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Polyhalomethanes combined with aluminum halides in one-step syntheses of carbonyl-containing compounds from alkanes and cycloalkanes*

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Data on new-generation superelectrophiles containing polyhalomethanes and aluminum halides are generalized. These systems open up broad prospects for organic syntheses based on alkanes and cycloalkanes. With these systems, reactions of various alkanes and cycloalkanes with CO were performed for the first time. Superelectrophiles underlay the development of new one-pot methods for the synthesis of carbonyl-containing compounds of various classes from readily available alkanes (or cycloalkanes) and CO. The reactions are usually selective and give the target products in high yields.

Key words: superelectrophilic complexes, aluminum halides, polyhalomethanes, carbonyl derivatives, transformations of alkanes and cycloalkanes, carbonylation, organic synthesis.

Introduction

The discovery of alkane activation by protic superacids[1,2] and transition metal complexes[3] shattered the myth of the intertness of alkanes under mild conditions. However, despite the substantial progress in this field of chemistry and the investigation of various approaches to the development of active systems,[4—41] alkanes still represent enormous undeveloped resources for organic synthesis, and elaboration of selective syntheses of valuable organic products directly from readily available oil raw materials is still among the most important and complicated challenges of organic chemistry.

The discovery of superelectrophilic properties of systems containing acyl halides in combination with excess aluminum halides[42] has served as the starting point in our search for new active systems able to initiate transformations of alkanes. The set of chemical and physicochemical data,[43] the results of quantum-chemical calculations,[44] and the known published data[45—52] concerning the reactions of acylium salts with saturated hydrocarbons in the presence of protic superacids led to the assumption that reactions of alkanes with the $RCOX\cdot 2AlX_3$ complexes, which have been studied in detail,[53—68] involve dicationic species in which the acylium cation is additionally coordinated to the aluminum halide molecule. In view of the foregoing, our approach to the development of new alkane-activating systems was based on the activation of molecules with several nucleophilic centers by one or several aluminum halide molecules. We expected that this route would give rise to active cationic systems or even dicationic species. As shown later by quantum-chemical calculations,[69—74] complexes formed in the newly developed systems are highly diverse and cannot be reduced in all cases to truly cationic or, all the more, dicationic systems. Nevertheless, this approach has proved fruitful and has resulted in the development of highly active organic and inorganic superelectrophiles of new generation

$RCOX\cdot 2AlX_3$ [42];
$CX_4\cdot nAlX_3$, $CHX_3\cdot nAlX_3$, $CH_2X_2\cdot nAlX_3$ [75];
$Hal_2\cdot nAlX_3$ [76];
$SOCl_2\cdot nAlX_3$ [77]; $RSO_2Cl\cdot nAlX_3$ [77]; $S_2Cl_2\cdot nAlX_3$ [77];
$BBr_3\cdot 2AlBr_3$,[78] and
$PBr_3\cdot 2AlBr_3$ [78]

(R = Alk, Ar; X = Cl, Br; Hal_2 = Cl_2, Br_2, I_2; n = 1—3).

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* This work is dedicated to the memory of our teacher, Mark Efimovich Vol´pin, an outstanding scientist and a brilliant person. He was interested in only important and complex problems. The chemistry of alkanes is among such challenges. Our research group started investigations in this field together with Mark Efimovich Vol´pin. We hope that the studies started in M. E. Vol´pin´s laboratory and continued by his followers would occupy a worthy place in the chemistry of saturated hydrocarbons, which has been developed by numerous splendid Russian scientists (N. D. Zelinsky, V. N. Ipat´ev, A. E. Shilov, and many others) and is now in progress.

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The new-generation superelectrophiles include the systems mentioned above in which aluminum halides are combined with acyl halides and new systems based on polyhalomethanes[75] (organic superelectrophiles). The group of inorganic superelectrophiles comprises halogen-,[76] sulfur-,[77] boron-, and phosphorus-containing[78] halides and oxohalides, which are also combined with aluminum halides. Superelectrophiles containing polyhalomethanes in combination with aluminum halides proved to be the most promising as regards selective functionalization of alkanes and cycloalkanes.

This review is devoted to carbonylation of linear C_2—C_{10} alkanes, C_5—C_8 cycloalkanes (and the isomeric monoalkylcyclohexanes), bi- and tricyclanes (norbornane, tetrahydrodicyclopentadiene, adamantane, and 1,3-dimethyladamantane) and the use of these reactions for one-step acylation of a broad range of substrates (alcohols, aromatic hydrocarbons, tetraalkyl- and trialkylarylsilanes, heteroaromatic compounds (thiophene, furan, and pyrrole), aliphatic, cyclic, and aromatic amines) by treatment with alkanes or cycloalkanes and CO in the presence of superelectrophilic systems containing polyhalomethanes combined with aluminum halides. The review also considers opening of the tetrahydrofuran ring to give esters $RCOO(CH_2)_4Br$, carried out for the first time by treatment with equivalents of acylium salts originated from saturated hydrocarbons RH (alkanes and mono-, bi-, and tricyclanes) and CO in the presence of superelectrophiles $CX_4 \cdot 2AlBr_3$ as well as reactions of cycloalkanes, CO, and ethylene to give the products of ethylene bromoacylation or acylation. Before we proceed to the material concerning carbonylation of alkanes and cycloalkanes and its application in organic synthesis, we will briefly consider other transformations of saturated hydrocarbons initiated by superelectrophiles based on polyhalomethanes.

Polyhalomethanes combined with aluminum halides as new superelectrophiles in the transformations of alkanes and cycloalkanes

Reactions without functionalization. Ionization of polyhalomethanes under the action of aluminum halides has been known since the early 20th century.[79,80] However, only in 1993, did we find that these systems actively initiate transformations of saturated hydrocarbons under mild conditions, such as cracking and isomerization of linear alkanes (Scheme 1)[75] and various oxidative reactions of cycloalkanes (Scheme 2).[81,82]

Scheme 1

$$C_mH_{2m+2} \xrightarrow[a]{E} i\text{-}C_4H_{10} + i\text{-}C_5H_{12} + \ldots \text{ oligomers}$$

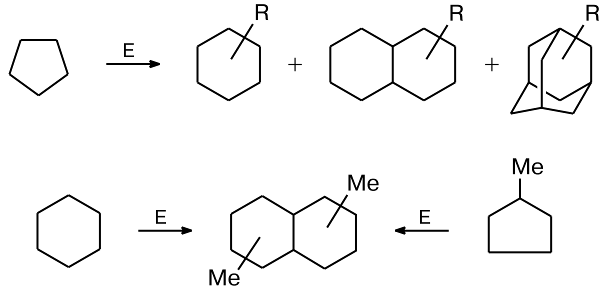
$m = 5$—12

$$n\text{-RH} \xrightarrow[b]{E} i\text{-RH}$$

$RH = n\text{-}C_4H_{10}, n\text{-}C_5H_{12}$

a. $E = CX_4 \cdot nAlBr_3$, $CHX_3 \cdot nAlBr_3$ (X = Cl, Br; *n* = 1, 2), 20 °C, 10—20 min; degree of conversion 70—80%.
b. $E = CX_4 \cdot 2AlBr_3$, $CHX_3 \cdot 2AlBr_3$ (X = Cl, Br), 20 °C, 3—6 h; yield 51—65% (20—25 moles in relation to E).

Scheme 2



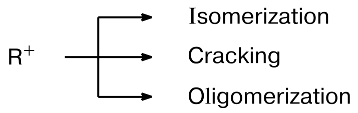
$E = CX_4 \cdot nAlBr_3$, $CHX_3 \cdot 2AlBr_3$ (X = Cl, Br; *n* = 1, 2); R is a set of alkyl groups.

The key step in each of these processes is the transfer of a hydride ion from the saturated hydrocarbon to the polyhalomethyl cation generated from the starting polyhalomethane on treatment with aluminum halide. This affords the reduced form of polyhalomethane and a carbocation, which undergoes further transformations (Scheme 3).[78]

Scheme 3

$$CBr_4 \xrightarrow{AlBr_3} CBr_3^+AlBr_4^- \xrightarrow{AlBr_3} CBr_3^+Al_2Br_7^-$$

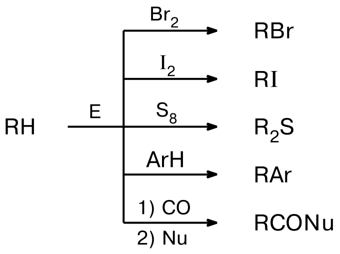
$$RH + CBr_3^+ \longrightarrow R^+ + CHBr_3$$



Types of functionalization reactions of alkanes and cycloalkanes. Selective one-step functionalization of alkanes and cycloalkanes is of particular interest. The types of functionalization reactions of alkanes and cycloalkanes induced by polyhalomethane/aluminum halide systems are summarized in Scheme 4.

Some examples of developed processes are shown in Schemes 5—8. They include selective monobromination of saturated hydrocarbons and dibromination of ethane to give 1,2-dibromoethane (Scheme 5).[83,84]

Scheme 4



E = $CX_4 \cdot 2AlX_3$

Scheme 5

$$RH + Br_2 \xrightarrow{-20\text{—}0\ ^\circ C} RBr$$

6 moles in relation to the catalyst

$$C_2H_6 + Br_2 \xrightarrow{55\text{—}65\ ^\circ C} 1,2\text{-}C_2H_4Br_2$$

100% in relation to Br_2

RH = C_3H_8, C_4H_{10}, *cyclo*-C_5H_{10}, *cyclo*-C_6H_{12} and so on.

Using the $CCl_4 \cdot 2AlI_3$ system, electrophilic ionic iodination of saturated hydrocarbons by I_2 was carried out for the first time (Scheme 6).[85]

Scheme 6

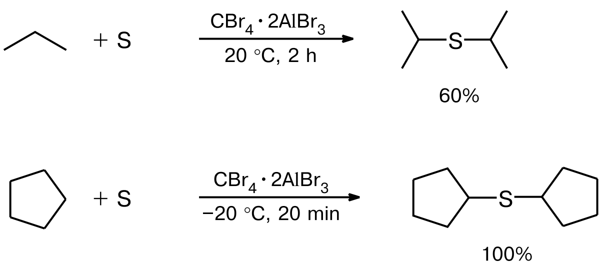
$$RH + I_2 \xrightarrow[-20\ ^\circ C,\ 1\text{—}2\ h]{CCl_4 \cdot 2AlI_3} RI$$

50—80%

RH = propane, cyclopentane, cyclohexane, norbornane, adamantane

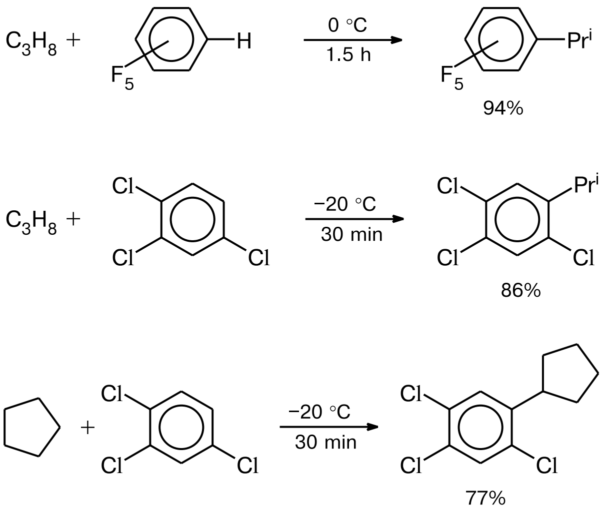
Yet another type of functionalization is sulfurization on treatment with elemental sulfur (Scheme 7).[86]

Scheme 7



The alkylation of deactivated arenes with alkanes and cycloalkanes is one more type of transformation (Scheme 8).[87,88]

Scheme 8



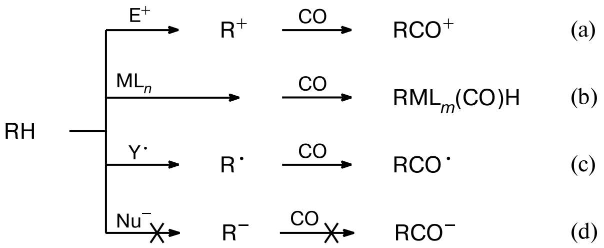
Many of these processes occur selectively and regioselectively to give products in high yields. Some reactions represent new types of transformation of alkanes (selective dibromination of ethane, ionic monoiodination of saturated hydrocarbons with I_2, and alkylation of deactivated aromatic hydrocarbons). Other functionalization reactions (propane and cyclopentane sulfurization, catalytic monobromination of cycloalkanes) were carried out selectively for the first time. Yet another type of functionalization is the reactions with CO giving rise to various carbonyl-containing compounds. Carbonylation of saturated hydrocarbons opens up the widest prospects for organic synthesis, and it is the subject of detailed discussion given below.

Reactions of alkanes and cycloalkanes with CO induced by superelectrophiles based on polyhalomethanes, resulting in esters of carboxylic acids

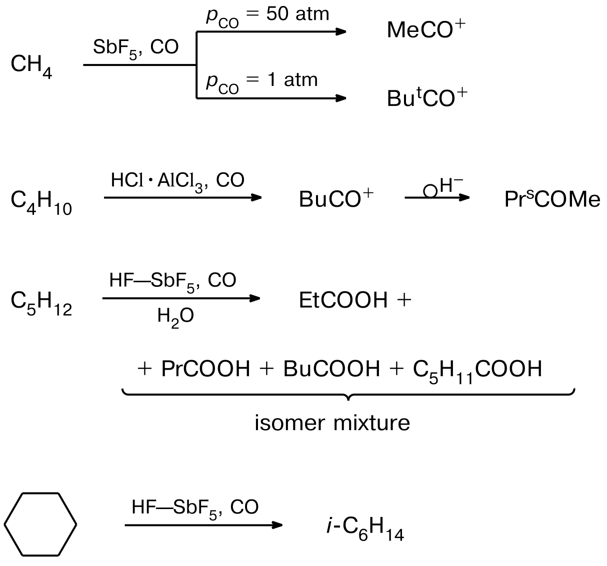
Reactions of alkanes and cycloalkanes with CO (state-of-the art). Selective reactions of saturated hydrocarbons with CO open up the possibility of one-pot synthesis of valuable carbonyl-containing compounds from readily available raw materials.[89] The research along this line was started in the early 1930s.[90—93] At present, numerous systems able to initiate carbonylation of saturated hydrocarbons have been described. They include transition metal compounds,[94—99] radical systems,[21,22,100—103] electrophiles[5,6,9,10,104—110] (mainly protic superacids). Of the possible transformation routes of saturated hydrocarbons (Scheme 9), only carbonylation induced by nucleophiles is unknown (d).

However, the selectivity of reactions studied previously is often very low and sharply decreases on passing from lower hydrocarbons to higher homologs, irrespec-

Scheme 9



Scheme 10

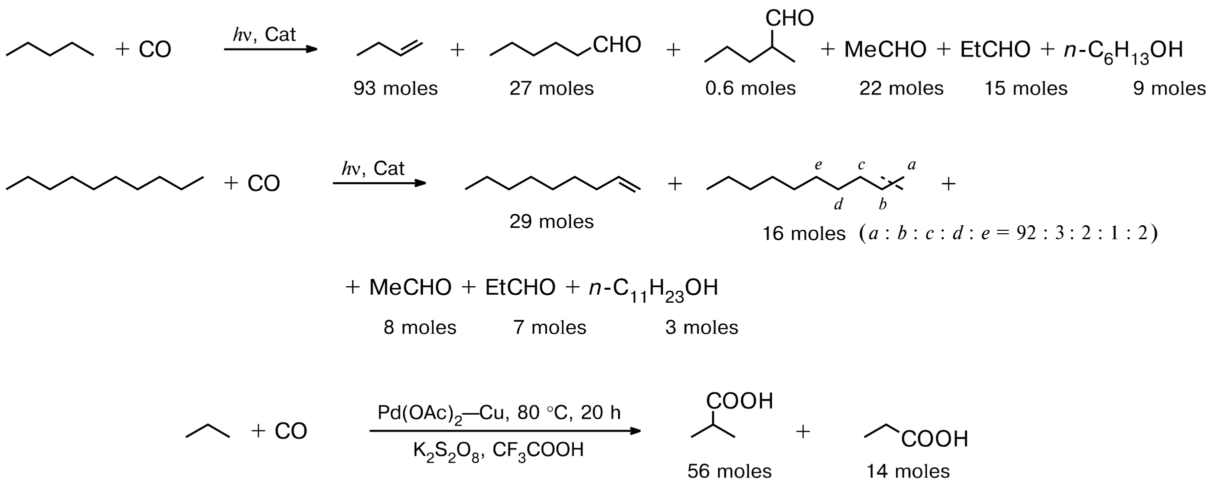


tive of the type of system. This is due to the increase in the lability of the key intermediates of reactions (a)—(c) (see Scheme 9), namely, R^+ cations, transition metal complexes R—ML_n with σ-bonds, and $R^•$ radicals, following an increase in the number of C atoms in the R group of the saturated hydrocarbon RH. Therefore, examples of selective carbonylation of alkanes by means of systems other than polyhalomethane-based superelectrophiles are limited to the C_1—C_3 alkanes.[9,94,97,99,102,105] Carbonylation initiaded by protic superacids usually proceeds in excess superacid and results in the products of destructive carbonylation, *i.e.*, carbonyl compounds containing either more or fewer C atoms in the R group attached to carbonyl than the initial hydrocarbon RH.[1a,90—93,105,109,111,112] This is a consequence of fragmentation reactions of saturated hydrocarbons. The reactions of cycloalkanes may be accompanied by ring opening.[1c,10,113] Secondary transformations of the initially formed acylium salts have been described.[90—93,114,115] Some side reactions involved in the carbonylation in the presence by protic or Lewis superacids[1,10,90a,91,93,105,109] are depicted in Scheme 10.

Few examples of catalytic carbonylation in the presence of transition metal complexes (with or without irradiation) are known. Usually, these reactions occur nonselectively. Scheme 11 shows reactions of alkanes with CO catalyzed by palladium[94] and rhodium[95b] complexes, and Scheme 12 presents carbonylation of alkanes and cycloalkanes induced by radical initiators such as tungsten polyoxo complexes[103] and excited mercury atoms.[101]

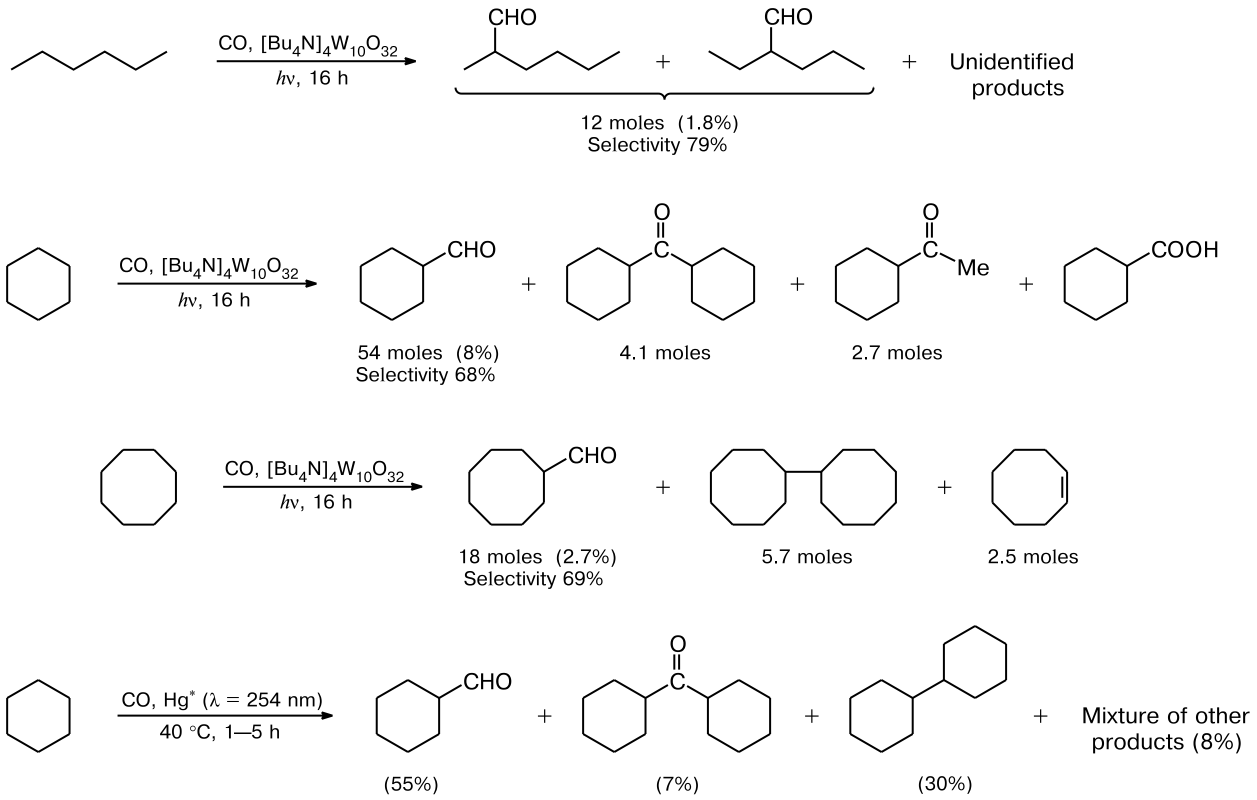
The use of superelectrophilic systems based on polyhalomethanes for selective carbonylation of alkanes and mono-, bi-, and tricyclanes proved to be rather successful. Apparently, the reactions follow a scheme that includes generation of a carbocation, which isomerizes to the most stable cation. The addition of the CO molecule to the latter results in the formation of the acylium cation. After treatment of the reaction mixture with alcohol, this

Scheme 11



Cat is $RhCl(CO)(PMe_3)_2$, 20 °C, 16 h; the yield is given relative to Rh.

Scheme 12*



* The yield given in parentheses is based on RH.

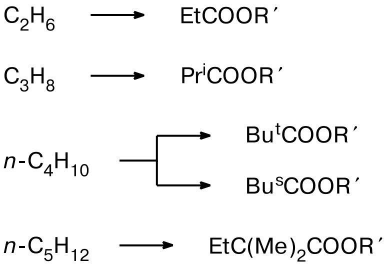
species is converted into the corresponding alkyl carboxylate (Scheme 13).

Scheme 13

$$\mathrm{RH} \xrightarrow{E^+} \mathrm{R^+} \xrightarrow{\mathrm{CO}} \mathrm{RCO^+} \xrightarrow{\mathrm{R'OH}} \mathrm{RCOOR'}$$

Carbonylation of alkanes. Examples of the reactions of alkanes with CO in the presence of polyhalomethane-based superelectrophiles are shown in Scheme 14 (the yields are 80—100% based on $CX_4 \cdot 2AlBr_3$). The reactions with ethane are carried out at 50 °C and those with propane, butane, and pentane, at –20 to –40 °C.

Scheme 14



$$C_2H_6 \longrightarrow \mathrm{EtCOOR'}$$

$$C_3H_8 \longrightarrow \mathrm{Pr^iCOOR'}$$

$$n\text{-}C_4H_{10} \longrightarrow \mathrm{Bu^tCOOR'},\ \mathrm{Bu^sCOOR'}$$

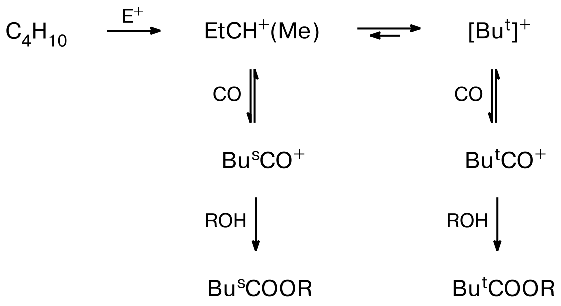
$$n\text{-}C_5H_{12} \longrightarrow \mathrm{EtC(Me)_2COOR'}$$

Lower alkanes (C_2—C_5) react selectively with CO to give in each case, after alcoholysis of the reaction mixture, either a single product or a major product with a selectivity of 85—90%. Electrophilic carbonylation of ethane was performed for the first time.[116,117] The reaction is carried out without solvents. Heating of a mixture of polyhalomethane (CBr_4, CCl_4, $CHCl_3$) with 2—3 moles of $AlBr_3$ with stirring at 80 °C for 5 min without a solvent furnishes superelectrophilic liquids,[118] which do not change the state of aggregation at 50—60 °C and can function as both the superelectrophile and the solvent in the reaction of ethane with CO. Under the optimal conditions, *i.e.*, at 50—60 °C and a CO : C_2H_6 : $CBr_4 \cdot 2AlBr_3$ molar ratio of 2.2 : 1 : 0.05 (p_{CO} = 45 atm, $p_{C_2H_6}$ = 20 atm), the yield of EtCOOBu obtained after alcoholysis of the reaction mixture with butyl alcohol was 86% over a period of 2 h. The yield of the side product, butyl 2-bromopropionate, was 6%.

Carbonylation of propane gives[119,120] (after alcoholysis of the reaction mixture) the ester Pr^iCOOR. The reactions are carried out by stirring a superelectrophilic system ($CBr_4 \cdot 2AlBr_3$, $CCl_4 \cdot 2AlBr_3$, or another) in a CH_2Br_2 solution in a C_3H_8/CO atmosphere. The yield of the ester noticeably depends on the C_3H_8 : CO (*n*) ratio and is a maximum at *n* = 1.5. An opposite dependence of the yield of the carbonylation product of propane on *n* has been observed in several other studies,[9,108,121] which reported selective carbonylation of propane in the HF—SbF$_5$ superacid in the presence of halogen-containing compounds (CCl$_4$, CHCl$_3$, Br$_2$, and even NaBr). It was shown[9,121a] that in the absence of halogen-containing additives, the reaction of propane with CO is nonselective and very inefficient. The presence of these additives increases in some cases both the reaction selectivity and the degree of propane conversion. For instance, in the presence of Br$_2$ (−10 °C, 1 h) and with treatment of the reaction mixture with ethanol, the yield of Pr^{i}COOEt is 67% based on propane or 11% based on SbF$_5$.[121c] The increase in the yield of the carbonylation products with an increase in the CO content in the gas mixture was regarded[9,121c] as an argument for the key role of the BrCO$^+$ cation in this reaction. The existence of this cation was proved by NMR spectroscopy.[122]

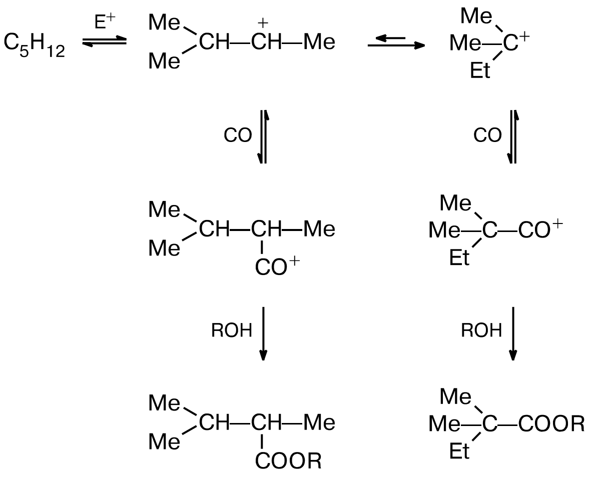
In the presence of polyhalomethane-based superelectrophiles, the reaction of butane with CO can proceed *via* two routes, giving alkyl carboxylate with either tertiary or secondary butyl group as the major product.[120,123] The yields of esters are ~80% in all cases. The route of butane carbonylation depends on the nature of the superelectrophile and the temperature. Lower temperatures in combination with a powerful superelectrophile are favorable for the predominant formation of the ester with the tertiary butyl radical, due to fast isomerization of the butyl cations to [Bu^t]$^+$, which is stable at low temperature and forms Bu^{t}CO$^+$, stable against decarbonylation under these conditions. Raising the temperature and an increase in the content of aluminum bromide in the system from two to three moles per mole of polyhalomethane results in the predominant formation of the ester Bu^{s}COOR. This is due to the enhanced tendency of the acylium cation to decarbonylation, which shifts the equilibrium toward the formation of the [Bu^s]$^+$ cation under these conditions (Scheme 15).

Scheme 15



At −20 °C, pentane gives the sole product, *tert*-C$_5$H$_{11}$COOR, in a quantitative yield.[123] The same product is selectively formed in 77% yield at 0 °C over a period of 30 min. The difference between the behaviors of butane and pentane is attributable to the fact that the barriers to the interconversion of the [Bu^s]$^+$ and [Bu^t]$^+$ cations are much higher than those for the pentyl cations, *sec*-C$_5$H$_{11}$$^+$ and *tert*-C$_5$H$_{11}$$^+$ (15.4 and 2 kcal mol^{-1}, respectively).[106] In addition, the equilibrium constant *K* for butane isomerization is lower than for pentane (in the gas phase, K = [Bu^{t}H]/[Bu^{n}H] = 4.5, whereas K = [*tert*-C$_5$H$_{12}$]/[*n*-C$_5$H$_{12}$] = 13).[124] Thus, the *sec*-C$_5$H$_{11}$$^+$ $\rightleftharpoons$ *tert*-C$_5$H$_{11}$$^+$ equilibrium is attained rapidly and the *tert*-C$_5$H$_{11}$$^+$ cation is virtually the only cation formed from pentane at low temperature, whereas in the case of butane, both butyl cations are probably present in the solution (Scheme 16).

Scheme 16



The selectivity of carbonylation of C$_2$—C$_5$ alkanes by polyhalomethane-containing systems is due to the ability of these powerful superelectrophiles to catalyze the generation and isomerization of alkyl cations under mild conditions. Hence, the most stable carbocations are accumulated in the reaction medium. It is noteworthy that at low temperatures, alkyl cations are stable against cracking, while the acylium cations formed from them are stable against decarbonylation. Therefore, the destructive carbonylation, resulting in products with smaller and greater numbers of C atoms in the alkyl group at the carbonyl, which is typical of carbonylation induced by protic superacids, does not occur in this case.

At low temperature (−40 °C, 1—2 h, p_{CO} = 1 atm), carbonylation of higher linear C$_6$—C$_{10}$ alkanes affords exclusively carbonyl-containing products with *tert*-alkyl substituents.[125] In all cases, they are represented mainly or exclusively (the content is 76—100%) by two isomers, which are shown in Scheme 17. The fact that these reactions always furnish these two esters (usually, AlkC(Me)$_2$COOR is the predominant isomer) is probably due to their close stabilities. The destructive carbonylation does not take place in this case.

Scheme 17

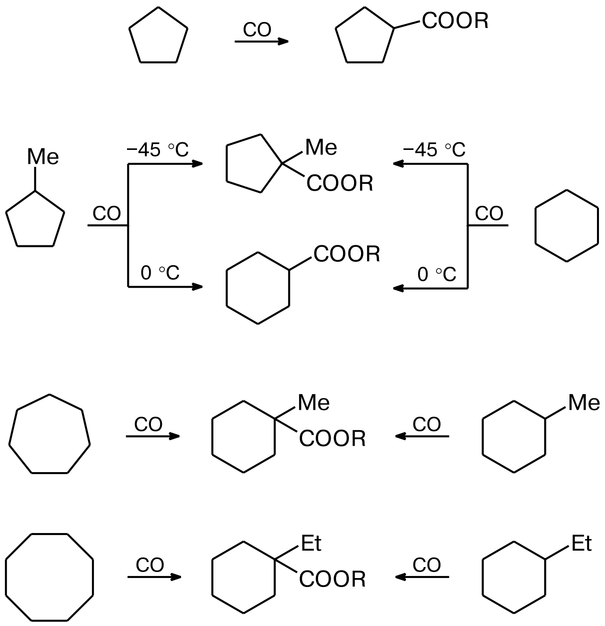
$$n\text{-RH} \xrightarrow[\text{R}'\text{OH}]{\text{CO}} \underset{60\text{—}95\%}{tert\text{-RCOOR}'}$$

$tert$-RCOOR′ = AlkC(Me)$_2$COOR′ + Alk′C(Me)(Et)COOR′

The carbonylation of C_4—C_{10} alkanes in the protic superacid media proceeds nonselectively if at all. For instance, at 30 °C and an RH : SbF_5 : HF molar ratio of 1 : 2 : 10, hexane is converted, after hydrolysis of the reaction mixture, into a complicated mixture of products consisting of *tert*-$C_6H_{13}COOH$ (15% based on hexane), *sec*-$C_6H_{13}COOH$ (29%), and a set of destructive carbonylation products, *i.e.*, the acids RCOOH (R = Et, Pr, Bu, C_5H_{11}).[109] Under the same conditions, heptane and octane form only products of destructive carbonylation; in particular, the former gives the C_4 and C_5 acids in comparable amounts,[126] while the latter, only the C_5 acids.[127] Carbonylation of these alkanes under the action of hydride ion acceptors (olefins or alcohols in the presence of H_2SO_4 or H_2SO_4/Ag^+) does not take place at all. The reactions afford exclusively the products of carbonylation of the olefin or the alcohol. In the presence of a Cu^I salt and in the HSO_3F—SbF_5 or HF—SbF_5 medium, octane reacts with CO to give Bu^tCOOH.[110]

Selective reactions of monocycloalkanes with CO. Superelectrophiles based on polyhalomethanes were found to be effective initiators of selective carbonylation of cycloalkanes. At low temperature (–20 to –45 °C), the C_6—C_8 cycloalkanes and isomeric monoalkylated cycloalkanes react with CO (E = $CX_4 \cdot 2AlBr_3$, 1 h) to give products with the carbonyl group at the tertiary carbon atom with high selectivity in 70—100% yields (Scheme 18).[128]

Scheme 18



The reaction of cyclopentane with CO in the presence of superelectrophilic systems, $CBr_4 \cdot 2AlBr_3$ and $CCl_4 \cdot 2AlBr_3$, results in an alkyl cyclopentanecarboxylate in an almost quantitative yield both in the absence of a solvent[67] and in CH_2X_2 (X = Cl, Br).[128] Cyclohexane and methylcyclopentane behave in a similar way: at –45 °C, 1-methylcyclopentanecarboxylate is formed irrespective of the reaction time, while at 0 °C, cyclohexanecarboxylate is formed over a period of 4 h as the major product.[129] A similar type of influence of the reaction temperature on the carbonylation route has been observed previously[10,107] in a study of the reaction of these cycloalkanes with CO in the HF—SbF_5 protic superacid medium. Of particular interest is the formation of 2-methylcyclohexanone, which takes place under certain conditions in the reactions initiated by polyhalomethane-based superelectrophiles. At –23 °C in the presence of $CBr_4 \cdot 2AlBr_3$, this ketone is formed from methylcyclopentane and CO in 80% yield; simultaneously, the reaction gives a 1-methylcyclopentanecarboxylate in 74% yield (the yields are based on the superelectrophile).[129] This ketone was absent in attempted carbonylation in HF—SbF_5,[10,107] although carbonylation of cyclohexane at p_{CO} = 150 atm initiated by HCl—$AlCl_3$ does give this product.[90]

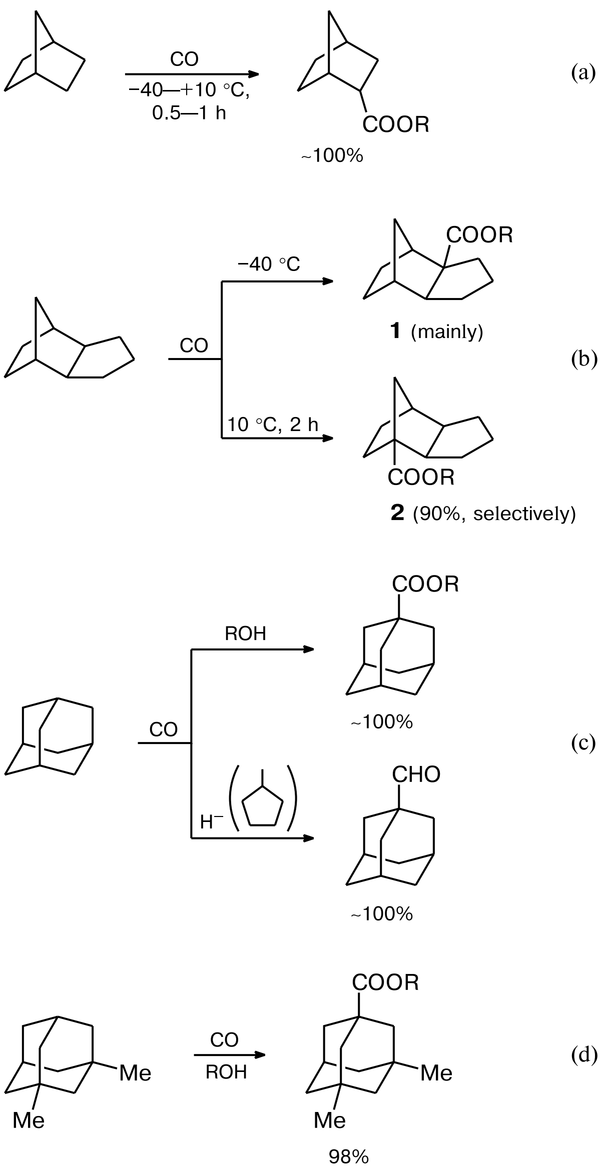
The $CBr_4 \cdot 2AlBr_3$ system was employed to perform the first selective electrophilic carbonylation of cycloheptane, cyclooctane, and ethylcyclohexane and the selective reaction of methylcyclohexane with CO without any additives.[130,131] Cycloheptane and methylcyclohexane behave in a similar way; at –40 °C and p_{CO} = 1 atm, they are converted into the same product, alkyl 1-methylcyclohexanecarboxylate, the product yields being similar in the two cases (~80%, 1—2 h). Under the same conditions, cyclooctane and ethylcyclohexane also form only one carbonylation product, an ester of 1-ethylcyclohexanecarboxylic acid, in ~70% yield. The reactions of cycloheptane and methylcyclohexane with CO at –20 °C are still selective, giving alkyl 1-methylcyclohexanecarboxylate, whereas the reactions of cyclooctane and ethylcyclohexane are nonselective at this temperature, resulting in a mixture of four isomers of *cyclo*-$C_8H_{15}COOR$ in which the 1-ethylcyclohexanecarboxylate is a minor component. The observed sharp decrease in the selectivity and the yield of 1-ethylcyclohexanecarboxylate (formed as the only product at –40 °C) is due to different temperature dependences of the stabilities of carbocations and the corresponding acylium cations.[106,132] As shown by PM3 quantum-chemical calculations,[130,131] among the tertiary cations, $[cyclo\text{-}C_6H_{10}Et]^+$ (ΔH_f = −152.6 kcal mol^{-1}) is more stable than the isomeric cations $[cyclo\text{-}C_6H_9Me_2]^+$ (ΔH_f = −150.5 kcal mol^{-1}), which have similar stabilities. This implies that the first-mentioned cation is accumulated on treatment of cyclooctane or ethylcyclohexane with the superelectrophile at −40 °C. With temperature rise, the decarbonylation of $cyclo\text{-}C_6H_{10}EtCO^+$ (which forms the more stable carbocation) proceeds much more easily than in the case of isomeric acylium cations $cyclo\text{-}C_6H_9Me_2CO^+$.[132] In addition, the difference between the stability of the $[cyclo\text{-}C_6H_{10}Et]^+$ and $[cyclo\text{-}C_6H_9Me_2]^+$ cations is less pronounced at higher temperatures.[124] As a consequence, raising the temperature results in the loss of selectivity and predominant formation of $cyclo\text{-}C_6H_9Me_2COOR$.

The isomerization of cycloalkanes induced by Lewis acids and accompanied by ring contraction is well known.[133,134] It was shown that this process occurs more readily for cycloheptane than for cyclooctane and gives, apparently, the same carbocations than the above-considered reactions with the $CBr_4 \cdot 2AlBr_3$ superelectrophile. Under comparable conditions, cycloheptane is converted quantitatively into methylcyclohexane, while cyclooctane yields a mixture of ethylcyclohexane (90%) and isomeric dimethylcyclohexanes (10%).[134] Previously,[10] it was reported that the reaction of methylcyclohexane with CO in the presence of $HF—SbF_5$ results in a mixture consisting of isomeric $cyclo\text{-}C_6H_9Me_2COOH$ (90%) and $cyclo\text{-}(1\text{-}Me)C_6H_{10}COOH$ (10%). Carbonylation of methylcyclohexane in 98% H_2SO_4 (or $BF_3—H_2O$) in the presence of copper or silver salts (as sources of metal carbonyls) and olefins or alcohols (as sources of carbocations) gives rise to methylcyclohexane-1-carboxylic acid in 20—70% yields.[135] The drawbacks of this method include not only the necessity to use a Cu or Ag salt and, in addition, olefins (or alcohols) but also the fact that carbonyl products derived from olefins or alcohols are formed in commensurable amounts with respect to the target product.

Carbonylation of bi- and tricyclanes. Carbonyl-containing derivatives of cage hydrocarbons are of considerable interest for practical use as potential pharmaceuticals, fragrance compound, and other valuable products.[136] However, except for adamantane, whose carbonylation was accomplished[137] back in the 1960s, the reactions of polycyclanes with CO have been little studied.[138]

Under the action of superelectrophiles based on polyhalomethanes, selective reactions of norbornane, tetrahydrodicyclopentadiene (trimethylenenorbornane), adamantane, and 1,3-dimethyladamantane with CO were accomplished, and the corresponding carbonyl-containing products were obtained in nearly quantitative yields (Scheme 19).*

Scheme 19



In the presence of these superelectrophiles, norbornane reacts with CO to give (after alcoholysis) alkyl 2-norbornylcarboxylate in nearly quantitative yields over a broad temperature range (−20 to +10 °C) under an atmospheric pressure of CO. Interestingly, the route of this reaction at −40 °C depends unexpectedly on whether CH_2Cl_2 or CH_2Br_2 is used as the solvent, the yield of the ester being

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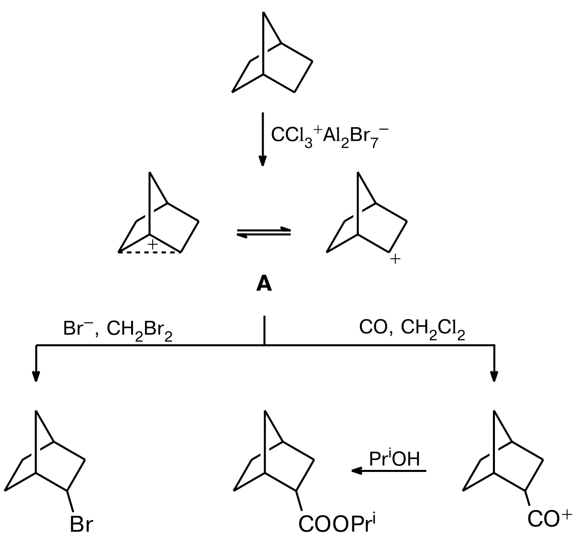
* I. S. Akhrem, L. V. Afanas´eva, D. V. Avetisyan, S. V. Vitt, P. V. Petrovskii, and A. L. Chistyakov, the material is being prepared for publication.

75—100% in the former case and only 16% in the latter case. The latter reaction is accompanied by the formation of 2-norbornyl bromide in 76% yield. The presumed scheme of the reaction includes the generation of the 2-norbornyl cation (or, more precisely, the nonclassical norbornyl cation **A**), which either accepts Br^- (–40 °C, CH_2Br_2) or adds CO to give the ester* (Scheme 20).

Scheme 20

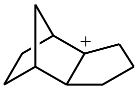


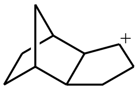
The selective transformation of norbornane into alkyl carboxylate with the CO group at the secondary C atom over a broad temperature range is at variance with the general tendency according to which C_4—C_{10} *n*-alkanes and C_6—C_8 monocycloalkanes (as well as isomeric monocyclohexanes) are converted at low temperatures only into products with a carbonyl group at a tertiary C atom. This outcome can be attributed to the exceptionally high stability of the 2-norbornyl cation. This cation is nearly as stable as the 1-adamantyl cation and is thermodynamically more favorable than the tertiary 1-norbornyl cation by 17 kcal mol^{-1}.[139] The reason for the unusual stability of the 2-norbornyl cation has been the subject of vigorous debate, which has lasted for 30 years and ended in the recognition of the nonclassical structure (**A**) for this ion.[6,139—144]

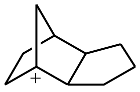
Thus, the generation of the stable nonclassical carbocation from norbornane accounts for the formation of 2-functionally substituted product in the reaction with CO. Yet another unexpected result,* namely, the predominant formation of 2-bromonorbornane in the transformation of norbornane at –40 °C in the presence of $CBr_4 \cdot 2AlBr_3$, in a CO atmosphere, and with CH_2Br_2 as the solvent, may be attributed to the fact that the norbornyl cation is more prone to add the Br^- ion from the solvating $Al_2Br_7^-$ anion than a neutral CO molecule, because intramolecular transformations of the cations proceed more readily than intermolecular ones.[106] The fact that at lower temperatures (unlike higher temperatures), the addition of the Br^- ion is irreversible accounts for the result observed.

Like norbornane, 5,6-trimethylenenorbornane reacts with CO in the presence of $CBr_4 \cdot 2AlBr_3$ even at –40 °C; however, unlike the reaction of norbornane with CO, carbonylation of trimethylenenorbornane is temperature-controlled. In the temperature range from –40 to +20 °C, the reaction give only products with the carbonyl group located at the tertiary C atom, namely, esters **1** and **2** (see Scheme 19, reaction (b)).* Neither the ester with the functional group in position 3 nor the products of destructive carbonylation with a modified hydrocarbon fragment are produced. However, the ratio of esters **1** and **2** depends appreciably on the temperature. At –40 °C, ester **1** is the major carbonylation product. The **1** : **2** isomer ratio is 6 : 1. At higher temperatures, ester **2** becomes the major product and at +10 °C, ester **2** is obtained selectively in a nearly quantitative yield. The seemingly strange fact of formation of ester **2** containing a bridgehead carbonyl group and the lack of the isomer with the functional group in position 3 was interpreted using quantum-chemical calculations.*

The DFT calculation of the stabilities and barriers to the interconversions of trimethylenenorbornyl cations showed that the tertiary cation (**1´**) has the lowest energy on the potential energy surface, the secondary cation (**2´**) is 7.8 kcal mol^{-1} less stable, and the tertiary cation (**3´**) lies 12.7 kcal mol^{-1} higher in energy.


1´


2´


3´

In view of these results, one could expect that the ester containing the carbonyl group in position 3 would predominate at higher temperatures. However, as shown by the calculations, the energy barrier to the transformation of the secondary cation **2´** into cation **1´** (8.5 kcal mol^{-1}) is comparable with the difference between the energies of formation of these cations. This implies that cation **2´** is readily converted into cation **1´**. A different situation is observed for cation **3´**. The barrier to its transformation into cation **1´** is exceptionally high (71 kcal mol^{-1}). This means that cation **3´** is rather stable against isomerization. Presumably, the acylium ion formed from cation **3´** is also rather stable against decarbonylation, as the bridgehead groups are very inert, because the formation of the corresponding high-energy carbocations is highly unfavorable.[145] For example, 1-chloronorbornane does not

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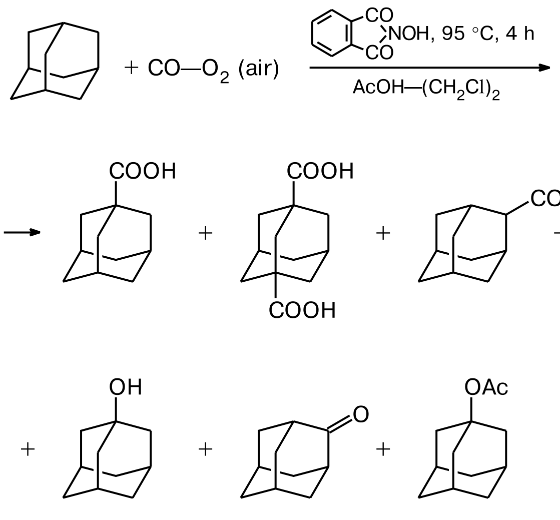
split off the Cl atom even upon long-term heating with a silver salt.[145]

It has been reported in short that radical carbonylation of *endo*-trimethylenenorbornane on treatment with CO catalyzed by *N*-hydroxyphthalimide (CO : air = 45 : 1, 85 °C, 15 h) leads, after hydrolysis, to two major products, trimethylenenorbornane-2-carboxylic acid (42%) and trimethylenenorbornane-2,6-dione (19%). When a slight amount of $Co(acac)_2$ is added to the reaction mixture, the yield of the acid increases to 55%, the process being nonselective (Scheme 21).[138]

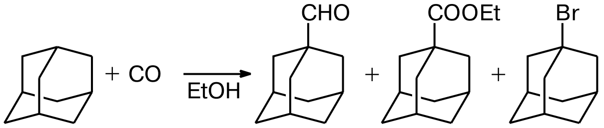
The reaction of adamantane with CO has been intensively studied. Adamantane-1-carboxylic acid and, under more drastic conditions, adamantane-1,3-dicarboxylic acid were synthesized from adamantane and CO (or HCOOH) in concentrated H_2SO_4 or oleum.[89,136c,d,146,147] Different modifications of this reaction have been the subjects of numerous papers and patents. The syntheses of adamantane-1-carboxylic acid described earlier (except for the reactions in question carried out in concentrated H_2SO_4 or oleum) have low selectivity. For instance, the yield of this acid in the *N*-hydroxyphthalimide-catalyzed reaction is 55% and the reaction is not selective (Scheme 21).[138]

Scheme 21



The reaction of adamantane with CO under atmospheric pressure in the presence of polyhalomethane systems ($CX_4 \cdot nAlX_3$ and $CH_2X_2 \cdot nAlX_3$, where X = Cl, Br; n = 1, 2) has been studied in detail in the temperature range from –45 to 20 °C.[148,149,*] Treatment of the reaction mixture with alcohol furnishes three products (Scheme 22) whose proportions depend on the nature of the electrophile, the reaction temperature and duration, the component ratio, and the nature and the amount of the solvent.

Scheme 22



It is significant that the reaction of adamantane with CO carried out under strictly fixed conditions allows quantitative and selective transformation of adamantane into either alkyl adamantane-1-carboxylate or adamantane-1-carboxaldehyde. Alkyl adamantane-1-carboxylate is formed selectively with a stoichiometric ratio of the reactants in the presence of a potent superelectrophile and when the reaction is carried out in a dilute solution.* The possibility of selective and quantitative transformation of adamantane into 1-AdCO^+ in an organic medium, as shown below, opens up broad prospects for selective one-step syntheses of various carbonyl compounds of the adamantane series.

The selective carbonylation of 1,3-dimethyladamantane induced by polyhalomethane-based systems to give alkyl 3,5-dimethyladamantane-1-carboxylate in a quantitative yield (see Scheme 19, reaction (d)) also requires specific conditions. When this reaction is carried out under the optimal conditions selected for the transformation of adamantane into adamantane-1-carboxylic acid or its esters, only 5-bromo-1,3-dimethyladamantane is formed in a quantitative yield.*

Other transformations of alkanes and cycloalkanes in reactions with CO induced by superelectrophiles

Adamantane formylation. The second route of reaction between adamantane and CO yielding adamantane-1-carboxaldehyde is of interest by itself. Unlike the widely used electrophilic formylation of aromatic hydrocarbons,[150] this route of electrophilic reaction of saturated hydrocarbons with CO is atypical and has been implemented only for adamantane. The formylation of adamantane under the action of CO was first performed in a protic superacid[151] and on treatment with $AlCl_3$ in CH_2Cl_2.[152] These reactions seem to follow different mechanisms in the protic and aprotic media.

The former mechanism includes the initial protonation of the CO molecule and the subsequent attack of the adamantane molecule by the electrophilic HCO^+ species (Scheme 23).[151]

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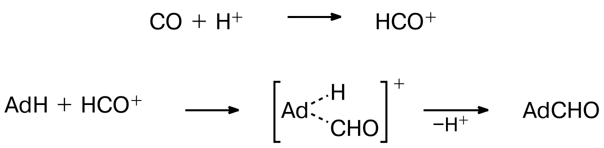
* I. S. Akhrem, L. V. Afanas´eva, D. V. Avetisyan, S. V. Vitt, P. V. Petrovskii, and A. L. Chistyakov, the material is being prepared for publication.

Scheme 23

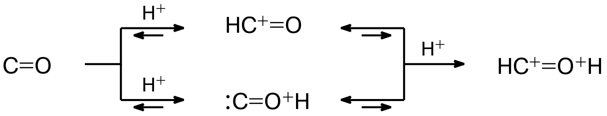


$$\mathrm{CO} + \mathrm{H}^+ \longrightarrow \mathrm{HCO}^+$$

$$\mathrm{AdH} + \mathrm{HCO}^+ \longrightarrow \left[\mathrm{Ad}\begin{matrix}\cdot^{\cdot}\mathrm{H}\\ \cdot_{\cdot}\mathrm{CHO}\end{matrix}\right]^+ \xrightarrow[-\mathrm{H}^+]{} \mathrm{AdCHO}$$

This mechanism was confirmed experimentally for the reaction of 1,3,5,7-tetradeuterioadamantane with CO in HF—SbF_5.[151] Quantum-chemical calculations showed the possible formation of two forms of the monoprotonated CO molecule, namely, the formyl cation HC^+O and the isoformyl cation $:C{=}O^+H$, and a diprotonated species, $HC^+{=}O^+H$.[153,154] The processes of generation of the formyl and isoformyl cations are exothermic and both cations (even the isoformyl cation, which is 38 kcal mol^{-1} higher in energy) are fairly stable against deprotonation (Scheme 24).[153]

Scheme 24



The second formylation mechanism operating in aprotic media is apparently a three-step process comprising generation of the carbocation, the addition of a CO molecule to the cation to give the acylium cation, and the abstraction of the hydride anion from the saturated hydrocarbon molecule by this acylium cation (Scheme 25).[148,149]

Scheme 25

$$\mathrm{RH} \xrightarrow{E^+} \mathrm{R}^+ \xrightarrow{\mathrm{CO}} \mathrm{RCO}^+ \xrightarrow{\mathrm{R'H}} \mathrm{RCHO} + [\mathrm{R'}]^+$$

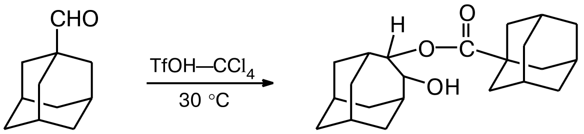
It is evident that the last step, namely, the transfer of a hydride ion from a hydrocarbon to the acylium cation, is the key step in the transformation of saturated hydrocarbons induced by $RCO^+Al_2X_7^-$ superelectrophilic complexes.[53,54] No aldehydes RCHO were found upon the reactions of alkanes with $RCO^+Al_2X_7^-$, which is due to the high reactivity of aldehydes with respect to superelectrophiles. However, benzaldehyde was detected in the reaction of adamantane with $PhCOCl \cdot 2AlBr_3$[56] (Scheme 26).

Scheme 26

$$\mathrm{AdH} + \mathrm{PhCO^+Al_2Br_7^-} \xrightarrow[-\mathrm{Al_2Br_6}]{} \mathrm{AdBr} + \mathrm{PhCHO}$$

Although the possibility of adamantane formylation was demonstrated, the reactions in the presence of various protic acids (either in organic solvents or without them)[151] or in the presence of $AlCl_3$ in CH_2Cl_2 [152] (p_{CO} = 80 atm, 0—30 °C, 4—20 h) gave 1-AdCHO in very low yields (0.2—21%). Meanwhile, adamantane-1-carboxylic acid was formed as the major product (yield 60—75%) in the reaction of adamantane with CO and a small amount of 1-AdOH (2—7%) was also formed. Japanese researchers, who reported a detailed study of the reactions of 1-AdOTf (TfOH = CF_3SO_2OH), AdH, and other sources of the adamantyl cation with CO in the presence of TfOH at 30 °C in CCl_4 did not find any adamantane-1-carboxaldehyde in the reaction products.[155,156] Instead, a homoadamantane derivative was isolated in a yield of up to 70% after treatment of the reaction mixture with water (Scheme 27). In special experiments, the researchers cited showed that 1-AdCHO was unstable under the reaction conditions.

Scheme 27



The use of systems composed of polyhalomethanes and aluminum halides for the formylation of adamantane proved to be much more successful.[148,149] As in other cases, the rates of these reactions with the $CBr_4 \cdot nAlX_3$ systems were higher than those with $CH_2X_2 \cdot nAlCl_3$. However, even with the latter type of system, it is possible to convert adamantane into the aldehyde at 20 °C with high selectivity and a in yield of up to 57% in 1 h (X = Br) or 26% in 2 h (X = Cl) (the yields are based on adamantane). The efficiency of the much less active CH_2X_2—AlX_3 systems (X = Cl, Br) toward the formylation of adamantane compared to that for the similar systems with CBr_4 can probably be due to two reasons. First, adamantane does not require a very strong electrophile to generate the cation. Second, the potent superelectrophile removes adamantane from the reaction area too fast, whereas the weaker electrophile induces the formation of the Ad^+ and then $AdCO^+$ cations at a lower rate, thus creating favorable conditions for the reaction of the acylium salt with adamantane, giving rise to the aldehyde (Scheme 28).[149]

Since Ad^+ adds CO, while $AdCO^+$ can, in turn, detach a hydride ion from AdH, one might expect development of a chain process. However, such process does not occur in reality. Apparently, the absence of catalysis can be explained as follows. When [AdH] = [E^+], the hydride ion is deficient in the reaction mixture, as the formation of $AdCO^+$ is a fast step, while the hydride ion transfer is a

Scheme 28

$$\mathrm{AdH + E^+ \rightleftharpoons Ad^+ + EH}$$

$$\mathrm{Ad^+ + CO \longrightarrow AdCO^+}$$

$$\mathrm{AdH + AdCO^+ \longrightarrow AdCHO + Ad^+}$$

$$\mathrm{2\,AdH + E^+ + CO \longrightarrow AdCHO + Ad^+ + EH}$$

slower step. It is the equality [AdH] = $[E^+]$ with a very strong electrophile, high dilution, and a temperature of 0 °C that allows this reaction to be carried out selectively to give alkyl adamantane-1-carboxylate after alcoholysis of the reaction mixture. However, when [AdH] > $[E^+]$, the system activity decreases due to the accumulation of AdCOH, able to be coordinated to the electrophile, in the reaction products.[149]

Despite the fact that polyhalomethane-based systems allow one to prepare adamantane-1-carboxaldehyde from adamantane in a satisfactory yield and with a rather good selectivity, the formylation can still be more efficient if methylcycolpentane is added to the reaction mixture as a hydride ion donor. In the presence of methylcyclopentane, at 20 °C, and at an [AdH] : $[CH_2Br_2 \cdot 2AlX_3]$: [*cyclo*-C_5H_9Me] molar ratio of 1 : 1 : 2, a quantitative yield of the aldehyde based on adamantane is attained over a period of 1 h (X = Br) or 2 h (X = Cl).[148,149]

The calculated reaction enthalpies[148,149] are in full agreement with the observed facts. The overall reaction of adamantane formylation is exothermic, whereas the hydride ion transfer requires an energy expenditure. Among the hydrocarbons shown in Scheme 29, methylcyclopentane proves to be the best hydride ion donor.

Scheme 29

$$\mathrm{AdH + CO \longrightarrow AdCHO}$$

$\Delta H_f = -20.7$ kcal mol^{-1}

$$\mathrm{AdCO^+ + RH \longrightarrow AdCHO + R^+}$$

R	*cyclo*-C_6H_{11}	Ad	Bu^t	*cyclo*-C_5H_8Me
ΔH_f/kcal mol^{-1}	17.0	15.7	8.2	5.5

Most of the reactions of saturated hydrocarbons with CO described in the review were either first carried out or first carried out selectively giving no products of destructive carbonylation (electrophilic carbonylation of ethane; carbonylation of C_4—C_{10} alkanes, C_7 and C_8 cycloalkaneas with isomeric monoalkylated cyclohexanes, norbornane, and trimethylenenorbornane; carbonylation of adamantane and 1,3-dimethyladamantane in an organic medium; and exhaustive formylation of adamantane).

It is very important that the reactions of saturated hydrocarbons with CO initiated by superelectrophiles give actually acylium salts. The problem of whether the role of the superelectrophiles in these reactions is only to generate the carbocations or they are also involved in the activation of the CO molecule has not been studied previously. The participation of protonated CO in the formylation of aromatic hydrocarbons and adamantane has been confirmed. Hence, the functions of superelectrophiles in the reactions with CO may be more complex than mere generation of carbocations. However, the generation of acylium cations in these reactions is beyond doubt. The formation of the Pr^iCO^+ and $EtCO^+$ acylium salts upon the reaction of propane with CO in a HF—SbF_5 medium was detected by NMR.[9] Hogeveen[105] has proved the formation of the $MeCO^+$ and Bu^tCO^+ cations from CH_4 and CO on treatment with SbF_5 in the reaction carried out at 50 and 1 atm, respectively.

The fact that superelectrophiles based on polyhalomethanes allow the generation of acylium salts from alkanes and mono-, bi-, and tricyclanes in an organic medium and, furthermore, the reaction is often selective, opens up unique prospects for the extensive use of saturated hydrocarbons and CO as reagents in organic synthesis. Note that acylation can be carried out as a one-pot procedure.

Acylation of arenes. Examples of acylation of aromatic hydrocarbons by treatment with saturated hydrocarbons and CO are presented in Scheme 30.[120,128]

Scheme 30

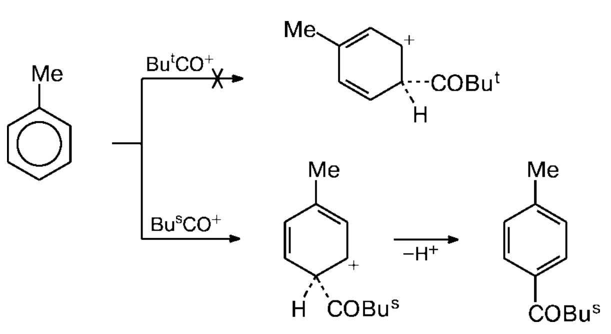
$$\mathrm{RH \xrightarrow{E^+} R^+ \xrightarrow{CO} RCO^+ \xrightarrow[-H^+]{ArH} RCOAr}$$

RH = *n*-C_4H_{10}, *n*-C_5H_{12}, *cyclo*-C_5H_{10}, *bicyclo*-C_7H_{12} (norbornane)
E = $CCl_4 \cdot 2AlBr_3$, $CBr_4 \cdot 2AlBr_3$
ArH = C_6H_5Me, PhOMe, 1,3,5-$Me_3C_6H_3$, $PhCH_2SiMe_3$

A specific feature of this reaction is high positional selectivity, as it gives only *para*-substituted ketones. The absence of *ortho*-isomers may be due to steric restrictions arising in the attack of the aromatic molecule by a bulky electrophilic species, $RCO^+Al_2Br_7^-$. The yields of ketones in the reactions with butane, cyclopentane, and norbornane amount to 63—92%; in the case of *n*-pentane, the product yields and the reaction selectivity are much lower. The reaction with butane mainly affords ketones containing a secondary butyl group. The difference between the structures of compounds formed after treatment of the carbonylation product of *n*-butane with alcohol, on the one hand, and with aromatic hydrocarbon, on the other hand, can be interpreted by comparing Schemes 15 and 31.

It was shown[75] that in the presence of polyhalomethane superelectrophiles, the $Bu^t \rightleftharpoons Bu^s$ equilibrium is

Scheme 31



shifted toward $\mathrm{Bu^t}$. Therefore, the fast reaction between the acylium cation and a strong nucleophile such as $\mathrm{Pr^iOH}$ or water (see Scheme 15) gives a $\mathrm{Bu^t}$-containing product, whereas slow reactions with less nucleophilic arenes (see Scheme 31) involve the more reactive $\mathrm{Bu^sCO^+}$ cation. The latter cations are present in the solution in a small amount; however, as they react with arenes, the equilibrium between the butyl cations shifts toward the secondary cation.

Conversely, mesityl *tert*-pentyl ketone is formed as the only product upon the reaction of *n*-pentane, CO, and mesitylene. In the reaction of *tert*-$\mathrm{C_5H_{11}CO^+}$ with less reactive arenes, namely, toluene and anisole, the alkylation products *tert*-$\mathrm{C_5H_{11}C_6H_4X}$ and the alkylation—acylation products *tert*-$\mathrm{C_5H_{11}C_6H_3}$(*tert*-$\mathrm{C_5H_{11}CO}$)X (X = Me, OMe) are formed in addition to the usual acylation products. The reaction of $\mathrm{Me_3SiCH_2Ph}$ with *cyclo*-$\mathrm{C_5H_9CO^+}$ generated from cyclopentane and CO affords an organiosilicon ketone in a quantitative yield. The conduction of this process with an excess of the acylium salt with respect to trimethylbenzylsilane is accompanied by cleavage of one Si—Me bond of the ketone and gives, after alcoholysis, alkoxydimethylsilyl-substituted ketone in 40—50% yield (Scheme 32).[120,128]

Scheme 32

$$\mathrm{Me_3SiCH_2Ph + C_5H_9CO^+} \longrightarrow$$

$$\longrightarrow \mathrm{Me_3SiCH_2C_6H_4COC_5H_9} \longrightarrow$$

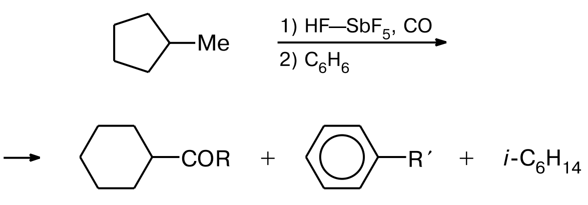
$$\xrightarrow{\mathrm{C_5H_9CO^+Al_2X_7^-}} \mathrm{Me_2Si(X)CH_2C_6H_4COC_5H_9} \longrightarrow$$

$$\xrightarrow{\mathrm{ROH}} \mathrm{Me_2Si(OR)CH_2C_6H_4COC_5H_9}$$

Thus, the acylation of activated aromatic compounds can be carried out in good yields. However, in some cases, it is difficult to avoid more easily proceeding alkylation of arenes with the carbocations resulting from decarbonylation of acylium salts. It is evident that the proportion of these processes increases on passing to less reactive arenes and on raising the reaction temperature. Chlorobenzene does not change at 0 °C on treatment with the *cyclo*-$\mathrm{C_5H_9CO^+}$ cation generated from cyclopentane and CO in $\mathrm{CH_2Cl_2}$. At 20 °C, instead of the acylation products of chlorobenzene, the reaction gives cycloalkylation and cycloalkenylation products of diarylmethane derivatives (together with nonalkylated diarylmethane).

The acylation of benzene with methylcyclopentane and CO in the HF—$\mathrm{SbF_5}$ system has been reported.[10] Although the yield of cyclohexyl phenyl ketone was relatively high, the reaction resulted in a five-component mixture (Scheme 33).

Scheme 33



R = Ph, $\mathrm{C_6H_{11}}$
R′ = Ph, $\mathrm{C_6H_{11}}$

Acyldesilylation of tetraorganosilanes. The use of tetraorganosilanes together with alkanes (cycloalkanes) and CO in the synthesis of ketones also proved to be quite successful. These reactions are accompanied by desilylation and afford alkyl aryl and dialkyl ketones in good yields and with high selectivity (Scheme 34).[120,128]

Scheme 34

$$\mathrm{RH} \xrightarrow{\mathrm{E^+}} \mathrm{R^+} \xrightarrow{\mathrm{CO}} \mathrm{RCO^+} \xrightarrow{\mathrm{R'SiR''_3}} \mathrm{RCOR'}$$

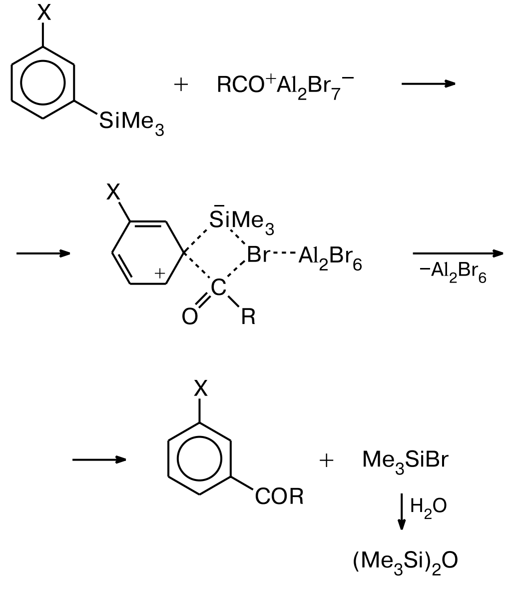
60-98%

RH = $\mathrm{C_3H_8}$, $\mathrm{C_4H_{10}}$, *cyclo*-$\mathrm{C_5H_{10}}$, *cyclo*-$\mathrm{C_6H_{12}}$, *cyclo*-$\mathrm{C_5H_9Me}$
E = $\mathrm{CCl_4 \cdot \mathit{n}AlBr_3}$ (*n* = 2, 3), $\mathrm{CBr_4 \cdot 2AlBr_3}$
R′ = Me, Et, *m*-$\mathrm{MeC_6H_4}$, *p*-$\mathrm{MeC_6H_4}$, *m*-$\mathrm{ClC_6H_4}$, *p*-$\mathrm{ClC_6H_4}$, *m*-$\mathrm{MeOC_6H_4}$, *p*-$\mathrm{MeOC_6H_4}$
R″ = Me, Et

As in the case of acylation of arenes with saturated hydrocarbons and CO, in this case, too, propane, butane, cyclopentane, and norbornane are converted into ketones containing isopropyl, *sec*-butyl, cyclopentyl, and 2-norbornyl groups, respectively. The reactions involving cyclohexane or methylcyclopentane result in either almost pure *cyclo*-$\mathrm{C_6H_{11}COR}$ or mainly *cyclo*-(1,1-$\mathrm{MeC_5H_8COR}$), depending on the conditions.

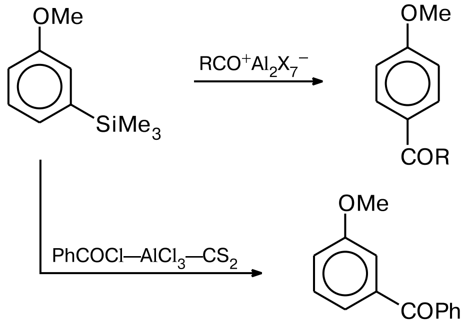
The use of tetraorganosilanes in the synthesis of ketones has a number of advantages. First, the reactions with tetraorganosilanes allow the synthesis of ketones containing both alkyl and aryl groups, including aryl groups with electron-withdrawing substituents. The last-mentioned compounds cannot be synthesized at low temperatures using saturated hydrocarbons and CO by direct acylation of deactivated arenes devoid of organosilicon substituents. Meanwhile, *m*- and *p*-$ClC_6H_4SiMe_3$ react with cyclopentane and CO in the presence of superelectrophiles at 0 °C to give ketones with the *cyclo*-$C_5H_9CO^+$ group in 81—89% yield over a period of 15 min. The second important advantage is regioselectivity of the syntheses of aromatic ketones. For instance, the reaction with *p*-$XC_6H_4SiMe_3$ gives the ketones *p*-XC_6H_4COR. Correspondingly, *m*-$XC_6H_4SiMe_3$ are converted into the ketones *m*-XC_6H_4COR. It should be emphasized that, although the reactions of activated arenes with RCO^+ according to Scheme 34 proceed easily to give ketones ArCOR in high yields, only the *para*-isomers can be obtained. The regioselectivity of the acyldesilylation of trialkylarylsilanes is probably indicative of the fact that the reaction follows the *ipso*-substitution mechanism,[157] which comprises an attack of the acylium cation on the site with the highest electron density of the benzene ring, *i.e.*, on the C atom attached to the trialkylsilyl group, and the subsequent displacement of this group by an acyl group (Scheme 35).

Scheme 35



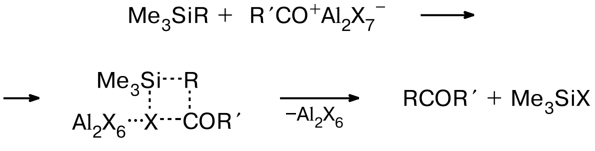
Acyldesilylation of aryltrimethylsilanes on treatment with $RCOCl \cdot AlCl_3$ has been described previously.[158,159] A specific feature of the proposed method for the synthesis of ketones is the *in situ* utilization of the acylium salts generated from alkanes or cycloalkanes and CO. The only example that does not fit into the general scheme of regioselective acylation of trialkylarylsilanes is the formation of *p*-$MeOC_6H_4COC_5H_9$ (instead of the expected *meta*-isomer) in the reaction of *m*-$MeOC_6H_4SiMe_3$ with *cyclo*-$C_5H_9CO^+$.[120,128] This result is all the more unexpected in view of the fact that acyldesilylation of *m*-$MeOC_6H_4SiMe_3$ with the $PhCOCl—AlCl_3—CS_2$ system, as follows from a previous publication,[160] occurs selectively giving rise to 3-methoxybenzophenone (Scheme 36). The formation of the *para*-isomer in the reaction of *m*-$MeOC_6H_4SiMe_3$ with *cyclo*-$C_5H_9CO^+Al_2Br_7^-$ might be due to the fact that the attack by the acylium cation is directed to the *para*-position with respect to the methoxy group (the concerted effect of two strong *ortho*-,*para*-directing groups). It can be suggested that the trimethylsilyl group in the cationic σ-complex thus formed (the Wheland complex) is intramolecularly displaced by a proton.

Scheme 36



As in other reactions of tetraalkylsilanes with electrophilic reagents, in this reaction, the transfer of the alkyl group from the tetraalkylsilane Si atom to the acylium cation is apparently facilitated by the formation of a complex of five-coordinate silicon with an enhanced mobility of the alkyl group (Scheme 37).

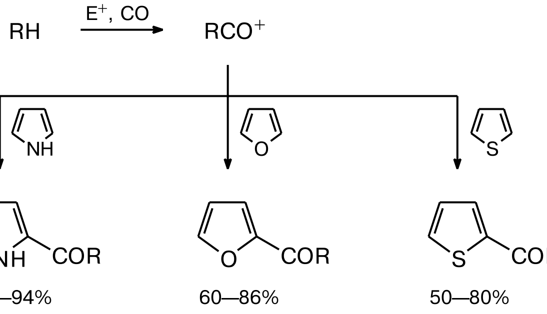
Scheme 37



Examples of acyldesilylation of tetraalkylsilanes have been reported.[160] Refluxing of $RCOCl \cdot AlCl_3$ (R = Alk, Ar) with Me_4Si and Et_4Si in CH_2Cl_2 for 18 h furnishes the ketones RCOR′ (R′ = Me, Et) in 30—80% yields. Before our studies,[120,128] no syntheses of ketones from alkanes (cycloalkanes), CO, and tetraorganosilanes were reported.

Acylation of heteroaromatic compounds. Alkanes (or cycloalkanes) and CO in the presence of polyhalomethane superelectrophiles have been successfully used for selective acylation of heteroaromatic compounds, namely, pyrrole, furan, and thiophene (Scheme 38).*

Scheme 38



RH = C_3H_8, C_4H_{10}, *n*-C_5H_{12}, *cyclo*-C_5H_{10}, *cyclo*-C_6H_{12}, *bicyclo*-C_7H_{12} (norbornane), $C_{10}H_{16}$ (adamantane)

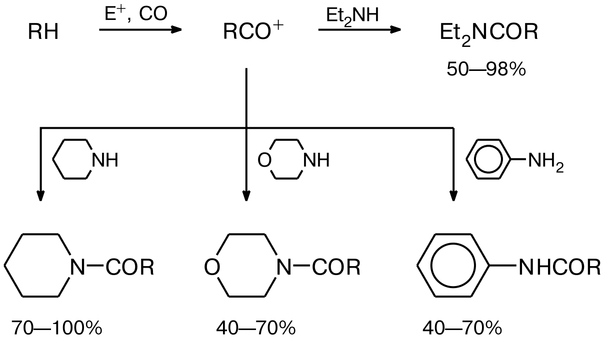
The reaction proceeds regioselectively to give, most often, a single ketone in a high yield. In these reactions (as in other acylation processes involving saturated hydrocarbons and CO), the group R has the same structure as that in the aromatic ketones formed according to Schemes 30 and 34.

Acylation of heterocycles is an important method for the synthesis of valuable heterocyclic derivatives or their precursors.[161,162] Five-membered heteroaromatic compounds with one heteroatom are known to be markedly less stable in electrophilic media than benzoid hydrocarbons. They can react as dienes, undergo ring opening, or polymerize under the action of electrophiles. Therefore, selective acylation of activated heterocycles even by conventional acylating reagents is not always a routine operation.[163] The success of the approach based on the use of the acylium salts generated *in situ* from saturated hydrocarbons for selective acylation of heteroaromatic hydrocarbons is apparently due to the fact that the acylium salts are highly ionized in the superelectrophilic media and, therefore, the acylation proceeds at high rates under very mild conditions.

Acylation of amines. The next type of reaction is acylation of amines with alkanes (cycloalkanes) and CO. Selective acylation of compounds containing amino groups is an important reaction resulting in the synthesis of amides many of which are of interest by themselves (in particular, may possess biological activities) or as intermediates for the synthesis of biologically active compounds. The acylation methods of the amino group are well developed.[164,165] They mainly consist of treatment of amines with activated derivatives of carboxylic acids, namely, acyl halides, anhydrides, and esters.

Amines of various types (aliphatic, cyclic, and aromatic) are readily acylated with saturated hydrocarbons and CO in the presence of superelectrophiles on the basis of polyhalomethanes.* The reactions proceed selectively and regioselectively to give amides, usually in good yields (Scheme 39).

Scheme 39



RH = C_3H_8, C_4H_{10}, *n*-C_5H_{12}, *cyclo*-C_5H_{10}, *cyclo*-C_6H_{12}, *bicyclo*-C_7H_{12} (norbornane), $C_{10}H_{16}$ (adamantane)

Under definite conditions, trimethylenenorbornane can be converted into the corresponding trimethylenenorbornyl derivatives containing a bridgehead amide group. It is worth mentioning that aromatic amines containing an acceptor group, for example, *o*- and *p*-nitroanilines can also be acylated by this method in good yields. Adamantanecarboxamides are of interest for the synthesis of biologically active compounds.[136,166,167]

Acylation and bromoacylation of ethylene. On treatment with systems based on polyhalomethanes and aluminum halides (in the presence or in the absence of a saturated hydrocarbon) at low temperature, ethylene is easily converted into a complex mixture of branched higher alkanes, cycloalkanes, and their halogen derivatives.** The reaction of ethylene, cycloalkane, and CO can be directed, with good selectivity, along two different routes by changing the reaction conditions.***

Stirring of cyclopentane with $CBr_4 \cdot 2AlBr_3$ in CH_2X_2 at a low temperature in a C_2H_4—CO (1 : 3) atmosphere affords alkyl 1-methylcyclohexanecarboxylate as the only product after alcoholysis of the reaction mixture (Scheme 40).***

The reaction includes the addition of the cyclopentyl cation to ethylene followed by isomerization of the pri-

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* I. S. Akhrem, D. V. Avetisyan, L. V. Afanas´eva, S. V. Vitt, and P. V. Petrovskii, the material is being prepared for publication.

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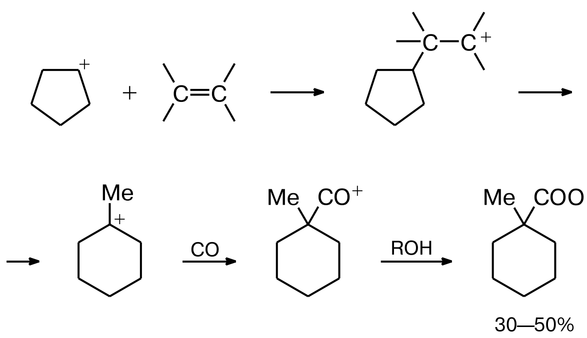
** A. V. Orlinkov, I. S. Akhrem, and S. V. Vitt, the material is being prepared for publication.

*** I. S. Akhrem, L. V. Afanas´eva, S. V. Vitt, and P. V. Petrovskii, the material is being prepared for publication.

Scheme 40



mary carbocation formed initially into a stable tertiary 1-methylcyclohexyl cation; this is accompanied by ring expansion. The addition of CO to 1-methylcyclohexyl cation results in the corresponding acylium salt, which is converted into the ester observed after treatment with an alcohol.

If ethylene is introduced in a solution of the acylium salt (formed from a cycloalkane), the same initial components (RH, CO, C_2H_4, $CBr_4 \cdot 2AlBr_3$) furnish the product of ethylene acylbromination in a satisfactory or good yield (Scheme 41).*

Scheme 41

$$RH \xrightarrow{CX_3^+Al_2Br_6X^-,\ CO} RCO^+Al_2Br_6X^-$$

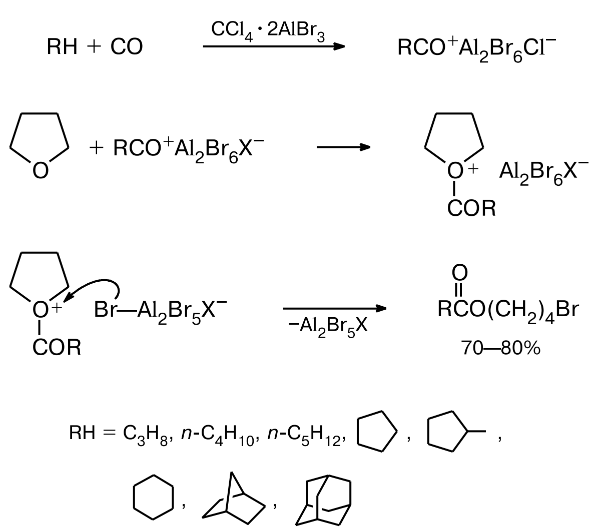
$$RCO^+Al_2Br_6X^- + H_2C{=}CH_2 \longrightarrow RCOCH_2CH_2Br$$

40—100%

RH = *cyclo*-C_5H_{10}, *bicyclo*-C_7H_{12} (norbornane)

Ring opening in tetrahydrofuran. The opening of the tetrahydrofuran ring under the action of electrophilic reagents is well known.[168] Recently, this reaction was successfully carried out using alkanes (cycloalkanes) and CO as equivalents of an acylium salt.** Apparently, the reaction includes the transformation of tetrahydrofuran and the acylium cation into an oxonium salt, which undergoes ring opening, resulting in an ester with the $(CH_2)_4Br$ group (Scheme 42). When the procedure is strictly followed, only one isomer is formed in each reaction. Owing to the enhanced stability of the oxonium salt against decarbonylation compared to the corresponding acylium cations, the reactions with tetrahydrofuran proceed at temperatures of 20—50 °C and give the target products in 70—80% yields.** In the absence of tetrahydrofuran, the reactions of alkanes or cycloalkanes (except for adamantane) with CO give carbonyl-containing products in very poor yields, if at all, even at 20 °C.

Scheme 42



The nature of complexes responsible for the superelectrophilic properties of polyhalomethanes in the presence of aluminum halides

The reasons for the superelectrophilic properties of polyhalomethanes in the presence of strong Lewis and protic acids have been investigated by quantum-chemical methods.[73,74,169] Semiempirical and *ab initio* calculations for the complexes $CCl_4 \cdot nAlX_3$ (n = 1—3, X = Cl, Br) and the free cations CX_3^+, CHX_2^+, CHX^{2+}, and CX_2^{2+} (X = Cl, Br, I, but not F) showed that polyhalomethyl cations, both free and incorporated in cationic and dicationic complexes $CX_3^+Y^-$ and $CX_2^{2+}Y_2^-$ (Y = $AlBr_4$ or Al_2Br_7), should be classified, strictly speaking, as the halonium cations or cationic complexes, $X_2C{=}X^+$ and $X^+{=}C{=}X^+$, containing positively charged halogen atoms at the electron-deficient C atom rather than as carbenium ions. In other words, the electron density transfer from the lone electron pairs of the halogen atom to the carbocation is so pronounced that the halogen atoms bear a substantial positive charge, while either zero or a great negative charge is concentrated on the C atoms.

The question arises of whether the superelectrophilic properties of the systems under study are related to the formation of the $CX_3^+Y^-$ cationic complexes or their specific properties are determined by some other, more electrophilic cations? It could be expected that protonation of polyhalomethyl cations (or the formation of donor-acceptor complexes of these cations with a Lewis acid) would increase the electrophilicity of the cationic species. These

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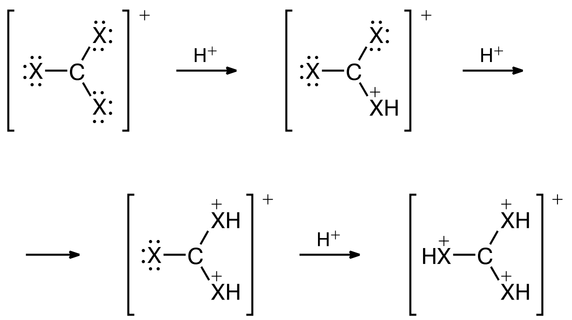
* I. S. Akhrem, L. V. Afanas´eva, S. V. Vitt, and P. V. Petrovskii, the material is being prepared for publication.

** I. S. Akhrem, D. V. Avetissyan, S. V. Vitt, and P. V. Petrovskii, the material is being prepared for publication.

multicharged cations could be responsible for the superelectrophilic properties of polyhalomethanes in the presence of protic and aprotic superacids (Scheme 43), as is the case for systems containing acylium salts in the presence of strong protic or aprotic acids.[43,44]

Scheme 43

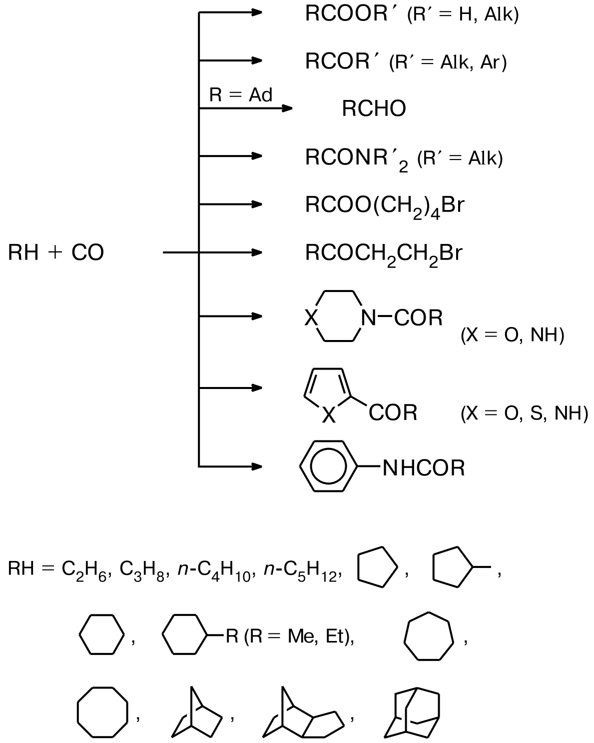


Calculations[169] showed that monoprotonation of the trihalomethyl cations requires an energy of 70—84 kcal mol^{-1} and diprotonation, 150—170 kcal mol^{-1}. However, both types of cations are stable against deprotonation. For example, the barriers to deprotonation for CBr_3H^{2+} and $CBr_3H_2^{3+}$ are 74 and 37 kcal mol^{-1}, respectively, *i.e.*, once formed, these di- and trications are rather stable. Thus, the data of calculations do not contradict the assumption that in a protic superacid, polyhalomethanes are converted into multicharged ions, which play a key role in the reactions with alkanes.

However, semiempirical and *ab initio* calculations ($CX_3^+ \to AlX_3$ and $[CX_3^+ \to AlX_3]AlX_4^-$) did not confirm the assumption that the activity of polyhalomethanes in the presence of aluminum halides is related to the formation of dication type complexes.[73] The question yet remaining unanswered is as follows: if complexes of the halomethyl cations CX_3^+ with different anions are generated in $CX_4 \cdot nAlX_3$ (and in related systems) with both $n = 1$ and $n = 2$, why these complexes differ so sharply in activity. Perhaps, only the donor-acceptor $CX_4 \to AlX_3$ complexes with a small positive charge on the halogen atom are formed in equilmolar systems in solution, whereas in the systems with excess aluminum halide, polar complexes having rather high positive charges on the halogen atom are produced. A similar situation is observed for the $RCOX \cdot nAlX_3$ systems; when $n = 1$, they entirely exist in solution as donor-acceptor complexes inert with respect to alkanes, whereas for $n = 2$, they represent mixtures of donor-acceptor complexes and acylium salts.[43,53,54] The final solution of the problem of the nature of the active species generated from polyhalomethanes under the action of aluminum halides requires further investigation.

Scheme 44 summarizes the types of carbonyl-containing compounds synthesized from alkanes (cycloalkanes) and CO in the presence of superelectrophiles on the basis of polyhalomethanes.

Scheme 44



The synthesis of carbonyl-containing products from alkanes and cycloalkanes has a number of serious advantages over the traditional routes based on the use of conventional acylating systems.

1. The ready availability of the starting compounds. It is noteworthy that, apart from the obvious availability of saturated hydrocarbons and CO compared to the traditional acylating systems (acyl halides, anhydrides, esters, carboxylic acids), many acids and their derivatives cannot be easily synthesized and some of them have not even been described.

2. The simplicity of one-step syntheses.

3. The selectivity of reactions.

4. Performing the reactions at low temperatures, which provides the possibility of effective and selective acylation of nucleophilic substrates unstable in electrophilic media.

5. The possibility of preparing products containing tertiary alkyl (cycloalkyl) and cage substituents at the carbonyl group.

It is clear that the scope of acylation reactions depicted in Scheme 44 can be markedly extended due to both involvement of other saturated hydrocarbons into selective reactions with CO and an increase in the range of nucleophilic reagents.

Mechanistic studies[170—172] of the key steps of reactions covered in the review, which represent cleavage of alkanes under the action of a superelectrophile (see Scheme 3) (taking the reaction of methane and propane with the CBr_3^+ cation and the $CBr_3^+AlBr_4^-$ cationic complex as an example), led to the unexpected conclusion stating that none of these reactions can be described in terms of the classical Olah scheme,[173,174] which assumes the formation of a two-electron three-center cyclic transition state but each of them follows a new unprecedented mechanism. Discussion of the mechanisms of the reactions of alkanes with superelectrophiles is beyond the scope of this review and will be the subject of another publication.

Conclusion

The discovery of superelectrophilic properies of the $RCOX \cdot 2AlX_3$ complexes in the 1980s marked the beginning of a new stage in the development of the chemistry of alkanes. The approach to the creation of superelectrophilic systems *via* the activation of molecules with several nucleophilic centers by one or several aluminum halide molecules proved to be fruitful and resulted in the design of new groups of very active organic and inorganic superelectrophiles. It is especially important that many transformations of alkanes and cycloalkanes induced by these superelectrophiles can be carried out selectively. Of most interest among the new superelectrophiles are polyhalomethanes used in combination with aluminum halides. These superelectrophilic systems of new generation efficiently initiate various reactions of alkanes and cycloalkanes, including selective functionalization in organic media under very mild conditions. Due to their ability to efficiently initiate the low-temperature transformations of alkanes and cycloalkanes, these superelectrophilic systems with record-breaking activity have considerable advantages in the reactions with alkanes compared to less active electrophilic and superelectrophilic systems known previously. These advantages include suppression of side processes, high stability of the functionalization products, high selectivity of reactions, and the predominant formation of products with branched organic radicals. The reactions of alkanes and cycloalkanes with CO initiated by polyhalomethane-based superelectrophiles open up the unique possibility for selective one-pot syntheses of diverse carbonyl-containing products from readily available raw materials.

I am grateful to collaborators who participated in the work and greatly contributed to obtaining of the results presented here, in particular, A. V. Orlinkov, L. V. Afanas´eva, D. V. Avetisyan, I. M. Churilova, S. Z. Bernadyuk, S. V. Vitt, and P. V. Petrovskii. I also wish to thank A. V. Orlinkov for assistance in preparing the publication.

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