FUNCTIONALIZATION OF SATURATED HYDROCARBONS BY MEANS

OF APROTIC SUPERACIDS.

1. IONIC BROMINATION OF ALKANES AND CYCLOALKANES

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Aprotic organic superacids with the composition $AcBr \cdot 2AlX_3$ (X = Cl, Br) are efficient catalysts (Cat) for the bromination of n-alkanes and cycloalkanes by molecular bromine. Under the given conditions, the reactions afford (predominantly or exclusively) monobromides in high yields.

One-step functionalization of alkanes and cycloalkanes is a promising method for synthesizing various organic compounds directly from readily available hydrocarbon raw material. One method for the functionalization of saturated hydrocarbons is their treatment with strong electrophiles [1-6].

Scheme 1

$$R-H + E^{+} \equiv \begin{bmatrix} R & \cdots & H \\ E \end{bmatrix}^{+} \xrightarrow{-H^{+}} R-E$$

$$\downarrow -HE$$

$$R^{+} \xrightarrow{AB:} R-B + A^{+}$$
(1a)
(1a)

The key functionalization step with electrophiles is an attack by the electron-deficient C-H σ -bond of the hydrocarbon (RH). There are two mechanisms for the substitution of RH hydrogen by a functional group: electrophilic functionalization (la) and nucleophilic functionalization, catalyzed by an electrophile (lb) (Scheme 1).

Bromination is a frequent method for the functionalization of hydrocarbons. Ionic bromination of saturated hydrocarbons by molecular bromine (in the presence or absence of acid catalysts) is effective only for a narrow range of hydrocarbons, for example, polyhedral [7] or strained cycloalkanes such as cyclopropane [8].

Ionic bromination of n-alkanes has not been described in the literature, and the number of such examples for iso- and cycloalkanes is very limited [5, 9]. A major limitation to effective ionic bromination of paraffins is the instability of alkyl bromide (R-Br) formed in the presence of strong Lewis acids, leading to dehydrobromination and formation of polybromides as well as fragmentation.

According to Olah [5], the best catalyst for ionic bromination of isoalkanes, $AgSbF_6$, catalyzes the reactions of isobutane and isopentane with Br_2 to form primarily mono- and dibromides, respectively. Cyclopentane and cyclohexane react to form only monobromides in a low yield (5-27%; here and below, yields are calculated with respect to the catalyst). The formation of dibromides was also observed during bromination of isoalkanes in the presence of SbF_5 or superacid system $HSO_3F-SbF_5[9]$. In these reactions isopentane was converted to 1,2-dibromo-2-methylbutane, and isobutane was converted to a mixture of isobutyl bromide and 1,2-dibromo-2-methylpropane. The same mixture was formed in the bromination of isooctane,

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RH	Cat	T,°C	Time, min	RH∶Br₂∶Cat (molar)	Monobro- mides, % of Cat	Bromide composi- tion, mole %		mposi- %
					total mono- bromide yield, %*	mono	đi	tri
$n-C_4H_{10}$	(I) (I) AlCl ₃	10 20 20	165 165 165	$ \begin{array}{c c} 10:4:1\\ 10:4:1\\ 10:4:2 \end{array} $	54 142 12	91	7	2
<i>n</i> -C ₅ H ₁₂ »	(1) (I) AlCl ₃	0 0 0	90 120 120	10:4:1 20:10:1 20:1:2	203 369 7	91	6	3
<i>n</i> -C ₆ H ₁₄ » »	(I) (I) AlCl ₃	0 0 0	30 40 30	10:4:1 10:4:1 10:4:2	$ \begin{array}{c} 66\\ 77\\ 0 \end{array} $	95 80	5 8	Traces 12
$n-C_7H_{16}$ weights h_{16}	(I) AlCl ₃ (I)	0 0 0	65 90 110	10:4:1 10:4:2 10:4:1	90 3 55	78 100	22	Traces
$cyclo- C_5H_{10}$ $cyclo- C_6H_{12}$	$\begin{array}{c} \text{AlCl}_3 \\ (I) \\ \text{AcBr}_2 \end{array}$	0 0 0	110 120 120	10:4:2 10:4:1 10:4:1	4 133 0	100		
"	AlCl ₃	v	120	10.7.1	v			

TABLE 1. Ionic Bromination of n-Alkanes and Cycloalkanes Catalyzed by $AcBr \cdot 2AlCl_3$ (I) and $AlCl_3$ in CH_2Br_2

*Calculated with respect to the catalyst.

TABLE 2. Ionic Bromination of n-Alkanes and Cycloalkanes by Bromine, Catalyzed by $AcBr \cdot 2AlBr_3$ (II) and $AlBr_3$, in CH_2Br_2

	Cat	T,°C	Time, min	RH : Br. : Cat	Total monobro- mide yield, %*	Bromide composi- tion, mole%		
RH						mono	di	tri
<i>n</i> -C ₄ H ₁₀	(11)	-20	180	10:4:1	161	100	Traces	None
»	(II) AlBr3	$\begin{array}{c} 0 \\ -20 \end{array}$	60 180	40:20:1 10:4:2	485 96	82	18	Traces
$n-C_5H_{12}$	(11)	-20	90	10:4:1	302	100	1	
» »	AlBr ₃ (II)	$\begin{vmatrix} -20 \\ 0 \end{vmatrix}$	90 60	10:4:2 100:50:1	97 914	65	18	17
n-C7H16 ·	(II)	0	40	10:4:1	114			
»	AlBr₃	0	40	10:4:2	19			
$cyclo-C_{5}H_{10}$ $cyclo-C_{6}H_{12}$	(II) (II)	$-20 \\ -20$	150 180	10:4:1 10:4:1	242 300	100 100		
• *	AlBr ₃	-20	180	10:4:2	86	100		
*	AcBr∙ ∙AlBr₃	0	180	10:4:1	0			
Exo-TDC	(II)	5	20	10:4:1	252			

*Calculated with respect to the catalyst.

which was subjected to fragmentation under these conditions. Unfortunately, the bromide yield is not specified in [9].

Earlier we found that systems with the compositon $RCOX \cdot 2AIX_3$ (X = C1, Br), named aprotic organic superacids (AOS), are exceptionally active with respect to paraffins; at room temperature (and below), they effectively catalyze fragmentation, isomerization, and alkylation of n-alkanes, oxidative coupling of cycloalkanes, etc. [10-13]. These systems thus differ qualitatively from corresponding equimolar complexes, which are inactive with respect to RH under such mild conditions, and from other Lewis acid-base catalysts. As a rule, AOS systems are even more active than protic superacids. The exceptionally high activity of AOS systems led us to hope that they would be good catalysts for ionic bromination of n-alkanes and cyclo-alkanes.

Indeed, systems with the composition $AcBr \cdot 2AIX_3$ (X = Cl (I), Br (II)) were shown to be effective catalysts for ionic bromination of $C_4 - C_7$ n-alkanes, cyclopentane, cyclohexane, and exotetrahydrodicyclopentadiene (TDC) under mild conditions in the dark.

In the presence of $AcBr \cdot 2AlCl_3$ (I), the hydrocarbons were effectively brominated by Br_2 at 0-20°C. Under selected conditions, monobromides were the major products regardless of the nature of RH; they were obtained in yields of 55-369% with respect to (I) (Table 1).

The n-alkane monobromination products are isomeric mixtures whose tertiary RBr content increases with reaction time. This is also true for di- and tribromides.

Cyclopentane and cyclohexane are brominated almost exclusively to monobromides.

 $n-C_{n}H_{2n+2} + Br_{2} \xrightarrow{AcBr \cdot 2AlX_{3}} C_{n}H_{2n+1}Br + C_{n}H_{2n}Br_{2} + C_{n}H_{2n-1}Br_{3}$ $\underset{\text{major product}}{\overset{(CH_{2})}{\prod} + Br_{2}} \xrightarrow{AcBr \cdot 2AlX_{3}} \begin{pmatrix} CH \\ CH_{2} \end{pmatrix}_{n}} Br$ n = 4, 5.

Optimal conditions for monobromination of saturated hydrocarbons in the presence of system (I) are shown in Table 1. An increase in reaction time or carrying out the reaction at a higher temperature results in decreased selectivity, not only due to a higher polybromide content but, primarily, because of active fragmentation, causing a sharp decrease in the yield of monobromides. It should be stressed that RBr fragmentation is negligible under the conditions shown in Table 1.

Unlike system (I), $AcBr \cdot AlCl_3$ (1:1) is completely inert under the given conditions, and $AlCl_3$ exhibits a very low activity in the ionic bromination of n-alkanes and unsubstituted cycloalkanes. In contrast, methylcyclopentane is smoothly brominated in the presence of $AlCl_3$ to form a tertiary monobromide.

As shown earlier, system (II) $(AcBr \cdot 2AlBr_3)$ is more active than system (I) in reactions with alkanes. This is also true for reactions of RH with Br_2 . Thus system (II) was an even more effective catalyst in the ionic bromination of RH, allowing this reaction to take part at -20 to 0°C. As seen in Table 2, RBr yields in reactions catalyzed by system (II) are 114-910%, calculated with respect to the catalyst (the maximal yield of RBr with respect to Br_2 is 75%).

The ability to carry out bromination at low temperatures (-20°C) permits selective synthesis of RBr not only from C_5-C_6 cycloalkanes, but from n-butane, n-pentane, and exo-TDC. The composition of the synthesized monobromides is similar to that observed in reactions catalyzed by complex (I). Exo-TDC forms at least six isomeric monobromides (GLC), which does not include 1-bromoadamantane. Under the given conditions (Table 2), destructive processes are absent.

Catalyst inhibition does not take place even at high bromine concentrations, but the bromination rate at -20°C is low in this case. When the reaction is carried out at 0°C at a high Br_2 concentration, the monobromination selectivity decreases. Thus at a Br_2 :(II) ratio of 50:1 the RBr fraction of the bromination reaction products of n-pentane is 65 mole % (see Table 2).

As seen from Table 2, the AcBr·AlBr₃ system, like AcBr·AlCl₃, does not catalyze ionic bromination of paraffins. At the same time, we were surprised by the marked activity exhibited by AlBr₃ alone, which is in sharp distinction to AlCl₃ (see Table 2). As far as we know, ionic bromination of n-alkanes and cycloalkanes by bromine in the presence of AlBr₃ (which is much less active than complex (II)) has not been described in the literature.

Earlier [14] we showed that an important difference between active systems (I) and (II) and inert (with respect to paraffins) equimolar complexes is the generation of acylium salts $Ac^{+}Al_{2}X_{7}^{-}$ in low-polar solutions of systems (I) and (II). Thus there are two likely bromination mechanisms for reactions catalyzed by systems (I) and (II) (Schemes 2 and 3).

According to Scheme 2, the role of complexes (I) and (II) is activation of a bromine molecule.

Scheme 2 $Br-Br + Ac^{+}Al_{2}Br_{7}^{-} \Rightarrow Br^{+}Al_{2}Br_{7}^{-} + AcBr$ $Br^{+}Al_{2}Br_{7}^{-} + R - H \rightleftharpoons$ $R - Br + HBr - Al_{2}Br_{6}$ $\xrightarrow{H} R - Br + Br^{+}Al_{2}Br_{7}^{-}$ $\xrightarrow{H} R^{+}Al_{2}Br_{7}^{-} \longrightarrow R - Br + Al_{2}Br_{7}^{-}$ $AcBr - Al_{2}Br_{6} \Rightarrow Ac^{+}Al_{2}Br_{7}^{-}$

The reaction of $Ac^+Al_2X_7^-$ salts, generated in system (I) or (II) solutions [14], with Br₂ leads to formation of the cation-like particles $Br^+Al_2X_7^-$ (Scheme 2). Reaction of these particles with C-H σ -bonds of the hydrocarbon produces a pentacoordinated carbonium ion, which decomposes to form either R-Br or the carbonium ion $R^+Al_2Br_7^-$. The latter may accept a bromide anion from Br_2 or from anion $Al_2X_7^-$ (X = Br), which also leads to the formation of R-Br. We would like to point out that the acceptance of Br⁻ from anion $Al_2Br_7^-$ was demonstrated by us in the bromination of adamantane by system (II) in the absence of bromine.

According to Scheme 3, complexes (I) and (II) activate the RH molecule by cleaving a hydride ion to form carbenium ion $R^+Al_2X_7^-$, which then converted (Scheme 2) to the desired products.

Scheme 3

$$R=H + Ac^{+}Al_{2}Br_{7}^{-} \xrightarrow{R^{+}Al_{2}Br_{7}^{-}} \xrightarrow{R^{+}Br_{7}} R-Br + Br^{+}Al_{2}Br_{7}^{-}$$

$$R^{+}Al_{2}Br_{7}^{-} + AcH \rightleftharpoons Ac^{+}Al_{2}Br_{7}^{-} + HBr$$

Monobromide formation may involve both of these mechanisms (Schemes 2 or 3). At high Br_2 concentrations in the reaction mixture the reaction probably proceeds according to Scheme 2. At low bromine concentrations, on the other hand, Scheme 3 is the preferred pathway.

Polybromination most likely results from further conversion of monobromides, including their dehydrobromination and formation of olefin intermediates [5].

EXPERIMENTAL

The bromination product yields were the same whether the experiments were carried out in the dark or in light.

Bromination of Liquid n-Alkanes and Cycloalkanes by Bromine in the Presence of AcBr 2AlX3 (general method). A 0.4-g portion (3 mmoles) of AlCl₃, 0.18 g (1.5 mmoles) AcBr, and 3.2 ml CH2Br2 were mixed in three-necked flask equipped with a Dewar condenser (-78°C), thermometer, and dropping funnel. The catalyst (I) solution thus obtained was cooled, with mixing, to the desired temperature, then 0.96 g (6 mmoles) Br, in 1.08 g (15 mmoles) n-pentane was added dropwise for 5 min. The reaction mixture was stirred in the dark for the specified time period (from the addition of Br_2), poured over ice, and extracted with ether. Unreacted Br₂ was neutralized with Na₂SO₃. The ether extracts were dried with MgSO₄ and analyzed quantitatively by means of GLC on a Biokhrom-1 apparatus with a glass capillary column, 50 m \times 0.2 mm (liquid phase: OV-101; temperature program: 40°C (4 min), 8°C/min, 230°C (4 min)), and n-decane as internal standard. A qualitative analysis of the reaction mixture was carried out by means of chromato-mass spectrometry on a Nermag R 10-10 instrument with a quartz capillary column, 50 m × 0.32 mm (liquid phase: methylphenylsiloxane; temperature program: -30°C (4 min), 3°C/min, 250°C (4 min)). Monobromides were identified by the presence of molecular ion peaks and their characteristic fragmentation patterns, which coincided with those described in the literature [15]. Di- and tribromides, which do not form molecular ions, were

identified by their characteristic fragmentation ions and retention times. In experiments with n-butane, cold n-butane was added directly to the catalyst solution and bromine in CH₂Br₂.

Synthesis of Bromocyclohexane. A 6.65-g (25 mmoles) portion of AlBr, 1.55 g (12.5 mmoles) AcBr, and 16 ml CH₂Cl₂ were mixed in a three-necked flask. The solution was cooled to -20° C, and 8.0 g (50 mmoles) of Br₂ in 10.5 g (125 mmoles) cyclohexane was added. The mixture was stirred for 3 h at -20°C, then was hydrolyzed and extracted with pentane. The extract (200 ml) was dried with MgSO₄ and eluted through an Al₂O₃ layer. The pentane, CH_2Cl_2 , and excess cyclohexane were evaporated, and the residue was fractionated at 5-6 mm; fractions with a bp of 28-32°C were collected. After repeat distillation, 3.7 g of bromocyclohexane were isolated (yield, 182% with respect to the catalyst). The structure of cyclohexyl bromide was confirmed by elemental analysis and by means of mass and PMR spectra, which were identical to those of a known sample (marker).

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