0 : 0.4.

$$C_4H_{10} \ + \ Br_2 \ \xrightarrow{\ CBr_4 \cdot 2AlBr_3\ }$$

$$\longrightarrow \ Me_3CBr \ + \ Me(Et)CHBr \ + \ Me_2CHCH_2Br \ + \ HBr$$
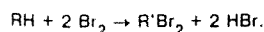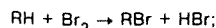
The $CCl_4 \cdot 2AlBr_3$ is markedly less active in this reaction: under the same conditions, the yield of butyl bromides decreases from 100 % to 13 %.

Bromination of cyclopentane, cyclohexane, and methylcyclopentane occurs even at −40 °C. At −20 °C, the reactions occur selectively, and the yields of monobromides based on Br_2 reach 76 % (600 % based on the catalyst). The products of polybromination are either not formed at all or formed only in trace amounts.
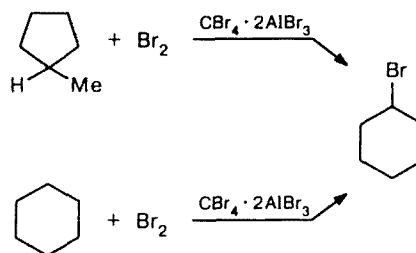
The reaction of cyclopentane with Br_2 affords cyclopentyl bromide as the only product.

* In this case and in all the following cases, the yields of bromides were calculated according to the following equations:
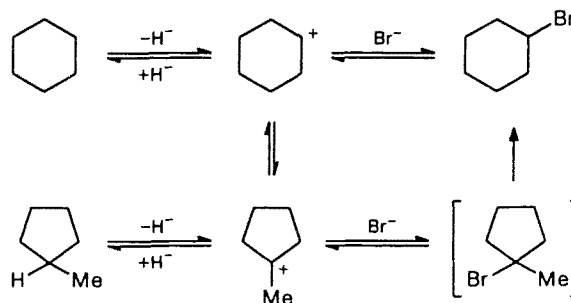
RH + Br_2 → RBr + HBr;

RH + 2 Br_2 → R'Br$_2$ + 2 HBr.

Cyclohexane and methylcyclopentane yield cyclohexyl bromide as the only product both at −40 °C and at −20 °C.

This result can be explained by the fact that 1-methyl-1-bromocyclopentane formed initially from both cycloalkanes is unstable and is irreversibly converted into the more stable secondary bromide (Scheme 2).

Scheme 2

The direction of the carbonylation of methylcyclopentane and cyclohexane in the presence of $CBr_4 \cdot 2AlBr_3$, unlike that of bromination, depends on the temperature: at −45 °C, the reaction gives the carbonyl derivative of the methylcyclopenane series, while at 0 °C, the cyclohexane derivative is produced.[4]

Below we present the activity series for catalysts of the bromination of cyclohexane at −20 °C (the yields of cyclo-$C_6H_{11}Br$ based on Br_2 and the reaction durations for $[cyclo$-$C_6H_{12}] : [Br_2] : [Cat] = 10 : 4 : 1$ are presented):

$CBr_4 \cdot 2AlBr_3$ (75 %, 1 h) > $CHBr_3 \cdot 2AlBr_3$ (50 %, 1 h) > $C_6F_5CF_3 \cdot 2AlBr_3$ (36 %, 2 h) > $CCl_4 \cdot 2AlBr_3$ (29 %, 2 h) > $CH_2Br_2 \cdot AlBr_3$ (22 %, 3 h).
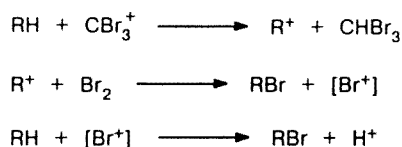
Thus, $CBr_4 \cdot 2AlBr_3$ is the most active catalyst.

The bromination of higher alkanes and cycloalkanes, like that of ethane, is accompanied by the reduction of the starting polyhalomethanes. However, these reactions are substantially different. First, the bromination of higher paraffins is a catalytic process with respect to $CBr_4 \cdot 2AlBr_3$, whereas bromination of ethane is a stoichiometric reaction. Second, cycloalkanes and higher homologs of ethane are brominated with Br_2 in the presence of $AlBr_3$ in CH_2Br_2, although in the absence of CBr_4, the reactions are markedly less efficient. And,

finally, ethane forms dibromide, whereas higher homologs of alkanes and cycloalkanes afford monobromides.

Two mechanisms for the ionic bromination of higher alkanes can be postulated. The first of them is similar to that presented in Scheme 1 (path *a*). It includes the initial abstraction of a hydride ion from the alkane through the action of the superacidic complex and the subsequent addition of Br^- to the carbocation (Scheme 3).
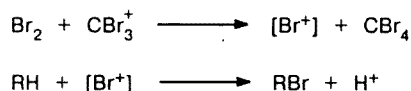
Scheme 3

$$RH + CBr_3^+ \longrightarrow R^+ + CHBr_3$$

$$R^+ + Br_2 \longrightarrow RBr + [Br^+]$$

$$RH + [Br^+] \longrightarrow RBr + H^+$$

The difference between the directions of bromination of ethane and higher alkanes is probably due to the dissimilar reaction conditions. Ethane reacts with Br_2 at a noticeably higher temperature than more reactive higher alkanes. An increase in the temperature being favorable for the transformations involving olefins (see Scheme 1, *b*).

The second possible mechanism of bromination of higher alkanes includes the initial attack by the superelectrophile on the Br_2 molecule. The resulting species, which contains a positively charged Br^+ ion, attacks a molecule of the alkane to give monobromide (Scheme 4).

Scheme 4

$$Br_2 + CBr_3^+ \longrightarrow [Br^+] + CBr_4$$

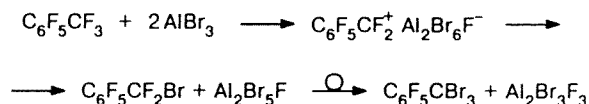$$RH + [Br^+] \longrightarrow RBr + H^+$$

Apparently, this scheme, which includes regeneration of the catalyst, plays a more important role in the bromination of reactive cycloalkanes than in the case of inert lower alkanes, which can be activated only by more electrophilic CX_3^+, rather than by $[Br^+]$. The fact that the reduction of the starting polyhalomethanes accompanies bromination of all alkanes and cycloalkanes indicates that Scheme 4 is not realized by itself.

The nature of the active complexes generated in the polyhalomethane—$2AlBr_3$ systems has been studied by quantum-chemical methods.[10] According to the results of the calculations, the formation of cationic $CBr_3^+Y^-$ (Y = $AlBr_4$, Al_2Br_7) and dicationic $Br^+=C=Br^+(Y^-)_2$ bromenium complexes, containing a one-coordinated positively charged Br^+ atom is, in principle, possible in the $CBr_4 \cdot nAlBr_3$ systems (*n* = 1, 2, and 4). The cationic bromenium complexes are the most probable superelectrophiles responsible for the reactions observed. The intermediacy of the dicationic complexes, which have a

higher charge but are considerably thermodynamically unstable, seems to be much less probable.

Conversely, the reactions catalyzed by $C_6F_5CF_3 \cdot 2AlBr_3$ involve apparently the $C_6F_5CF_2^+$ carbocationic complex.[11] The low activity of this system must be due to the substantial displacement of the electron density from the F atoms to the carbenium center and by the observed F/Br exchange, resulting in the formation of a Lewis acid weaker than $AlBr_3$.

$$C_6F_5CF_3 + 2AlBr_3 \longrightarrow C_6F_5CF_2^+ Al_2Br_6F^- \longrightarrow$$

$$\longrightarrow C_6F_5CF_2Br + Al_2Br_5F \xrightarrow{\Omega} C_6F_5CBr_3 + Al_2Br_3F_3$$

Experimental

Quantitative analysis of the reaction products was carried out by GLC using internal standards and a Model'-3700 chromatograph equipped with a flame ionization detector (FID) and a quartz capillary column (25 m × 0.23 mm, SE-54 as the stationary phase). The reaction products were identified by GC/MS on a VG 7070 E spectrometer (EI, 70 eV).

Bromination of ethane in tubes. A mixture of $AlBr_3$ (0.32 g, 1.2 mmol), CBr_4 (0.2 g, 0.6 mmol), and bromine (0.11 g, 0.68 mmol) was heated in a glass tube (2.5×200 mm) at 80—90 °C until a homogeneous solution was formed, then liquid ethane (0.06 g, 2 mmol) was condensed into the tube on cooling. The tube was sealed, heated to 50—65 °C, and held at this temperature in the dark for the 6 h needed for the disappearance of bromine. The contents of the tube were transferred into ice water, the aqueous layer was extracted with CH_2Br_2, and the organic extract was washed with an aqueous solution of $NaHCO_3$ and dried to give 1,2-dibromomethane (0.10 g, 0.53 mmol) and EtBr (0.008 g, 0.073 mmol) (GC and GC/MS data).

Bromination of propane under atmospheric pressure. CBr_4 (0.37 g, 1.12 mmol) was added to $AlBr_3$ (0.6 g, 2.25 mmol) in 1.5 mL of anhydrous CH_2Br_2. A round-bottom flask (0.5 L) containing the solution of the resulting $CBr_4 \cdot 2AlBr_3$ complex and equipped with a dropping funnel was filled with dry propane (23 mmol) and cooled to −20 °C. Bromine (0.36 g, 2.25 mmol) in 0.5 mL of CH_2Br_2 was added dropwise, and the reaction mixture was stirred in the dark for 3 h at the same temperature. Then the mixture was hydrolyzed with ice water, treated with Na_2SO_3 to remove the unreacted bromine, and extracted with CH_2Br_2, and the extract was washed with an aqueous solution of $NaHCO_3$ and dried to give 0.13 g (1.07 mmol) of Pr^iBr (GC and GC/MS data), yield 48 % based on Br_2 and 96 % based on CBr_4. The proportion of the corresponding dibromide did not exceed 2 % of Pr^iBr.

Bromination of *n*-butane under atmospheric pressure. $AlBr_3$ (0.96 g, 3.6 mmol) and CBr_4 (0.6 g, 1.8 mmol) were mixed in 1.5 mL of CH_2Br_2 in a round-bottom flask (50 mL) connected to a dropping funnel. The solution was cooled to −20 °C, liquid butane (1.7 mL, ~18 mmol) was added to it in one portion and then bromine (1.14 g, 7.2 mmol) in 1 mL of CH_2Br_2 was added dropwise, and the reaction mixture was stirred at −20 °C for 2 h until bromine completely disappeared. The mixture was worked-up as described above to give 0.98 g (7.16 mmol) of isomeric butyl bromides (GC and GC/MS data), yield 100 % based on Br_2. The molar ratio ([Bu^iBr] + [Bu^sBr]) (nonseparated chromatographic peaks) : [Bu^iBr] = 1 : 2.

Bromination of cycloalkanes (general procedure). AlBr$_3$ (0.59 g, 2.2 mmol) and CBr$_4$ (0.37 g, 1.1 mmol) were mixed in 1 mL of CH$_2$Br$_2$ in a round-bottom flask equipped with a dropping funnel. A solution of bromine (0.7 g, 4.4 mmol) in 1.2 mL of methylcyclopentane (0.92 g, 11 mmol) was added dropwise to this solution cooled to −20 °C. The reaction mixture was stirred at −20 °C for 70 min until bromine disappeared. The standard workup gave cyclohexyl bromide, yield 75 % based on Br$_2$ and 301 % based on CBr$_4$.

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