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Low-temperature functionalisation of alkanes and cycloalkanes by 'classical' and 'non-classical' (superacidic) Friedel–Crafts complexes

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Abstract. The results of studies on direct functionalisation of activated alkanes and cycloalkanes under the action of 'classical' Friedel–Crafts complexes (*viz.* equimolar complexes of acyl halides with aluminium halides) and related systems containing smaller or somewhat larger amounts of aluminium halide are surveyed. The studies carried out during the last decade on functionalisation of saturated hydrocarbons devoid of tertiary carbon atoms, by aprotic organic superacids $RCOX \cdot 2AlCl_3$ are summarised. Reactions of alkanes with acylium cations in superacidic media are considered. The published data on the structure of complexes $RCOX \cdot AlCl_3$ and $RCOX \cdot 2AlCl_3$ and on the nature of the active complexes in the reactions of arenes with acylium cations and with complexes $RCOX \cdot AlCl_3$ in both acidic and organic media as well as in the reactions of alkanes with acylium salts in protic superacids and with superacidic complexes $RCOX \cdot 2AlCl_3$ in aprotic solvents are analysed. The prospects for the synthesis of organic compounds from alkanes and cycloalkanes under the action of complexes of acyl halides with aluminium halides are outlined. The bibliography includes 128 references.

I. Introduction

Alkanes and cycloalkanes, which are the major components of oil and natural gas, still remain the most promising raw material for the synthesis of organic compounds. Although there is a possibility, in principle, to carry out direct functionalisation of alkanes and cycloalkanes and although some selective reactions of this type have been reported, only few saturated hydrocarbons are used currently in organic synthesis. Therefore, Mendeleev's words that to use petroleum as a fuel is like firing a furnace with banknotes are still timely.

The main difficulties that hamper selective one-stage functionalisation of alkanes (or cycloalkanes) arise because compounds of this class are inert and, hence, the products of their transformations are more reactive than the initial hydrocarbons.

In the early 1970s, a new stage in the chemistry of alkanes began. Since then, two non-traditional approaches are being developed successfully, which have given an impetus to the new 'low-temperature' chemistry of alkanes. (Low-temperature catalysts for transformations of alkanes have indubitable advantages over catalysts that are active at elevated temperatures, since the former make it possible to perform more selective processes and to work under thermodynamically more favourable conditions.[1]). The activation of the C–H bonds in alkanes, including methane, by transition metal complexes in solution has been discovered.[2–4] Over the past two and half decades, a wide range of transition metal complexes and lanthanide and actinide derivatives that are capable of activating alkanes have been described, the scientific fundamentals for the metallocomplex activation of C–H σ-bonds have been created, and processes for the transformation of alkanes and cycloalkanes into their derivatives (alkenes, oxidation products, carbonyl compounds, *etc.*) have been developed. The 'biomimetic' approach based on the development of activating systems, similar to metalloenzymes acting in living nature, proved quite promising.

At about the same time as the first transition metal complexes activating alkanes were described, the activation of saturated hydrocarbons by protic superacids was discovered.[5–7] The use of these systems made it possible to accomplish for the first time cracking, isomerisation, alkylation, and some other reactions of alkanes under mild conditions, at high rates, and with good yields of products. It has been shown that direct functionalisation of nonactivated cycloalkanes and alkanes including methane in protic acid media is, in principle, possible, and some examples of selective reactions of this type have been reported.

A great achievement in the chemistry of alkanes has been the elucidation of the mechanism of σ-bond activation by protic superacids and evidence for the existence of hypervalent carbon and for the formation of a two-electron three-centre (2e–3c) transition state. The intermediates in these reactions, namely, derivatives of pentacoordinated and hexacoordinated carbon, carbonium ions, and carbenium ions, the existence of which had been postulated previously, were generated and studied experimentally.[5] As a result of these studies, the views on the mechanism of the electrophilic activation of alkanes, which had previously been speculative, became substantially more profound and acquired a reliable theoretical base. The Nobel prize in chemistry awarded to Olah in 1994 for his pioneering studies on the activation of alkanes by protic superacids reflected the recogni-

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tion of his fundamental contribution to the chemistry of alkanes[7] and, simultaneously, the recognition of the current interest in this subject.

Among the new approaches to the chemistry of alkanes, which have been successfully developed during the past two decades, gas-phase reactions of alkanes with metal ions[8-17] and with metal atoms or small clusters[17-28] are noteworthy. The former have provided valuable information concerning the mechanisms of the activation of C–H and C–C bonds and on the energies of M–H and M–C bonds. The studies on the reactions of alkanes with metal atoms and small clusters have led to the development of new active heterogeneous catalysts[17,18] and to the direct synthesis of organometallic compounds from alkanes.[26,27]

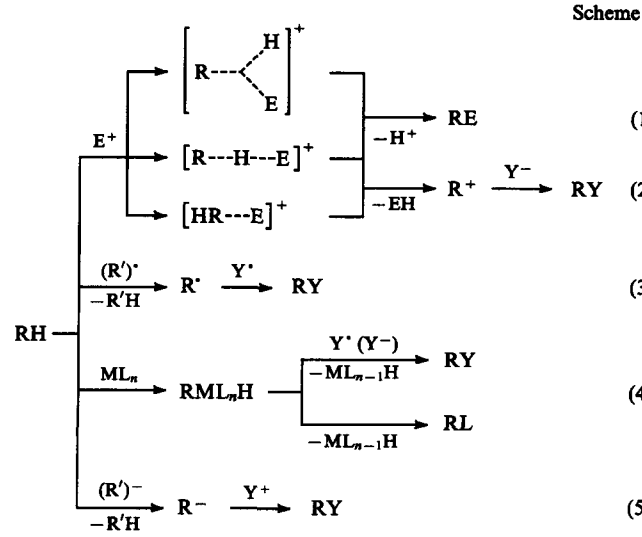
The traditional field involving gas-phase reactions of alkanes in the presence of heterogeneous catalysts, which still occupy a prominent position among industrial processes, has also been substantially revolutionised. Great progress has been achieved in studies on the structures of heterogeneous catalysts and mechanisms of reactions involving them (including industrial processes) as well as in the development of a new generation of catalysts.[20-34] The elaboration of novel catalysts for the oxidation of alkanes based on polyoxometallates ('inorganic porphyrin'), which combine the advantages of homogeneous systems (selectivity and controllability of processes; see Chapter VIII in the published book[2]) with stability, which is the basic advantage of heterogeneous catalysts, especially significant for industry, demonstrates the fruitfulness of using different approaches for solving a common problem.

In recent years, some selective radical processes of functionalisation of alkanes have been reported. The photoinduced single electron transfer (SET), which has been achieved using photochemical oxidising agents (for example, tetracyanobenzene) generating radical cations from saturated hydrocarbons, can serve as an example. The subsequent exothermal transformation of the alkyl radical cation into the alkyl cation, which then adds to the radical derived from the oxidising agent, affords a functional derivative of the alkane.[35] Somewhat earlier, Crabtree (see for example, Chapter III in the published book[2]) has proposed another method for the generation of alkyl radicals from alkanes; this involved the use of photoexcited mercury atoms. The alkyl radicals thus formed can undergo cross-coupling with other radicals generated in the system. For example, the interaction of cyclohexane and methanol yields the cross-coupling product, cyclo-$C_6H_{11}CH_2OH$, in addition to the products of dimerisation of the radicals — (cyclo-$C_6H_{11})_2$ and $(CH_2OH)_2$. Crabtree believes that this approach is quite promising for practical purposes, because it permits a large number of catalytic cycles. In this respect, the 'mercury' method compares favourably with the dehydrogenation of alkanes under the action of phosphine complexes of transition metals, which are readily deactivated during the reactions. Unfortunately, the Hg/*hν* and Hg/*hν*/H_2 systems are relatively ineffective for the transformation of methane or other alkanes with strong C–H bonds.

The simplest pathways to the functionalisation of alkanes are shown in Scheme 1. Obviously, compounds of the same type can react by different mechanisms. For example, metal complexes can act either as electrophiles or as radicals or react by the oxidative addition mechanism.

The electrophilic functionalisation (1), electrophile-promoted nucleophilic functionalisation (2),[5,6] the radical mechanism (3), and the metallocomplex mechanism (4) of hydrogen substitution in a saturated hydrocarbon[2-4] shown in the Scheme have been proved, while reaction (5) has not been performed so far. However, since the H/D isotope exchange in saturated hydrocarbons including methane under the action of strong nucleophiles is well known,[36-39] this functionalisation pathway seems possible, although it is unlikely to play a noticeable role in the chemistry of alkanes, because the reagents needed for the irreversible functionalisation are difficult to select.

Scheme 1



In can be concluded from the foregoing that the chemistry of alkanes has developed vigorously over the last 20–25 years. It has been reported[2] that the number of publications devoted to the activation of alkanes and their catalytic reactions increases exponentially and doubles every 3–4 years. The advances made in this field bring closer the solution of the problem of the direct synthesis of organic compounds from alkanes and cycloalkanes.

The present review is devoted to the functionalisation of alkanes and cycloalkanes by complexes of acyl halides with aluminium halides.

Studies on the transformations of saturated hydrocarbons under the action of equimolar Friedel–Crafts complexes have been carried out desultorily for 65 years. The reported examples of functionalisation of activated saturated hydrocarbons seemed to be of purely abstract interest. However, recently it has been shown that, in some cases, the acylation of activated cycloalkanes with these systems can be applied to organic synthesis.

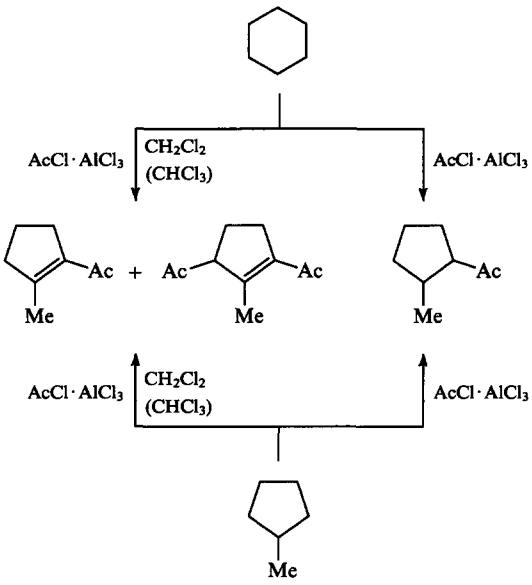
The discovery of the 'superacidic' properties of the $RCOX \cdot 2AlX_3$ complexes has opened new prospects in the chemistry of alkanes.[40] The $RCOX \cdot 2AlX_3$ complexes, which were called by us aprotic organic superacids (AOS) proved extremely reactive toward *n*-alkanes and non-activated cycloalkanes under mild conditions,[41] which markedly distinguishes them from the equimolar complexes $RCOX \cdot AlX_3$, which are inert with respect to these substrates. Regarding their activity in the initiation of transformations of alkanes, AOS surpass not only the known systems based on aluminium halides but also the strongest protic superacids. In the presence of AOS, functionalisation of linear alkanes and nonactivated cycloalkanes has been accomplished; among these processes, novel reactions of alkanes were found. It is also essential that, although AOS readily initiate transformations of alkanes and cycloalkanes accompanied by the rupture of C–C bonds, the fragmentation processes can be suppressed under certain conditions and a one-stage selective functionalisation of saturated hydrocarbons can be performed.

II. Functionalisation of isoalkanes and activated cycloalkanes by equimolar complexes $RCOX \cdot AlCl_3$ and related systems

The discovery of the activating influence of aluminium chloride on acyl halides made by Friedel and Crafts in the late XIX century marked the beginning of the fruitful use of the complexes $RCOX \cdot AlX_3$ in organic chemistry and, actually, the beginning of the use of catalysis in organic synthesis. However, the use of $RCOX \cdot AlX_3$ complexes has long been confined only to reactions of unsaturated or aromatic compounds.[42-45] The use of these

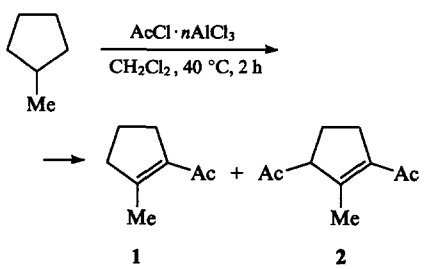
complexes for transformations of alkanes and cycloalkanes was far from being equally successful. The first studies in this field were carried out by Nenitzescu, Zelinsky, Hoppf, and other researchers[46–53] as early as the 1930s. The results of these studies have been discussed in monographs[42,43] and in a review.[54]

In early papers, only qualitative experiments were carried out. For example, it was found that stirring cyclopentane, acetyl chloride, and aluminium chloride in a molar ratio of 3 : 1 : 1.1 for two days affords acetylcyclopentane.[47] If methylcyclopentane is used instead of cyclopentane and the ratio of the reagents is 5 : 1 : 1.2, 2-acetyl-1-methylcyclopentane is formed in three days.[46] Later, reactions of cyclohexane, methylcyclopentane, methylcyclohexane, and decalin in the presence of $AcCl \cdot nAlCl_3$ (n = 0.8–1.5) were studied in detail by various researchers. It was found that the transformations of cyclohexane and methylcyclopentane carried out in the medium of the hydrocarbon itself lead to the corresponding saturated ketones, while in a solvent (CH_2Cl_2 or $CHCl_3$), α,β-unsaturated ketones or diketones of the cyclopentane series are formed.[55–64]



Acetylation of methylcyclopentane, cyclohexane, methylcyclohexane, and decalin with the reaction conditions are shown in Scheme 2.[55–58]

Thorough investigation of the acetylation of methylcyclopentane carried out recently has made it possible to increase the overall yield of the monoacetylated product **1** and diacetylated product **2** to 65%–70%.[64]



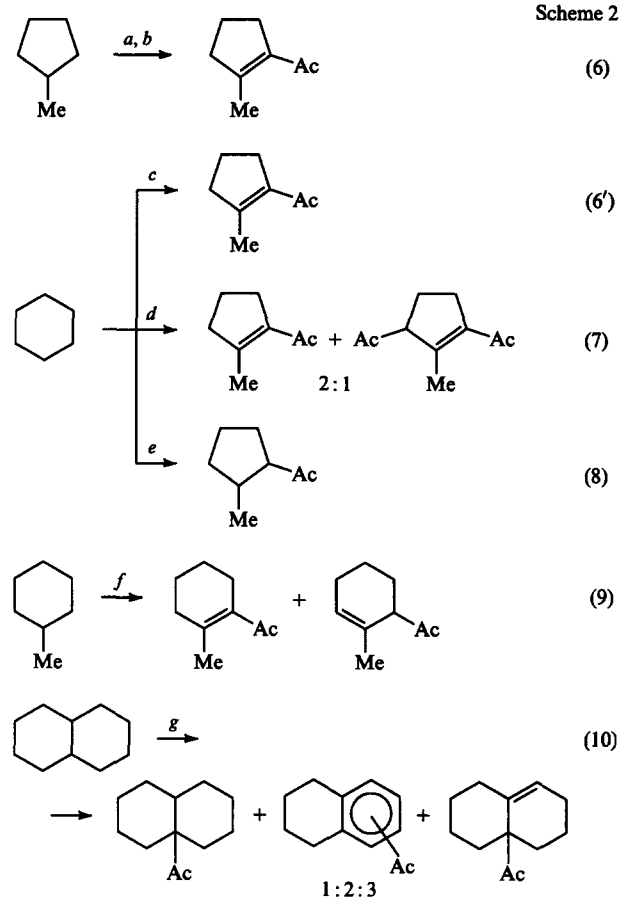
1 **2**

The ratio of **1** and **2** depends on the [AcCl] : [$AlCl_3$] ratio. When this is 2 : 1.5, the yield of the compound **2** is 50%.

Although the exact mechanism of the formation of the diketone **2** is unknown, the researchers cited presented some facts indicating that it is formed *via* enol derivative **3** rather than by the direct acylation of the unsaturated ketone **1** (Scheme 3).

In keeping with this scheme is the fact that treatment of the enol derivative **3** with $AlCl_3$ or $TiCl_4$ gives the diketone **2** in a quantitative yield. Conversely, acylation of **1** leads mostly to heavy products in which the proportion of the diketone **2** is very low.[64]

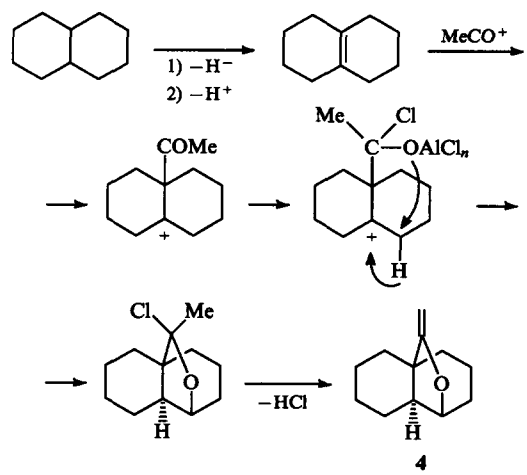
Scheme 2



(*a*) $AcCl \cdot AlCl_3$, 20 °C, 5 h (yield 27%);[55]
(*b*) $AcCl \cdot AlCl_3$, 40 °C, 2 h (yield 50%);[56]
(*c*) $AcCl \cdot AlCl_3$, 60 °C, 5 h, 20 °C, 12 h (yield 36%);[57]
(*d*) $AcCl \cdot AlCl_3$, 40 °C, 24 h + 20 °C, 18 h (yield 58%);[56]
(*e*) $AcCl \cdot AlCl_3$, 20 °C, 17 h (yield 30%);[58]
(*f*) $AcCl \cdot 0.8AlCl_3$, 60 °C, 70 h (total yield 13%);[58]
(*g*) $AcCl \cdot 1.5AlCl_3$, 20 °C, 48 h (total yield 71%).[59]

The acetylation of methylcyclohexane and decalin occurs with the retention of the structures of the initial cycloalkanes.

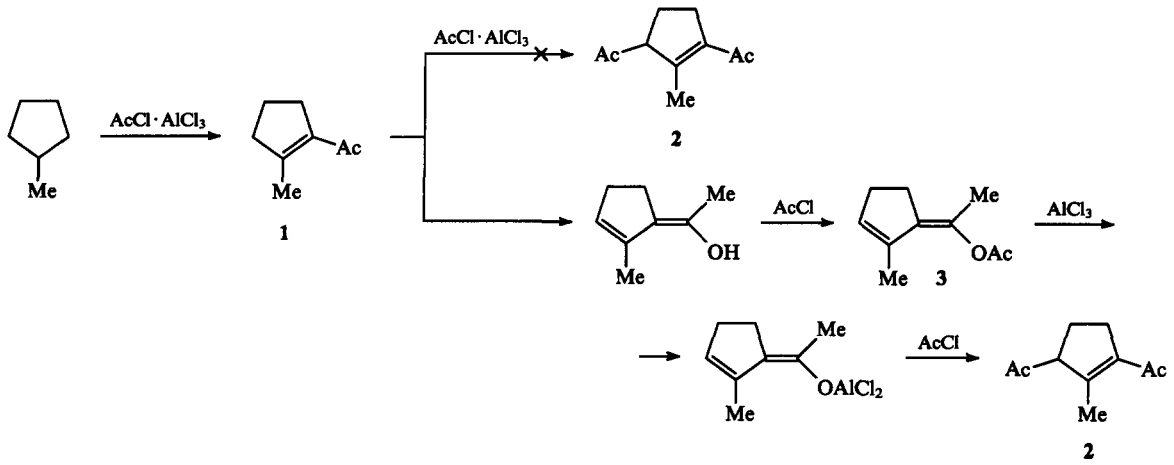
Unlike reactions (6)–(9) (Scheme 2), acetylation of decalin [reaction (10)] is conducted with a substantial excess of aluminium



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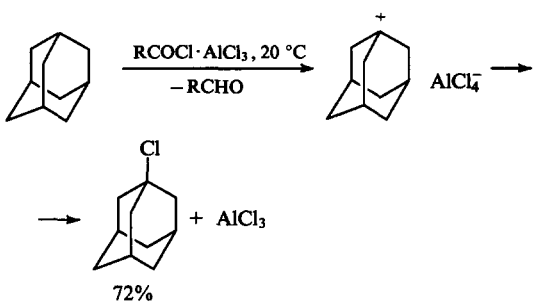
[RH] : [AcCl] : [$AlCl_3$] = 1 : 2.4 : 1.5; CH_2Cl_2, 10 °C, 10 h (yield 46%).

Scheme 3



chloride. Although this reaction is not selective, the overall yield of acylated products is quite high. A decrease in the amount of aluminium chloride in the $AcCl \cdot nAlCl_3$ system to $n < 1$ and a decrease in the temperature change sharply the direction of the reaction. Instead of the decalin acylation products, vinyl ether **4** is formed.[63] It was shown that only *cis*-decalin enters into this process, while *trans*-decalin is inactive. The scheme proposed for the transformation of *cis*-decalin into the vinyl ether **4** involves the formation of 9,10-decalene, which is then acylated giving a tertiary carbocation. The latter undergoes an axial shift and cyclisation and, after elimination of HCl, it is finally converted into the vinyl ether **4**.[63,64]

When cyclic hydrocarbons that are not prone to form alkenes are made to react with $RCOCl \cdot AlCl_3$ systems, halogenation products rather than acylaton products are formed.[65] For example, treatment of adamantane with $RCOCl \cdot AlCl_3$ leads to 1-chloroadamantane.



72%

[AdH] : [$RCOCl \cdot AlCl_3$] = 1 : 1; R = Me, Pr^n, Pr^i, cyclo-C_6H_{11} ($R \neq Ph$).

At 50 °C and at the molar ratio [$RCOCl \cdot AlCl_3$] : [AdH] = 6 : 1, dichloroadamantane is formed in a good yield, instead of 1-chloroadamantane.[65]

The only transformation observed for linear and branched alkanes in earlier studies, was their acylation, which led predominantly to the formation of saturated ketones and, to a lesser degree, of unsaturated ketones.[47,55,66–69] The yields of the acylation products were extremely low even after prolonged heating of the reactants.

$$C_nH_{2n+2} \xrightarrow{AcCl \cdot AlCl_3} \text{iso-}C_nH_{2n+1}Ac + \text{iso-}C_nH_{2n-1}Ac,$$

$n = 4-6$.

n-Butane does not react with $AcCl \cdot AlCl_3$ at room temperature. However, if a mixture of *n*-butane with $AcCl \cdot AlCl_3$ (molar ratio 3 : 1) is stirred for 15 h at 60 °C without a solvent, Me_2CHCH_2Ac, formed in a very low yield can be detected. The same product is also obtained from isobutane.[66]

Pentane and hexane can be acylated by prolonged stirring with $AcCl \cdot AlCl_3$ at room temperature without a solvent. For example, when *n*-pentane reacted with $AcCl \cdot AlCl_3$ for 8 h, the formation of a mixture of $Me_2CHCH(Me)Ac$ and $Me_2C{=}C(Me)Ac$ was qualitatively detected.[67] Under similar conditions, *n*-hexane is converted into $Me_2CHCH(Et)Ac$ and $Me_2C{=}C(Et)Ac$. The indirect data reported by Nenitzescu et al.[47] suggest that the yield of $Me_2CHCH(Et)Ac$ relative to AcCl does not exceed 5%. Japanese workers[55] have studied the interaction of isopentane with $AcCl \cdot AlCl_3$ by heating the reactants ([RH] : [$AcCl \cdot AlCl_3$] = 1 : 1) in a solvent. Under these conditions, only the unsaturated ketone **5** was obtained in a yield of no more than 6%.[55]

$$Me_2CH-CH_2Me \xrightarrow[60\ ^\circ C,\ CHCl_3]{AcCl \cdot AlCl_3} Me_2C{=}C(Me)Ac$$

5

Prolonged heating of isooctane, which readily undergoes cracking, with the $AcCl \cdot AlCl_3$ complex gives rise to the unsaturated ketone **6** and compound **7**, resulting from its further chlorination, the degree of conversion of the initial hydrocarbon not exceeding 37%.

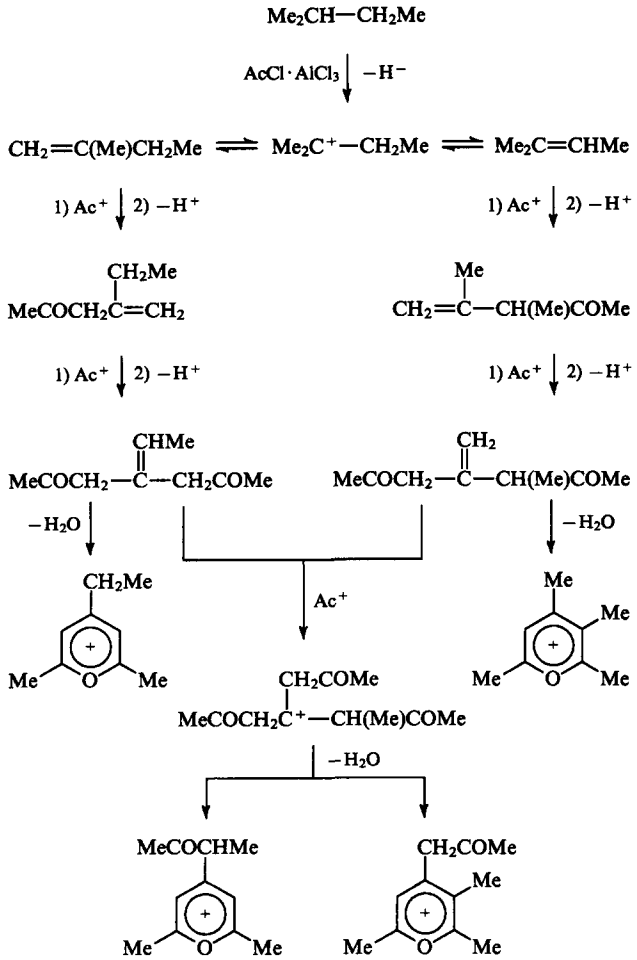
$$Me_3C-CH_2CHMe_2 \xrightarrow[60\ ^\circ C,\ 12\ h]{AcCl \cdot AlCl_3} Me_2C{=}CHAc + Me_2C(Cl)CH_2Ac$$

6 : **7** = 8 : 1

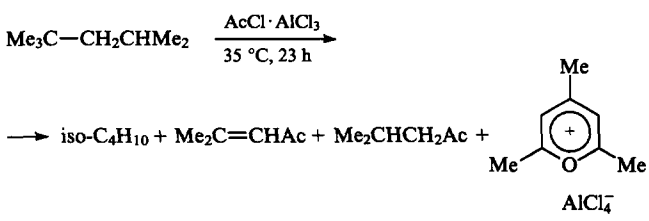
Yet another interesting route for the transformation of alkanes containing a tertiary carbon atom in the presence of $AcCl \cdot AlCl_3$ systems (excess AcCl is normally used) has been reported by French researchers.[70,71] They found that, apart from the products resulting from monoacylation of isoalkanes (2-methylbutane, 2-methylpentane, 3-methylpentane, and 2,3-dimethylbutane), diacylated and triacylated compounds are formed intermediately; under the reaction conditions, they are converted into a mixture of pyrylium salts and, after treatment of the reaction mixture with NH_4OH, they are transformed into a mixture of pyridinium salts. The transformation of isopentane into a mixture of four pyrylium salts is illustrated in Scheme 4.[70]

Pyrylium salts are synthesised at 25–53 °C over a period of 5–23 h without a solvent or in $CHCl_3$. The yields of the products depend strongly on the reaction conditions and do not exceed 20%–25%.[70] The reactions of 2,2,4-trimethylpentane, which readily undergoes cracking, with $RCOCl \cdot AlCl_3$ systems (R = Me, Et, Pr^i) afford isobutane, saturated and unsaturated

Scheme 4



ketones of the isobutane series, and a 2,4,6-trialkylpyrylium salt arising *via* transformations of diacylated isobutene.[71]



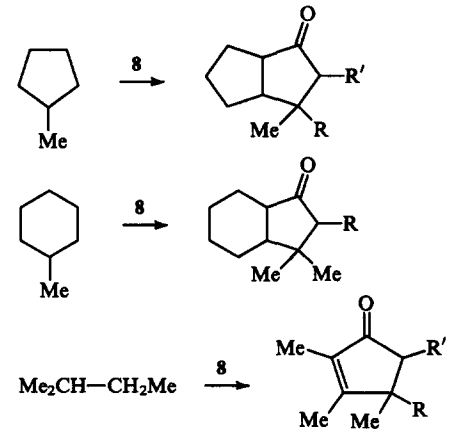
Mixtures of pyrylium salts obtained from isopentane and isohexane also contain a 2,4,6-trimethylpyrylium salt as a side product; this salt results from a transformation of isobutene, which is formed upon cracking of the initial alkanes. An increase in the content of aluminium chloride in the $RCOCl \cdot nAlCl_3$ systems ($n > 1$) sharply decreases the yield of the pyrylium salts from isoalkanes. *n*-Alkanes do not enter into a similar reaction at any ratios of AcCl and $AlCl_3$.[70,71]

Based on the acylation of methylcyclopentane, methylcyclohexane, and 2-methylbutane with alkenoyl chlorides in the presence of $AcCl \cdot AlCl_3$, pentalenes, hydrindenones, and cyclopentenones have been synthesised from saturated hydrocarbons in yields of up to 60%.[64]

Examples of these reactions in which the chlorides of α,β-unsaturated acids **8** of the general formula RCH = CR'COCl have been used as the acylating agents are presented in Scheme 5. The reactions are carried out in the presence of $AlCl_3$ (sometimes, of the $AcCl \cdot AlCl_3$ complex).

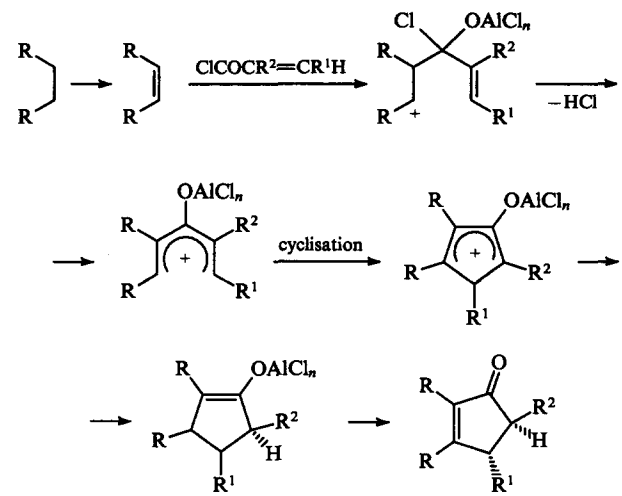
The researchers[64] suggested that these processes involve the acylation of the alkene generated in situ and subsequent cyclisation (Scheme 6).

Scheme 5



So, when sixty years have elapsed after the first acylations of cycloalkanes were performed, these reactions become interesting from the synthetic viewpoint.

Scheme 6



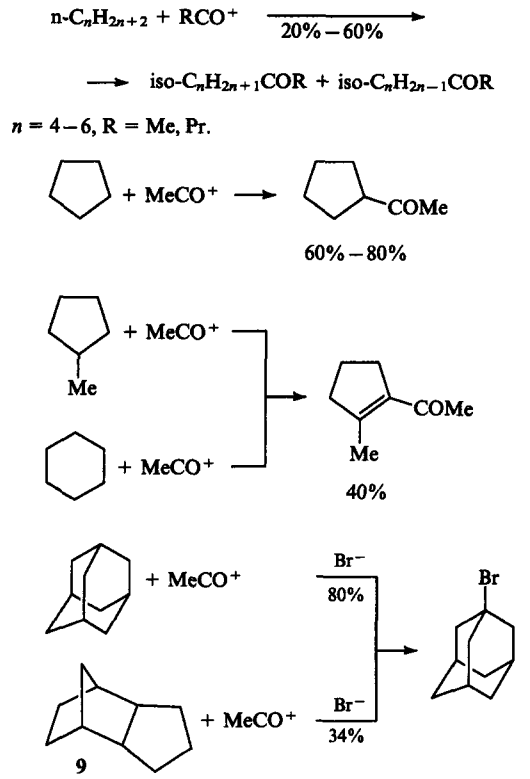
Thus, the classical Friedel–Crafts complexes $RCOX \cdot AlCl_3$ can be used for functionalisation and, especially, for acylation of isoalkanes and cycloalkanes capable of generating tertiary carbocations. However, no examples have been reported of any successful use of equimolar $RCOX \cdot AlCl_3$ complexes for the functionalisation of linear alkanes and cycloalkanes containing no tertiary carbon atoms.

III. Functionalisation of alkanes and cycloalkanes with aprotic organic superacidic complexes $RCOX \cdot 2AlCl_3$

1. $RCOX \cdot 2AlCl_3$ complexes as sources of functional groups

The disclosure of superacidic properties of $RCOX \cdot 2AlX_3$ complexes has offered new ways for the low-temperature functionalisation of saturated hydrocarbons including linear alkanes and nonactivated cycloalkanes.[40,41] In this case, two routes for the functionalisation are possible. The first route is electrophilic functionalisation, which results in the introduction of an RCO group into an alkane or cycloalkane molecule [see Scheme 1, route (1), $E^+ = RCO^+$]. The second route is nucleophilic functionalisation initiated by an electrophile and resulting in the introduction of a halogen atom into the molecule of a saturated hydrocarbon [see Scheme 1, route (2), $Y^- = Hal^-$ from $Al_2Hal_7^-$]. Both functionalisation routes have been accomplished (see the acylation, dehydroacylation, and bromination reactions

Scheme 7



discussed below).[40,41,72] In some cases, the yields of products are sufficiently high and the reactions are fairly selective.

Examples of functionalisation of alkanes and cycloalkanes under the action of the superacidic $RCO^+ Al_2Cl_7^-$ complexes (1–2 h, 20 °C) are presented in Scheme 7.

The last example, namely, the transformation of tricyclo[5.2.1.$0^{2,6}$]decane (**9**) into 1-bromoadamantane, includes two consecutive reactions: isomerisation and bromination.

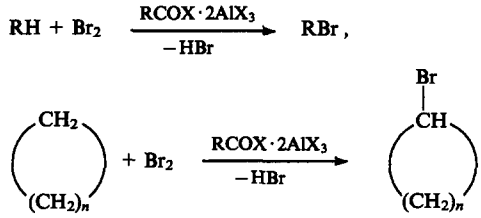
2. Functionalisation involving other reagents

When saturated hydrocarbons are functionalised with other reagents, the $RCO^+ Al_2X_7^-$ complexes act either as promoters or as both initiators and reagents.

a. Ionic bromination with Br_2

The ionic bromination of saturated hydrocarbons with molecular bromine in the presence or in the absence of acid catalysts has been accomplished for a limited series of hydrocarbons such as polyhedral or strained cycloalkanes.[73,74] The ionic bromination of *n*-alkanes was not described until 1988;[75] and only a few examples of this reaction involving isoalkanes and cycloalkanes have been reported.[76,77] For example, bromination of C_4 and C_5 isoalkanes and of cyclohexane in the presence of $AgSbF_6$ gives monobromides in 2%–27% yields relative to $AgSbF_6$, the reactions being complicated by polybromination.[76] The ionic bromination of isoalkanes in the $HSO_3F–SbF_5$ protic superacid also affords monobromides in low yields, and polybromides and the products of hydrocarbon fragmentation are formed as side products.[77]

Unlike other electrophilic reagents, AOS catalyse effectively the ionic bromination of $C_3–C_7$ *n*-alkanes, cyclopentane, cyclohexane, trimethylenenorbornane **9**, and other cycloalkanes with molecular bromine in the dark at temperatures ranging from –20 to 20 °C.[75,78] Conditions can be chosen under which monobromides are formed exclusively or predominantly, their yields being 55%–370% relative to $AcBr·2AlCl_3$ or 110–910% relative to $AcBr·2AlBr_3$ (Tables 1 and 2).[78]



The maximum yield of RBr relative to Br_2 reaches 75%. Under the conditions studied, the bromination is not complicated by fragmentation. The reactions involving the $C_4–C_7$ *n*-alkanes result in the formation of monobromides as mixtures of isomers, while in the case of cycloalkanes, individual cycloalkyl bromides are obtained. Equimolar $AcX·AlX_3$ complexes do not catalyse the ionic bromination of alkanes, the complexes containing $AlCl_3$ being virtually inert. Aluminium bromide exhibits low activity in CH_2Br_2; it is substantially less active than the $Ac^+Al_2Br_7^-$ complex.

The role of AOS in these reactions can reduce to the activation of the Br_2 molecule, which gives rise to species containing a positively charged bromine atom (e.g. as Br_3^+) and acting as a superacid, which withdraws a hydride ion from an alkane molecule (Scheme 8).

Scheme 8a

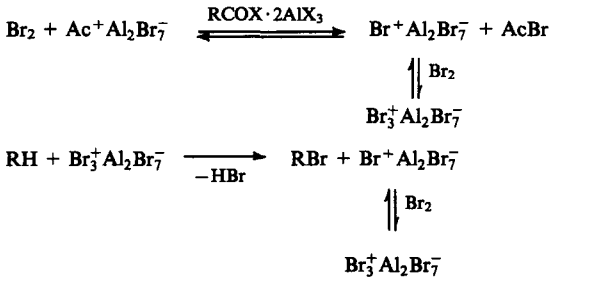


Table 1. Ionic bromination of *n*-alkanes and cycloalkanes, catalysed by $AcBr·2AlBr_3$ and $AlBr_3$ in CH_2Br_2 (according to a published work[78]).

RH	Catalyst (Ct)	*T*/°C	*t*/h	[RH]:[Br_2]:[Ct]	Yields of monobromides (%, relative to Ct)	Proportion of monobromides in the bromide mixture (%)
n-C_4H_{10}	$AcBr·2AlBr_3$	–20	3.0	10:4:1	161	100
	$AcBr·2AlBr_3$	0	1.0	40:20:1	485	82
n-C_5H_{12}	$AcBr·2AlBr_3$	–20	1.5	10:4:1	302	100
	$AlBr_3$	–20	1.5	10:4:1	97	–
	$AcBr·2AlBr_3$	0	1.0	100:50:1	914	65
n-C_7H_{16}	$AcBr·2AlBr_3$	0	0.6	10:4:1	114	–
	$AlBr_3$	0	0.6	10:4:2	19	–
cyclo-C_5H_{10}	$AcBr·2AlBr_3$	–20	2.5	10:4:1	242	100
cyclo-C_6H_{12}	$AcBr·2AlBr_3$	–20	3.0	10:4:1	300	100
	$AlBr_3$	–20	3.0	10:4:2	86	100
	$AcBr·AlBr_3$	0	3.0	10:4:1	0	–

Table 2. Ionic bromination of *n*-alkanes and cycloalkanes catalysed by the $AcBr \cdot 2AlCl_3$ complex and $AlCl_3$ in CH_2Cl_2 at 0 ° (according to a published study[78]).

RH	Catalyst (Ct)	*t*/h	[RH] : [Br_2] : [Ct]	Overall yield of monobromides (%, relative to Ct)	Proportion of monobromides in the bromide mixture (%)
n-C_4H_{10}	$AcBr \cdot 2AlCl_3$	2.7	10:4:1	54[a]	91
	$AcBr \cdot 2AlCl_3$	2.7	10:4:1	142[b]	–
n-C_5H_{12}	$AcBr \cdot 2AlCl_3$	1.5	10:4:1	203	91
	$AcBr \cdot 2AlCl_3$	2.0	20:10:1	369	–
	$AlCl_3$	2.0	20:10:1	7	–
n-C_6H_{14}	$AcBr \cdot 2AlCl_3$	0.5	10:4:1	66	95
	$AlCl_3$	0.5	10:4:2	0	–
n-C_7H_{16}	$AcBr \cdot 2AlCl_3$	1.0	10:4:1	90	78
cyclo-C_5H_{10}	$AcBr \cdot 2AlCl_3$	2.0	10:4:1	55	100
	$AlCl_3$	2.0	10:4:2	4	100
cyclo-C_6H_{12}	$AcBr \cdot 2AlCl_3$	2.0	10:4:1	133	100
	$AcBr \cdot AlCl_3$	2.0	10:4:1	0	–

[a] At 10 °C. [b] At 20 °C.

Another possibility is that a carbocation (R^+) is generated from RH by the action of the superacid $RCO^+Al_2Br_7^-$; this carbocation withdraws Br^- from Br_2 thus forming a bromide.

Scheme 8b

$$RH + Ac^+Al_2Br_7^- \underset{-AcH}{\rightleftharpoons} R^+Al_2Br_7^-,$$

$$R^+Al_2Br_7^- + Br_2 \rightleftharpoons RBr + Br^+Al_2Br_7^- \overset{Br_2}{\rightleftharpoons} Br_3^+Al_2Br_7^-,$$

$$AcH + Br_3^+Al_2Br_7^- \xrightarrow[-Br_2,\ -HBr]{} Ac^+Al_2Br_7^-.$$

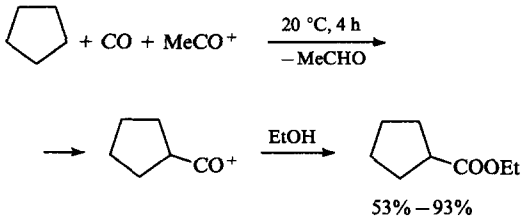
Both schemes include stages in which the catalyst is regenerated. The $Ac^+Al_2Br_7^-$ complex is the catalyst of the bromination shown in Scheme 8b, whereas in the process shown in Scheme 8a, this complex initiates the reaction catalysed by the $Br_3^+Al_2Br_7^-$ complex. By increasing the amount of Br_2 in the initial mixture and the reaction period, one can accomplish polybromination of alkanes, for example, of propane.

$$C_3H_8 + Br_2 \longrightarrow C_3H_7Br + C_3H_6Br_2 + C_3H_5Br_3 + C_3H_4Br_4 + C_3H_3Br_5.$$

The overall yield of polybromopropanes is quantitative relative to Br_2.

b. Carbonylation of cyclopentane

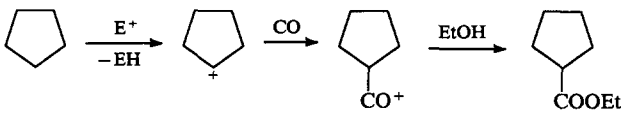
Acetyl bromide initiates carbonylation of cyclopentane with CO in the presence of excess $AlBr_3$ ($AlBr_3$: MeCOBr > 1.8).[79] This reaction occurs at room temperature and under atmospheric pressure and, after treatment of the reaction mixture with ethanol, it leads to the corresponding ester.



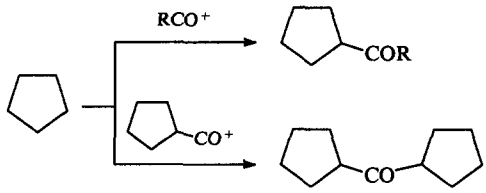
53%–93%

The selectivity of this reaction is 90%–99% and the yield of the ester varies from 53% to 93% depending on the proportion of $AlBr_3$. Dicyclopentyl ketone and acetylcyclopentane are formed as side products. The equimolar $AcBr \cdot AlBr_3$ complex is inert under these conditions.

The mechanism suggested for this reaction is similar to that of the known Haaf–Koch reaction,[80] which includes generation of a carbocation from a cycloalkane through the action of an electrophile and subsequent addition of a CO molecule leading to the formation of an acylium-cation.



Side reactions:



It is significant that in the presence of AOS, alkanes and cycloalkanes have been introduced into reactions of new types (see Sections **c** and **d**).

c. The synthesis of RSCOR′

Compounds RSCOR′ have been synthesised from alkanes (or cycloalkanes) RH, elementary sulfur, and the $R'COX \cdot 2AlX_3$ complexes in 25%–60% yields relative to the initial sulfur (Table 3).[81]

$$RH + S + R'CO^+Al_2X_7^- \xrightarrow{0 \text{ to } 20\ ^\circ C} \textit{sec}\text{-}RSCOR',$$

RH = C_3H_8, n-C_4H_{10}, n-C_5H_{12}, cyclo-C_5H_{10}, cyclo-C_6H_{12};
$R'CO^+$ = $MeCO^+$, $PrCO^+$, $PhCO^+$.

With cycloalkanes, the corresponding dicycloalkyl sulfides R_2S (R = cyclo-C_5H_9, cyclo-C_6H_{11}) are formed in small yields. The mechanisms possible for this reaction are shown in Scheme 9.

In the case of hydrocarbons containing tertiary carbon atoms (isobutane, methylcyclohexane, adamantane), which are usually more reactive than *n*-alkanes and than unsubstituted cycloalkanes, organosulfur compounds either are not formed at all under the conditions studied or are formed in low yields.

In the presence of Al_2Br_6 or the equimolar $MeCOBr \cdot AlBr_3$ complex, no organosulfur compounds are formed from alkanes and sulfur, which is in agreement with published data indicating that alkanes are inert with respect to sulfur at low temperatures.

Table 3. One-stage synthesis of organosulfur compounds RSCOR′ from alkanes (cycloalkanes), elemental sulfur, and R′COCl·2AlBr$_3$ complexes (according to a published study[81]).

RH	R′	T/°C	t/h	RSCOR′	Yield relative to S (%)
C_3H_8	Me	20	2	Pr^{i}SCOMe	47
n-C_4H_{10}	Me	0	2.5	Bu^{i}SCOMe	29
cyclo-C_5H_{10}	Me	0	2	cyclo-C_5H_9SCOMe	45
cyclo-C_6H_{12}	Me	0	4	cyclo-C_6H_{11}SCOMe	60
	Pr	0	4	cyclo-C_6H_{11}SCOPr	52
	Ph	0	4	cyclo-C_6H_{11}SCOPh	34

At elevated temperatures, the reactions of alkanes with sulfur are non-selective and ineffective.[82,83]

Scheme 9

a) $Ac^+Al_2Br_7^- + S_8 \longrightarrow AcS^+Al_2Br_7^-$,

$RH + AcS^+Al_2Br_7^- \xrightarrow[-HBr,\ -Al_2Br_6]{} sec\text{-}RSAc$;

b) $RH + Ac^+Al_2Br_7^- \longrightarrow sec\text{-}R^+Al_2Br_7^- + AcH$,

$sec\text{-}R^+Al_2Br_7^- + S_8 \longrightarrow RS^+Al_2Br_7^-$,

$AcH + RS^+Al_2Br_7^- \xrightarrow[-HBr,\ -Al_2Br_6]{} AcSR$.

Note for comparison that sulfurisation of alkanes (or cycloalkanes) with elementary sulfur in CF_3SO_3H giving rise to the corresponding (or isomeric) disulfides proceeds only upon prolonged reaction at a high temperature.[84]

$2RH + S \longrightarrow R_2S + H_2S$

RH	T/°C	t/h	Reaction product	Yield relative to the reacted sulfur (%)
cyclo-C_5H_{10}	150	12	(cyclo-C_5H_9)$_2$S	46
C_3H_8	150	62	Pr_2S (mixture of isomers)	47
iso-C_4H_{10}	125	10	Bu$^i_2$S	33

d. Alkylacylation of aromatic hydrocarbons with alkanes (or cycloalkanes) in the presence of $RCO^+Al_2X_7^-$ complexes

The ability of superacidic $RCO^+Al_2X_7^-$ complexes to acylate under mild conditions not only unsaturated compounds[85] but also alkanes[40,41,72] seemingly precludes the possibility of alkylation of aromatic compounds in the presence of these complexes. However, it has been found that the acylating ability of these complexes is suppressed in the presence of alkyl halides, and they act as catalysts for alkylation, for instance, of benzene.[86]

tert-$C_5H_{11}Cl$ + C$_6$H$_6$ $\xrightarrow[20\ °C,\ 1.5\ h]{Ac^+Al_2Cl_7^-}$ *tert*-$C_5H_{11}C_6H_5$ (85%) + *tert*-C_5H_{11}-C$_6$H$_4$-C_5H_{11}-*tert* (10%)

$[C_6H_6]:[tert\text{-}C_5H_{11}Cl]:[Ac^+Al_2Cl_7^-] = 180:36:1$.

Alkylated aromatic ketones *tert*-$C_5H_{11}C_6H_4COMe$ are formed as side products in these reactions. The yield of the alkylated aromatic ketones can be increased to 57% (relative to $Ac^+Al_2Cl_7^-$) when the molar ratio of the reactants is 5:15:1. The reaction is completed over a period of 5 min at 20 °C.

Apparently, the alkylacylation of benzene with alkyl halides involves generation of a carbenium ion, which alkylates benzene. Subsequently acylation of the alkylated benzene occurs (Scheme 10).

Scheme 10

$R^tX + RCO^+Al_2X_7^- \longrightarrow R^{t+} Al_2X_7^- + RCOX$,

C$_6$H$_6$ + $R^{t+}Al_2X_7^-$ $\xrightarrow[-HX,\ -Al_2X_6]{}$ C$_6$H$_5$-R^t,

C$_6$H$_5$-R^t + $RCO^+Al_2X_7^-$ $\xrightarrow[-HX,\ -Al_2X_6]{}$ RCO-C$_6$H$_4$-R^t.

Since alkanes can give rise to carbenium ions in the presence of $RCO^+Al_2X_7^-$ complexes, they can be successfully used, instead of alkyl halides, as alkylating agents for aromatic hydrocarbons.[86,87] These reactions result in the formation of alkylated aromatic ketones (Scheme 10). The one-stage alkylacylation of benzene with isoalkanes or *n*-alkanes in the presence of the $RCO^+Al_2X_7^-$ complexes occurs at 0–20 °C. The yields of alkylacylation products reach 65%–87% (Table 4). The yields of non-alkylated aromatic ketones, the products of a competing reaction, are relatively low (3%–20%). Isobutane and *n*-butane can be used as alkylating agents. Butylated ketones are normally obtained in somewhat lower yields (up to 68%) but they are also the major reaction products.

$C_6H_6 + R'H + 2RCO^+Al_2X_7^- \xrightarrow[-HX,\ -RCHO,\ -Al_2X_6]{0\text{ to }20\ °C} p\text{-}R'C_6H_4COR$

R′ = Bu^i, Bu^n, n-C_5H_{11}, 2,3-$Me_2C_4H_7$, cyclo-C_5H_8Me;

R = Me, Pr, Ph; X = Cl, Br.

Alkylacylation reactions result in good yields of products only when an excess of the 'alkylating system' ($R'H + RCO^+Al_2X_7^-$) is used, the molar ratio $[R'H]:[RCO^+Al_2X_7^-]:[C_6H_6]$ is (10 to 15):(3 to 12):1, and the experimental procedure is thoroughly followed.[86,87]

Alkylacylation of benzene with isobutane occurs regioselectively and leads to the *para*-isomers of the corresponding ketones.

C$_6$H$_6$ + iso-C_4H_{10} + $R'CO^+Al_2X_7^-$ $\longrightarrow$ Bu^t-C$_6$H$_4$-COR′.

The reaction of benzene with isopentane gives equal amounts of *para*-substituted ketones differing in the structure of the pentyl group.

C$_6$H$_6$ + iso-C_5H_{12} + $R'CO^+Al_2X_7^-$ $\longrightarrow$

$\longrightarrow$ $Me_2(Et)C$-C$_6$H$_4$-COR′ + $Me(Pr^i)CH$-C$_6$H$_4$-COR′.

Alkylacylation of bromobenzene is more selective than that of benzene, the yield of the corresponding ketone reaching 74%–82% (see Table 4). The reaction with isobutane affords only one isomer, 2-bromo-4-*tert*-butylacetophenone.[86]

C$_6$H$_5$-Br + iso-C_4H_{10} + $MeCO^+Al_2X_7^-$ $\longrightarrow$

$\longrightarrow$ Bu^t-C$_6$H$_3$(Br)-COMe.

Table 4. One-stage alkylacylation of benzene and bromobenzene with alkanes (cycloalkanes) and $RCO^+Al_2X_7^-$ complexes.

Run	R'H	$RCO^+Al_2X_7^-$		$[RCO^+Al_2X_7^-]$:[PhY]	T/°C	t/min	Yield of products relative to ArH (%)	
		R	X				$R'C_6H_3(Y)COR$	YC_6H_4COR
Benzene								
1	iso-C_4H_{10}	Me	Cl	12:1	0	30	62	35
2	iso-C_4H_{10}	Me	Cl	12:1	20	40	68	32
3	iso-C_4H_{10}	Me	Br	6:1	0	30	48	41
4	iso-C_4H_{10}	Pr	Br	6:1	0	30	54	23
5	iso-C_4H_{10}	Ph	Cl	6:1	0	30	35	18
6	iso-C_5H_{12}	Me	Br	6:1	20	5	87	3
7	iso-C_5H_{12}	Me	Br	3:1	20	5	65	12
8	iso-C_5H_{12}	Me	Cl	6:1	20	5	81	20
9	iso-C_5H_{12}	Me	Br	6:1	20	5	73	3
10	iso-C_6H_{14}	Me	Cl	6:1	20	5	82	18
11	cyclo-C_5H_9Me	Me	Cl	6:1	20	5	58	11
Bromobenzene								
12	iso-C_4H_{10}	Me	Br	6:1	0	60	82	4
13	iso-C_4H_{10}	Me	Cl	6:1	0	60	79	22
14	iso-C_5H_{12}	Me	Cl	6:1	0	20	74	Traces
15	n-C_4H_{10}[a]	Me	Cl	6:1	0	30	40	5

[a] Before the reaction, the initial alkane was held for 3 h with a catalytic amount of $RCO^+Al_2X_7^-$.

Apparently, the *para*-bromo-*tert*-butylbenzene formed initially isomerises into the more stable *meta*-isomer in the presence of a strong aprotic superacid. The acylation of the *meta*-isomer into the *para*-position with respect to the *tert*-butyl group gives rise to the reaction product observed. Activated arenes (toluene, naphthalene, and *meta*-xylene) also form alkylacylation products, but their yields do not exceed 10% of the yields of products obtained by the direct acylation of arenes. At the same time, arenes that contain strong electron-withdrawing groups (nitrobenzene and acetophenone) remain unchanged under the reaction conditions. This fact suggests that the reactions under consideration occur as the initial alkylation of arenes followed by acylation of the alkylated arenes. Apparently, in the case where the aromatic compound is activated toward an electrophilic attack, the acylation and alkylation reactions proceed at comparable rates. Therefore, in the presence of excess acylating agent, the acylation occurs as the prevailing process. The difference between the acylation and alkylation rates increases on passing from activated aromatic compounds to benzene and, especially, to bromobenzene, which is inert toward electrophiles. Therefore, in these cases, the initial alkylation is the predominant or even the only reaction pathway.

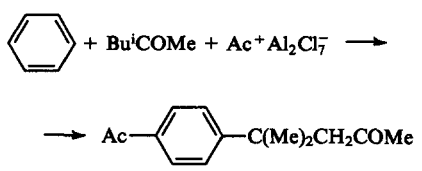
Apparently, the scheme of the alkylacylation with alkanes (or cycloalkanes) is similar to Scheme 10 and differs from it only by the absence of the stage for the regeneration of the acylium cation.[86]

$$R'H + RCO^+Al_2X_7^- \longrightarrow (R') + Al_2X_7^- + RCHO,$$

$$YC_6H_5 + (R') \longrightarrow YC_6H_4R',$$

$$YC_6H_4R' + RCO^+ \longrightarrow YC_6H_3(R')COR.$$

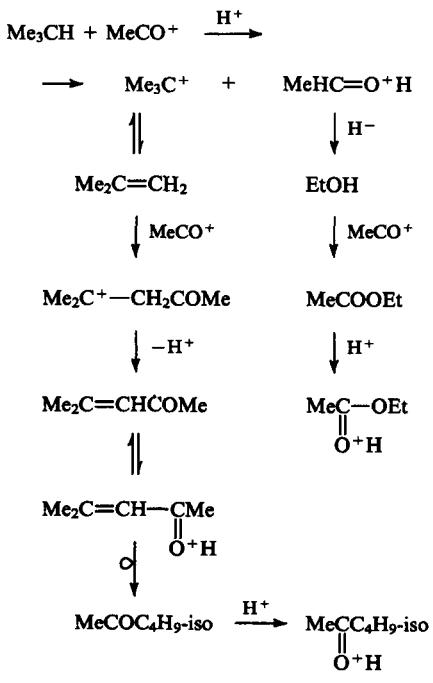
We have also detected the 'alkane-type' reactivity of Bu^iCOMe in its interaction with benzene, which resulted in the formation of the corresponding product of the alkylacylation of benzene in 40% yield.[86]



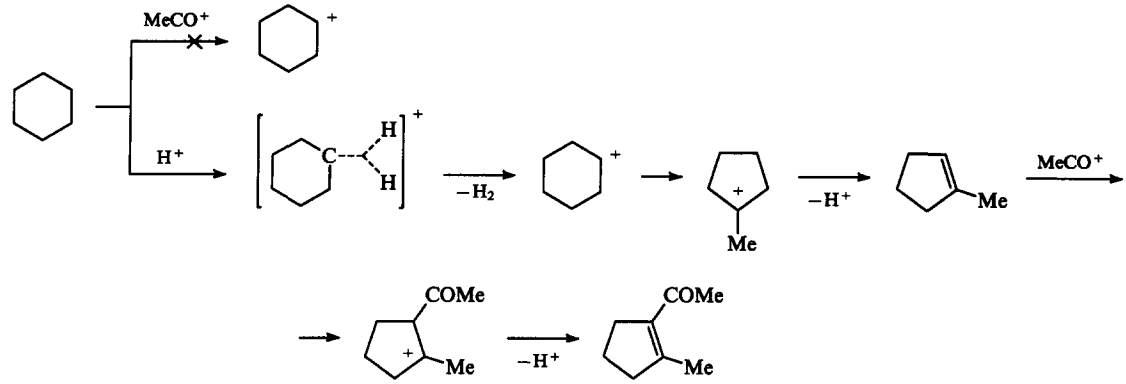
IV. Reactions of acylium salts with saturated hydrocarbons in protic superacids

Reactions of saturated hydrocarbons with acylium salts in a medium of a protic superacid were described for the first time by Brouwer and Kiffen.[88] They showed that in the $HF-BF_3$ and $HF-SbF_5$ systems at 25 °C, acylium ion detaches a hydride ion from the tertiary carbon atom in isobutane, isopentane, or methylcyclopentane. In the case of isobutane, the degree of conversion of an acylium salt amounts to 90% over a period of 12 h. The acylium salt is transformed into protonated ethyl acetate, which arises, in the authors' opinion,[88] *via* the interaction of $MeCO^+$ with the ethanol resulting from the reduction of $MeCO^+$ by the isoalkane. The conversion of isobutane leads initially to protonated mesityl oxide (Scheme 11). The second-order rate constant for this reaction is 3×10^{-5} l mol^{-1} s^{-1}.

Scheme 11

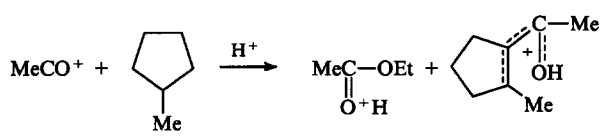


Scheme 12

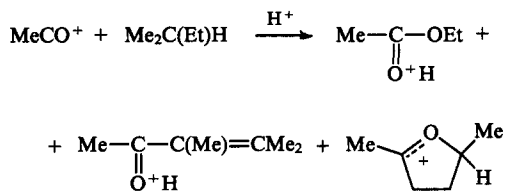


When the duration of the process is more than 12 h, the mesityl oxide formed is reduced by isobutane to give protonated isobutyl methyl ketone.

Methylcyclopentane reacts with $MeCO^+$ in a protic acid in a similar way and gives rise to protonated 1-acetyl-2-methylcyclopentene and ethyl acetate.



The reaction involving isopentane yields a more complex mixture of products.



When cyclohexane is treated with $MeCO^+$ in excess HSO_3F-SbF_5, an α,β-unsaturated ketone — 1-acetyl-2-methylcyclopentene — is formed in 44% yield.[89] It was suggested that the dehydrogenation of cyclohexane is due to the generation of a carbocation upon the action of the superacid HSO_3F-SbF_5 on the cycloalkane rather than to the hydride transfer to the $MeCO^+$ cation.[90,91] Thus, the role of $MeCO^+$ reduces only to acylation of the alkene existing in an equilibrium with the carbenium ion (Scheme 12).

It should be noted that with *n*-alkanes, hydride transfer barely takes place under the same conditions. For example, when butane has been in contact with a solution of $MeCO^+BF_4^-$ in $HF-BF_3$ for 72 h, the transformation occurred by no more than 1%, and the rate constant for this reaction, as estimated by Brouwer and Kiffen,[88] did not exceed $2\cdot10^{-8}$ l mol^{-1} s^{-1}. No transformations of *n*-alkanes have been observed when they were treated with $MeCO^+$ in excess HSO_3F-SbF_5.[89]

V. The nature of the active complexes in acyl halide – aluminium halide systems

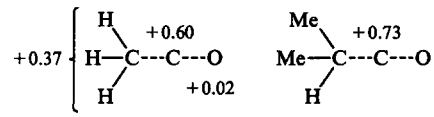
Evidently, the abstraction of a hydride ion from a saturated hydrocarbon by a superelectrophile leading to a carbocation is the key stage of the functionalisation of alkanes and cycloalkanes. This process includes one or several stages and occurs either by the classical Olah scheme [Eqns (1) and (2) in Scheme 1][92] or by a different mechanism.

From studies of equimolar $RCOX-MX_n$ systems, which were started as early as the beginning of this century and developed most significantly in the 1960–1970s, the structures of these systems in the solid state and in solution are well known (see, for example, reviews[44,93,94] and monographs[43–45,93–96]).

The solid $RCOX\cdot AlX_3$ complexes (R = Alk, X = Cl, Br) exist as ionic acylium salts or donor-acceptor complexes.[94] The structures of $MeCO^+AlCl_4^-$,[97] and $RC(Cl)=O\rightarrow AlCl_3$ [R = Et,[98] C_6H_5,[99] and *o*- and *p*-MeC_6H_4[100]] were determined by X-ray diffraction analysis. The cationic fragment $MeCO^+$ in the ionic complex $MeCO^+AlCl_4^-$ is linear, which corresponds to *sp*-hybridisation of the carbonyl carbon atom. The C–C–O angle is close to 180°, and the C–O bond is markedly shorter than the $C_{sp^2}=O$ bonds in ketones and acyl halides and even than that in CO. The structure of the $AlCl_4^-$ moiety is close to tetrahedral.

X-Ray diffraction data provide valuable information also on the electron density distribution in acylium cations. The positive charge in the acylium cation $C(2)H_3C(1)O^+$ has been shown to be mostly localised on the C(1) atom and on the hydrogen atoms attached to C(2) but not on the oxygen atom. In fact, the C(1)···Cl and $C(2)H_3$···Cl intramolecular distances between the nonbonded atoms are almost always smaller than the sums of the van der Waals radii of the corresponding atoms, whereas the Cl···O distances are greater than the sum of the covalent radii of Cl and O. This conclusion was totally confirmed by the data of an *ab initio* LCAO MO SCF calculation.[101] The results of this quantum-chemical calculation are in good agreement with the experimental values of bond lengths and bond angles shown in Scheme 13.

Scheme 13



The electron density distribution in the $MeCO^+$ ion inferred from an X-ray diffraction structural study of $MeCO^+SbF_6^-$ (see Ref. 102) is, in our opinion, less probable,[94] because, according to these data, the charge on the hydrogen atom (+0.07) in CH_3CO^+ is close to that in ethane, which is at variance with a number of other studies indicating that the hydrogen atoms in the acylium cation carry a substantial positive charge.

According to X-ray diffraction studies, the Lewis acid in nonionic $RCOX\cdot AlX_3$ complexes is coordinated to the electron pair of the oxygen atom of the acyl halide. This follows from the presence of Al–O bonds in these compounds. The Al–O bond lengths vary in the range 1.820–1.847 Å, and they are only slightly larger than the Al–O bond lengths in such stable compounds as aluminosilicates (1.79 Å). The complex formation involving oxygen results in the elongation of the C–O bond (1.21–1.24 Å) compared to this bond in noncoordinated RCOX (1.17 Å).[103] It is significant that the C–O and C–Cl bond lengths are much the same in various donor–acceptor complexes, which apparently indicates that their strengths are similar. Conversely, the C–C bond lengths in donor–acceptor complexes of the aliphatic and aromatic series are markedly different. For example, the C(1)–C(2) bond length in the complex $EtC(Cl)=O\rightarrow AlCl_3$ is close to the length of the classical $C_{sp^3}-C_{sp^2}$ bond, while the Ar–C bond

in complexes like $ArC(X)=O\rightarrow AlX_3$ is shorter than the Ar–C bond in a non-coordinated ArC(X)=O molecule.[94] A specific feature of the geometry of the donor-acceptor complexes $ArC(X)=O\rightarrow AlX_3$ is a substantial increase in the bond angles with respect to 120° typical of an sp^2-hybridised carbon atom. This distortion of the angles has been attributed[104] to steric effects occurring upon packing of the molecules in a crystal. The geometry of the $O-AlCl_3$ fragment is that of a somewhat distorted tetrahedron.[94]

According to ^{81}Br NQR data,[105] the $AcBr\cdot AlBr_3$ complex at 77 K is an ionic acetylium salt. The same complex obtained in a solution in CH_2Br_2 at 77 K exists as the ionic salt $MeCO^+[AlBr_4\rightarrow CH_2Br_2]^-$.

The $RCOX\cdot AlX_3$ systems have been studied in a broad range of solvents (CH_2Cl_2, CH_2Br_2, $CHCl_3$, $C_2H_4Cl_2$, $C_6H_5NO_2$, $MeNO_2$, SO_2, HF, CF_3SO_3H, *etc.*) by IR, Raman, and ^1H, ^{13}C, and ^{27}Al NMR spectroscopy.[41,94,106–109] The whole set of the results obtained indicate that in the solvents listed above, except for strong protic acids, the systems under study exist exclusively as donor-acceptor complexes (the state of these systems in SO_2 is less definite[94]).

1. Acylation of arenes

Since 1877, when the $AlCl_3$-catalysed acylation of aromatic hydrocarbons was discovered by Friedel and Crafts,[110] the mechanism of this reaction has been intensely studied both by the same researchers and by many others. The current views on the nature of the active species involved in this process and the arguments in favour of the concept outlined are the following.[111]

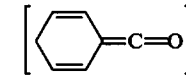
The acetylium cation is a relatively weak electrophile due to the resonance stabilisation of the carbocation centre by the electron pairs of the oxygen atom.

$$Me-C^+=\ddot{O}: \longleftrightarrow Me-C\equiv\ddot{O}^+ .$$

Therefore, it seems unlikely that benzene or other non-activated arenes would react with the acetylium cation or with the donor-acceptor complex, which is even less reactive. In fact, a study of the influence of the acidity of the medium on the rate of acetylation and benzoylation of benzene, toluene, and chlorobenzene with $MeCO^+SbF_6^-$ and $PhCO^+SbF_6^-$ has led to the conclusion that in an acidic medium, the protonated acetylium $MeC^+=O^+H$ or $PhC^+=O^+H$ is the main reacting species.[111] For example, the reaction of benzene with $MeCO^+SbF_6^-$ carried out in CF_3COOH ($H_0 = -2.7$) at 5 °C for 12 h, yields less than 10% of acetophenone, while chlorobenzene remains unchanged over a period of 24 h under the same conditions. The rate of acetylation increases by a factor of 10 and more on passing from a solvent with $H_0 = -12$ (a mixture of CF_3COOH with CF_3SO_3H) to a solvent with $H_0 = -14$ (CF_3SO_3H).[111] The NMR data indicate that for $H_0 = -12$, the proportion of the $MeCO^+$ ion in the complex is 60%, whereas for $H_0 = -14$, it reaches 75%. Calculations show that if it were the acetylium cation that acted as the reactive species, the acylation rate would increase by a factor of less than 2 following the change in the acidity from $H_0 = -12$ to $H_0 = -14$.

Unlike benzene and chlorobenzene, toluene, which is more reactive, gives acetylation products in 55% yield over a period of 12 h at 0 °C in CF_3COOH. However, the ratios of the isomers resulting from the acetylation of toluene in CF_3COOH and CF_3SO_3H are markedly dissimilar, which indicates that the process occurs by different mechanisms in the media with different acidities. Conversely, the isomeric compositions of the acylation products obtained in media with $H_0 = -10$ and -18 are identical. It has been assumed that toluene, which is an activated arene, is capable of being acetylated with the $MeCO^+$ ion in low-acidity media. The strong acid $HSbF_5X$ formed in this reaction also can catalyse subsequent reactions. In a medium with higher acidity, the reaction involving the protonated acetylium cation is the main route for the acylation of toluene.

The benzoylation of arenes with $PhCO^+SbF_6^-$ follows the same regularities. It is noteworthy that an increase in the benzoylation rate is observed at a higher acidity than $H_0 = -14$, although spectral studies indicate that at $H_0 = -14$, the system exists exclusively as the ionic salt $PhCO^+SbF_6^-$.[111] The fact that benzoylation requires more acidic media than acetylation has been explained[111] by the lower reactivity of aroyl cations $ArCO^+$ compared to that of the acylium cations $AlkCO^+$, which is due to the contribution of ketene-like structures.

$$PhC^+=O \longleftrightarrow PhC\equiv O^+ \longleftrightarrow \left[\text{}\right]^+ .$$

It has also been suggested that the species formed from two acceptor molecules play an important role in the acylation of arenes in organic media. This hypothesis was stated for the first time by Gillet to account for the activating influence of $AlCl_3$ on the synthesis of ketones from arenes and $RCOX\cdot AlCl_3$ complexes.[112] The hypothesis of Gillet was soon confirmed experimentally.

A kinetic study of the $AlCl_3$-catalysed benzoylation of aromatic hydrocarbons[113] has led to a complex equation for the rate constant, most closely consistent with the concept of participation of complexes of two types

$$PhC(X)=O\rightarrow AlCl_3 \quad \text{and} \quad PhC(=O\rightarrow AlCl_3)(X\rightarrow AlCl_3)$$

Based on a kinetic study of the acylation of arenes with acetyl chloride in the presence of $AlCl_3$ in dichloroethane, *ortho*-dichlorobenzene, or in excess acetyl chloride, the workers cited[113] concluded that complexes of three types participate in the reaction, namely, $MeCO^+AlCl_4^-$, $MeC(Cl)=O\rightarrow AlCl_3$, and $Cl_3Al\leftarrow ClC(Me)=O\rightarrow AlCl_3$.

Other investigators,[114] who have also studied the acylation of benzene with $RCOCl\cdot AlCl_3$ complexes in dichloroethane, have shown that this reaction can be described by a simpler equation

$$v = k[ArH][RCOCl\cdot AlCl_3] .$$

The benzoylation of arenes with acyl halides in the presence of $AlBr_3$, at $[AlBr_3]:[PhCOBr]$ molar ratios of 1 and 1.5 has been shown[115] to obey second-order kinetics. Further increase in the amount of $AlBr_3$ results in a change in the reaction mechanism. In this case, the reaction rate is described by a third-order equation. The rate constants (k) for the benzoylation in a trichlorobenzene solution are given below.

$[AlBr_3]:[PhCOBr]$	1	1.5	2	2.5	3
k	0.4	6.0	128	225	327

It is seen from the above data that on passing from the $PhCOBr\cdot AlBr_3$ system to the $PhCOBr\cdot 2AlBr_3$ system, the rate constant for benzoylation increases by a factor of 320. When the quantity of $AlBr_3$ is further increased, the rate constant smoothly and slightly increases. The researchers[115] could not explain this phenomenon, and they stated only that the electrophilicity of $PhCOBr\cdot nAlBr_3$ systems at $n = 2$ is markedly higher than that at $n = 1$.

2. The nature of active species in reactions of activated alkanes with acylium salts in media of protic superacids

The results obtained for reactions of isobutane with the acetylium cation are in full agreement with the above data on the protonated acylium cations as the species responsible for the acylation of arenes in acidic media. Brouwer and Kiffen[88] have reported on the hydride transfer from isobutane to the acetylium cation generated from acetic acid in an $HF-BF_3$ medium.

$$MeC^+{=}O + H^+ \rightleftharpoons MeC^+{=}O^+H,$$

$$Me_3CH + MeC^+{=}O^+H \rightleftharpoons Me_3C^+ + MeCH{=}O^+H.$$

At the same time, Olah and coworkers [116] have shown that in aprotic solvents such as SO_2, SO_2ClF, AsF_3, and CH_2Cl_2 this reaction with the acetylium cation does not occur.

$$Me_3CH + MeC^+{=}O \xrightarrow{SO_2} Me_3C^+ + MeCHO.$$

The views about a crucial role for protonated acetylium are in agreement with the results of calculations, which indicate that the abstraction of a hydride ion from isobutane by the acetylium cation in the gas phase requires 8.5 kcal mol^{-1}. The protonated acylium dication has not been detected by ^1H NMR; however, in the IR spectrum of the acetylium cation in a protic superacid, a shift of the frequency corresponding to the carbonyl group has been observed. Calculations have shown that a global minimum on the potential energy surface corresponds to the $[MeC{-}OH]^{2+}$ structure.[117] It should be noted that the $C_2H_4O^{2+}$ dication has also been observed in the gas phase by mass spectrometry.[118]

3. The nature of active species generated in aprotic superacids $RCOX \cdot 2AlX_3$ and responsible for their reactivity toward alkanes

In order to understand the reason for the high reactivity of the $RCOX \cdot 2AlX_3$ complexes, which differs so markedly from the reactivity of the corresponding equimolar $RCOX \cdot AlX_3$ complexes, we have studied the structures of both types of complexes in the solid state and in solutions in CH_2X_2 using ^{81}Br NQR, ^1H, ^{13}C, ^{27}Al, and ^{17}O NMR (in the solid state and in solutions), IR, and Raman spectroscopy.[41, 105, 109] It was found that in the solid state complexes of both types are ionic acylium salts differing only in the structure of the anions: $MeCO^+Al_2X_7^-$ for $MeCOX \cdot 2AlX_3$ or $MeCO^+AlX_4^-$ for $MeCOX \cdot AlX_3$. This conclusion is at variance with the suggestion of Bertoluzza, who has attributed the structure $(Ac{\cdots}AlCl_3)^+AlCl_4^-$ to the isolated complex $AcCl \cdot 2AlCl_3$.[119]

In CH_2X_2 solutions, the former complexes exist as equilibrium mixtures of acylium salts $MeCO^+Al_2X_7^-$ and donor-acceptor complexes $MeC(X){=}O{\rightarrow}Al_2X_6$, whereas the latter exist exclusively as coordination complexes $MeCO(X){=}O{\rightarrow}AlX_3$.

$$MeCOX + AlX_3 \rightleftharpoons$$

$$\rightleftharpoons MeC(X){=}O{\rightarrow}AlX_3 \not\rightarrow MeCO^+AlX_4^-,$$

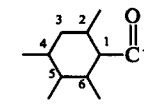
$$MeCOX + 2AlX_3 \rightleftharpoons MeC(X){=}O{\rightarrow}Al_2X_6 \rightleftharpoons$$

$$\rightleftharpoons MeCO^+Al_2X_7^-.$$

Thus, only $RCOX \cdot 2AlX_3$ (R = Alk), which are active in the reactions with alkanes, are able to generate effectively acylium cations in low-polarity solutions, and this is their basic difference from the corresponding equimolar complexes. A comparison of two pairs of complexes: $MesCO^+Al_2Br_7^-$ and $MesCO^+AlBr_4^-$ (Mes = 2,4,6-$Me_3C_6H_2$), on the one hand, and $Ac^+Sb_2F_{11}^-$ and $Ac^+SbF_6^-$ in SO_2, on the other hand, has shown that only acylium salts with dimeric anions are active in the reactions with alkanes under mild conditions (Table 5).[120]

The very close similarity of the ^1H and ^{13}C NMR spectra of active and inactive complexes of the composition $RCOX \cdot nAlX_3$ (n = 1, 2) differing only in the structure of the anion (Table 6) gave grounds to suggest that it is not the acylium salts themselves that

Table 6. ^{13}C NMR spectra of $MesCO^+X^-$ salts with anions $X^- = AlBr_4^-$ and $X^- = Al_2Br_7^-$ (δ, ppm).[120]

δ, ppm		Assignment
$X^- = AlBr_4^-$	$X^- = Al_2Br_7^-$	
21.4	21.7	C(2)–CH_3
23.7	24.2	C(4)–CH_3
85.3	84.6	C(1)
153.7	153.9	C(2)
130.9	131.5	C(3)
162.1	163.1	C(4)
159.2	159.7	CO

Note. In the ^{27}Al NMR spectra of the $MesCO^+AlBr_4^-$ and $MesCO^+Al_2Br_7^-$ complexes, the corresponding shifts of the ^{27}Al nuclei are 79.4 (Δ = 12 Hz) and 93.0 ppm (Δ = 930 Hz).

are responsible for the superacidic properties of the $RCOX \cdot 2AlX_3$ systems. It was suggested that in solutions, the acylium salts with the dimeric anions $Al_2X_7^-$ occur in an equilibrium with more electrophilic ionic complexes, namely, cationic acylium complexes of the type **10a** or **10b** in which the cation is additionally coordinated to the Lewis acid.[41, 94, 120]

$$RCO^+Al_2X_7^- \rightleftharpoons$$

$$\rightleftharpoons RC^+{=}O{\rightarrow}Al_2X_7^- \rightleftharpoons [RC^+{=}O{\rightarrow}AlX_3]AlX_4^-$$

$$\updownarrow \qquad\qquad \updownarrow$$

$$RC^{2+}{-}O{-}Al_2X_7^- \qquad [RC^{2+}{-}O{-}AlX_3^-]AlX_4^-$$

10a **10b**

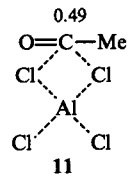
Table 5. Comparison of the activities of acylium salts with monomeric and dimeric anions in the cracking of n-alkanes and in the isomerisation of trimethylenenorbornane **9** (according to a published study [120]).

Hydrocarbon (RH)	Acylium salt (A)	[RH] : [A]	t/h	Conversion of RH (%)	Products (yields relative to RH, mass %)
n-C_8H_{18}	$Ac^+SbF_6^-$	1 : 1	3.0	0	–
n-C_8H_{18}	$Ac^+Sb_2F_{11}^-$	1 : 1	3.0	100	iso-C_4H_{10} (31) + oligomer (59)
n-C_8H_{18}	$Ac^+Sb_2F_{11}^-$	1 : 1	1.0	100	iso-C_4H_{10} (36) + oligomer (56)
n-$C_{12}H_{26}$ [a]	$Ac^+Sb_2F_{11}^-$	1 : 1	2.0	85	see [b]
n-C_8H_{18} [c]	$MesCO^+AlBr_4^-$	1 : 4	0.5	0	–
n-C_8H_{18} [c]	$MesCO^+Al_2Br_7^-$	1 : 4	0.5	100	see [b]
n-$C_{12}H_{26}$ [c]	$MesCO^+AlBr_4^-$	1 : 2	0.5	0	–
n-$C_{12}H_{26}$ [c]	$MesCO^+Al_2Br_7^-$	1 : 2	0.5	100	see [b]
9	$MesCO^+AlBr_4^-$	1 : 10	5.0	0	–
9	$MesCO^+Al_2Br_7^-$	1 : 10	5.0	37	adamantane (37)
9	$MesCO^+Al_2Br_7^-$	1 : 10	8.0	86	adamantane (54)

[a] In SO_2. [b] Not determined. [c] In CH_2Br_2.

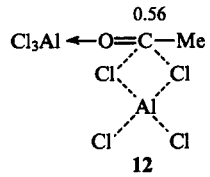
It is clear that the additional coordination should lead to a more electrophilic cation, which in its extreme form, can be represented as the acylium dication. The fact that these species are difficult to detect experimentally must be due to their very low concentration.

Data about the complexes that can be generated in the $MeCOCl \cdot nAlCl_3$ systems ($n = 1-3$) have also been obtained by semiempirical CNDO quantum-chemical calculations. The most significant conclusion which can be drawn from these calculations is that in the systems containing an excess of aluminium chloride ($n = 2$ and 3), the formation of complexes **12** and **13**, in which the carbonyl carbon atoms carry larger positive charges than this carbon atom in the acetylium cation **11**, is in principle possible.[121]



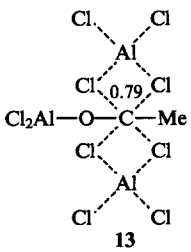
11

$H_0 = -185$ kcal mol^{-1}



12

$H_0 = -322$ kcal mol^{-1}



13

$H_0 = -423$ kcal mol^{-1}

In the complex **12**, which can be regarded as the acetylium cation with a donor–acceptor bond $=O\rightarrow AlCl_3$ (**10b**) postulated previously as a key intermediate, the electron density on all the atoms in the $MeC=O$ fragment is substantially lower than that in the non-coordinated cation **11**: the positive charge on the carbonyl carbon atom is +0.56. The structure of **13**, which also corresponds to a local minimum on the potential energy surface, is of special interest. The complex **13** can be regarded as a system incorporating a $Cl_2Al-OC^{2+}Me$ dication and two $AlCl_4^-$ anions. The charge on the carbon atom in this complex reaches a record value of +0.79.

Table 7 presents the enthalpies of the reactions, which characterise the relative stabilities of the $MeCOCl \cdot nAlCl_3$ complexes. From the data given in the Table, it follows that the reactions (1) and (2) leading to charged species are strongly endothermal. The formation of the polar complex **11** requires less energy than the formation of separated ions. It should be taken into account that these data refer to the gas phase, whereas the energies of formation of the ions in solution can be much lower due to solvation and agglomeration. In fact, the existence of acetylium salts in solution has been proved, although calculations for the reactions (1) and (2) indicate that their formation requires a lot of energy (110.5 kcal mol^{-1}). The formation of donor-acceptor complexes of the composition 1 : 1 and 1 : 2 involves either release of energy or absorption of a small quantity of energy. It is significant that the formation of the complex **12** and even of the dicationic complex **13** in the reaction of acetyl chloride with $AlCl_3$ (but not with Al_2Cl_6) is energetically favourable, unlike the formation of the acetylium complex **11**.

Thus, the complexes **12** and **13** can be regarded as the most likely key superelectrophiles, which are responsible for the high activity of acyl halides (in the presence of excess aluminium halides) with respect to alkanes. Apparently, the role of the complex **13** is manifested only when the reaction mixture contains a substantial excess of aluminium halide. The generation of the carbenium ions from alkanes under the action of $RCOX \cdot 2AlX_3$ can be represented as follows:

$$RH + [R'C^+=O\rightarrow AlX_3]AlX_4^- \longrightarrow R^+Al_2X_7^- + R'CHO,$$

$$RH + [R'C^{2+}OAlX_2]2AlX_4^- \longrightarrow$$

$$\longrightarrow R^+Al_2X_7^- + R'CHO + AlX_3.$$

At present, the idea concerning the participation of dications or even of multicharged positive ions in organic reactions is becoming more and more popular.[117,121]

Table 7. Enthalpies (ΔH) of reactions, characterising the stability of the $MeCOCl \cdot nAlCl_3$ complexes (according to a published study [121]).

Number of the reaction	Reaction	ΔH/kcal mol^{-1}
(1)	$MeCOCl + \frac{1}{2}Al_2Cl_6 \longrightarrow O=C^+Me + AlCl_4^-$	110.5
(2)	$MeC(Cl)=O\rightarrow AlCl_3 + \frac{1}{2}Al_2Cl_6 \longrightarrow MeC(Cl)=O\rightarrow AlCl_2^+ + AlCl_4^-$	98.3
(3)	$MeCOCl + \frac{1}{2}Al_2Cl_6 \longrightarrow (MeC^+O)AlCl_4^-$ **11**	35.7
(4)	$MeC(Cl)=O\rightarrow AlCl_3 \longrightarrow MeC(Cl)_2OAlCl_2$	24.9
(5)	$MeCOCl + \frac{1}{2}Al_2Cl_6 \longrightarrow MeC(Cl)=O\rightarrow AlCl_3$	−7.5
(6)	$MeCOCl + \frac{1}{2}Al_2Cl_6 \longrightarrow MeC(O)Cl\rightarrow AlCl_3$	5.4
(7)	$MeCOCl + Al_2Cl_6 \longrightarrow MeC(Cl)=O\rightarrow Al_2Cl_6$	−2.9
(8)	$MeCOCl + Al_2Cl_6 \longrightarrow [MeC=O\rightarrow AlCl_3]^+AlCl_4^-$ **12**	−4.4
(9)	$MeCOCl + \frac{3}{2}Al_2Cl_6 \longrightarrow [MeC^{2+}OAlCl_2]2AlCl_4^-$ **13**	75.4
(10)	$MeCOCl + 3AlCl_3 \longrightarrow [MeC^{2+}OAlCl_2]2AlCl_4^-$ **13**	−2.3

VI. Conclusion

The high selectivity and the ease of one-stage functionalisation reactions, the high yields of products, and the accessibility of both initial compounds and $RCOX \cdot nAlX_3$ complexes (which are obtained by mere mixing of acyl halides with aluminium halides) suggest that the reactions considered above can be of interest as methods for the laboratory syntheses of organic compounds from alkanes and cycloalkanes.

The 'classical' Friedel–Crafts complexes can find application in the functionalisation of activated saturated hydrocarbons. The superacidic $RCOX \cdot 2AlX_3$ complexes substantially extend the possibilities for the direct functionalisation of alkanes and make it possible to perform selective and effective transformations of linear alkanes and simple cycloalkanes into functional derivatives.

The conclusion that dication-type species play a key role in the reactions of alkanes with $RCOX \cdot 2AlX_3$ complexes has stimulated the search for new superelectrophilic complexes, which would be more accessible and more convenient to work with than the complexes based on acyl halides and would open the way to new types of functionalisation. Testing of a number of systems in which the generation of dications is, in principle, possible has led in recent years to new aprotic superacids, which are quite promising regarding the functionalisation of alkanes.[123–128] The direct one-stage synthesis of organic compounds from saturated hydrocarbons may be accomplished in the near future, at least, for lower alkanes and cycloalkanes, which are relatively resistant to cracking. The subsequent important and complicated task is to develop new superacids containing no aluminium halides. The advantages of such systems are obvious. In this case, the problem of catalyst regeneration as well as ecological problems would be solved more easily.

Advances in the development of homogeneous aprotic superacids also seem very important for the elaboration of solid superacids of a new generation, which play a crucial role in the chemistry of alkanes.

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