

Polyhalomethanes Combined with Lewis Acids in Alkane Chemistry

Irena Akhrem* and Alexander Orlinkov

A.N.Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilova Street, 117813 Moscow, Russia

Received August 30, 2004

Contents

1. Introduction	2037	4.1.4. Electrophilic Attack on Hydrogen with “Open” 3c-2e Bonding	2066
2. Polyhalomethane–SbF ₅ -Mediated Transformations of Alkanes and Cycloalkanes	2040	4.2. The Nature of Complexes Responsible for the Superselectivity of Polyhalomethanes in the Presence of Aluminum Halides or Protic Superacids	2068
2.1. Polyhalomethane–SbF ₅ Systems as Generators of Polyhalomethyl Cations	2040	4.3. Mechanisms of Reactions of Alkanes with Bromine-Centered Superselectophiles	2070
2.2. Reactions of Alkanes and Cycloalkanes Initiated by Polyhalomethane–SbF ₅ Systems	2040	4.3.1. Reactions of Propane with CBr ₃ ⁺ and CBr ₃ ⁺ AlBr ₄ [–]	2070
2.2.1. Ionic Monohalogenation	2040	4.3.2. Reaction of Methane with CBr ₃ ⁺	2071
2.2.2. Polyhalomethane-Mediated Propane Carbonylation in HF–SbF ₅ Media	2040	4.3.3. Reactions of Methane with the CBr ₃ ⁺ AlBr ₄ [–] Cationic Complex	2071
3. Polyhalomethanes Combined with Aluminum Halides as a Novel Family of Aprotic Organic Superselectophiles for Alkane and Cycloalkane Transformations	2042	5. Conclusions	2073
3.1. Reactions without Functionalization	2042	6. Abbreviations	2073
3.1.1. Cracking, Isomerization, and Oligomerization of Alkanes	2042	7. Acknowledgments	2073
3.1.2. Oxidative Transformations of Cycloalkanes	2043	8. References	2073
3.2. Functionalizations	2044		
3.2.1. Polyhalomethanes as Sources of a Halide Functional Group	2044		
3.2.2. Types of Functionalization with Participation of Substrates	2045		
3.2.3. Ionic Bromination with Molecular Bromine	2045		
3.2.4. First Ionic Iodination	2046		
3.2.5. Dichlorophosphorylation with PCl ₃	2047		
3.2.6. Ritter-Type Reaction of Adamantane	2048		
3.2.7. Unprecedented Facile Sulfurization with Elemental Sulfur	2048		
3.2.8. Alkylation of Deactivated Arenes	2049		
3.2.9. Carbonylation with CO Leading to Carboxylic Acids and Esters	2051		
3.2.10. Alkanes and Cycloalkane with CO in One-Pot Syntheses of Various Carbonyl-Containing Compounds	2057		
4. Mechanistic Studies of the Reactions of Alkanes with Polyhalomethane-Based Superselectophiles	2062		
4.1. Early Studies of Mechanisms of Electrophilic Reactions of Alkanes	2062		
4.1.1. Electrophilic Attack on the C–H Bond with Cyclic 3c-2e Bonding (the Classical Olah Mechanism)	2062		
4.1.2. Reactions with Al(OH) ₃ and Related Compounds	2064		
4.1.3. Electrophilic Attack on Alkane Carbon Atoms	2065		

1. Introduction

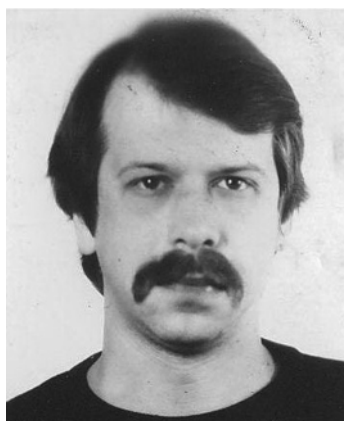
Alkanes and cycloalkanes, which are the major components of oil and natural gas, present great but hitherto unrealized resources for organic synthesis. Therefore, the development of one-pot selective syntheses of fine chemicals from available alkanes and cycloalkanes is one of the most important problems of organic chemistry. The realization of single-stage transformations of alkanes and cycloalkanes into valuable organic products would revolutionize petrochemistry by replacing the multistep nonselective processes currently used in industry. This capability will predictably soon become more topical as ecological reforms lead to the elimination of the market for saturated hydrocarbons as fuel for cars and thus also lead to increased availability of the hydrocarbons as substrates for these transformations.

The end of the 1960s brought about two sensational discoveries in this field. Almost simultaneously, the first transition metal complexes which activate alkane C–H bonds in solutions under mild conditions were described,¹ and the activation of alkanes with protic superacids was discovered.^{2,3} The reactivity of the weakly solvated proton turned out to be so high that, under mild conditions in the protic superacid media, efficient transformations of alkanes, even including the most inert alkane, methane, became possible.^{4–8} The discovery of new systems which activate alkanes under mild conditions gave impetus to extensive studies of alkane chemistry. The beginning of a new stage in the field of “low-temperature” alkane chemistry is mostly connected with George Olah’s works. The Nobel Prize in chemistry awarded to George Olah in 1994 for his pioneering studies on the activation of alkanes by protic superacids was a gesture of recognition of the current interest in this subject.⁶ To

* To whom correspondence should be addressed. E-mail: cmoc@ineos.ac.ru.



Irena S. Akhrem, D. Sc, Professor, Head of the Group of inert molecules activation at the Institute of Organoelement Compounds (INEOS) RAS, has about 250 publications. She was born in Moscow (USSR) in 1932, graduated from Moscow State University in 1955 and began work under the supervision of Prof. Mark E. Vol'pin at the INEOS. Her Ph.D. study (1961) was devoted to the chemistry of tropylium. Then she studied activation of S–C and C–C bonds in paraffines and silaparaffines by transition metal complexes. Together with her collaborates, she found effective catalysts based on ligand-deficient small metal clusters and Ziegler-type systems for hydrocracking of saturated hydrocarbons and new active transition metal compounds for Si–C bond cleavages. She and her collaborates were the first who described the activation of Si–H bonds in Alk_3SiH by ionic fluorides and applied this approach for syntheses. She obtained her D. Sc. in 1991 from the INEOS. In 1982 she, for a short time, worked in the field of metalloporphyrines under the supervision of Dr. J.-P. Battioni (lab. of Prof. D. Mansuy) in L'Ecole Normale Superiere in Paris. Her current research interests are the development of super-electrophiles of a new generation for low-temperature transformations and selective functionalizations of alkanes and cycloalkanes. The nature of active species in new superelectrophilic systems and mechanisms of superelectrophilic alkane functionalizations are in the focus of her interests also.



Alexander V. Orlinkov was born in Moscow, Russia, in 1957. He graduated from the Moscow State University in 1979. Since this year, he started investigations in the Laboratory of Complex Organoelement Catalysts of A.N. Nesmeyanov Institute of Organoelement Compounds RAS (INEOS RAS) under scientific directions of Prof. Mark. E. Vol'pin and Prof. Irena S. Akhrem. He received his Ph.D. degree in 1989 from said Institute working in the field of alkanes and cycloalkanes activation. In 1992–93, he worked as visiting scientist at the University of Southern California (Loker Hydrocarbon Research Institute) under the supervision of Prof. George A. Olah. At present, Alexander V. Orlinkov is the Senior Researcher of the Group of Activation of Inert Molecules of the INEOS RAS. In recent years his research interests involve the development of new types of functionalizations of alkanes and deactivated arenes by new aprotic and protic superacids.

appreciate at the present time the importance of the above discoveries, one should remember that alkanes, called “parafins” for their lack of reactivity with the majority of

active reagents under ordinary conditions, were referred to then as one of the most inert classes of organic compounds (the “noble gases of organic chemistry”). All monographs⁹ and reviews devoted to alkanes stress that they are extremely weak acids and bases, that they lack both nonbonded electron pairs as well as low-lying vacant orbitals, and that their C–H and C–C bonds are of high energy. Before the early 1970s, it was thought that reactions of alkanes only occur, as a rule, either at high temperature or with high-energy species.⁹

In the last quarter of the 20th century, alkane chemistry has developed with remarkable success. A number of brilliant scientific teams have made considerable contributions to alkane chemistry. In addition to the above-mentioned achievements, namely, the development of the activation of alkanes both by proton superacids^{4–8,10} and by transition metal complexes,^{10–21} as well as the elaboration of the reactions induced by these nontraditional activating systems, this period provided many new approaches including also the development of traditional activating systems to a new level. Among these new approaches are making new groups of radical agents^{22–37} and analogues of metalloenzymes.^{38–45} Organometallic chemistry of alkanes in the vapor phase has also advanced greatly during this time.^{46–52} Mass-spectral studies of reactions of alkanes with metal ions elucidated the steps involved in these reactions and made it possible to estimate the energies of M–H and M–C bonds.^{46–52} Functionalization of methane constitutes the most important topic of research both since it challenges alkane inertness, and since there is substantial economic interest in the use of natural resources. The known and projected world reserves of natural gas, more than 2.5×10^{17} L, are comparable to those of petroleum.⁵³ Therefore, methane activation by a “naked” transition metal cation M^+ has been the subject of a number of fundamental gas-phase ion studies.^{47,49} Schwarz has shown how easy it is to functionalize C–H and C–C bonds in the gas phase in a mass spectrometer using metal ions, especially those derived from iron. The gas-phase reactions of $\text{M}(\text{CH}_2)^+$ species with various nucleophiles have been studied recently⁵² to elucidate the elementary steps of industrially important processes such as conversions of CH_4 into CH_3OH , CH_2O , CH_3COOH , HCN , and so forth.

The traditional field of heterogeneous alkane reactions occurring on metal surfaces experienced a renaissance^{54–56} that, in turn, stimulated the development of the homogeneous organometallic chemistry of alkanes. The development of solid and supported acidic catalysts, which are of great industrial potential, is a high point in petrochemistry.^{57–59} For example, $\text{TaF}_5/\text{Nafion-H}$, $\text{SbF}_5/\text{graphite}$, and even zeolites have been used as catalysts for selective chlorination and bromination of methane.^{59c,d} Thus, the reaction of MeH with Br_2 over a synthetic aluminosilicate ZSM-5 becomes available as a key stage for converting gaseous alkanes into liquid hydrocarbons useful for the production of fuel.^{59d} By the 1980s, the properties of zeolites or “boiling stones” (discovered in the mid 18th century⁶⁰) had made these minerals a subject of increasing interest in chemistry and chemical technology. The studies of alkane reactions with metal atoms and metal clusters as well as other metal-containing heterogeneous systems^{61–75} led to a novel new group of active catalysts for alkane transformations (see, for example, references 64–75) and to the elaboration of new syntheses of organometallic complexes directly from alkanes and cycloalkanes.⁶³ During the last few decades, considerable advances have been made in understanding the mechanisms

of alkane activation by proton superacids^{4–6,76a,77–81} and by transition metal complexes.^{18–21,82–91} The concept of electrophilic activation of C–H and C–C σ -bonds based on the formation of CX_5^+ intermediates or on transition states with a hypervalent carbon was a major breakthrough in organic chemistry happening after the late 1970s. The first direct observations and descriptions of alkyl carbenium ions,^{2c,4–6,76a} which had been postulated earlier only as intermediates in electrophilic alkane reactions,^{76b} also occurred during this time.

Another method for alkane C–H bond activation involving oxidative addition of the bond to a coordinatively unsaturated metal atom was also documented, mostly in excellent works of R. Bergman,⁸² W. Graham,⁸³ W. Jones,⁸⁴ and others.^{18,21} The formation of weak alkane-metal σ -complexes (or “sol-vates”) has been shown to precede alkane C–H bond scission by transition metal complexes.^{90,91} Recently, the development of computers has enabled many mechanistic calculations of alkane and cycloalkane reactions with radicals and cation radicals,³⁷ transition metal complexes,^{18,86–87} bare metal ions,⁸⁸ enzymatic systems,⁹² and solid superacids, the last of which includes coordinatively unsaturated aluminum compounds⁹³ serving as models of aluminosilicates, through the application of density functional theory (DFT)⁹⁴ and high level *ab initio* calculations (see section 4).

The activation of saturated hydrocarbons by radicals and radical cations has been the topic of detailed consideration in recent reviews.^{36,37} The activation of C–H bonds by metal complexes has also been covered in several recent reviews.^{16–18,21} Organometallic alkane chemistry has now become a promising and important field of catalysis and of organometallic, organic, and coordination chemistry. Over the last 2 to 3 decades, a large number of complexes of transition metals, lanthanides, and actinides for alkane activation were described. In contrast, progress in the elaboration of novel strong electrophilic systems which do not contain transition metals and which are not protic acids was not as remarkable. In this connection, it is necessary to recall that, in spite of a worldwide trend to restrict the use of liquid acids such as HF and H₂SO₄ as well as Lewis acids such as aluminum halides, BF₃, and so forth, due to environmental concerns, these systems are still used because of their high activity at low temperature.⁹ Acid-catalyzed hydrocarbon reactions comprise the largest volume of transformations in the oil refining and chemical industry.⁹ As to heterogeneous alkane transformations into functional derivatives, they are used industrially very rarely because of inherent practical limitations (low conversions, poor selectivity, high-energy consumption). Conversion of *n*-butane by the VOPO₄/SiO₂ system at 320 °C to maleinic anhydride, widely used in polyester resin production, is the only heterogeneously catalyzed alkane-selective functionalization reaction in commercial use.^{59b} Recently, effective catalytic functionalizations of methane and ethane have been performed by using highly electrophilic transition metal cationic species generated *in situ* in strong acid media.^{89,95–97} For example, methane and ethane were selectively carbonylated with CO by Pd(OAc)₂/Cu(OAc)₂ in the presence of K₂S₂O₈ in CF₃COOH to give the corresponding acids.^{89,95a} Vanadium-containing catalysts also were found to be very effective for carbonylation of low alkanes. Methane was converted to acetic acid almost quantitatively with VO(acac)₂ as catalyst (the turnover is 18).^{89,95b} It was suggested that Pd-catalyzed alkane carbonylation involves electrophilic attack of PdO₂CCF₃⁺ cation

on the C–H bond of alkanes to give an alkyl-Pd(II)O₂CCF₃ species.⁸⁹ For the V-catalyzed reactions, a radical mechanism^{89,95b} has been proposed, wherein the V(V)=O species serves both as a generator of CH₃[•] radical and as an oxidant for CH₃CO[•]. Various compounds of transition metals in strong protic acid media have been found to be good catalysts for conversions of alkanes, especially methane, to alcohol derivatives.^{89,96,97} The transformation of methane by V-containing heteropolyacids in CF₃COOH/(CF₃CO)₂O to give methyl trifluoroacetate in 95% yield has been described.^{96d} A. Sen et al. reported the first electrophilic conversion of methane to a methanol derivative by H₂O₂ in CF₃COOH, using the Pd^{II}/CF₃COOH system.^{96a,b} R. Periana et al. described the highly effective esterification of methane in the presence of Hg^{II}/H₂SO₄ or Pd^{II}/H₂SO₄ systems. These electrophilic reactions gave esters in 43% and 72% yields, respectively.⁹⁷ Thus, a new strategy for catalytic functionalization of low alkanes, and especially methane, by the application of highly electrophilic cationic complexes of transition metals generated *in situ* in a strong acid medium turned out to be very promising. Indeed, such an approach will probably lead to industrial processes in the near future. As to the state of alkane chemistry now, one can say that in spite of the swift development of this field in the last quarter of the 20th century, alkanes and cycloalkanes still provide an unrealized wealth of opportunity for organic synthesis. Therefore, Mendeleev’s often repeated statement that “to use petroleum as a fuel is like firing a furnace with banknotes” still rings true today. However, one can believe that discoveries in alkane chemistry in recent years have gradually brought us closer to a solution of this problem.

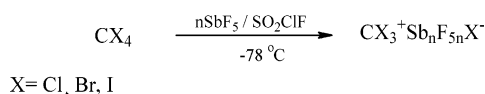
New aprotic superelectrophiles, which are the topic of this review, offer unique possibilities for the application of alkanes and cycloalkanes in organic synthesis.

The discovery in the 1980s of the superelectrophilic properties of acylhalide/aluminum halide complexes of the form RCOX•2AlX₃,^{98–100} as opposed to the classical Friedel–Crafts RCOX•AlX₃ equimolar complexes,^{101–106} was the high point in electrophilic low-temperature alkane chemistry for that decade. These systems are far superior in their reactivity in alkane reactions to all previously known systems based on either mineral acids or Lewis acids, usually even including the strongest protic superacids.^{98–100} They have been shown to be extremely active in initiating various transformations of alkanes accompanied by C–C bond cleavage, such as in¹⁰⁷ isomerization,^{108–110} alkylation,^{111,112} and oxidative coupling.^{98,99} In those cases for which cracking reactions can be suppressed, selective single-stage functionalization can be successfully achieved.^{98–100,113–119}

It is the purpose of this review to acquaint the reader with a new family of aprotic organic superelectrophiles for effective transformations, including selective functionalizations, of alkanes and cycloalkanes. The matter concerns the polyhalomethanes combined with Lewis acids (mostly with aluminum halides, especially bromide).

The halide exchange between CHCl₃ and AlBr₃¹²⁰ has been known since 1901. In the early 1950s, Willard et al.¹²¹ showed that exchange of the chlorine atoms of CCl₄ or CHCl₃ and AlCl₃ labeled with ³⁶Cl occurs even at –20 and –63 °C, thus, indicating their ionization to cations CCl₃⁺ and CHCl₂⁺, respectively. It was not until a century later, after the first publication concerning ionization of polyhalomethanes, that the first direct observations of polyhalomethyl cations in a liquid¹²² and in a solid¹²³ state were reported.

Scheme 1

**Table 1.** Comparison of ^{13}C NMR Chemical Shifts of Trihalomethyl Cations^{122b} and Relative Haloforms^{132, a}

X	CHX ₃ , δ ^{13}C	CX ₃ ⁺ , δ ^{13}C	$\Delta\delta$
Cl	77.7	236.3	158.6
Br	12.3	207.0	194.7
I	-139.7	95.0	234.7

^a In excess SbF₅/SO₂ClF at -78 °C. (Adapted from Ref 122b, Table 2. Copyright 1996 American Chemical Society).

At the same time, the superelectrophilic properties of polyhalomethanes both in the presence of SbF₅ in proton superacid media¹²⁴ and in the presence of aluminum halides in organic media¹²⁵ were discovered. Even with this short history, the role of polyhalomethane–AlX₃ systems in the chemistry of alkanes has become very rich and most promising. This novel family of superelectrophiles has opened new perspectives for selective and regioselective syntheses of organic compounds from alkanes and cycloalkanes by a one-pot procedure. This review covers different transformations of alkanes and cycloalkanes mediated by the polyhalomethane-based superelectrophiles. We will consider both the nature of the species which might be responsible for the high activity of these systems and also the mechanisms of their reactions with alkanes, which are novel for electrophilic alkane chemistry.

This review consists of an introduction and three major sections treating polyhalomethane–SbF₅-mediated alkane reactions, polyhalomethane–AlX₃-mediated alkane reactions, and polyhalomethane superelectrophile alkane reaction mechanisms.

2. Polyhalomethane–SbF₅-Mediated Transformations of Alkanes and Cycloalkanes

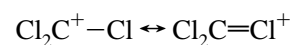
2.1. Polyhalomethane–SbF₅ Systems as Generators of Polyhalomethyl Cations

Ionization of polyhalomethanes by aluminum halides at low temperatures had been described as early as the beginning of the 20th century.^{120,121} More recently, free halomethyl cations have been produced and spectroscopically characterized as matrix photoionization products and photolysis products of halomethanes.^{126–128} The CCl₃⁺ ion was first observed by Jacox in an argon matrix at 14 K among the products both of ultraviolet and of microwave radiation decomposition of CHCl₃.^{129,130} The list of experimental vibrational frequencies for the CHCl₂⁺ cation is also available.^{130,131}

Olah and co-workers were the first to succeed in preparing trihalomethyl cations in solution under conditions giving long-lived stable ions.¹²² Tetrahalomethanes were shown to ionize in an excess of SbF₅/SO₂ClF solution at -78 °C to yield the corresponding trihalomethyl cations as shown in Scheme 1. The assignment of the carbenium structure to the products was based on a noticeable downfield shift of their C-atom signals compared with those for the corresponding CX₃H in the ^{13}C NMR spectra (Table 1). The thermodynamic stability of the CX₃⁺ cations as opposed to the CH₃⁺ cation, which is not observable in solutions, was explained by the

efficient p–n interaction between the nonbonded electron pairs of the halogens and the positively charged carbon atom¹²² as illustrated in Scheme 2. To confirm the formation of the trichloromethyl cation, it was produced independently according to Scheme 3.

Chloroform did not give a stable CHCl₂⁺ cation under similar conditions.¹²² A rapid exchange reaction between CHCl₂⁺ and SbF₅ is proposed to be responsible for the failure to produce this ion in HF–SbF₅ media. However, Vancik et al. were successful in generating it in the solid state.¹²³ Co-deposition of each of the chloromethanes, CCl₄, CCl₃H, and CH₂Cl₂, with SbF₅ at 77 K on a CsF window followed by warming to 150 K produced polyhalomethyl cations, that is, CCl₃⁺, CHCl₂⁺, and (ClCH₂)₂Cl⁺, respectively, as ion pairs with Sb₂F₁₀Cl⁻ anion, which were identified by their IR-spectra (Table 2).¹²³ A strong absorption band observed at 1037 cm⁻¹ was assigned to the asymmetrical C–Cl stretching vibration of these cations. The relatively high frequency is indicative of the partial double bond character of this bond:



The appearance of the band at $\approx 1040\text{ cm}^{-1}$ in the solid SbF₅ matrix at 150 K was accompanied by the disappearance of the absorption at 785 cm⁻¹, which is characteristic for the C–Cl stretching vibration in CCl₄.¹²³ CCl₃⁺ Sb₂F₁₀Cl⁻ in solution and CHCl₂⁺ Sb₂F₁₀Cl⁻ in the solid-state were stable below -50¹²² and -123 °C,¹²³ respectively. When the matrix was warmed to -73 °C, the CHCl₂⁺ peaks disappeared, and new peaks, which were assigned to CHF₃, appeared.¹²³

The trichloromethyl cation has been shown to be an excellent reagent for the generation of carbocations in the SbF₅ matrix (Table 3).¹²³ Thus, the trichloromethyl cation formed initially is consumed by a saturated hydrocarbon as the equilibrium is shifted in favor of the thermodynamically more stable alkyl or cycloalkyl cation (Scheme 4). Figure 1 demonstrates the successive formation of CCl₃⁺ at first and then of the nonclassical norbornyl cation⁶ in the reaction of norbornane in the SbF₅/CCl₄ matrix.¹²³

2.2. Reactions of Alkanes and Cycloalkanes Initiated by Polyhalomethane–SbF₅ Systems

Reactions of alkanes and cycloalkanes with polyhalomethanes in the presence of SbF₅ are not numerous. They are limited to ionic monochlorination or bromination of saturated hydrocarbons by CH₂X₂ (X = Cl, Br)¹³³ and polyhalomethane-mediated propane carbonylation in HF–SbF₅ media.¹²⁴

2.2.1. Ionic Monohalogenation

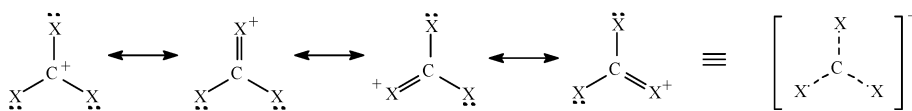
At an equimolar ratio of RH to SbF₅, ionic halogenation of saturated hydrocarbons by CH₂X₂ occurs selectively (Scheme 5).¹³³

Two alternative mechanistic schemes were considered for the halogenation reactions (Scheme 6a,b).¹³³ In both of them, the participation of the bis (chloromethyl) chloronium ion was accepted. Its formation from CH₂Cl₂ and SbF₅ in liquid SO₂¹³⁴ as well as in cryogenic SbF₅ matrices¹²³ was proved.

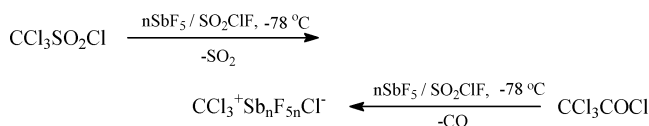
2.2.2. Polyhalomethane-Mediated Propane Carbonylation in HF–SbF₅ Media

Carbonylation of propane in HF–SbF₅ media is extremely poor with the propane conversion being 4% and 1% for 1 h

Scheme 2



Scheme 3

Table 2. Infrared Frequencies of Polychloromethyl Cations^a

initial polyhalomethane	corresponding cation	IR data, cm ⁻¹	
		lit. ^{130,131}	lit. ¹²³
CCl ₄	CCl ₃ ⁺	1035 ¹²⁹	1040vs
		1291	1290s
CHCl ₃	CHCl ₂ ⁺	1045	1045vs
		845	850s
		3033	
CH ₂ Cl ₂	(ClCH ₂) ₂ Cl ⁺	3070m, 3068m, 2980m, 1233w, 1030s, 870vs, 796s, 780s	

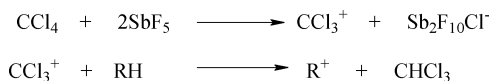
^a Adapted from Ref 123, Table 1. Copyright 1990 American Chemical Society.

Table 3. Experimental Infrared Frequencies of Carbocations Generated in the Matrix Experiment at 150 K^a

Precursor	Ion	Frequencies, cm ⁻¹
		2910s, 2850s, 2750s, 1456m, 1400m, 1310vs, 1270vs, 1210m, 1150w, 1105w, 980m, 910m, 900w
		3100m, 2970m, 2940m, 1480s, 1430vs, 1380s, 1350vs, 1300vs, 1280s, 1245w, 1225m, 1150m, 1125s, 1100s, 1090m, 1035m, 980m, 960w, 920w, 865s
		2890s, 2840w, 1480s, 1450m, 1350m, 1320m, 1255m, 1190w, 1170s, 1150w, 1100w, 1080s, 1070s, 1005s, 973s, 900s
		2950m, 1485s, 1455s, 1215s, 1150m, 1105s, 980s, 915s
		2955m, 2880w, 2770w, 1460s, 1380m, 1360m, 1310m, 1265m, 1215m, 1150vs, 1100s, 980vs, 915vs, 900s
		2830m, 1465m, 1300s, 1280w, 1270w, 1100m, 1085w, 1040vs, 980s, 910w, 900m

^a Adapted from ref 123, Table 2. Copyright 1990 American Chemical Society.

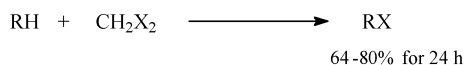
Scheme 4



at -10 and -30 °C, respectively. In addition, the selectivity of this reaction at -10 °C is also low, since both ⁱPrCO⁺ (**1**) and EtCO⁺ (**2**) cations are formed.^{124a} Formation of **2** is due to the cracking of the propyl cation generated (Scheme 7).

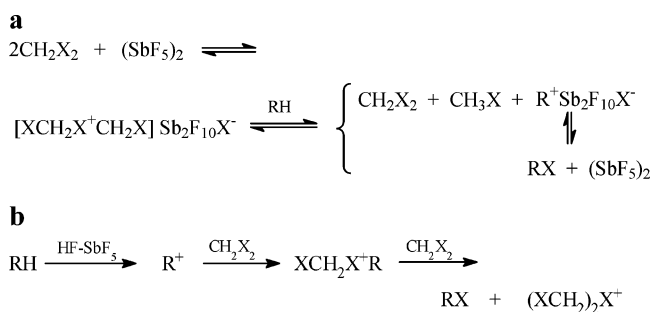
Sommer reported a dramatic effect of polyhalomethanes on the effectiveness and selectivity of propane carbonylation in HF-SbF₅.^{124a} In the presence of a catalytic amount of CCl₄, the conversion of propane reaches 50% after 1 h even at -30 °C, and **1** is the only ion produced under these conditions. CHCl₃ and CH₂Cl₂ act similarly, although their

Scheme 5

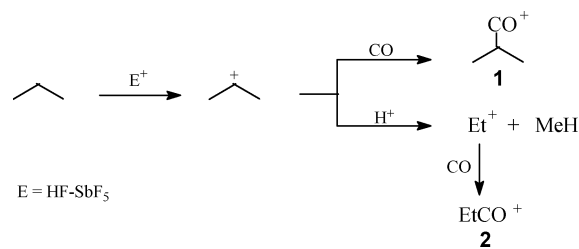


RH = C₃H₈, ⁱC₄H₁₀, *neo*-C₅H₁₂, *cyclo*-C₅H₁₀, C₁₀H₁₆ (adamantane)

Scheme 6



Scheme 7



activation effect is less, that is, the reactivity of halomethanes decreases in the order: CCl₄ > CHCl₃ ≫ CH₂Cl₂. The surprising increased reactivity of propane in the presence of catalytic amounts of CCl₄ or CHCl₃ can be rationalized by

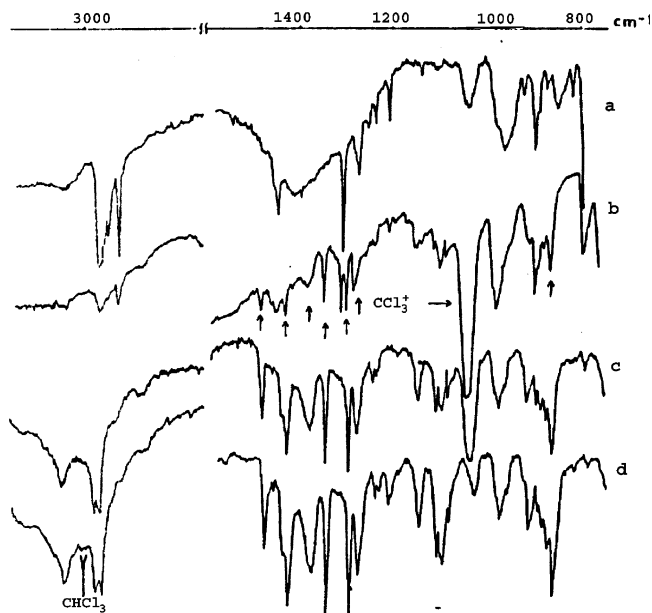
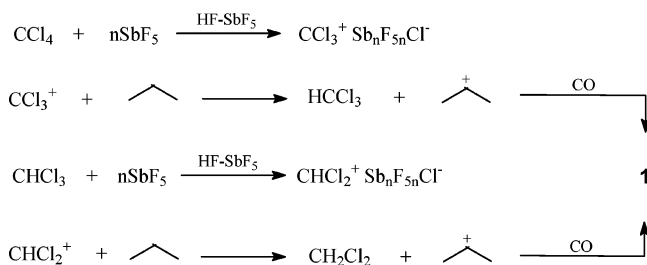


Figure 1. The reaction of norbornane with CCl₃⁺ in the CCl₄/SbF₅ matrix: (a) starting material; (b-d) after successive warming from 77 to 150 K (the signals of 2-norbornyl cation are labeled with arrows) (reprinted from ref 123, Figure 1. Copyright 1990 American Chemical Society).

Scheme 8

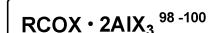


the generation of polychloromethyl cations under these conditions. Free SbF_5 is present in an HF-SbF_5 medium when the concentration of SbF_5 exceeds 20% HF .^{7c} The activity of CCl_3^+ and CHCl_2^+ cations is probably higher than that of the protic acid $\text{H}^+\text{Sb}_2\text{F}_{11}$, which is present in a large excess in the medium. The emergent halomethyl cation abstracts selectively the secondary C–H bond of propane to give **1**, as in Scheme 8.

The selectivity may be caused by steric hindrance suppressing the electrophilic attack of the bulky polyhalomethyl cations on the propane C–C bond.¹²⁴

3. Polyhalomethanes Combined with Aluminum Halides as a Novel Family of Aprotic Organic Superelectrophiles for Alkane and Cycloalkane Transformations

The discovery of the superelectrophilic properties of systems containing acyl halides in combination with excess aluminum halides^{98–100} has served as the starting point in the search for new superelectrophilic complexes which would provide selective and effective functionalization of alkanes and cycloalkanes, and which would be simultaneously more accessible and more convenient to work with than the complexes based on acyl halides. Testing of a number of systems in which the generation of cations or even dications^{135–144} seems to be, in principle, possible has led to the novel families of organic^{125,145} and inorganic^{145–148} superelectrophiles shown in Figure 2. With respect to selective functionalization of alkanes and cycloalkanes, we find that among these systems the polyhalomethanes in combination with aluminum halides are particularly interesting.



(R = Alk, Ar; X = Cl, Br; n = 1–3)



(n = 1–2; Hal₂ = Cl₂, Br₂, I₂)



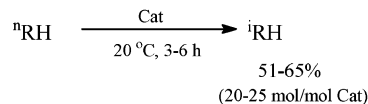
(R = Me, Cl; X = Cl, Br; n = 1–3)



Figure 2. Organic and inorganic superelectrophiles of a new generation.

Scheme 9

Isomerization

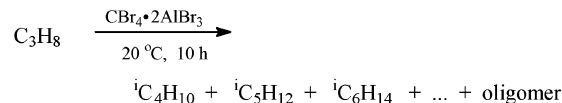


${}^n\text{RH} = \text{C}_4\text{H}_{10}, \text{C}_5\text{H}_{12}$

Cat = $\text{CBr}_4 \cdot 2\text{AlBr}_3, \text{CHCl}_3 \cdot 2\text{AlBr}_3$

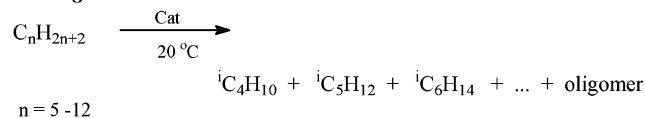
TOF = 4–9 h^{–1}

Oligomerization



Conversion - 0.27 mol/mol Cat

Cracking



Conversion - 70–80% of C₈–C₁₂ alkanes for 10–20 min

TOF = 10–42 h^{–1}

Cat = $\text{CX}_4 \cdot n\text{AlBr}_3, \text{CHX}_3 \cdot n\text{AlBr}_3$

(X = Cl, Br; n = 1 or 2)

3.1. Reactions without Functionalization

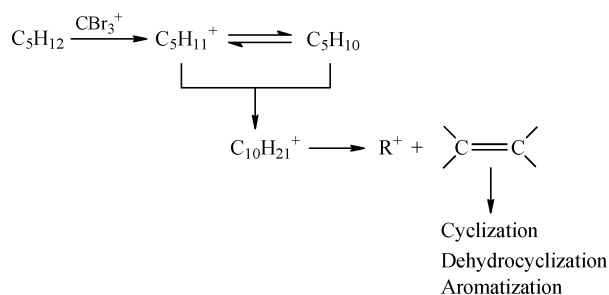
3.1.1. Cracking, Isomerization, and Oligomerization of Alkanes

Polyhalomethanes in the presence of aluminum halides, particularly bromides, are the strongest organic superelectrophiles. The $\text{CBr}_4 \cdot n\text{AlBr}_3$, $\text{CHBr}_3 \cdot n\text{AlBr}_3$ (n = 1 or 2), $\text{CCl}_4 \cdot 2\text{AlBr}_3$, and $\text{CHCl}_3 \cdot 2\text{AlBr}_3$ systems under mild conditions are effective initiators of n-alkane isomerization, of lower alkane oligomerization, of the cracking of alkanes (mostly into oligomers and low C₄–C₆ isoalkanes), and of similar processes¹²⁵ (Scheme 9).

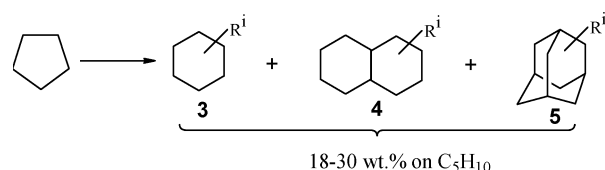
At 20 °C, either with CH_2Br_2 as solvent or with no solvent, and with a $[{}^n\text{C}_5\text{H}_{12}]/[\text{CBr}_4 \cdot 2\text{AlBr}_3]$ molar ratio in the range 5–10, pentane undergoes complex transformations. Among the products are C₄–C₆ isoalkanes, including mostly isopentane, higher branched isoalkanes up to C₁₂H₂₆, and small amounts of dehydrocyclization products from pentane, that is, various hydrocarbons with varying degrees of unsaturation, such as cycloalkanes, cycloalkenes, cyclodienes, linear trienes, and aromatics. The total yield of hydrocarbon products (starting from C₈) is ca. 20% on the initial pentane (recalculated for a stoichiometric reaction). The dehydrocyclization of pentane under such mild conditions has not been reported since this work.¹⁴⁹ A suggested pathway for these pentane transformations involves alkylation of the conjugated alkene with a pentyl cation. The C₁₀H₂₁⁺ cation from the alkylation undergoes fragmentation to give lower alkanes and alkenes according to the classical path in Scheme 10. Under catalytic conditions, the conversion of pentane into isomerization and cracking products reaches 200 mol per mole of superelectrophile.

Contrary to the $\text{RCOX} \cdot n\text{AlX}_3$ complexes,^{98–100} whose activity is extremely high at n = 2 and completely absent at n = 1, both 1:1 and 1:2 polyhalomethane·nAlBr₃ systems show high activity.¹²⁵ The influence of AlBr₃ content on activity of polyhalomethane is not uniform. In the transformations involving low-activity alkanes, the 1:2 systems are

Scheme 10



Scheme 11



considerably more active than the corresponding 1:1 systems, and indeed, the latter sometimes do not promote alkane transformations at all. Conversely, both systems display high activity in reactions with more active saturated hydrocarbons such as adamantane. In agreement with the Sommer's data,¹²⁴ the activity of polyhalomethanes in the presence of $AlBr_3$ increases with the number of halogens in the molecule.

3.1.2. Oxidative Transformations of Cycloalkanes

The search for active systems to initiate the conversion of alkanes and cycloalkanes into alkylated bicyclic hydrocarbons and adamantanes¹⁵⁰ is stimulated by the interest in these compounds as parents for the preparation of valuable biologically active products, polymers, and other industrially important compounds. The polyhalomethane-based super-electrophiles were the first systems shown to be capable of mediating such transformations of cyclopentane under very mild conditions. Even at 20 °C under the action of the complex $CBr_4 \cdot 2AlBr_3$ either in CH_2X_2 ($X = Cl$ or Br) as solvent or with no solvent, cyclopentane converts rapidly into a mixture in which alkylated cyclohexanes, decalins, and adamantanes are the main components (Scheme 11).

In addition to saturated cycloalkanes of types 3–5, small amounts of cyclic hydrocarbons C_nH_{2n-6} (6) are also produced. A suggested scheme¹⁵¹ for the cyclopentane oxidative transformations involves abstraction of a hydride ion from cyclopentane. The cyclopentyl cation attacks the cyclopentene in equilibrium with itself and apparently gives rise to dicyclopentyl and then to decalin and adamantane. These oxidative transformations should also be accompanied by the reduction of CBr_4 . In addition to the processes involving the formation of C–C bonds, cyclopentane ring-opening also occurs, and this yields amyl cations in equilibrium with pentenes. Thus, cyclopentane also acts as a hydrogen acceptor in the oxidative cyclooligomerization of cyclopentane. These amyl cations and pentenes start a series of alkyl cations and olefins which alkylate cyclic hydrocarbons. The observed products are apparently the result of a set of numerous reactions involving making and breaking C–C bonds. The driving force of these reactions is the formation of the thermodynamically most stable hydrocarbons (Scheme 12).

Alkyladamantanes and alkylcyclohexanes have been detected on prolonged heating decalins of dicyclopentyl¹⁵² or cyclopentane¹⁵³ with $AlBr_3$ – t BuBr at 160 °C. The formation

of derivatives of decalin has been reported from cyclopentanol¹⁵⁴ and cyclopentene¹⁵⁵ as precursors of the cyclopentyl cation in acidic media. Cyclopentane ring-opening under the action of FSO_3H – SbF_5 or HF – SbF_5 at –10 °C to yield the *tert*-pentyl cation has been described.¹⁵⁶

Apart from the low-temperature transformations of pentane and cyclopentane, oxidative dimerization of cyclohexane and methylcyclopentane has been known since the early 1930s. Contrary to one publication¹⁵⁷ in which these cycloalkanes were reported to remain unchanged in the presence of 20–30% (w/w) of $AlCl_3$ at 120–150 °C, it has been reported in later publications that both cycloalkanes dimerize upon treatment with aluminum halide-based systems to give a mixture of dimethyldecalins (DMDs).^{98,158–160} Heating cyclohexane at 40–60 °C for 15–20 h with activated $AlCl_3$ gives DMDs in 10–15% yield.¹⁶⁰ The use of a promoted HF – BF_3 system makes it possible to prepare DMDs from cyclohexane in 54% yield at 100 °C over the period of 6 h.¹⁶¹ Some electrophilic systems are active in this reaction at 20 °C: *tert*-BuCl– $AlCl_3$,^{159b} $Cu(Al_2Cl_8)$,¹⁶² and $AcX \cdot 2AlBr_3$ ⁹⁸ are examples. The yields of DMDs based on super-electrophile are 27% (2 h),^{159b} 33% (4 h),¹⁶² and 100% (1 h).⁹⁸

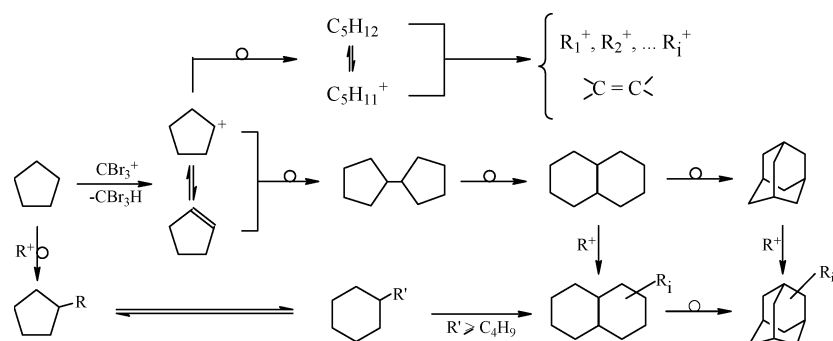
Upon treatment with any of the electrophilic systems $CBr_4 \cdot nAlBr_3$, $CCl_4 \cdot nAlCl_3$, or $CHCl_3 \cdot nAlCl_3$ at 20 °C, cyclohexane and methylcyclopentane undergo rapid oxidative dimerization to give DMDs in yields with respect to the super-electrophile of 25% and 100–140% over a period of 0.5 h. and 2 days, respectively. In the presence of an excess of cycloalkane, the reaction occurs rather selectively, giving only traces of trimerization products and other byproducts¹⁴⁹ (Scheme 13).

The mechanism conjectured for these reactions (Scheme 14) involves formation of the active cationic complex (a), generation of the cycloalkylcarbenium ion from a cycloalkane (b), addition of the cycloalkane to the carbocation to the conjugated cycloolefin to give the dicycloalkylcarbenium ion (c), rearrangement of the latter into the thermodynamically stable dimethyldecalinium ion (d), and finally, the formation of DMD and regeneration of the electrophile (e).¹⁴⁹

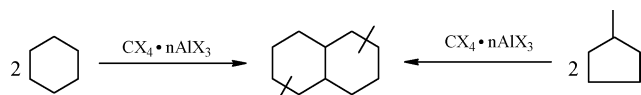
According to Scheme 14, the formation of one DMD molecule requires two molecules of super-electrophile, and only one of them can be regenerated. The formation of DMDs in a yield of more than 100% is explained by the reaction of CBr_4 with cycloalkane to be reduced to $CHBr_3$, which is also able (although less efficiently than CBr_4) to initiate oxidative dimerization of the cycloalkane. Dimerization of C_6 cycloalkanes is accompanied by the reduction of initial polyhalomethanes; conversely, aluminum halides function in these reactions as catalysts. However, the yield of DMD based on $AlCl_3$ was 150% only, when the reaction of methylcyclopentane or cyclohexane was carried out in an excess of CCl_4 at 40 °C.¹⁴⁹

The schemes presented in this review and the general problem of the mechanisms of electrophilic reactions of alkanes suggest that close attention should be paid to the concept of A. Fokin, P. Schreiner, and coauthors.^{37,163} These authors have emphasized the importance of the electron-transfer steps in alkane reactions with electrophiles, and they have proposed some criteria to distinguish between two different alkane C–H activation modes: an inner sphere one-electron pathway (SET, Scheme 15a), and a two-electron hydride transfer (Scheme 15b). The authors propose that reactions with weak electrophiles which are powerful oxidants should occur *via* Scheme 15a rather than *via*

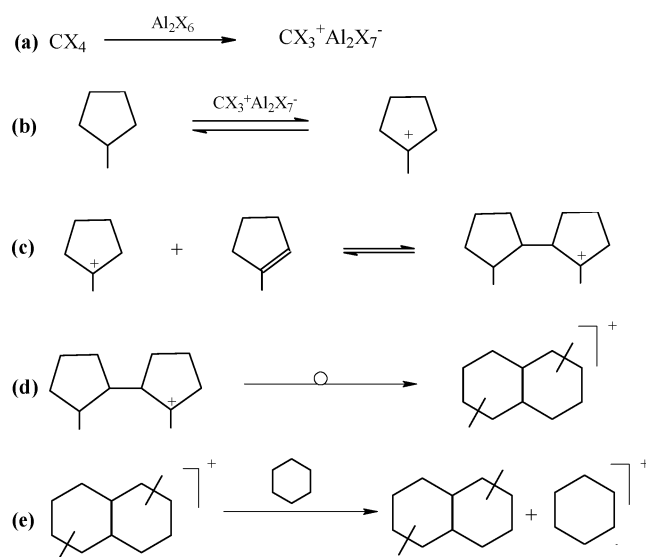
Scheme 12



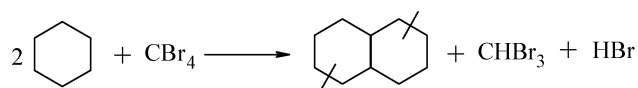
Scheme 13



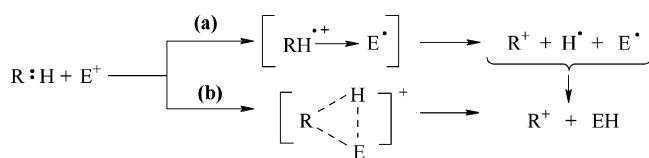
Scheme 14



Overall reaction



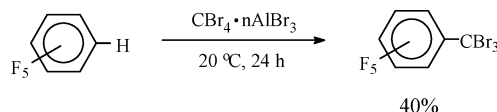
Scheme 15



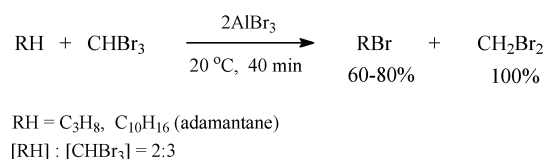
Scheme 15b. These SET reactions should be characterized by high kinetic isotope effects, and in their transition states, both a considerable charge transfer to the electrophile and a close structural similarity between the hydrocarbon moieties and the corresponding radical cation should be observed. Conversely, reactions with strong electrophiles should display low kinetic isotope effects as suggested by Scheme 15b.

At this point, a radical cation mechanism cannot be excluded for any reaction initiated by polyhalomethane-based superelectrophiles, but this pathway cannot be experimentally supported for them, either. Therefore, we consider only the

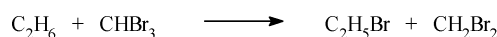
Scheme 16



Scheme 17



Scheme 18



overall process, that is, the transfer of what is only formally a “hydride” from a hydrocarbon to an electrophile.

3.2. Functionalizations

In some cases, at least for hydrocarbons of comparable stability toward cracking, C–C bond cleavage can be suppressed, and transformations of alkanes and cycloalkanes into their functionalized products or their isomeric forms occur.

3.2.1. Polyhalomethanes as Sources of a Halide Functional Group

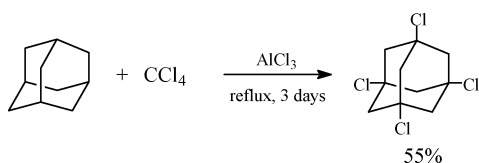
The substitution of saturated hydrocarbon hydrogen for a halomethyl group (CX_3 , CHX_2 , CH_2X) did not occur in the reactions initiated by polyhalomethane – aluminum systems. Reactions of that type were observed only for pentafluorobenzene (Scheme 16).¹⁶⁴

On the contrary, selective transformations into the corresponding or isomeric monobromides of alkanes and cycloalkanes which are relatively stable to cracking were achieved with $\text{CBr}_4 \cdot n\text{AlBr}_3$ and $\text{CHBr}_3 \cdot n\text{AlBr}_3$ systems in satisfactory yields (Scheme 17).^{125,165–166}

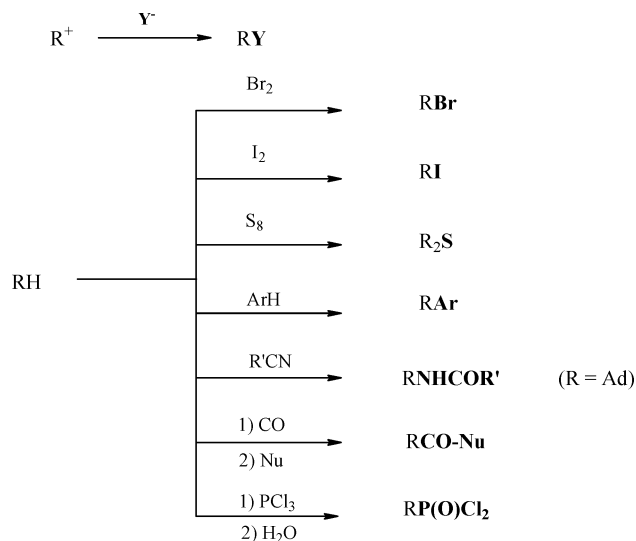
However, due to the instability of bromides toward these powerful superelectrophilic systems, even with cyclopentane at 0°C the cyclopentylbromide yield based on CHBr_3 is not higher than 20%. Ethane is brominated by CHBr_3 or CBr_4 in the presence of AlBr_3 for 6 h at $55\text{--}65^\circ\text{C}$.^{165,166} The single product, *viz.* ethylbromide, is formed in 60% yield (Scheme 18).

Tetrachloromethane in the presence of AlCl_3 was shown to be a good polychlorinating system for adamantane; thus, 1,3,5,7-tetrachloroadamantane was obtained in a satisfactory yield under the conditions shown in Scheme 19.^{167a}

Scheme 19



Scheme 20



Note that CBr_4 has been used in combination with NaOH for the bromination of saturated hydrocarbons in a two-phase system in the presence of a phase-transfer catalyst,^{167b} but the bromination was inefficient. For example, under reflux for 90 h, adamantane gives a mixture of 1-bromo- and 1,3-dibromoadamantanes in 70% and 15% yield, respectively. In 16 h, cyclohexane forms the monobromide in 44% yield. This approach was successfully applied for the first selective monohalogenation of the highly strained molecule cubane without concomitant loss of the cubane structure. The yields of RX ($R = \text{cubyl}$) are as follows: $X = Br$, 75% on RH (37.5% on CBr_4) at 25 °C for 24 h.; $X = Cl$, 81% on RH under refluxing in CCl_4 for 5 days; $X = I$, 67% on RH (33.5% on CHI_3) at 25 °C for 36 h.^{167c} Catalytic bromination of decane, dodecane, and cyclohexane was done using CBr_4 in the presence of catalysts containing either copper or nickel.^{167d} From reaction at 150–180 °C for 5–8 h, alkanes gave a mixture of secondary bromoalkane isomers in high yields, and cyclohexane gave cyclohexylbromide, also in high yield.^{167d} A radical mechanism was suggested for all these reactions.^{167b–d}

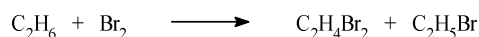
3.2.2. Types of Functionalization with Participation of Substrates

The types of functionalization reactions of alkanes and cycloalkanes induced by polyhalomethane–aluminum halide systems are summarized in Scheme 20.

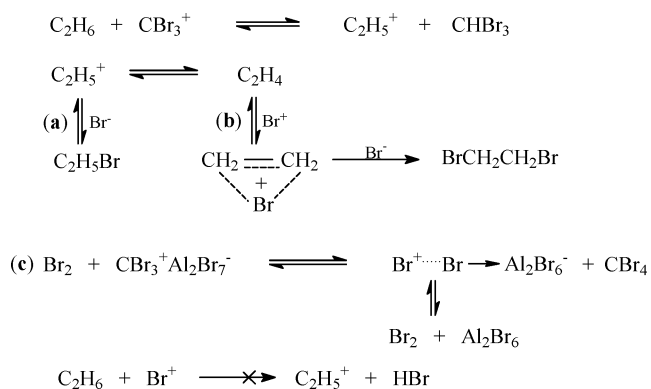
3.2.3. Ionic Bromination with Molecular Bromine

The bromination of adamantane with Br_2 in the absence of an electrophile was performed in the early 1960s.^{168a,b} Olah and co-workers were the first to report ionic bromination of alkanes and cycloalkanes with Br_2 in the presence of Lewis acids.^{169a} However, the activity of $AgSbF_6$, the best promoter among the studied ionic bromination promoters, was low: for linear alkanes, the reaction was not acceptable, while for

Scheme 21



Scheme 22



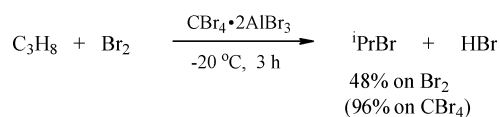
isoalkanes the reaction was not selective and was accompanied by polybromination. For cycloalkanes, the reaction gave monobromide yields of 5–27% based on the catalyst. Ionic bromination of isoalkanes in HSO_3F-SbF_5 media also led to low yields of monobromides. In addition, polybromides and fragmentation products were formed as byproducts.^{169b} The aprotic organic superelectrophiles $RCOX \cdot 2AlX_3$ were shown to catalyze low-temperature ionic bromination of C_4-C_7 *n*-alkanes, C_5-C_6 cycloalkanes, and so forth.¹¹³

Polyhalomethanes in combination with $AlBr_3$ were shown to promote liquid-phase ionic bromination of cycloalkanes and alkanes including ethane, which had heretofore been unreactive toward Br_2 under mild conditions.^{165,166} Ethane effectively reacts with Br_2 in the presence of $CBr_4 \cdot 2AlBr_3$ both in CH_2Br_2 solution and under solvent-free conditions at 55–65 °C affording 1,2-dibromoethane as the main product along with a small amount of ethyl bromide (Scheme 21).^{165,166}

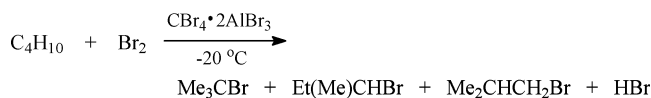
The reaction with ethane can be carried out without solvent since at 60 °C with $[Br_2] \geq [CBr_4 \cdot 2AlX_3]$ a homogeneous solution is formed. At 60 °C, the $\{Br_2-CX_4 \cdot 2AlBr_3\}$, $\{CX_4 \cdot 2AlBr_3\}$, and related systems are ionic liquids.¹⁷⁰ If the reaction is carried out as a stoichiometric reaction under solvent-free conditions, that is, in an ampule, then at 55–60 °C the Br_2 is consumed completely during 18 h, and the total yield of brominated products is 100% based on Br_2 .^{165,166} This shows that formally both bromine atoms of the Br_2 molecule are involved in the brominated products. Under similar conditions for 6 h, the same products are formed with overall yield of 84% based on Br_2 . Increasing the $[Br_2]:[CBr_4 \cdot 2AlBr_3]$ molar ratio reduces the effectiveness of bromination: when this ratio is equal to 4, the yield falls to 26% based on Br_2 . The maximum yield of the brominated products does not exceed 1.5 mol based on superelectrophile. Qualitatively, the reaction in CH_2Br_2 solution proceeds analogously. Ethane bromination by Br_2 in the presence of $CBr_4 \cdot 2AlBr_3$ can be achieved at atmospheric pressure of ethane. In this case, ethylbromide, 1,2-dibromoethane, and 1,1,2,2-tetrabromoethane (in a molar ratio of *ca.* 1:3:5) are formed with a total yield of 73% based on Br_2 after 3 h. On the other hand, Br_2 in the presence of $AlBr_3$ in CH_2Br_2 does not react with ethane at 55–65 °C. These results were interpreted as in Scheme 22.¹⁶⁶

According to Scheme 22, the CBr_3^+ cation abstracts a hydride ion from ethane to form the ethyl cation and $CHBr_3$.

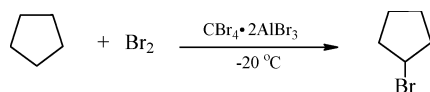
Scheme 23



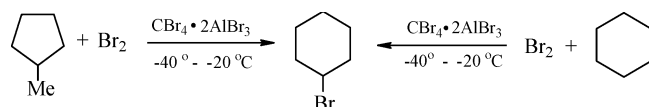
Scheme 24



Scheme 25



Scheme 26



In pathway (a), which appears to be the only one available in the absence of Br_2 , ethyl cation adds a Br^- anion to give EtBr . In the presence of Br_2 , pathway (b), which involves the participation of ethylene, becomes the predominant pathway. The reaction is not a catalytic one, since $\text{Br}^+ \cdot \text{Br}^- \rightarrow \text{Al}_2\text{Br}_6^-$ does not react with ethane under the conditions studied. Moreover, increasing the $[\text{Br}_2]:[\text{CBr}_4 \cdot 2\text{AlBr}_3]$ molar ratio leads to decreasing system activity since it lowers the content of the CBr_3^+ cation in the reaction medium by shifting equilibrium (c) to the right. The essential difference between the composition of the brominated products in the reactions at atmospheric and higher pressures is explained by the lower stationary ethane concentration at atmospheric pressure leading to further bromination of the 1,2-dibromoethane formed initially. At room temperature, ethane bromination does not occur. On the other hand, the more active propane readily reacts with Br_2 even at $-20\text{ }^\circ\text{C}$ with selective formation of ${}^i\text{PrBr}$ (Scheme 23).¹⁶⁶

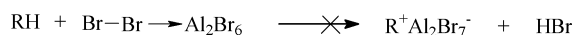
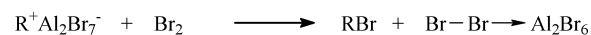
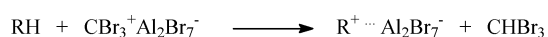
At -10 or $0\text{ }^\circ\text{C}$, propane is fully brominated. With the increase of temperature; however, dibromide is also formed, and the ratio $[\text{}^i\text{PrBr}]:[\text{C}_3\text{H}_6\text{Br}_2]$ decreases to 6:1 ($-10\text{ }^\circ\text{C}$, 3 h) or 2:1 ($0\text{ }^\circ\text{C}$, 2 h). At $20\text{ }^\circ\text{C}$, bromination of propane is nonselective.

n-Butane is completely brominated at $-20\text{ }^\circ\text{C}$ for 2 h with the selective formation of the monobromide isomers in the ratio $[\text{}^{\text{tert}}\text{BuBr}]:[\text{}^i\text{BuBr} + \text{}^{\text{sec}}\text{BuBr}] = 1:0.4$ (Scheme 24).¹⁶⁶ In this reaction, $\text{CCl}_4 \cdot 2\text{AlBr}_3$ is markedly less active: the yield of butylbromides decreases to 13%. Bromination of cyclopentane, cyclohexane, and methylcyclopentane proceeds noticeably at $-40\text{ }^\circ\text{C}$ and more effectively at $-20\text{ }^\circ\text{C}$. The yields of monobromides reach 76% based on Br_2 and 600% based on catalyst. Polybrominated products are either absent or formed as traces. The reaction with cyclopentane leads only to cyclopentylbromide (Scheme 25).

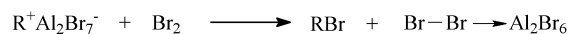
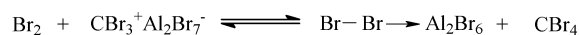
Both cyclohexane and methylcyclopentane at -40 or $-20\text{ }^\circ\text{C}$ afford the same single product, *viz.*, cyclohexylbromide (Scheme 26).

This result was explained by the formation from both cycloalkanes of the same initial tertiary product, 1-methylcyclopentylbromide, which is irreversibly transformed into the secondary product, cyclohexylbromide, which is more stable toward the superelectrophile. The order of catalyst activity for bromination of cyclohexane at $-20\text{ }^\circ\text{C}$ is as follows

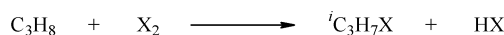
Scheme 27



Scheme 28



Scheme 29



$$\Delta H_f = -105.3 \text{ (}\Delta H_f^0 = -106.5\text{), X = F; } -28.5 \text{ (-31.0), X = Cl;}$$

$$-8.9 \text{ (-12.3), X = Br; } 10.2 \text{ (3.3), X = I}$$

(the yields of cyclohexylbromide based on Br_2 are given for $[\text{c-C}_6\text{H}_{12}]:[\text{Br}_2]:[\text{cat}] = 10:4:1$ molar ratio): $\text{CBr}_4 \cdot 2\text{AlBr}_3$ (75%, **1 h**) > $\text{CHBr}_3 \cdot 2\text{AlBr}_3$ (50%, **1 h**) > $\text{C}_6\text{F}_5\text{CF}_3 \cdot 2\text{AlBr}_3$ (36%, **2 h**) > $\text{CCl}_4 \cdot 2\text{AlBr}_3$ (29%, **2 h**) > $\text{CH}_2\text{Br}_2 \cdot 2\text{AlBr}_3$ (22%, **3 h**).

Thus, $\text{CBr}_4 \cdot 2\text{AlBr}_3$ is the most active catalyst among those studied. In all cases, the above bromination is accompanied by reduction of the initial polyhalomethanes. In other respects, however, ethane bromination differs from that of higher alkanes and cycloalkanes. First, the higher paraffin bromination is a catalytic reaction, while ethane bromination is a stoichiometric one. Second, ethane gives the dibromide, while higher alkanes and cycloalkanes give monobrominated products. Third, cycloalkanes and higher homologues of ethane (but not ethane itself) react with Br_2 in the presence of AlBr_3 in CH_2Br_2 , although in the absence of CBr_4 these reactions are noticeably less effective.

Two mechanistic schemes for bromination of higher alkanes were postulated.¹⁶⁶ The first one, a stoichiometric reaction, assumes initial hydride abstraction by a superelectrophile from the alkane followed by addition to the emerging carbocation of a Br^- anion from Br_2 (Scheme 27).

The second path, a catalytic reaction, involves the initial attack of a superelectrophile on the Br_2 molecule to give a positive bromine species which attacks the alkane to give the brominated product (Scheme 28).

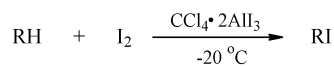
It should be noted that Scheme 28 is never fully realized since bromination is invariably accompanied by reduction of a starting polyhalomethane. However, the contribution of this mechanism to the reactions of activated alkanes is probably more significant than its contribution to reactions of low-reactivity alkanes, for which activation requires strong electrophiles.

3.2.4. First Ionic Iodination

In recent years, not only thermodynamically favorable reactions of alkanes but also those consuming energy have become objects of study.^{151,171–173} Iodination of saturated hydrocarbons is an example of this type of reaction. The enthalpies of propane halogenation, that is, ΔH_f and the zero-point energy ΔH_f^0 , were calculated¹⁷⁴ by a DFT-PBE method¹⁷⁵ shown in Scheme 29 in kcal/mol.

These calculations show that fluorination, chlorination, and bromination are exothermic, and the enthalpies for Cl_2 and Br_2 are 3 times and 10 times smaller, respectively, than the

Scheme 30



RH = propane, cyclopentane, cyclohexane, norbornane, adamantane

enthalpy for F₂. In contrast, iodination is endothermic. Nevertheless, the free-radical iodination of alkanes and cycloalkanes has been performed in photoinduced reactions using either the ^tBuCOI–HgCl₂ system as a source of *tert*-butylhypoiodide¹⁷¹ or a mixture of I₂–Cl₂ as a source of the ICl species.¹⁷² Recently, a promising method has been reported for the preparation of monoiodides from saturated hydrocarbons by the reaction with CHI₃–solid NaOH.¹⁷³

The substitution of hydrocarbon hydrogen by iodine in electrophilic reactions has been feasible only for aromatics.^{176–182} Most typically, iodinating systems were based on I₂ combined with oxidizing agents^{176–181} (Ag⁺ salts,¹⁷⁶ (NH₄)₂S₂O₈,¹⁷⁷ NO⁺BF₄[–],¹⁷⁸ Ce,¹⁷⁹ etc.) and iodosuccinimide in CF₃SO₃H.¹⁸² The latter system iodinate even deactivated aromatics effectively. The [CF₃SO₂OI]⁺[CF₃SO₃][–] complex is assumed to be responsible for the high activity of this system.¹⁸² Electrophile initiated iodination of alkanes and cycloalkanes has not been described since the work cited above.¹⁷⁴

One-pot transformations of alkanes and cycloalkanes into the corresponding monoiodides have been performed by using the superelectrophilic systems CX₄•2AlI₃ (X = Cl, Br). At –20 °C, propane and some mono-, bi-, and tricycloalkanes react with I₂ in the presence of an equimolar amount of the CX₄•2AlI₃ complex in CH₂Br₂ to give the corresponding monoiodides in 50–80% yields after 1.5–2 h (Scheme 30).¹⁷⁴

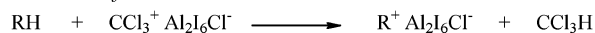
All of the reactions noted in Scheme 30 give rise to a single isomer with diiodides and bromides absent or produced in trace amounts only. However, at –40 °C the yields of monoiodides decrease to above 10%, and at 0 °C, these reactions become unselective. If the reaction is applied to *n*-pentane, the iodination even at –20 °C is not effective and affords a 2:1 mixture of two isomers in a total yield of 19%. At the stoichiometric I₂/CX₄ ratio, CX₄ is quantitatively reduced to CHX₃.

The systems CX₄•2AlI₃ (X = Cl, Br) were shown to be unique since aluminum iodide alone, that is, in the absence of CX₄, does not initiate iodination of alkanes and cycloalkanes with I₂. At the same time, the CCl₄•2AlI₃ complex itself (without I₂) causes iodination of cyclopentane, although the yield of cyclopentyl iodide is 2 times smaller than that for the reaction run with the I₂ + CCl₄•2AlBr₃ system. The use of the CCl₄•2AlBr₃ complex instead of CCl₄•2AlI₃ completely suppresses the iodination by I₂, with the corresponding bromides becoming the products of the reactions. Scheme 31 was suggested for the iodination of alkanes and cycloalkanes.¹⁷⁴

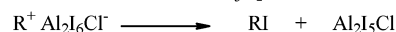
According to this scheme, the CX₃⁺Al₂I₆Cl[–] abstracts hydride ion to afford a carbocation. The latter immediately captures an iodide anion either from the Al₂I₆Cl[–] anion or from the I₂ molecule. Therefore, this reaction can be considered as a superelectrophile-initiated nucleophilic substitution of iodide for hydrogen on an alkane or cycloalkane. In this respect, it is noteworthy that the above calculations seem to exclude the alternative direct electrophilic iodination mechanism, and in fact, the formation of alkyl iodides was not observed in the reaction of alkanes with the I₂–Al₂I₆ system.¹⁷⁴ Thus, the two types of superelectrophilic systems, that is, CCl₄•2AlI₃ and Hal₂•2AlI₃, differ considerably in

Scheme 31

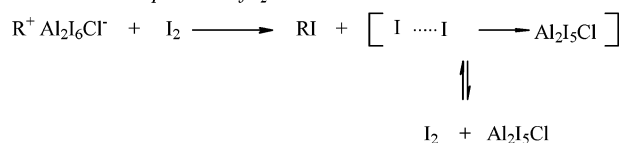
(a) Generation of a carbocation



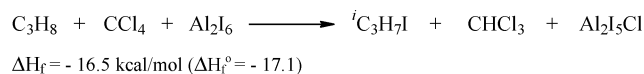
(b) Iodination in the absence of I₂



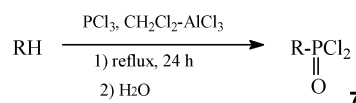
(c) Iodination in the presence of I₂



Scheme 32



Scheme 33



activity at –20 °C. The lower activity of CCl₄•2AlI₃ as compared to that of I₂–CCl₄•2AlI₃ is probably connected to the rapid I/Cl exchange between Al₂I₆ and CCl₄ or its reduced forms. As a result, in the presence CCl₄•2AlI₃, the more favorable chlorination occurs rather than iodination. Similarly, the I₂–CCl₄•2AlBr₃ system acts only as a brominating agent.¹⁷⁴

The DFT-PBE quantum-chemical calculations¹⁷⁴ revealed that, in contrast to the endothermic nature of reaction 29, the iodination of propane by the I₂–CCl₄•2AlI₃ system (Scheme 32) becomes exothermic by 16.5 kcal/mol.

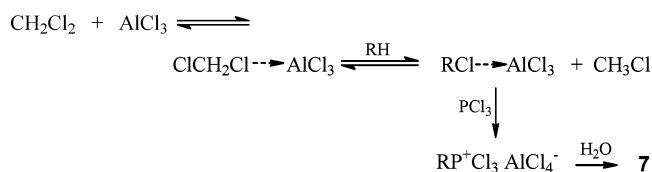
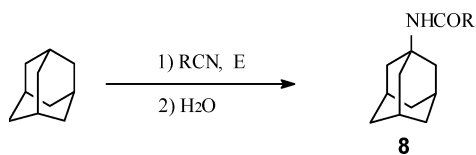
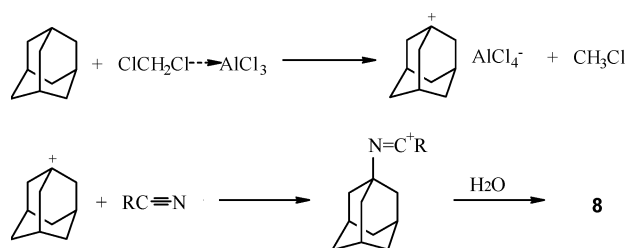
3.2.5. Dichlorophosphorylation with PCl₃

High-temperature direct phosphorylation in the gas phase of lower alkanes, even including methane, was reported.^{183,184} For example, upon heating methane and ethane at 500–700 °C with PCl₃, the corresponding dichlorophosphines were obtained in high yield. Gas-phase phosphorylation of hydrocarbons was also carried out under similar conditions using CoCl₂ as catalyst,¹⁸⁵ but only poor yields of phosphorylation products were obtained.

Earlier attempts to react adamantane with PCl₃–AlBr₃ under reflux did not result in phosphorylation products.¹⁸⁶ G. Olah et al. described the dichlorophosphorylation of saturated hydrocarbons. Refluxing a hydrocarbon with PCl₃ in the presence of CH₂Cl₂–AlCl₃ for over 20 h followed by workup with water gave product 7 (Scheme 33).¹⁸⁷

The yields of dichlorophosphorylated products for adamantane, dialkyadamantanes, and diamantane amount to 40–60%, while isobutane, monocyclic hydrocarbons, and bicyclic hydrocarbons gave only poor yields (10–20%) of phosphorylated products.¹⁸⁷ The participation of a polarized methylene chloride–aluminum chloride complex is assumed for this reaction. The attempts to prove the formation of bis(chloromethyl) chloronium in the CH₂Cl₂–AlCl₃ system by NMR spectroscopy failed. The single observable species was the donor–acceptor complex ClCH₂Cl → AlCl₃ (Scheme 34).¹⁸⁷

AlCl₃-catalyzed phosphorylation of alkylchlorides by PCl₃ (the Clay reaction) was described as resulting in 7 upon workup of the reaction mixture with water.¹⁸⁸ The important

Scheme 34**Scheme 35****Scheme 36**

role of dichloromethane in the reactions of saturated hydrocarbons with PCl₃ in the presence of AlCl₃ was proved. Indeed, the phosphorylation of adamantane practically did not occur when Freon-113 or other solvents were used instead of CH₂Cl₂. The alternative scheme involving the participation of the PCl₂⁺ cation seems to these authors¹⁸⁷ to be unlikely. In agreement with this conclusion, the PCl₂⁺ cation, which was identified as the most abundant positive ion in the mass spectrum of PCl₃,¹⁸⁹ was never observed in the condensed phase.^{190,191}

3.2.6. Ritter-Type Reaction of Adamantane

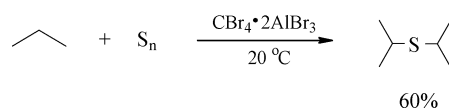
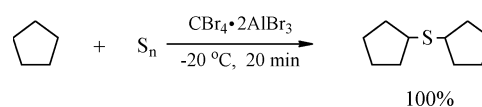
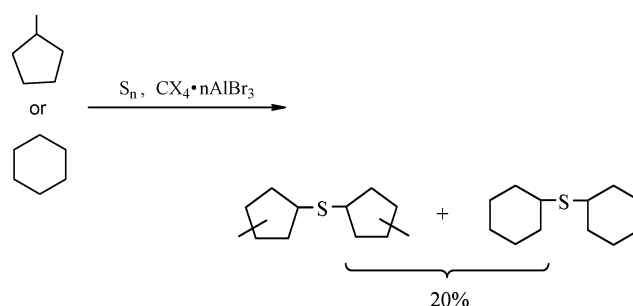
The facile generation of adamantyl cation from the parent hydrocarbon and the high reactivity of this nonplanar carbocation make possible effective adamantane functionalization mediated by comparatively low activity electrophiles such as CH₂X₂-AlX₃. The transformation of adamantane into 1-*N*-(adamantyl) amides (**8**) has been reported (Scheme 35)¹⁹² to occur under the action of RCN in the presence of CHCl₃-AlCl₃ or CH₂Cl₂-AlCl₃ (a Ritter-type reaction^{193,194}).

The reactions were carried out on a mixture of adamantane, a nitrile, and aluminum chloride in the molar ratios 1:2:(3.1–3.7) under reflux. The yields of **8** amounted to 60–70%. The participation of the Ad⁺ cation as illustrated in Scheme 36 was suggested.¹⁹²

A model reaction of adamantane radical cation with acetonitrile was calculated^{163a} by B3LYP/6-31G*. It was shown that the TS for the conversion of the initial {AdH⁺...CH₃CN} complex into the resulting product involves the insertion of a CH₃CN molecule into the activated C–H bond of the AdH⁺ moiety *via* proton migration. This conclusion follows from the low value of the H/D kinetic isotope effect for hydrogen migration to acetonitrile ($k_{\text{H}}/k_{\text{D}} = 1.35$).

3.2.7. Unprecedented Facile Sulfurization with Elemental Sulfur

Reaction of propane with sulfur at 20 °C for 2 h in the presence of CBr₄•2AlBr₃ in CH₂Br₂ gives diisopropyl sulfide in 60% yield based on sulfur (Scheme 37).¹⁹⁵

Scheme 37**Scheme 38****Scheme 39**

The reaction of cyclopentane with elemental sulfur in the presence of CBr₄•2AlBr₃ occurs particularly readily. At -20 °C, dicyclopentyl sulfide is formed in 71% yield based on sulfur even in 5 min, and it is formed in nearly quantitative yield in 20 min. The reaction is highly selective: the corresponding di- and trisulfides are either completely absent or formed in an overall yield of no greater than 6% (Scheme 38).

The equimolar CBr₄•AlBr₃ complex is noticeably less active in this reaction, while the CH₂Br₂-AlBr₃ system is totally inert. The yield of the sulfides is as small as 30% in the presence of CCl₄•2AlBr₃ as opposed to the 99% yield when the reaction is initiated with CBr₄•2AlBr₃ under the same conditions. In addition to a 3-fold decrease of the sulfide yield, the use of CCl₄•2AlBr₃ markedly increases the content of di- and trisulfides. On the other hand, the systems CCl₄•nAlBr₃ with $n \geq 3$ can be used successfully instead of CBr₄•2AlBr₃. The yields of dicyclopentyl sulfide decrease abruptly with an increase in the [S_n]:[CBr₄•2AlBr₃] molar ratio (“m”). At $m = 1.2$, the yield is 72%, while at $m = 2.0$, it is only 8%; in parallel with the decrease in the yield, the selectivity of monosulfide formation also decreases. In the absence of a saturated hydrocarbon, sulfur reacts in CH₂Br₂ with both the CBr₄•2AlBr₃ complex and the CCl₄•nAlBr₃ complex with liberation of molecular bromine. It is this reaction of sulfur with the superelectrophilic system which suppresses the sulfurization of saturated hydrocarbons. Indeed, sulfur pretreated with the CCl₄•2AlBr₃ system in CH₂Br₂ at 20 °C for 20 min is inactive in the reaction with cyclopentane.

The reaction of cyclohexane or methylcyclopentane with sulfur in the presence of the CCl₄•2AlBr₃ system or the CBr₄•2AlBr₃ system at -20 °C results in a small amount of di (methylcyclopentyl) sulfide or a mixture of the latter with dicyclohexyl sulfide in an overall yield not exceeding 20% and with low selectivity (Scheme 39).

Thus, the difference between the behavior of cyclopentane and cyclohexane (or methylcyclopentane) in the reaction with sulfur is quite significant, as opposed to their similar reactivity in other transformations initiated by these super-electrophiles.

Scheme 40



Adamantane does not form a sulfur-containing product in the presence of $\text{CBr}_4 \cdot 2\text{AlBr}_3$ at -20°C . However, the action of the much weaker electrophilic system $\text{CH}_2\text{Br}_2\text{-AlBr}_3$ at room temperature for 20 h results in the transformation of adamantane into methyladamantyl sulfide along with a mixture of 1,1'- and 1,2'-diadamantyl sulfides in a 4:1 ratio with an overall yield of 60% (Scheme 40).

Two alternative mechanistic schemes for these reactions were considered.¹⁹⁵ The first mechanism considered involves the initial generation of a carbocation which alkylates the sulfur cycle (e.g., S_8) followed by sulfur ring-opening. The cation then attacks the sulfur atom of the S-R fragment since the electron-donating properties of this atom are enhanced in comparison with those of nonalkylated S-atoms. The final reaction products include R_2S , HBr , and reduced polyhalomethane. Exhaustive reduction of CX_4 to CHX_3 is actually observed during the sulfurization (Scheme 41).

The second mechanism considered involves an initial attack on the sulfur cycle by the superelectrophilic complex. It is possible that just this pathway transforms sulfur to an inactive compound through an irreversible redox process (Scheme 42).

Sulfur has been proved to form ionic species both in oleum and in CF_3COOH .^{196,197} For example, S_{19}^{2+} and S_8^{2+} dications are formed from S_8 in $\text{SO}_3\text{-H}_2\text{SO}_4$, while a more convenient synthesis utilizing $\text{AsF}_5\text{-SO}_2$ permits isolation of the salt $\text{S}_8(\text{AsF}_6)_2$.¹⁹⁸ Warming a frozen mixture of $\text{S}_8(\text{AsF}_6)_2$ and propane affords a mixture of *iso*- and *n*- Pr_2S as well as PrSSPr with a total yield of 30%. *N*-Butane forms a more complex mixture of mono-, di-, and trisulfides including some unsaturated organosulfides.

The difference in the behavior of cyclopentane and cyclohexane (or methylcyclopentane) in the reactions mediated by $\text{CBr}_4 \cdot 2\text{AlBr}_3$ may be explained by the quicker alkylation of sulfur by the secondary cyclopentyl cation than by the tertiary methylcyclopentyl cation which is formed from both C_6 cycloalkanes at low temperature. At -20°C , the competing reaction of sulfur with a superelectrophilic system occurs very quickly, as do also transformations of cyclohexane or methylcyclopentane in the absence of sulfur to give DMDs, bromides, and other products. The failure of adamantane sulfurization using $\text{CBr}_4 \cdot 2\text{AlBr}_3$ has been explained by the instability of Ad_2S in the presence of a powerful superelectrophile.

Alkanes and cycloalkanes were shown to react with elemental sulfur in the presence of $\text{R}'\text{COX} \cdot 2\text{AlX}_3$ complexes giving thioesters in 25–60% yield based on sulfur (Scheme 43).¹¹⁵

For the sulfurization of alkanes and cycloalkanes, the difference in the product structures obtained using the $\text{R}'\text{COX} \cdot 2\text{AlX}_3$ system and the product structures obtained using the $\text{CBr}_4 \cdot 2\text{AlBr}_3$ system is probably caused by the relative stability of the S-COR' bond as compared to the S-CBr₃ bond.

The sulfurization of alkanes and cycloalkanes with elemental sulfur in $\text{CF}_3\text{SO}_3\text{H}$ was found to give the corresponding disulfides or the isomeric disulfides upon prolonged reaction at 150°C (Scheme 44).²⁰⁰

Other reported transformations of alkanes and cycloalkanes by sulfur at higher temperatures are nonselective and have low efficiency.^{201,202}

3.2.8. Alkylation of Deactivated Arenes

Schmerling reported the first examples of benzene alkylation with isoalkanes and cycloalkanes by the $\text{CuCl}_2\text{-AlCl}_3$ salt mixture.²⁰³ The reaction of benzene with isopentane resulted in a mixture of amylbenzenes in 20% overall yield with respect to the copper salt. Additionally, ethylbenzene, isopropylbenzene, 1,2-diphenylethane, and *p*-polyphenylene were among the reaction products. The reaction of cyclohexane with benzene resulted in *p*-polyphenylene as the main product (60%), while alkylation products were formed in trace amounts only. The addition of isopentane to the reaction mixture increased the cyclohexylbenzene yield to 20%.

Direct acylation of benzene and bromobenzene was done^{116,117} using alkanes (cycloalkanes) as alkylating agents and $\text{RCOX} \cdot 2\text{AlX}_3$ complexes as acylating systems. The products were formed in good yields and, in some cases, selectively and regioselectively (Scheme 45).

Like the superelectrophilic complexes $\text{RCOX} \cdot 2\text{AlX}_3$, the $\text{CX}_4 \cdot n\text{AlBr}_3$ systems initiate the alkylation of aromatic compounds with alkanes and cycloalkanes.^{164,204} However, one difference in these reactions is that, in reactions with the $\text{RCOX} \cdot 2\text{AlX}_3$ complex, the first alkylation step is followed by acylation of the alkylated arenes to give eventually alkylated alkylaromatic ketones^{116,117}, while the use of $\text{CX}_4 \cdot n\text{AlBr}_3$ gives alkylated products only. Another difference is the possibility for alkylation of deactivated arenes in the presence of the $\text{CX}_4 \cdot n\text{AlBr}_3$ systems.

Thus far, the alkylation of aromatics even with traditional alkylating agents has mainly been limited to weakly passivated arenes, such as monohalobenzenes and polyfluoroarenes,²⁰⁵ which are slightly deactivated toward electrophiles. The alkylation of deactivated arenes with alkanes and cycloalkanes has been carried out for the first time.^{164,204} For instance, propane alkylates pentafluorobenzene in the presence of $\text{CBr}_4 \cdot n\text{AlBr}_3$ ($n = 1$ or 2) at 0°C for 1.5 h to give pentafluoroisopropylbenzene in almost quantitative yield¹⁶⁴ (Scheme 46).

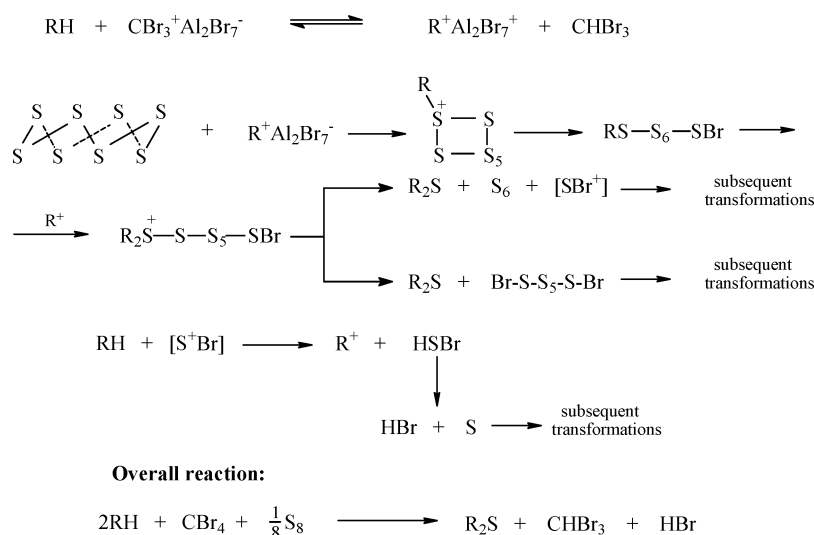
In this unusual reaction, the $\text{CBr}_4 \cdot 2\text{AlBr}_3$ and $\text{CBr}_4 \cdot \text{AlBr}_3$ systems display similar high activity. The $\text{CCl}_4 \cdot 2\text{AlBr}_3$ system is noticeably less active, whereas the corresponding equimolar complex is not active at all. At 20°C , the reaction promoted by the $\text{CBr}_4 \cdot 2\text{AlBr}_3$ system is completed within 10 min to give pentafluoroisopropylbenzene in 60% yield, while CBr_4 disappears completely to give CHBr_3 in 68% yield. In the absence of propane at 20°C , the $\text{CBr}_4 \cdot 2\text{AlBr}_3$ slowly reacts with pentafluorobenzene to give $\text{C}_6\text{F}_5\text{CBr}_3$ ¹⁶⁴ (see Scheme 16).

Pentafluorobenzene was reported to react in the presence of AlCl_3 at 150°C with CH_2Cl_2 to give $(\text{C}_6\text{F}_5)_2\text{CH}_2$ in 77% yield after 4.5 h and with CHCl_3 to give $(\text{C}_6\text{F}_5)_3\text{CH}$ in 92% yield after 8 h.²⁰⁵

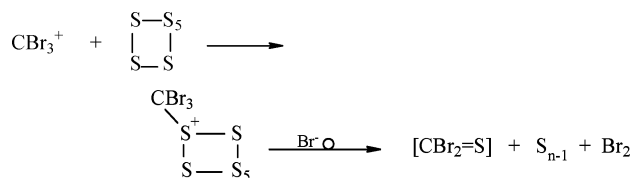
As with pentafluorobenzene, other passivated arenes, (i.e., di- and trichlorobenzenes, dibromobenzenes, acetophenone, benzophenone, and methylbenzoate), are also alkylated with propane, with butane, and with cyclopentane at -40 to 0°C in the presence of the $\text{CBr}_4 \cdot 2\text{AlBr}_3$ system in CH_2Br_2 solution. Using this system, the reaction of propane and of cyclopentane with 1,2,4-trichlorobenzene at -20°C for 30 min gives the corresponding single alkylation product in high yield (Scheme 47).

The alkylation of dihalobenzenes occurs less selectively. The reaction of *p*-dibromobenzene is accompanied by disproportionation to give mono- and tribromobenzenes. Dichlorobenzenes do not undergo disproportionation, but

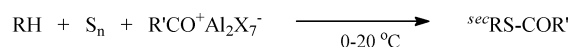
Scheme 41



Scheme 42



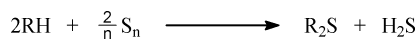
Scheme 43



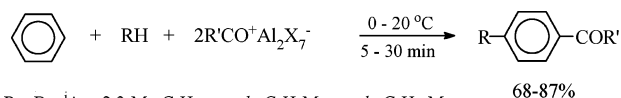
RH = C₃H₈, n-C₄H₁₀, n-C₅H₁₂, cyclo-C₅H₁₀, cyclo-C₆H₁₂

R'CO⁺ = MeCO, PrCO, PhCO

Scheme 44

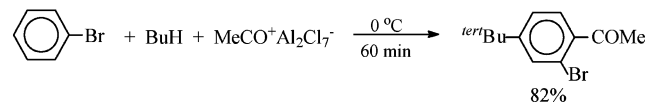


Scheme 45

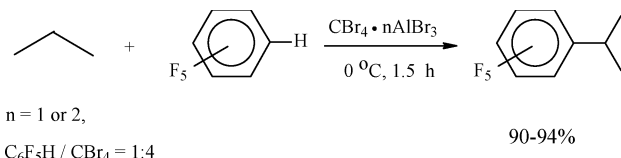


R = Bu, ⁱAm, 2,3-Me₂C₆H₁₁, cyclo-C₅H₈Me, cyclo-C₆H₁₀Me

R' = Alk, Ar, X = Cl, Br



Scheme 46

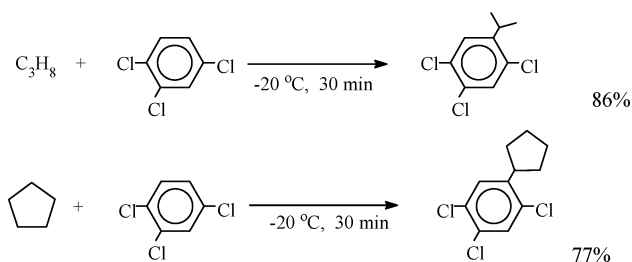


they do form a mixture of mono- and dialkylated products²⁰⁴ (Scheme 48).

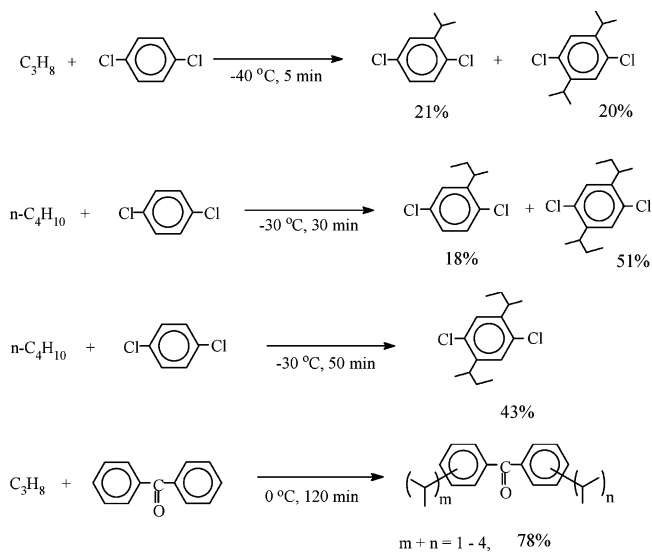
In the presence of excess arene in CH₂X₂ solvent, reactions with alkanes and cycloalkanes follow a different pathway to give alkylated diarylmethane derivatives²⁰⁶ (Scheme 49).

Most likely, the alkylation of arenes with alkanes occurs according to the usual electrophilic substitution mechanism as shown in Scheme 50.

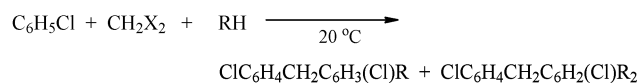
Scheme 47



Scheme 48



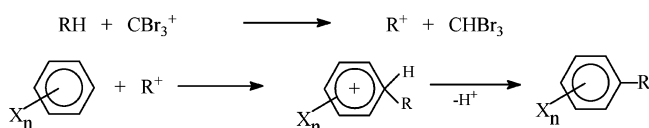
Scheme 49



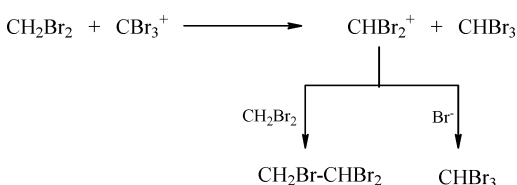
R = cyclo-C₅H₉, cyclo-C₅H₇

The evidence does not support an alternative mechanistic scheme analogous to that for the reactions of superelectrophiles with alkanes in which the superelectrophile accepts a hydride ion from an arene to give an Ar⁺ cation.^{207,208} In fact, when an alkane was absent, not even traces of CHBr₃ were detected upon treatment of C₆F₅H or m-C₆H₄Br₂ with CBr₄•2AlBr₃ in CH₂Br₂. It is interesting that in the absence

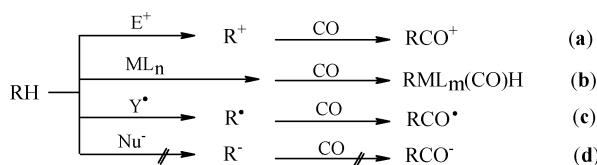
Scheme 50



Scheme 51



Scheme 52



of an arene, reduction of the $\text{CBr}_4 \cdot 2\text{AlBr}_3$ with dibromomethane to give CHBr_3 in 20% yield was observed under the same conditions (Scheme 51).²⁰⁴

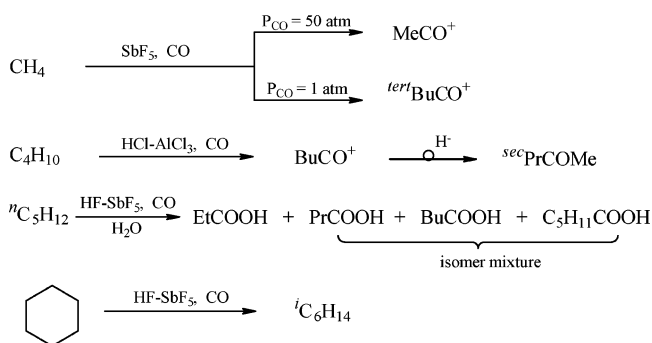
The explanation for the suppression of hydride transfer from CH_2Br_2 to the cation by arenes is probably that the electrophilic attack of a cation on the arene with formation of Wheland σ -complexes is the dominating process. Thus, arenes, or at least those arenes which do not contain strong electron acceptor groups, are poorer hydride ion donors than alkanes or dihalomethanes. The results described for alkylation of passivated arenes with alkanes dispel the notion that arenes any more passivated than monohalobenzenes cannot be alkylated under mild conditions by electrophiles.²⁰⁹

3.2.9. Carbonylation with CO Leading to Carboxylic Acids and Esters

3.2.9.1. 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 syntheses of valuable carbonyl-containing compounds from readily available raw materials.^{155b} Neither alkanes nor carbon monoxide are reactive by themselves. Powerful electrophiles, active metal complexes, or free radicals are required to generate active species capable of reacting with CO. The research along these lines was started in the early 1930s,^{210–213} and by now, numerous systems which are able to initiate carbonylation of saturated hydrocarbons have been described. These include (a) electrophiles,^{5,7,8,220–223} mainly the protic superacids, (b) transition metal compounds,^{95,214–216} and (c) radical systems.^{26,28,29,31,217–219} Of the possible transformation routes for saturated hydrocarbons, only (d) nucleophilic carbonylation is unknown (Scheme 52).

However, the selectivity of reactions studied previously is often very low and sharply decreases on passing from lower hydrocarbons to higher homologues, irrespective of the type of activating system. This is caused by the increasing lability of the key intermediates of reactions (a–c) (Scheme 52), that is, of the R^+ cations, of the transition metal–carbon σ -bonded complexes R–ML_n , and of the R^{\bullet} radicals, respectively, with the increasing number of C atoms in the saturated hydrocarbon RH. Therefore, examples of selective nondestructive carbonylation of linear alkanes by means of

Scheme 53



systems other than polyhalomethane-based superelectrophiles are limited to the C_1 – C_3 alkanes.^{3c,7,28,89,95a–c,216} Carbonylation initiated by protic superacids usually proceeds in excess superacid and results in the products of destructive carbonylation, that is, carbonyl compounds containing either more or fewer C atoms in the R group attached to carbonyl than were in the initial hydrocarbon RH.^{2a,210a–213,222} Destructive carbonylation is a consequence of fragmentation reactions of saturated hydrocarbons.^{224,225} The reactions of cycloalkanes may be accompanied by ring-opening.^{2c,8,156} Secondary transformations of the carbonylation products formed initially have been described.^{140,210–213,226} Examples of side reactions involved in carbonylation in the presence of protic or Lewis superacids^{3c,8,210a,211,212,222} are depicted in Scheme 53.

Few examples of catalytic carbonylation in the presence of transition metal complexes, either with or without irradiation, are known. Usually, these reactions occur unselectively. Some reactions of alkanes with CO catalyzed by palladium^{95a} and rhodium^{214b} complexes are shown in Scheme 54. (In Schemes 54 and 55, the numbers under formulas show the molar ratio of products).

Examples of carbonylation induced by radical initiators such as tungsten polyoxo complexes²¹⁸ and excited mercury atoms²⁶ are depicted in Scheme 55.

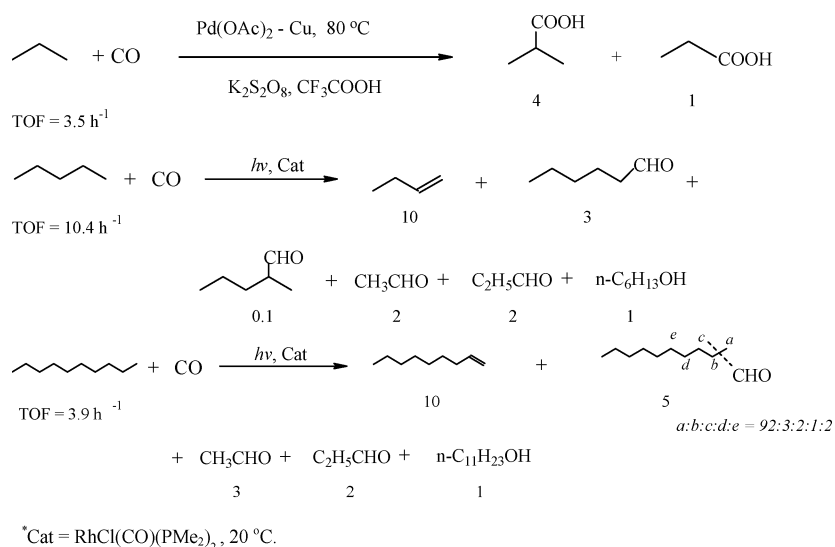
The use of superelectrophilic systems based on polyhalomethanes for selective carbonylation of alkanes as well as monocyclanes, bicyclanes, and tricyclanes proved to be rather successful. Apparently these reactions proceed as in Scheme 56 with the initial generation of a carbocation which isomerizes to the most stable cationic structure available. That stable cation then adds the CO molecule to yield an acylium cation which, upon treatment of the reaction mixture with alcohol, is converted into the corresponding alkyl carboxylate (Scheme 56).

3.2.9.2. Carbonylation of *n*-Alkanes C_2 – C_{10} . Ethane. Among the alkanes, ethane is the only methane in both its inertness and its abundance in natural gas. Therefore, the elaboration of direct methods for ethane functionalization is one of the more important problems in alkane chemistry. The electrophilic carbonylation of ethane had not been reported until 1999.²²⁷ However, catalytic selective carbonylation of methane and ethane in CF_3COOH in the presence of a $\text{Pd}(\text{OAc})_2 + \text{CuCl}_2$ mixture with $\text{K}_2\text{S}_2\text{O}_8$ as the reoxidant had been described before that.^{95a}

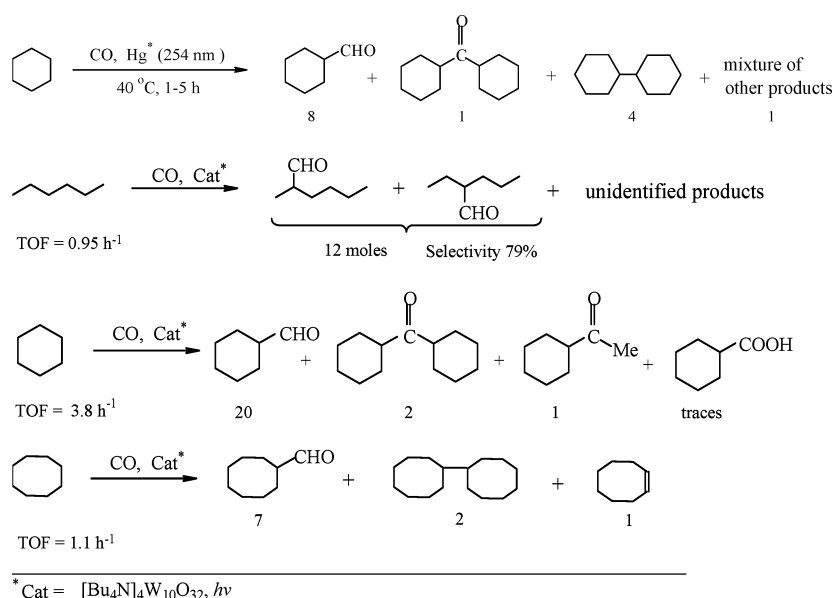
Ethane reacts with CO without a solvent at 50 °C in the presence of polyhalomethane– AlBr_3 superelectrophilic systems to give EtCOOBu (9) after treatment of the reaction mixture with *n*-butanol (Scheme 57).^{170a,227}

Heating a mixture of a polyhalomethane (CBr_4 , CCl_4 , or CHCl_3) with 2–3 mol of AlBr_3 at 80 °C for 5 min with

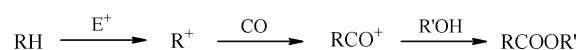
Scheme 54



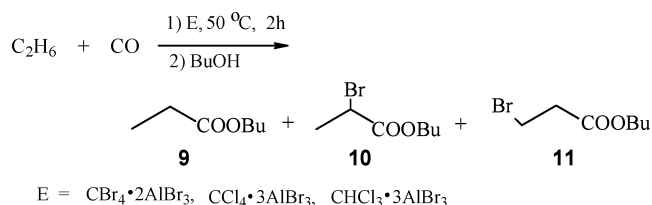
Scheme 55



Scheme 56

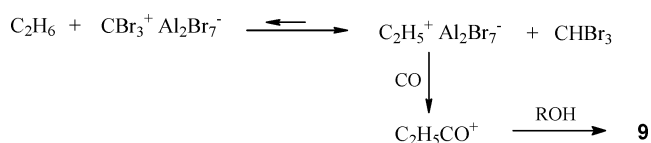


Scheme 57



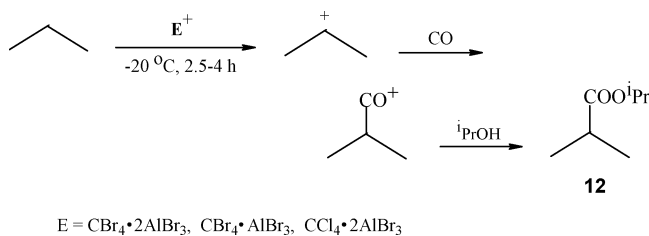
stirring but without a solvent furnishes a superelectrophilic liquid¹⁷⁰ which does not change its state of aggregation at 50–60 °C and can function both as the superelectrophile and as the solvent in the reaction of ethane with CO. Under the optimal conditions, that is, at 50–60 °C and a [CO]:[C₂H₆]:[CBr₄•2AlBr₃] molar ratio of 2.2:1:0.05 (P_{CO} = 45 atm, P_{C₂H₆} = 20 atm), the yield of **9** obtained after 2 h followed by alcoholysis of the reaction mixture with butyl alcohol was 86%. Yield of the side product, butyl 2-bro-

Scheme 58

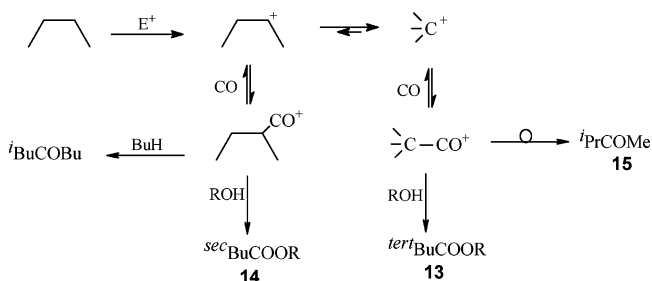


mopropionate (**10**), was 6%. The second byproduct (**11**) was present in trace amounts. Under similar conditions, 50–60% yields of **9** can be achieved by using CCl₄•3AlBr₃ and CHCl₃•3AlBr₃, while AlBr₃ in CH₂Br₂ is completely inactive. In the case of CHCl₃•3AlBr₃, the ethane carbonylation occurs with very high selectivity, although the yield of **11** is less. In the presence of CBr₄•2AlBr₃, the yields of **9** strongly depend on the temperature and the CO/C₂H₆ ratio *m*, with the higher yields of **9** being obtained at 50 °C. On passing from *m* = 1 to 2.2, the yields of **9** increase significantly but decrease again at *m* = 3. The proposed scheme for ethane carbonylation (Scheme 58) involves generation of the ethyl cation followed by CO trapping to form the EtCO⁺ cation and finally, EtCOOBu (**9**). Increasing either the superelectrophile strength or, up to a limit, the CO/C₂H₆ ratio, favors

Scheme 59



Scheme 60



the generation of, as well as the CO trapping of, the ethyl cation (Scheme 58).

Propane. The first example of effective and regioselective carbonylation of propane with CO in organic solvent was described in reference 228 where, as shown in Scheme 59, propane was found to react with CO in CH_2Br_2 solution and, after treatment with $iPrOH$, to form as the sole product $iPrCOO^iPr$ (**12**) in nearly quantitative yield based on the superelectrophile.

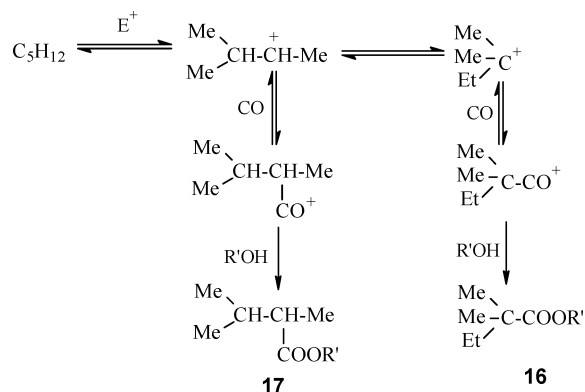
The activity of both the $CBr_4 \cdot 2AlBr_3$ and the $CCl_4 \cdot 2AlBr_3$ system is high, but that of $CHBr_3 \cdot 2AlBr_3$ is markedly lower. Systems such as $AlBr_3$ in CH_2Br_2 , $Br_2 \cdot 2AlBr_3$,¹⁴⁶ and $SOCl_2 \cdot 2AlBr_3$,¹⁴⁷ which are capable of initiating cracking of C_5 – C_{12} alkanes at ordinary temperature, are inert under the conditions studied.

At $-20^\circ C$, the yields of **12** in the presence of $CBr_4 \cdot 2AlBr_3$ are slightly dependent on the C_3H_8/CO ratio, with the higher yield being obtained at a ratio of 1.5. The opposite and more pronounced dependence of the yield of $iPrCOOR$ on the C_3H_8/CO ratio has been observed in propane carbonylation in $HF-SbF_5$ media in the presence of Br_2 .^{7a,229} This provided evidence in support of the suggestion that the $BrCO^+$ cation serving as the superelectrophilic species is generated *in situ* from CO and Br^+ and only this superelectrophile participates in the activation stage. Although the halocarbonyl cations XCO^+ ($X = Cl, Br$) have been prepared^{230,231} as long-lived species at low temperature and were characterized by ^{13}C NMR spectroscopy, they can hardly be active.

Butane. In the presence of polyhalomethane-based superelectrophiles, the reaction of butane with CO can occur via two routes, giving as the major product an alkyl carboxylate which from one route contains a tertiary (**13**) butyl group, and from the other route contains a secondary butyl (**14**) group (Scheme 60).^{232,233} The yields of esters are not less than 80% in all cases.

The route of butane carbonylation depends on the nature of the superelectrophile and on the temperature. Lower temperatures in combination with a powerful superelectrophile are favorable for the predominant formation of the ester from the tertiary butyl radical. This is due to fast isomerization of the butyl cations to $tertBu^+$, which is stable at low temperature and forms $tertBuCO^+$, which is stable against decarbonylation under these conditions. Either raising the

Scheme 61



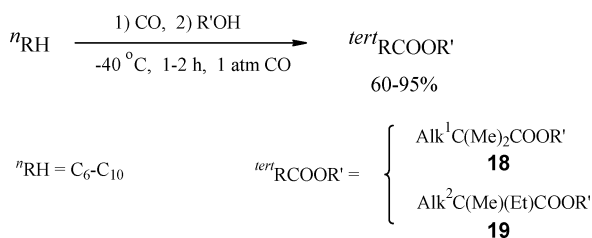
temperature or increasing the content of $AlBr_3$ from 2 to 3 mol per mole of polyhalomethane results in the predominant formation of the ester $secBuCOOR$. This is because of the enhanced tendency of the acylium cation to decarbonylation, which shifts the equilibrium toward the formation of the $secBu^+$ cation under these conditions. Thus, although the yields of **13** are high in the reactions of butane in the presence of $CBr_4 \cdot 2AlBr_3$ at $0^\circ C$, the selectivity of its formation is much lower. At $0^\circ C$, the quantities of **13** and **14** are near equal in some cases. The $CCl_4 \cdot 2AlBr_3$ system is noticeably less active in butane carbonylation, while Al_2Br_6 in CH_2Br_2 solution is completely inert. Moreover, with $CCl_4 \cdot 2AlBr_3$ as the superelectrophilic system, the ester **14** becomes the main carbonylation product, and this tendency increases on passing from $CCl_4 \cdot 2AlBr_3$ to $CCl_4 \cdot 3AlBr_3$. At $-20^\circ C$ in the presence of $CCl_4 \cdot 3AlBr_3$, **14** is formed in yields of up to 90% together with small amounts of **13**.²³²

The reaction of butane with CO under 100–150 atm pressure at 20 – $40^\circ C$ for 20–36 days in the presence of $AlCl_3$ or $HCl-AlCl_3$ led after treatment with water to a mixture of $iPrCOMe$ (**15**), $BuCO^iBu$, and acid **14** with $R = H$. Under the same conditions, isobutane produced a mixture of **15**, $tertBuCO^iBu$, and acid **13** with $R = H$.^{210,211} The electrophilic transformations described previously for butane with CO ²¹¹ and also for $tertBuCOCl$ in the presence of a large excess of $AlCl_3$ and isopentane as a hydride donor,²²⁶ which yield $iPrCOMe$ together with $BuCOBu^i$ or $iPrCOMe$ with $tertBuCO^iBu$, respectively, do not occur in the carbonylation of butane mediated by polyhalomethane-based systems.

Pentane. At $-20^\circ C$, pentane gives $tertC_5H_{11}COOR$ (**16**) as the sole product and in quantitative yield. Ester **16** is also selectively formed in 77% yield at $0^\circ C$ over a period of 30 min. The isomeric ester **17** is practically absent among the reaction products (Scheme 61).²³²

The difference between the behaviors of butane and pentane is attributable to the fact that the barrier to interconversion of the butyl cations $secC_4H_9^+$ and $tertC_4H_9^+$ is 15.4 kcal/mol, while the barrier to interconversion of the pentyl cations $secC_5H_{11}^+$ and $tertC_5H_{11}^+$ is only 2.0 kcal/mol. In addition, the equilibrium constant for isomerization, K , is lower for butane than for pentane (in the gas phase, $K = [tertBuH]/[secBuH] = 4.5$, whereas $K = [tertAmH]/[secAmH] = 13$).²³⁴ Thus, the $secC_5H_{11}^+ \rightleftharpoons tertC_5H_{11}^+$ equilibrium is attained rapidly and the $tertC_5H_{11}^+$ 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. Carbonylation of *n*-pentane with CO in $HF-SbF_5$ media followed by hydrolysis gives a mixture of isomeric

Scheme 62



acids $\text{C}_n\text{H}_{2n+1}\text{COOH}$ for $n = 2-5$ in an overall yield of 50% based on C_5H_{12} (25% based on HF-SbF_5) with the yield of the single isomer $\text{tert}'\text{C}_5\text{H}_{11}\text{COOH}$ being 11% based on C_5H_{12} (5.5% based on HF-SbF_5), as is shown in Scheme 53.

The selectivity of carbonylation of $\text{C}_2\text{-C}_5$ 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, thus, leading to the accumulation of the most stable carbocations 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 which is typical for carbonylation induced by protic superacids does not occur in this case.

n-Alkanes $\text{C}_6\text{-C}_{10}$. The first examples of the nondestructive carbonylation of $n\text{RH}$ to give $\text{tert}'\text{RCOOR}'$ for $\text{R} = \text{C}_6\text{H}_{13}$, C_7H_{15} , C_8H_{17} , C_9H_{19} , and $\text{C}_{10}\text{H}_{21}$ were reported in 2002.²³⁵ With a CO pressure of 1 atm and a temperature of either -40 or -60 $^\circ\text{C}$, carbonylation of the higher linear alkanes, C_6H_{14} through $\text{C}_{10}\text{H}_{22}$, gives only carbonyl-containing products with *tert*-alkyl substituents. The workup of the reaction mixtures with PrOH or MeOH led to the esters of tertiary carboxylic acids in selectivities of 88–100%. At -40 $^\circ\text{C}$, the yields of esters amounted to 74–95% in 1–2 h ($\text{C}_6\text{-C}_9$) and 54% in 2 h (C_{10}). In all cases, they are represented mainly or exclusively, that is, with the content ranging from 76% to 100%, by the two isomers **18** and **19** (Scheme 62).

That these reactions always give these two esters, and usually with the $\text{AlkC}(\text{Me})_2\text{COOR}'$ isomer predominating, is probably because of the comparable stabilities of the corresponding tertiary alkyl cations **18'** and **19'**. Practically no other isomeric esters were formed in significant yield in the $\text{C}_6\text{-C}_8$ alkane carbonylations, but others such as $\text{tert}'\text{RCOO}'\text{Pr}$ were produced at yields of 15–37% in the reactions of the $\text{C}_9\text{-C}_{10}$ alkanes. Hexane exhibited a small peculiarity: at -40 $^\circ\text{C}$ and at -60 $^\circ\text{C}$, small amounts of the ester of 1-methylcyclopentane carboxylic acid (**20**) were also formed in 13–18% yield, and lowering the temperature favored its formation. At -20 $^\circ\text{C}$, $\text{sec}'\text{hexylCOOPr}$ (**21**) instead of (**20**) was formed in amounts comparable to $\text{Et}_2\text{C}(\text{Me})\text{COOR}'$. Scheme 63 explains the formation of the main products of the carbonylation of $\text{C}_6\text{-C}_{10}$. This scheme involves the generation of carbocations from alkanes followed by isomerization of the initial cations into stable tertiary cations,^{221,236} trapping of the tertiary cations by the CO molecule to form acylium cations, and finally formation of the corresponding esters from the acylium cations. The byproduct of the hexane carbonylation probably arises from a multistep process starting from the deprotonation and cyclization of the amyl-2-carbenium cation leading to 1-methylcyclopentane which gives first **20'** and then **20** (Scheme 63).

The carbonylation of $\text{C}_4\text{-C}_{10}$ alkanes in protic superacid media proceeds unselectively if at all. For instance, at 30 $^\circ\text{C}$ and a $[\text{RH}]:[\text{SbF}_5]:[\text{HF}]$ molar ratio of 1:2:10, hexane is

converted, after hydrolysis of the reaction mixture, into a complicated mixture of products consisting of *tert*- $\text{C}_6\text{H}_{13}\text{COOH}$ (15% based on hexane), *sec*- $\text{C}_6\text{H}_{13}\text{COOH}$ (29%), and a set of destructive carbonylation products, that is, the acids RCOOH with $\text{R} = \text{Et, Pr, Bu, and C}_5\text{H}_{11}$.²²² 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, but the latter forms only the C_5 acids.²²² The carbonylation of hexane with HCOOH in 99% H_2SO_4 in the presence of hydride ion acceptors consisting of olefins or alcohols does not take place at all,²³⁶ but instead, the products of the carbonylation of the olefin or alcohol are formed. The carbonylation of *n*-octane with CO in the presence of hexanol and $\text{Ag}_2\text{O}/\text{H}_2\text{SO}_4$ results in the *tert*- C_7 -acids only.²³⁷ In either the $\text{HSO}_3\text{F-SbF}_5$ or the HF-SbF_5 medium, octane reacts in the presence of $\text{Cu}(\text{I})$ with CO to give $\text{tert}'\text{BuCOOH}$.²²³

Thus, polyhalomethane–aluminum bromide superelectrophiles are unique systems which are capable of transforming linear $\text{C}_4\text{-C}_{10}$ alkanes by reaction with CO exclusively into tertiary carbonyl-containing products. Taking into account the considerable interest in practical applications of tertiary carboxylic acids and their derivatives, both as mixtures and as individual compounds,^{155b,238} the first examples of their selective preparation from alkanes are significant.

3.2.9.3. Carbonylation of Monocyclanes $\text{C}_5\text{-C}_8$. Cyclopentane. The reaction of cyclopentane with CO at 1 atm is induced by $\text{CX}_4\bullet 2\text{AlBr}_3$ and results in the alkylcyclopentanecarboxylate **22** in an almost quantitative yield both in the absence of solvent¹¹⁸ and in CH_2X_2 as solvent with $\text{X} = \text{Cl}$ or Br (Scheme 64).²⁰⁶ The only byproduct of the reaction in solvent-free conditions at room temperature is ketone at yield of less than 1–5% (Scheme 64).

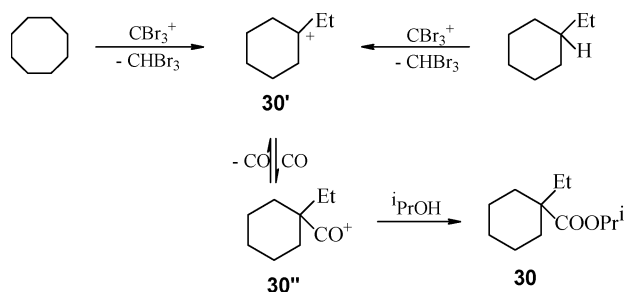
The $\text{CHBr}_3\bullet n\text{AlBr}_3$ and $\text{CCl}_4\bullet n\text{AlBr}_3$ systems are more effective than the $\text{RCOX}\bullet n\text{AlBr}_3$ superelectrophiles based on acyl halides.¹¹⁸ In addition, the former show activity in the presence of smaller quantities of AlBr_3 , although their activity increases with increasing n .

After 1 h of carbonylation in CH_2X_2 solvent at 0 $^\circ\text{C}$ promoted by $\text{CX}_4\bullet 2\text{AlBr}_3$ with $\text{X} = \text{Br}$ or Cl , the compound **22** is the single product and is formed in quantitative yield based on the electrophile.

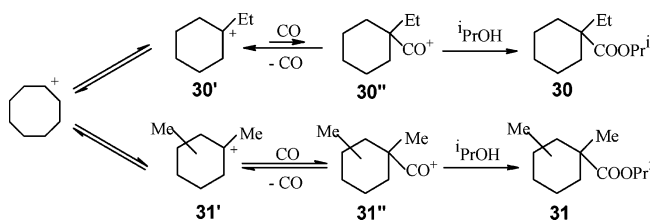
Cyclohexane and Methylcyclopentane. Cyclohexane (**24**) and methylcyclopentane (**25**) react with CO under atmospheric pressure in the presence of $\text{CX}_4\bullet 2\text{AlBr}_3$ ($\text{X} = \text{Br, Cl}$) in a CH_2X_2 solution to give after EtOH workup three products (**26–28**) in yields dependent on the conditions (Scheme 65).²³⁹

Cycloalkanes **24** and **25** behave similarly: at -45 $^\circ\text{C}$, 1-methylcyclopentanecarboxylate (**26**) is formed irrespective of the reaction time, while at 0 $^\circ\text{C}$, cyclohexanecarboxylate (**27**) is formed over a period of 1 h as the major product.²³⁹ The carbonylation route for the reactions of these cycloalkanes with CO in the HF-SbF_5 superacid medium was observed to be similarly influenced by temperature.^{8,240} However, in contrast with the results for the reactions in HF-SbF_5 , the carbonylation of **24** in the presence of $\text{CBr}_4\bullet 2\text{AlBr}_3$ proceeds more effectively and selectively than that of **25**. Of particular interest is the formation of 2-methylcyclohexanone (**28**) in the presence of $\text{CBr}_4\bullet 2\text{AlBr}_3$.²³⁹ At -23 $^\circ\text{C}$, **28** is formed from **25** in 80% yield; simultaneously, the reaction gives **26** in 74% yield based on the superelectrophile.²³⁹ This ketone was absent in the attempted carbonylation in HF-SbF_5 ,^{8,240} although reaction of **24** with $P_{\text{CO}} =$

Scheme 68



Scheme 69



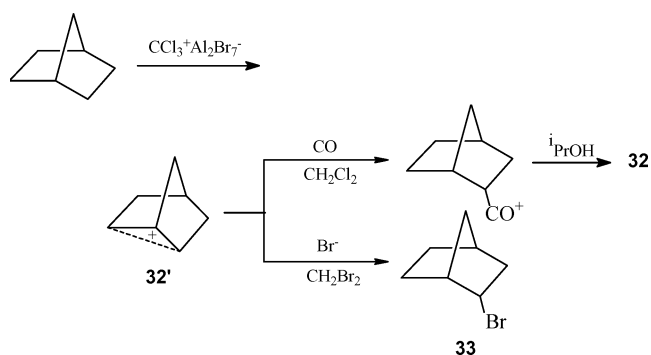
carbonyl containing product in a yield of 67–70% after 0.5–1 h (Scheme 68).

At $-20\text{ }^\circ\text{C}$, the reactions of cycloheptane and methylcyclohexane with CO are still selective, giving **29**, whereas the reactions of cyclooctane and ethylcyclohexane are nonselective, resulting in a mixture of four isomers of $\text{cyclo-C}_8\text{H}_{15}\text{COOR}$ in which **30** is a minor component (Scheme 69).

The observed sharp decrease in both the selectivity and the yield of **30**, which is formed as the only product at $-40\text{ }^\circ\text{C}$, is caused by the different temperature dependence of the carbocation and corresponding acylium cation stabilities.^{106,221} As shown by PM3 quantum-chemical calculations,^{241,242} among the tertiary cations, $[\text{cyclo-C}_6\text{H}_{10}\text{Et}]^+$ ($\Delta H_f = -152.6\text{ kcal/mol}$) is more stable than the isomeric cations $[\text{cyclo-C}_6\text{H}_9\text{Me}_2]^+$ ($\Delta H_f = -150.5\text{ kcal/mol}$), which have similar stabilities. This implies that the **30'** cation accumulates on treatment of cyclooctane or ethylcyclohexane with the superelectrophile at $-40\text{ }^\circ\text{C}$. At higher temperatures, the decarbonylation of $\text{cyclo-C}_6\text{H}_{10}(\text{Et})\text{CO}^+$ (**30''**), which forms the more stable carbocation, proceeds much more easily than in the case of isomeric acylium cations $\text{cyclo-C}_6\text{H}_9(\text{Me}_2)\text{CO}^+$ (**31''**).¹⁰⁶ In addition, the difference between the stabilities of the $[\text{cyclo-C}_6\text{H}_{10}\text{Et}]^+$ and $[\text{cyclo-C}_6\text{H}_9\text{Me}_2]^+$ cations is less pronounced at higher temperatures.²³⁴ As a consequence, raising the temperature results in the loss of selectivity and the predominant formation of isomers **31**.

The isomerization of cycloalkanes induced by Lewis acids and accompanied by ring contraction is well-known.^{243,244} Under comparable conditions, cycloheptane is converted quantitatively into methylcyclohexane, while cyclooctane yields a mixture of ethylcyclohexane (90%) and isomeric dimethylcyclohexanes (10%).²⁴⁴ The reaction of methylcyclohexane with CO in the presence of HF-SbF_5 results after hydrolysis in a mixture of isomeric $\text{cyclo-C}_6\text{H}_9(\text{Me})_2\text{COOH}$ (90%) and $\text{cyclo-C}_6\text{H}_{10}(1\text{-Me})\text{COOH}$ (10%).⁸ Carbonylation of methylcyclohexane in 98% H_2SO_4 or in $\text{BF}_3\text{-H}_2\text{O}$ gives methylcyclohexane-1-carboxylic acid in 20–70% yields when carried out with a copper salt or silver salt acting as the metal carbonyl source and with an olefin or alcohol acting as the carbocation source.²⁴⁵ The drawbacks of this method include not only the requirement for either a copper salt or a silver salt as well as either an alcohol or an olefin, but

Scheme 70



also the fact that carbonyl products derived from the alcohol or olefin used are formed in amounts comparable to the yield of the target product.

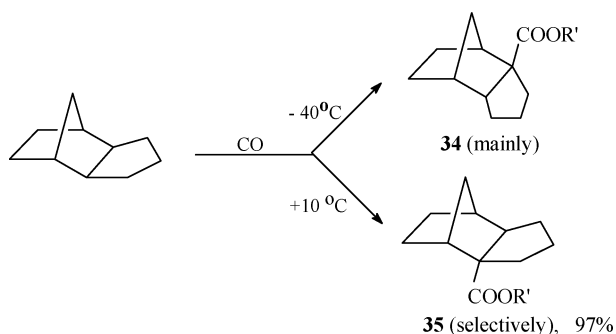
3.2.9.4. Carbonylation of Bi- and Tricyclanes. Norbornane. Carbonyl-containing cage-shaped compounds are of considerable interest for practical use as potential pharmaceuticals, fragrance compounds, and other valuable products.¹⁵⁰ However, except for adamantanes, for which carbonylation was first accomplished as far back as the 1960s,²⁴⁷ the reactions of polycyclanes with CO have scarcely been studied.²⁴⁸ Carbonylation of norbornane has only recently been accomplished.²⁴⁹

Norbornane reacts with CO at atmospheric pressure in the presence of $\text{CX}_4 \cdot n\text{2AlBr}_3$ in CH_2X_2 ($n = 1.5\text{--}2$; $\text{X} = \text{Cl}, \text{Br}$) with $i\text{PrOH}$ workup to give a single product, the ester of 2-norbornylcarboxylic acid (**32**), in nearly quantitative yield over a broad temperature range (-20 to $+10\text{ }^\circ\text{C}$) (Scheme 70).

Surprisingly, the route of this reaction at $-40\text{ }^\circ\text{C}$ depends on whether CH_2Cl_2 or CH_2Br_2 is used as the solvent, with the yield of the ester being 75–100% in CH_2Cl_2 but only 16% in CH_2Br_2 . The latter reaction is accompanied by the formation of 2-bromonorbornane (**33**) in 76% yield. The presumed reaction scheme (Scheme 70) involves the generation of the nonclassical norbornyl cation **32'**, which at $-40\text{ }^\circ\text{C}$ then either accepts Br^- in CH_2Br_2 solvent to give the 2-bromonorbornane or adds CO in CH_2Cl_2 solvent to give the ester.

The selective transformation over a broad temperature range of norbornane into alkyl carboxylate with the CO group at the secondary C atom is at variance with the general tendency according to which $\text{C}_4\text{--C}_{10}$ n -alkanes and $\text{C}_6\text{--C}_8$ monocycloalkanes as well as their isomeric monoalkylcyclohexanes are converted at low temperatures only into products with a carbonyl group at a tertiary C atom. This outcome can be attributed to an exceptionally high stability for cation **32'**. This cation is nearly as stable as the 1-adamantyl cation and is thermodynamically more favorable by 17 kcal/mol than the 1-norbornyl cation.²⁵⁰ The reason for the unusual stability of cation **32'** was the subject of a vigorous debate which lasted for 30 years and ended in the recognition of the nonclassical structure for **32'**.^{6,76a,250–253} Thus, the generation of the stable nonclassical carbocation from norbornane accounts for the formation of the 2-substituted product in the reaction with CO . Yet another unexpected result, namely, the predominant formation of 2-bromonorbornane from the reaction of norbornane under a CO atmosphere at $-40\text{ }^\circ\text{C}$ in the presence of $\text{CBr}_4 \cdot 2\text{AlBr}_3$ in a CH_2Br_2 solvent may be attributed to the fact that the norbornyl cation is more prone to add the Br^- ion from the

Scheme 71



solvating Al_2Br_7^- anion than it is to add a neutral CO molecule since intramolecular reactions of the cations proceed more rapidly than do intermolecular ones.²²¹ The fact that at low temperatures the addition of the Br^- anion is irreversible accounts for the result observed.

Trimethylenenorbornane. Like norbornane, trimethylenenorbornane (TMNB) reacts with CO in the presence of $\text{CBr}_4 \cdot 2\text{AlBr}_3$ even at -40°C .²⁴⁹ However, the carbonylation of TMNB is temperature-dependent. Regardless of whether *exo*- or *endo*-TMNB is used as the initial hydrocarbon, the ester of *endo*-trimethylenenorbornane-2-carboxylic acid (**34**) is formed as the main carbonylation product at -40°C . Another isomer formed in lower yield is the ester of *exo*-trimethylenenorbornane-2-carboxylic acid (**35**). Increasing the temperature changes the ratio of the carbonylation products dramatically. At 0°C , **35** is formed predominantly, and at $+10^\circ\text{C}$, the reaction occurs selectively affording **35** in almost quantitatively (Scheme 71).

Previously, based on the fact that both *exo*- and *endo*-TMNB form the same products at temperatures from -40 to $+10^\circ\text{C}$, the structures of esters of trimethylenenorbornane-2-carboxylic acid and trimethylenenorbornane-1-carboxylic acid were attributed to **34** and **35**, respectively.^{145b} However, a detailed reinvestigation of this question by high resolution ^{13}C NMR compelled us to dismiss this first attribution. At 20°C , **32** is the sole volatile carbonylation product from norbornane, and **35** is the sole volatile carbonylation product from TMNB, but their yields are considerably decreased. This reduction is probably caused by the facile decarbonylation of the corresponding acylium salts under these conditions.

It has been reported in short, that radical carbonylation of *endo*-TMNB with CO catalyzed by *N*-hydroxyphthalimide (CO/air = 45:1, 85°C , 15 h) after hydrolysis leads to trimethylenenorbornane-2-carboxylic acid (42%) and trimethylenenorbornane-2,6-dione (19%)²⁴⁸ as the major products.

Adamantane, 1,3-Dimethyladamantane. 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.^{150c,d,155b} Different modifications of this reaction have been the subjects of numerous papers and patents.²⁵⁴ The previously described adamantane-1-carboxylic acid syntheses, except for those carried out in concentrated H_2SO_4 or oleum, have low selectivity. For instance, the yield of this acid in an *N*-hydroxyphthalimide-catalyzed reaction is 55%, and the reaction is not selective (Scheme 72).²⁴⁸

The reaction of adamantane with CO under atmospheric pressure in the presence of the polyhalomethane systems $\text{CX}_4 \cdot n\text{AlX}_3$ and $\text{CH}_2\text{X}_2 \cdot n\text{AlX}_3$, where X = Cl, Br and $n =$

1, 2, has been studied in detail in the temperature range from -45 to 20°C .^{249,255,256} After alcohol workup, the resulting products, 1-AdCOOEt (**36**), 1-AdCHO (**37**), and 1-AdBr (**38**) are formed in a ratio depending on the nature of the superelectrophile, the temperature and duration of reaction, the ratio of the components, and the nature of the solvent (Scheme 73).

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 (**36**)²⁴⁹ or adamantane-1-carboxaldehyde (**37**).^{255,256} Compound **36** is formed selectively when the reaction is carried out at 0°C in a dilute solution with a stoichiometric ratio of the reactants in the presence of a potent superelectrophile (Scheme 74a). The possibility of selective and quantitative transformation of adamantane into 1-AdCO⁺ in an organic medium, as shown in Scheme 74a, 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 3,5-dimethyladamantane-1-alkylcarboxylate in a quantitative yield also requires specific conditions (Scheme 74b). 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 1-bromo-3,5-dimethyladamantane is formed in a quantitative yield.²⁴⁹

Most of the reactions of saturated hydrocarbons with CO, which were described in section 3.2.9, were first carried out either first or selectively for the first time and with no destructive carbonylation products. These reactions are the electrophilic carbonylation of ethane, the selective carbonylation of C_4 – C_5 alkanes, of C_7 – C_8 cycloalkanes, and isomeric monoalkylated cyclohexanes, the selective carbonylation of norbornane and TMNB, the nondestructive carbonylation of linear C_6 – C_{10} alkanes giving tertiary carbonyl products, and finally the quantitative carbonylations of adamantane and 1,3-dimethyladamantane in an organic medium.

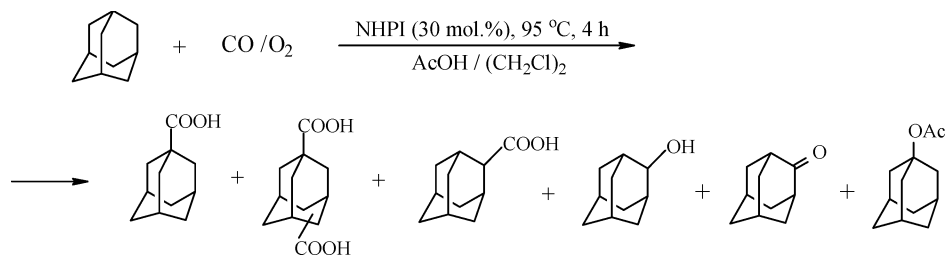
It is very important that the reactions of saturated hydrocarbons with CO initiated by superelectrophiles actually give acylium salts. The formation of the $^i\text{PrCO}^+$ and EtCO^+ acylium salts upon the reaction of propane with CO in an HF-SbF_5 medium was detected by NMR.^{7a} Hogeveen^{3c} proved that MeCO^+ cation is formed from CH_4 and CO at 50 atm treated with SbF_5 , and also that $^{\text{tert}}\text{BuCO}^+$ cation is formed from CH_4 and CO at 1 atm treated with SbF_5 .

The facts that superelectrophiles based on polyhalomethanes allow the generation of acylium salts in an organic medium from acyclic alkanes as well as mono-, bi-, and tricyclanes and, furthermore, that such reactions are often selective, open up unique prospects for the wide use of saturated hydrocarbons and CO as reagents in organic synthesis. It is also important that the acylation can be carried out as a one-pot procedure.

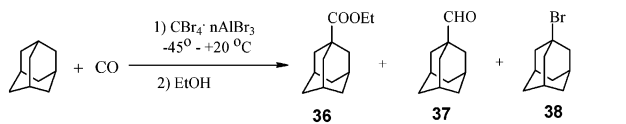
3.2.10. Alkanes and Cycloalkane with CO in One-Pot Syntheses of Various Carbonyl-Containing Compounds

3.2.10.1. Effective Formylation of Adamantane with CO. The second reaction route between adamantane and CO, which yields adamantane-1-carboxaldehyde (**37**), is itself interesting. Unlike the widely used electrophilic formylation of aromatics,²⁵⁷ this route for electrophilic reactions of saturated hydrocarbons is atypical and has been implemented only for adamantane.

Scheme 72



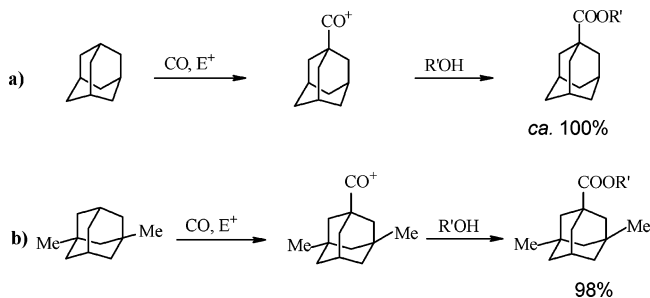
Scheme 73



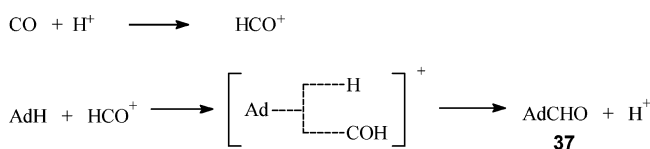
T, °C	-45	-23	0	20	Products	E, CH ₂ X ₂	[E], M
Yields [*] , for 1 h	6 ^{**}	28/10 ^{**}	32/2 ^{**}	22 ^{***}	(36)		
	traces ^{**}	1/2 ^{**}	8/45 ^{**}	30	(37)	CBr ₄ ·2AlBr ₃	1.87
	12 ^{**}	40/16 ^{**}	30/6 ^{**}	28	(38)		
		51 ^a	100 ^b	32 ^c	(36)		^a) 0,51
		34 ^a	0 ^b	65 ^c	(37)	CCl ₄ ·2AlBr ₃	^b) 0,34, 3h
		0 ^a	0 ^b	0 ^c	(38)		^c) 0,85

^{*}) on AdH; ^{**}) At [AdH]: [E] = 4:1, the remaining data were obtained at the molar ratio 1:1; ^{***}) Additionally, 2-AdCOOEt was obtained in 10% yield

Scheme 74



Scheme 75

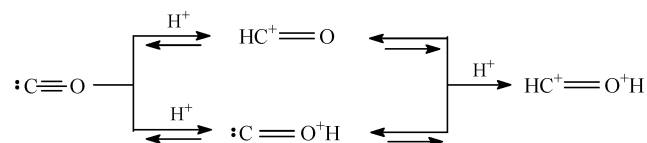


Olah and co-workers were the first to succeed in the electrophilic formylation of adamantane with CO both in proton superacid media²⁵⁸ and in CH₂Cl₂ solution under the action of AlCl₃.²⁵⁹ These reactions seem to proceed *via* two different mechanisms in protic and aprotic media.

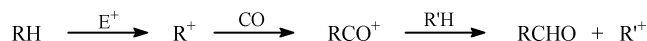
The first formylation mechanism, which operates in protic media, involves the protonation of CO and the subsequent attack of the adamantane molecule by the electrophilic HCO⁺ species, thus, affording **37** (Scheme 75).

Indeed, along with the usual 1-AdOH and 1-AdCOOH as the main product, the reaction of 1,3,5,7-tetradeuteriumadamantane with CO in CF₃SO₃H gave C₁₀H₁₂D₃COH and C₁₀H₁₂D₃COD in the ratio 16.5:1, respectively. In a control reaction of 1,3,5,7-tetradeuteriumadamantane with CF₃SO₃H in the absence of CO, no H/D exchange was observed. This fact served as evidence of formyl cation participation in the reaction.²⁵⁸ Quantum-chemical calculations supported the possibility of formation of two monoprotonated forms of CO, that is, the HC⁺=O (formyl) and :C=O⁺H (isoformyl)

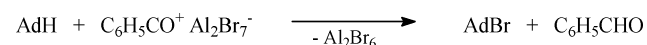
Scheme 76



Scheme 77



Scheme 78



cations. The diprotonated CO, that is, HC⁺=O⁺H, also has minimum on the PES^{144,260} (Scheme 76).

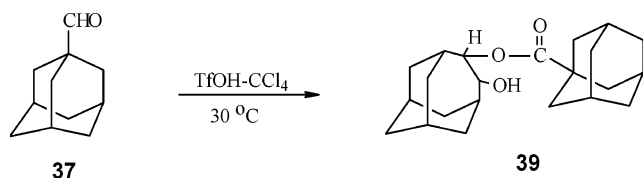
The formation of monoprotonated species from CO is exothermic. In addition, both of these species, even the isoformyl cation, which is less stable by 38 kcal/mol, once formed should be relatively stable because of a large barrier to deprotonation.²⁶⁰ Both protonated carbon monoxides were detected in the gas phase,²⁶¹ but neither of them could be directly observed in superacidic solutions.²⁵⁸

The second formylation mechanism, which operates in aprotic media, is apparently a three-step process comprising the generation of a carbocation, the addition of a CO molecule to that cation to give the acylium cation, and the abstraction of a hydride ion from the saturated hydrocarbon molecule by this acylium cation.^{255,256,259} It is evident that the last step of this process, namely, the transfer of a hydride ion from a hydrocarbon to an acylium cation, is the crucial step in the reactions of saturated hydrocarbons with the aprotic organic superelectrophiles RCO⁺Al₂X₇⁻.^{98,99} (Scheme 77).

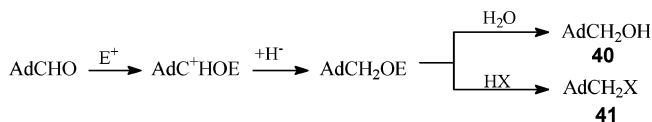
The formation of aldehydes by treatment of alkanes with AlkCO⁺Al₂Br₇⁻ has not been found, which is probably because of the high reactivity of aldehydes toward super-electrophiles. However, benzaldehyde¹¹¹ was detected in the reaction of adamantane with PhCOCl·2AlBr₃ (Scheme 78).

Since the work reported in reference 255, all attempts to prepare **37** from AdH or other precursors of Ad⁺ cation in proton superacid media of different acidities and under CO pressures up to 85 atm²⁵⁸ were minimally successful, as were also attempts using AdH in the presence of AlCl₃ in CH₂-Cl₂.²⁵⁹ The yield of **37** amounted to 0.2–21%. Meanwhile, adamantane-1-carboxylic acid was the major product, with yields of 60–75%, together with small amounts of 1-AdOH in yields of 2–7% as a minor product.²⁵⁹ Japanese workers who studied in detail the reactions of CO at 30 °C in TfOH·CCl₄ with 1-AdOTf (Tf = CF₃SO₂) and with AdH as well as with other sources of adamantanyl cation did not detect even traces of **37** in the reaction products.^{262,263} Instead, after water treatment, they isolated a homoadamantane derivative, that is, 3-hydroxy-4-homoadamantyl-1-adamantanecarboxyl-

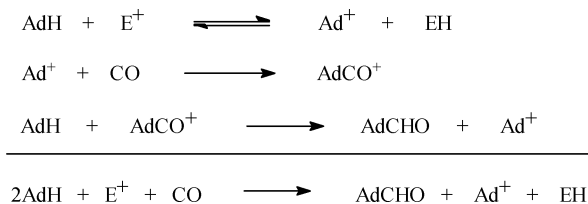
Scheme 79



Scheme 80



Scheme 81



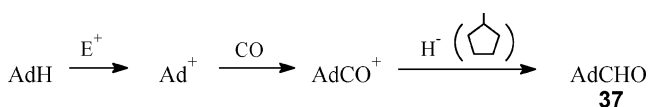
ate **39**, as the major product in yields up to 70%. In special experiments, these researchers showed that 1-AdCHO was unstable under the reaction conditions (Scheme 79).

The use of polyhalomethanes combined with aluminum halides for adamantane formylation have been markedly more successful.^{255,256} Although the rates of AdH formylation are higher in the reactions mediated by $\text{CBr}_4\cdot n\text{AlBr}_3$ compared with those mediated by $\text{CH}_2\text{X}_2\cdot\text{AlBr}_3$ ($\text{X} = \text{Cl}$ or Br) systems, similar or even higher yields of **37** can be achieved with the latter if more prolonged reactions are carried out. For example, at $20\text{ }^\circ\text{C}$ and the ratio [adamantane]: $[\text{CH}_2\text{X}_2\cdot 2\text{AlX}_3] = 1$, the yields of **37** are 57% for 1 h ($\text{X} = \text{Br}$) and 36% for 2 h ($\text{X} = \text{Cl}$). In some cases, however, at longer reaction times, products **40** and **41** from the further reduction of AdCO^+ are also formed in addition to **36–38** (Scheme 80).²⁵⁶

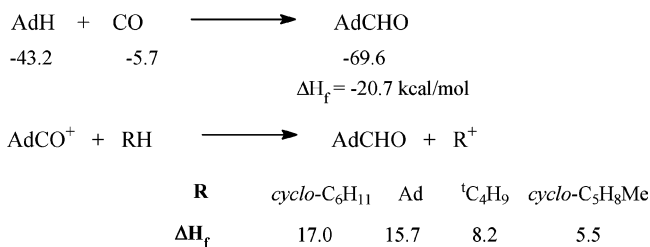
The increased effectiveness of adamantane formylation by the milder $\text{CH}_2\text{X}_2\cdot n\text{AlX}_3$ ($\text{X} = \text{Cl}, \text{Br}$) systems as compared with the stronger $\text{CBr}_4\cdot 2\text{AlBr}_3$ systems can be explained by the observations that AdH does not require a strong electrophile to generate the Ad^+ , and that very active systems such as $\text{CBr}_4\cdot n\text{AlBr}_3$ remove AdH from the reaction sphere too rapidly, while the milder electrophiles, which generate Ad^+ relatively slowly, create conditions favorable for the reaction of AdCO^+ with AdH. According to Scheme 81, the maximum theoretical yield of **37** is 50% based on the initial AdH.

Since Ad^+ adds CO to give AdCO^+ , which can in turn abstract a hydride from AdH, one might expect a chain process to result. However, such a process does not occur in reality. Apparently, when $[\text{AdH}] = [\text{E}]$, the hydride ion is deficient in the reaction mixture since the formation of AdCO^+ is a fast reaction and the hydride ion transfer is a slower step. However, when $[\text{AdH}] > [\text{E}]$, the system activity decreases due to the accumulation of aldehyde **37**, which is able to coordinate to the superelectrophile. 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 be made still more efficient if methylcyclopentane is added to the reaction mixture as a hydride ion donor. In the presence of methylcyclopentane, at $20\text{ }^\circ\text{C}$, and at an

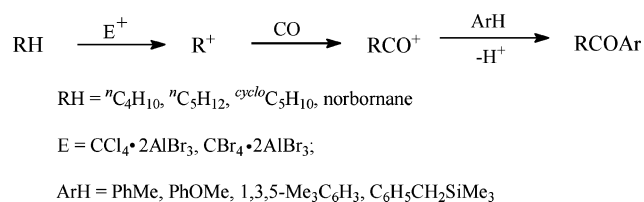
Scheme 82



Scheme 83



Scheme 84



[AdH]: $[\text{CH}_2\text{Br}_2\cdot 2\text{AlX}_3]$: $[\text{cyclo-C}_5\text{H}_9\text{Me}]$ molar ratio of 1:1:2, a quantitative yield of the aldehyde based on adamantane is attained over a period of 1 h for $\text{X} = \text{Br}$ and 2 h for $\text{X} = \text{Cl}$.^{255,256} It was assumed that in the presence of methylcyclopentane, an alternative process (Scheme 82) involving methylcyclopentane occurs in parallel with the reaction depicted in Scheme 81.

It is important that methylcyclopentyl cation does not form any stable products with CO in the presence of adamantane under these reaction conditions.

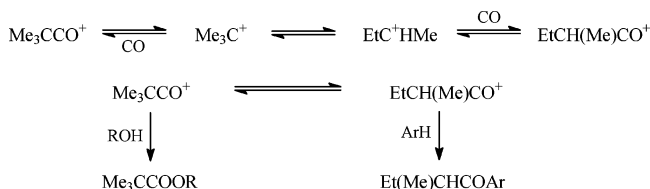
The enthalpies of the reactions depicted in Scheme 83 imply that the overall reaction of AdH formylation is exothermic, while the hydride transfer from RH to AdCO^+ is accompanied by the absorption of heat. It can be seen from the enthalpies in the scheme that the transfer of a hydride ion to AdCO^+ from methylcyclopentane is 10.2 kcal/mol more favorable than from AdH, and that methylcyclopentane is the best hydride donor among the listed hydrocarbons.²⁵⁶

3.2.10.2. Synthesis of Ketones from Aromatics. A direct synthesis of both alkyl as well as cycloalkyl aromatic ketones from the corresponding alkane or cycloalkane, CO, and arenes by using aromatics as the trapping agents for the acylium cations generated was elaborated^{145,206} (Scheme 84).

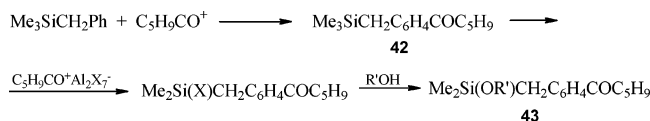
The advantage of these reactions is high position selectivity, since in contrast to the usual electrophilic arene reactions, only *para*-isomers are produced. The absence of *ortho*-isomers may be due to steric restrictions arising from the attack on the aromatic molecule by a bulky electrophilic species, $\text{RCO}^+\text{Al}_2\text{Br}_7^-$. 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 affords mainly 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 as in Scheme 85.

In the presence of polyhalomethane superelectrophiles, the ${}^{\text{tert}}\text{Bu} \rightleftharpoons {}^{\text{sec}}\text{Bu}$ equilibrium is shifted toward ${}^{\text{tert}}\text{Bu}$. Therefore,

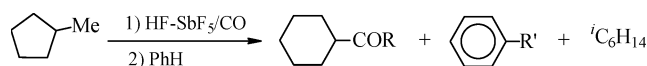
Scheme 85



Scheme 86



Scheme 87



R = Ph, C₆H₁₁, C₆H₄-*cyclo*-C₆H₁₁

R' = Ph, *cyclo*-C₆H₁₁

the fast reaction between the acylium cation and a strong nucleophile such as ⁱPrOH (see Scheme 60) gives a product (**15**) containing ^{tert}Bu, whereas slow reactions with less nucleophilic arenes (see Scheme 84) involve the more reactive ^{sec}BuCO⁺ 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.

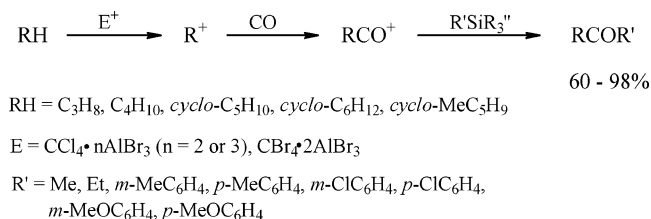
The C₆H₂(Me)₃CO^{tert}Amyl is the sole product of the reaction of AmylCO⁺ with mesitylene. The reactions of AmylCO⁺ with toluene or anisole give the usual acylation product along with alkylation and alkylacylation products in yields of 20–40%. Chlorobenzene is not changed in the presence of RCO⁺ at 0 °C. At 20 °C, the conversion of chlorobenzene increases markedly, but cycloalkylated diarylmethanes are formed instead of carbonyl-containing aromatic compounds (Scheme 49). The reaction of Me₃-SiCH₂Ph with *cyclo*-C₅H₉CO⁺ occurs by acylation of the starting silane to give an organosilicon ketone **42** in quantitative yield. When an excess of *cyclo*-C₅H₉CO⁺ with respect to the benzylsilane is used, one of the Si–Me bonds of the ketone **42** is cleaved, and alcoholysis with R'OH (R' = Et, ⁱPr) gives ketones **43** in 40–50% yield (Scheme 86).

Paatz described a single example of such an approach for the synthesis of a ketone in HF–SbF₅ media.⁸ The yield of cyclohexylphenyl ketone was rather high, but a mixture containing six components was produced under these conditions (Scheme 87).

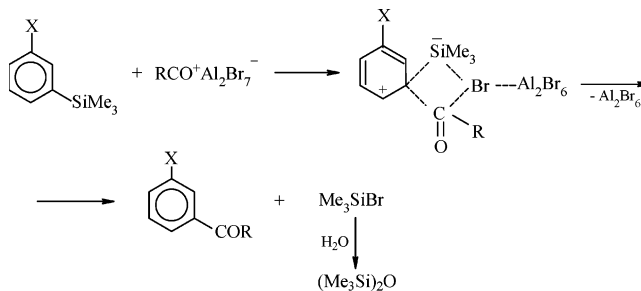
3.2.10.3. Synthesis of Ketones with Tetraorganosilanes (Acyl-desilylation). The use of alkanes (or cycloalkanes), CO, and tetraorganosilanes in the synthesis of ketones has also proved to be quite successful. These reactions are accompanied by desilylation and afford alkylaryl and dialkyl ketones in good yields and with high selectivity²⁰⁶ (Scheme 88).

As in the case of the acylation of arenes with saturated hydrocarbons and CO, in this case also, propane, *n*-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*-C₆H₁₁COR or mainly *cyclo*-1,1-MeC₅H₈COR, depending on the conditions. The reactions starting from cyclohexane/Me₄-

Scheme 88



Scheme 89



Si and from methylcyclopentane/Me₄Si both result in either pure ketone *cyclo*-C₆H₁₁COMe (**44**) or a mixture of **44** and *cyclo*-1,1-MeC₅H₈COMe (**45**) depending on the reaction temperature. Starting from cyclopentane or norbornane, that is, *cyclo*-RH compounds, and Me₃SiR' (R' = Me, Et) gives the corresponding ketones, *cyclo*-RCOR', in high yields.

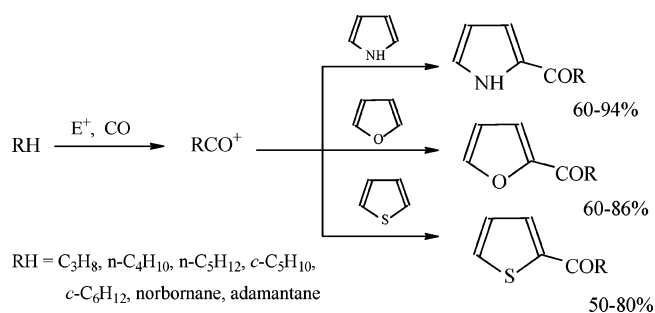
The use of tetraorganosilanes in the synthesis of ketones has two important advantages. The first advantage is the applicability of the method to the synthesis of ketones containing both alkyl and aryl groups, including aryl groups with electron-withdrawing substituents. The last-mentioned compounds cannot be synthesized at low temperatures using saturated hydrocarbons and CO by direct acylation of deactivated arenes devoid of organosilicon substituents. Meanwhile, at 0 °C, *m*- and *p*-ClC₆H₄SiMe₃ react with cyclopentane and CO in the presence of superelectrophiles to give ketones with the *cyclo*-C₅H₉CO group in 81–89% yield over a period of 15 min.

The second important advantage is the regioselectivity exhibited in the synthesis of aromatic ketones. For instance, the reaction with *p*-XC₆H₄SiMe₃ gives the ketones *p*-XC₆H₄-COR. Correspondingly, *m*-XC₆H₄SiMe₃ are converted into the ketones *m*-XC₆H₄COR. It should be emphasized that, although the reactions of activated arenes with RCO⁺ according to Scheme 84 proceed easily to give ketones ArCOR in high yields, only the *para*-isomers can be obtained. The regioselectivity of the acyl-desilylation of trialkylarylsilanes is probably indicative of the fact that the reaction follows the *ipso*-substitution mechanism,²⁶⁴ which comprises an attack of the acylium cation on the site with the highest electron density of the benzene ring, that is, on the C atom attached to the trialkylsilyl group, and the subsequent displacement of this group by an acyl group, as shown in Scheme 89.

The only example that does not fit into the general scheme of regioselective acylation of trialkylarylsilanes is the formation of the *p*-MeOC₆H₄COC₅H₉ instead of the expected *meta*-isomer in the reaction of *m*-MeOC₆H₄SiMe₃ with *cyclo*-C₅H₉CO⁺.²⁰⁶ This result is all the more unexpected since the acyl-desilylation of *m*-MeOC₆H₄SiMe₃ with the PhCOCl–AlCl₃–CS₂ system occurs selectively giving only 3-methoxybenzophenone.²⁶⁵

The acyl-desilylation of substituted trimethylphenylsilanes on treatment with RCOCl•AlCl₃ has been described.^{266,267}

Scheme 90



Refluxing a mixture of RCOCl•AlCl₃ (R = alkyl, aryl) with Me₄Si and Et₄Si in a CH₂Cl₂ solution for 18 h was reported to result in the formation of RCOR' ketones in 30–80% yields.²⁶⁷ The key feature of this ketone synthesis method is the use of either alkanes or cycloalkanes with CO as the equivalents of acylium cations.

3.2.10.4. Synthesis of Ketones from Heteroaromatics.

One-pot acylation of pyrrole, furan, and thiophene with alkanes (or cycloalkanes) and CO as acylating agents in the presence of the polyhalomethane-based superelectrophiles has been recently performed (Scheme 90).²⁶⁸ The reaction proceeds regioselectively to give a single ketone, most often in high yield. In these reactions, as in other acylation reactions involving saturated hydrocarbons and CO, the group R has the same structure as that in the aromatic ketones, which are formed according to Schemes 84 and 88.

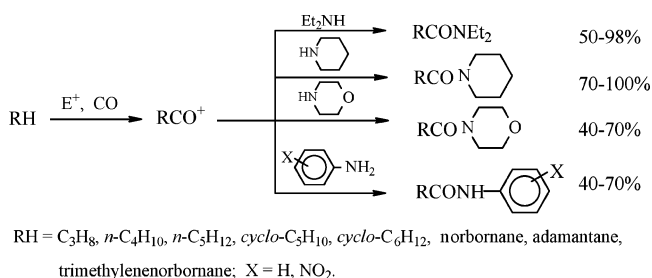
The acylation of heterocycles is an important method for the synthesis of valuable heterocyclic derivatives or their precursors.^{269,270} Five-membered heteroaromatic compounds with one heteroatom are known to be markedly less stable in electrophilic media than benzoid hydrocarbons: under the action of electrophiles, they can react as dienes, undergo ring opening, or polymerize. Therefore, selective acylation of activated heterocycles even by conventional acylating reagents is not always a routine operation.²⁷¹ The selective acylation of five-membered heteroaromatics by acylium salts generated *in situ* from saturated hydrocarbons is apparently successful because the acylium salts are highly ionized in the superelectrophilic media so that the acylation proceeds at high rates under very mild conditions.

3.2.10.5. Synthesis of Amides. The selective acylation of compounds containing amino groups is an important reaction for the synthesis of amides, many of which are of interest because of their own biological activity or because they serve as intermediates in the synthesis of other biologically active compounds.^{272,273} Adamantanecarboxamides are of particular interest for the synthesis of biologically active compounds.^{150,274} Acylation methods for the amino group are well-developed.^{272,273} They consist mainly of the treatment of amines with activated derivatives of carboxylic acids, namely, acyl halides, anhydrides, and esters.

Aliphatic, cyclic, and aromatic amines are readily acylated with saturated hydrocarbons and CO in the presence of superelectrophiles based on polyhalomethanes.²⁷⁵ Reactions of aliphatic amines, piperidine, morpholine, and aniline occur selectively and regioselectively to give amides, usually in good yields (Scheme 91).

It is worth mentioning that aromatic amines containing an acceptor group, that is, *o*- and *p*-nitroanilines, can also be acylated in high or moderate yields by this method. The structures of the RCO groups are the same as in the acylated products. Carbonylation of trimethylenenorbornane

Scheme 91



at 10 °C followed by treatment with an amine at the same temperature leads to the exo-trimethylenenorbornyl products containing a functional group in the 2-position.²⁷⁵

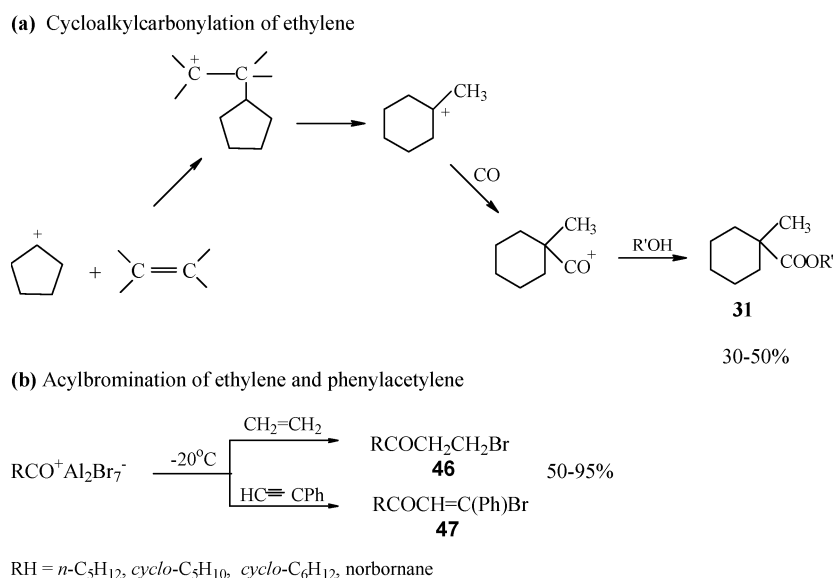
3.2.10.6. Alkyl- and Acyl-Bromination of Unsaturated Hydrocarbons. Upon treatment with the polyhalomethane-based superelectrophilic systems in the presence or in the absence of a saturated hydrocarbon) at low temperature, ethylene is easily converted into a complex mixture of branched higher alkanes, cycloalkanes, and their halogen derivatives. The reaction of ethylene, a cycloalkane, and CO can be directed with rather good selectivity along either of two different routes by changing the reaction conditions. Stirring of cyclopentane with CBr₄•2AlBr₃ in CH₂X₂ at a low temperature in a C₂H₄/CO (1:3) atmosphere affords alkyl 1-methylcyclohexanecarboxylate (**31**) as the only product after alcoholysis of the reaction mixture (Scheme 92a). The reaction includes the addition of the cyclopentyl cation to ethylene followed by isomerization of the primary 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 observed ester after treatment with an alcohol. If ethylene is introduced into a solution of the acylium salt formed from a cycloalkane, the same initial components (RH, CO, C₂H₄, and CBr₄•2AlBr₃) furnish the product of ethylene acylbromination (**46**) in a satisfactory to good yield (Scheme 92b). One-step acylbromination of phenylacetylene by RH and CO acting as acylium salt equivalents and thus leading to **47** has also been successfully achieved.²⁷⁶

In acylbromination reactions of unsaturated hydrocarbons, the above acylation systems serve as donors of two functional groups to the substrate molecules.

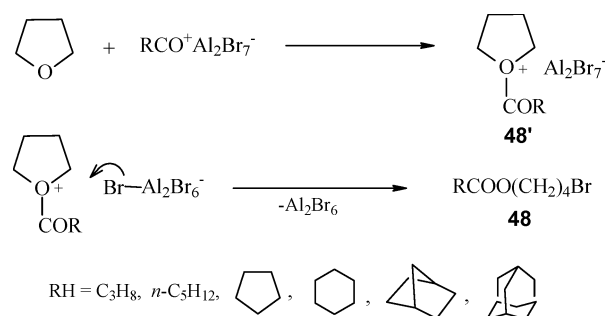
3.2.10.7. Ring-Opening of THF. The opening of the tetrahydrofuran ring under the action of electrophilic reagents is well-known.²⁷⁷ Use of some electrophiles proved to be rather effective and also useful for synthetic purposes. For example, cleavage of the THF ring by acyl halides^{277b-d} in the presence of Lewis or protic acids has been reported by several groups to yield halogen-substituted butyl esters which are otherwise difficult to obtain. Recently, this reaction was successfully carried out using alkanes (cycloalkanes) and CO as equivalents of an acylium salt (Scheme 93).²⁷⁸

Apparently, the reaction includes the transformation of THF and the acylium cation into an oxonium salt **48'**, which undergoes ring-opening, resulting in an ester **48** with the (CH₂)₄Br group. Under the conditions used, only one isomer is formed in each reaction. Because of the enhanced stability toward decarbonylation of the oxonium salt as compared to the corresponding acylium cations, the reactions with THF proceed at temperatures of 20–50 °C and give the target products in 70–80% yields.²⁷⁸ In the absence of THF, even at 20 °C, the reactions of alkanes and cycloalkanes (except

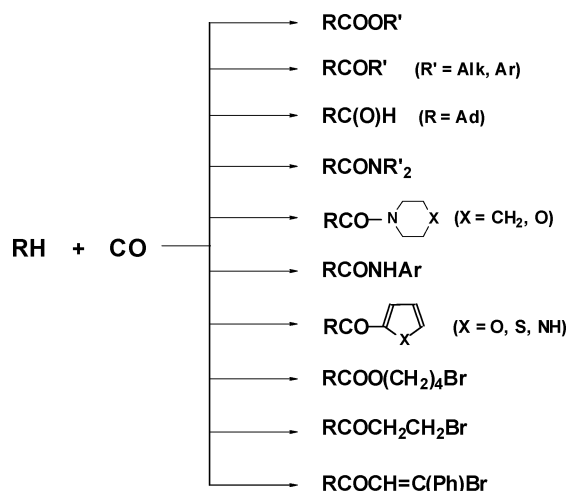
Scheme 92



Scheme 93



Scheme 94



for adamantane) with CO give carbonyl-containing products only in very poor yields if at all.

Scheme 94 summarizes the types of carbonyl-containing compounds synthesized from alkanes (cycloalkanes) and CO in the presence of polyhalomethane-based superelectrophiles.

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, and 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. The possibility of effective and selective acylation of nucleophilic substrates, which are unstable in electrophilic media, by performing the reactions at low temperatures.
5. The possibility of preparing products containing tertiary alkyl (cycloalkyl) and cage substituents at the carbonyl group.

It is clear that the scope of the acylation reactions in Scheme 94 can be markedly extended both by the involvement of other saturated hydrocarbons in selective reactions with CO and by increasing the range of nucleophilic reagents.

4. Mechanistic Studies of the Reactions of Alkanes with Polyhalomethane-Based Superelectrophiles

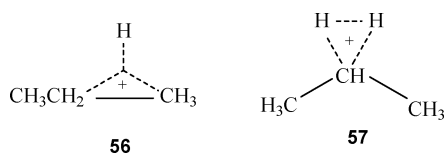
4.1. Early Studies of Mechanisms of Electrophilic Reactions of Alkanes

The unusual results that were obtained for the mechanisms of reactions involving CBr₃⁺ and CBr₃⁺AlBr₄⁻ prompted us to pay special attention to the mechanisms of electrophilic reactions of alkanes in general. These mechanisms are the subject of many papers already cited in this review. At this point, we would like to discuss the mechanistic data in more detail. Reported mechanisms of electrophilic alkane activation involve electrophilic attack on (i) the C–H bond, which is often referred to as the classical cyclic three-center two-electron (*3c-2e*) mechanism; (ii) the C atom, giving rise to a pentacoordinated carbonium cation; and (iii) the H atom to give a *3c-2e*, open C–H–E⁺ bond with hypervalent hydrogen. All three types of reactions are discussed below.

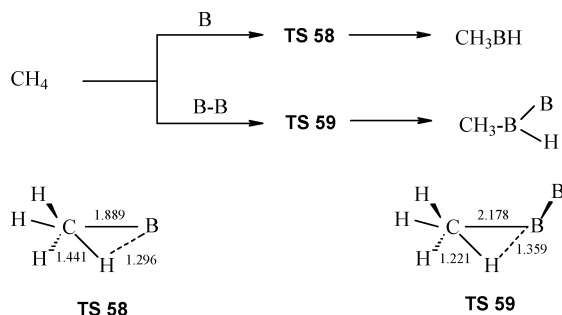
4.1.1. Electrophilic Attack on the C–H Bond with Cyclic *3c-2e* Bonding (the Classical Olah Mechanism)

4.1.1.1. Protolytic Reactions. The classical Olah mechanism of electrophilic reactions of alkanes was first proposed for protolytic reactions. It involves direct coordination of an

Scheme 100



Scheme 101



for the C–C protonated species **54** which is 4.4 kcal/mol lower than that of **55**, the C–H protonated isomer.²⁹¹ *Ab initio* calculations at the HF/4-31G level of protonated propane $C_3H_9^+$ have demonstrated^{292a} that the C–C protonated form (**56**) is only 1 kcal/mol more stable than the C–H protonated species (**57**) (Scheme 100).

A detailed study has recently been reported^{292b} of all possible isomers of C–H and C–C protonated *n*-butane by using both *ab initio* calculations and analysis of the theory of atoms in molecules (AIM), developed by Bader.^{292c} It was shown that the stability of the *n*-butonium cations $C_4H_{11}^+$ increases with an increase in the degree of substitution in the corresponding carbenium ion $C_4H_9^+$.

4.1.1.2. Reactions with B and B₂. The reactions of methane with B and B₂ have been shown to proceed *via* Olah's scheme. Calculations at the highest theoretical level suggest that the activation energies for B and B₂ insertions into methane are 16.2 and 4.1 kcal/mol, respectively (Scheme 101).

4.1.1.3. Reactions of Methane with Br₂•AlBr₃. The systems Br₂•*n*AlBr₃ for *n* ≥ 1 have been found to behave as superelectrophiles to initiate, under mild conditions, the cracking of linear alkanes and the selective monobromination of other saturated hydrocarbons more stable to fragmentation.^{146a,165,166} The nature of the complexes, which can be generated in the simplest system Br₂•AlBr₃, as well as the mechanisms of their reactions with methane and propane have been investigated.^{146b,294–296} A detailed study of the PES for the system Br₂•AlBr₃ by the semiempirical MNDO/PM3 method revealed five local minima,²⁹⁴ two of which respond to intermediates carrying positive charges of 0.35 and 0.45 au on the Br atoms. Only those two structures, both of which exhibited a pronounced ionic character, turned out to be important for methane activation. The initial stage of the interaction of methane with the Br₂•AlBr₃ complexes such as **60** (Scheme 102) involves barrierless electrophilic attack on the hydrogens or on the carbon.^{294,295} The H-coordination path leads to H₃CH•BrAlBr₄ as an intermediate (**61**), whereas C-coordination results in the formation of H₄C•BrAlBr₄. The C–H bond attacked in the H-solvated complexes is lengthened and weakened, whereas in all of the C-complexes, no significant changes in the structure of the methane fragment are observed, and therefore, methane activation does not take place. The mechanism of the reaction of methane with the Br₂•AlBr₃ complexes involves the transformation of the

H-solvated complex to a bromonium species, followed by the formation of CH₃Br and HBr. This is exemplified by the conversion of **61** to **63**. TS **62** for this and other similar transformations is of the *3c-2e* type that is characteristic of the classical Olah mechanism.

The overall reaction involves some steps with high-energy barriers, such as *ca.*30 kcal/mol for the formation of the bromonium complexes and *ca.* 20 kcal/mol for the transformation of these complexes into the final complex of CH₃Br and HBr with AlBr₃. The reaction of propane with Br₂•AlBr₃ occurs via a similar mechanism.²⁹⁶

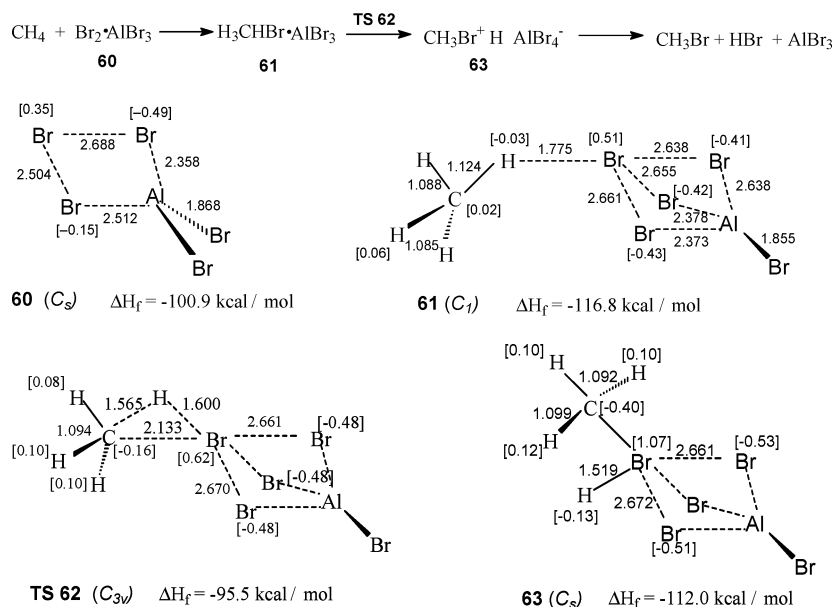
4.1.1.4. Reaction of Methane with F⁺. The results of theoretical studies of a model reaction of methane with the F⁺ cation leading to the intermediate CH₃F⁺H are in accord with F⁺ insertion into the C–H bond.^{297a} Failure to find the expected *3c-2e* TS was rationalized in terms of the high electrophilicity of the F⁺ and the barrierless formation of CH₃F⁺H. However, since single electron-transfer oxidation of CH₄ by the F⁺ to the radical-cation CH₄^{•+} is highly exothermic ($\Delta H = -115$ kcal/mol), doubts have been expressed^{297b} about the existence of F⁺, and a radical cation mechanism has been proposed for the fluorination of methane.

4.1.2. Reactions with Al(OH)₃ and Related Compounds

The mechanism of alkane activation by solid superacids, particularly zeolites, has been the topic of numerous studies.^{7c,58,59a,93} Various mechanistic schemes have been proposed, including proton transfer to C–H^{93c} and C–C^{93d} bonds, hydride abstraction by Lewis acid sites on the surface,^{7c,93e,h} heterolysis of the C–H bond with proton transfer to a negatively charged oxygen along with transfer of the methyl anion to a metal center,^{93f} and finally a concerted four-center mechanism.^{93g}

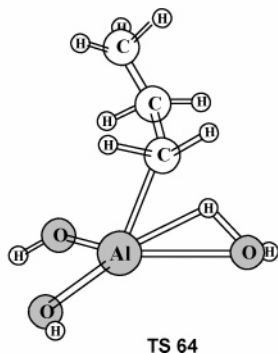
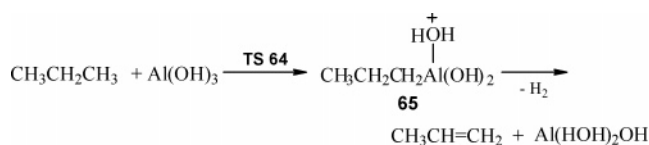
Interaction of propane with coordinatively unsaturated Al atoms has been studied by theoretical calculations to model the process occurring on the zeolites. DFT calculations with a large basis set have shown that the mechanism of chemisorption of propane *via* the primary C–H bonds on the tricoordinate aluminum center in Al(OH)₃ consists of aluminum insertion into the C–H bond followed by proton migration from Al to an O atom to give complex **65**.^{93a,b} In TS **64**, the imaginary frequency is the bending of the Al–H bond toward O, that is, hydrogen migration from the aluminum to oxygen. The distance of the migrating hydrogen from the oxygen is 20–25% longer than that for a normal O–H bond, whereas the Al–H distance is elongated by only 10–15% as compared to a conventional Al–H bond. Intermediate **65** can react further to form dihydrogen and propene which is apparently bound to an aluminum cluster (Scheme 103).

The tetracoordinate aluminum species (OH)₃Al(OH₂)_x (*x* = 1) reacts with the alkane *via* the same mechanism as its tricoordinate aluminum congener (*x* = 0), albeit with higher barriers for both the chemisorption and elimination steps. The critical feature of the mechanism of alkane cleavage by a coordinatively unsaturated aluminum compound is that the hydrogen of the C–H bond to be cleaved displays bonding interaction with the aluminum before migrating to the oxygen. These reactions involving insertion of aluminum into the C–H bond should not be considered as electrophilic alkane transformations. Instead, they are governed by mechanisms similar to those of alkane activation by transition metal complexes.^{93a,b}

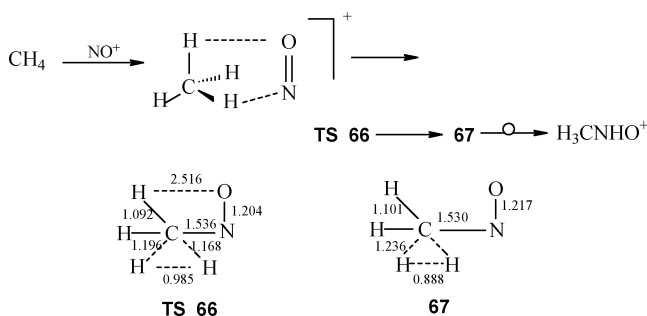
Scheme 102^a

^a In all cases atomic Mulliken charges are shown in square brackets.

Scheme 103



Scheme 104



4.1.3. Electrophilic Attack on Alkane Carbon Atoms

4.1.3.1. Reactions of Methane and Ethane with NO⁺.

On the basis of high level *ab initio* calculations, Schreiner et al.^{298,299} have concluded that the reactions of the NO⁺ cation with methane and ethane involve neither C–H bond insertion nor 3*c*-2*e* bonding between the C–H bond and the electrophile. These reactions involve direct electrophilic attack of NO⁺ on a carbon atom (Scheme 104).

Previously, Schreiner^{298,299} suggested that alkanes react with NO⁺ by developing a nonbonding electron pair on the carbon atom along with the synchronous formation of a 3*c*-2*e* bond between the carbon and H₂. Comments have been made on this mechanism.³⁰⁰ More recently, in the development of a new conception of an inner-sphere SET (single electron transfer) mechanism for reactions of alkanes with weak electrophiles such as NO⁺ which are nevertheless strong oxidizers, Fokin and Schreiner³⁷ concluded that the most realistic representation of the reactions of methane and ethane with NO⁺ is inner-sphere electron transfer from the alkane to the electrophile, and that free alkane radical cation transfer can be ruled out. This conclusion was based on the structures of the CH₄ and C₂H₆ fragments of the TSs being very close to those of the CH₄⁺ and C₂H₆⁺ radical cations. Transfer of large charges to the electrophile occurs in each case.

4.1.3.2. Dibromination of Methane with Br₂·AlBr₃.

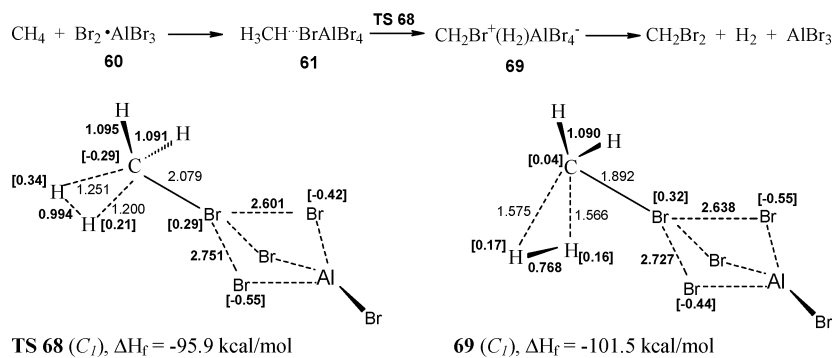
Another example of a reaction involving attack on a saturated C atom is the dibromination of methane with Br₂·AlBr₃.^{294,295} (Scheme 105). This process differs from the methane monobromination reaction by the same complex already discussed and illustrated in Scheme 102 above.

Intermediate **69** in Scheme 105 represents a donor–acceptor complex of the cation CH₂Br⁺ with a quasimolecular H₂. The positively charged Br atom is “solvated” by the AlBr₄[−] anion in a tridentate fashion. The structures of TS **68** and intermediate **69** are similar to those of TS **66** and intermediate **67**, respectively, which were found by Schreiner et al.^{298,299} The dibromination reaction occurring *via* the Schreiner mechanism has a lower barrier than that of the monobromination reaction that proceeds *via* the Olah mechanism with the former pathway being favored by 8.8 kcal/mol overall.

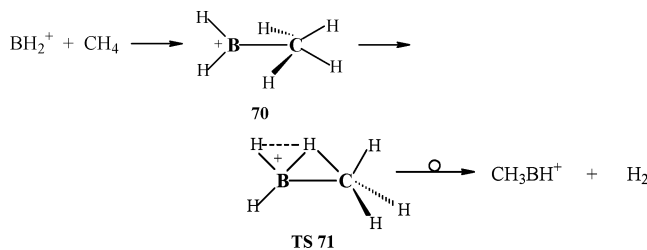
4.1.3.3. Reactions with BH₂⁺.

The reactions of both methane and ethane with BH₂⁺ also involve electrophilic attack on the C atom to form stable five-coordinate carbon intermediates (e.g., for **70**, $\Delta H_f^\ddagger = ca.$ 33 kcal/mol). TS **71** for the transformation of **70** into the B(H₂)⁺CH₃ shown in Scheme 106 is more complex as compared with those shown in Schemes 104 and 105. The reaction of ethane occurs

Scheme 105



Scheme 106



similarly.³⁰¹ The intermediates $\text{B}(\text{H}_2)^+\text{HR}$ ($\text{R} = \text{Me}$ or Et) eliminate H_2 to give RBH^+ .

4.1.3.4. Reactions of Hydroxylation. Oxidation of saturated hydrocarbons in general, a key reaction in biological processes,^{38–45} as well as electrophilic hydroxylation of saturated hydrocarbons^{304–305} have been the subject of intensive experimental and theoretical studies. Bach and co-workers have made a significant contribution to the theoretical studies of electrophilic hydroxylation of alkanes with water oxide^{303a} and the hydroperoxonium cation.^{303b} A frontier molecular orbital model (FMO) was suggested for the attack of the electrophilic oxygen atom on saturated hydrocarbons.³⁰⁵ The qualitative FMO analysis supported by *ab initio* molecular orbital calculations led to the conclusion that considerations in terms of isolated $\sigma\text{-C-H}$ or C-C bonds can be an oversimplification. In the idealized FMO model, the electrophilic reagent E is defined as having an electron-deficient orbital and an unshared electron pair. A series of TSs and intermediates has been found for alkane hydroxylation with water oxide^{303a} and the hydroperoxonium cation.^{303b} The suggested mechanism involves the attack of an electrophile on the C-atom with simultaneous 1,2-hydrogen shift of the proton from the alkane to the lone electron pair of the electrophile. Therefore, Bach et al. have described a novel kind of electrophilic alkane reaction which involves electrophilic attack on the C-atom with the TS being of the *3c-4e* type (Scheme 107).

The reaction of alkanes with carbenes occurs via a similar mechanism and involves electrophilic attack of the carbene C-atom on the alkane carbon in synchrony with proton transfer to the carbene HOMO.³⁰⁴

4.1.3.5. Hydroxylation by Cytochrome P-450, Monooxygenases, and Their Analogues. The homolytic “rebound mechanism” involving the formation of a radical followed by its rebounding with the OH^\bullet radical had been initially proposed,³⁰⁶ and for a long time remained widely accepted as the mechanism of alkane hydroxylation with cytochrome P-450, monooxygenases, and their analogues (Scheme 108).³⁰⁷

In the early 1990s, however, it became clear that such reactions are more complicated than initially believed and

cannot be rationalized in terms of the simple radical mechanism.^{308–311} For example, the hydroxylation reaction of 1-methyl-2-phenylcyclopropane with MMO occurs without isomerization and ring-opening. To account for this observation by the radical mechanism, one must assume that the rate constant for the “oxygen rebound” step is higher than $4 \times 10^{13} \text{ s}^{-1}$, which is hardly realistic.^{309,310} The oxidation of methylcubane with MMO leads to homocubane-1-ol, which cannot be formed via a radical pathway.³¹¹ The thermodynamics for the primary and secondary alkane hydroxylation also contradict the radical mechanism.³⁰⁹ The results of C–H hydroxylation with monooxygenases and their analogues indicate that in addition to the classical radical mechanism, there is another, parallel, pathway involved. Shestakov and Shilov suggested a pentacoordinate carbon mechanism involving the addition of the oxygen atom of the Fe=O group to the carbon atom of the C–H bond to form an intermediate Fe-O-CH_4 , followed by the insertion of the O atom into the C–H bond, leading finally to an alcohol.^{43,309}

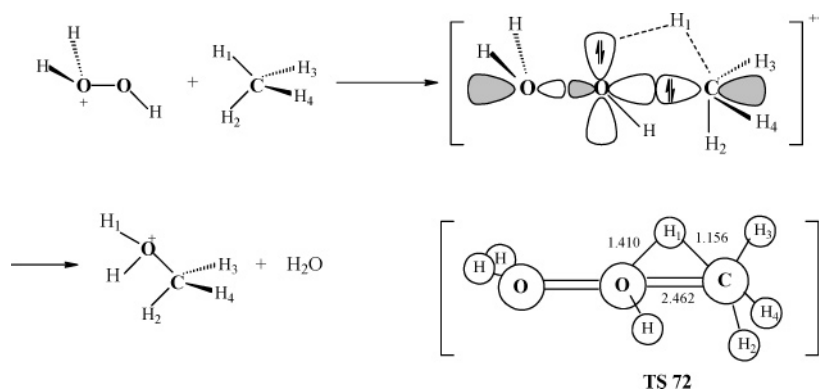
On the basis of the DFT calculations for methane abstraction by bare FeO complexes with a differently charged metal atom, Yoshizawa and coauthors suggested a concerted methane hydroxylation mechanism which also involves a TS with a pentacoordinate carbon. However, the TS calculated³¹² contained a $\text{H}_4\text{C} \rightarrow \text{Fe}$ rather than a $\text{H}_4\text{C} \rightarrow \text{O-Fe}$ interaction. Two types of H atom abstraction from methane were considered. The H-abstraction *via* four-centered TS **73** (in the sextet state of the FeO^+) was shown to be energetically more favorable by 4.5 kcal/mol than the direct H-abstraction *via* TS **74** with the linear C–H–O–Fe array (Scheme 109).³¹²

The concerted Yoshizawa mechanism³¹² should be classified as a more complex example of a reaction involving electrophilic attack on the C atom with simultaneous proton transfer from the alkane to the lone electron pair on O as the Fe and H atoms approach each other.

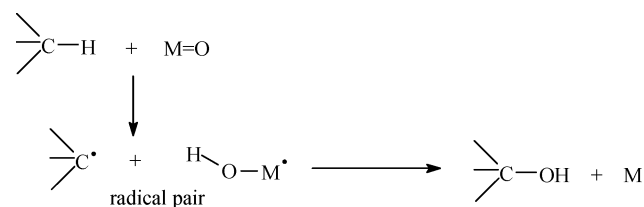
It is beyond the scope of this review to cover the broad area of mechanistic studies of alkane hydroxylation by cytochrome P-450 and similar species. In reference 308c, a radical cation mechanism was suggested for methane hydroxylation by cytochrome P-450 (see also reference 37 and cited works on this topic).

4.1.4. Electrophilic Attack on Hydrogen with “Open” 3c-2e Bonding

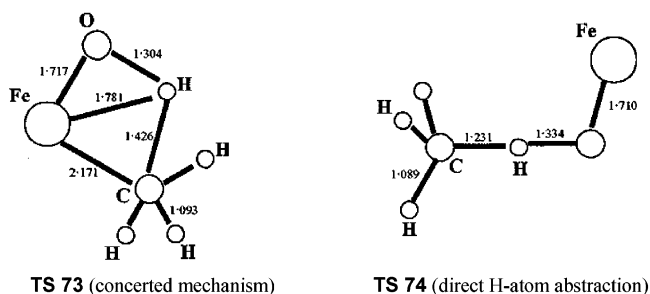
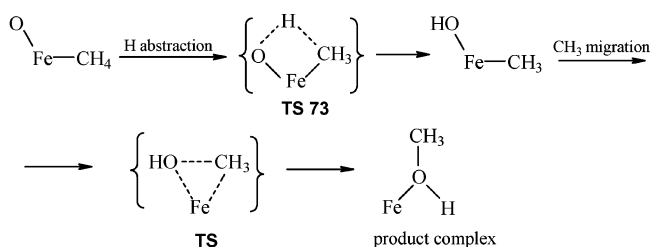
Open *3c-2e* bonds containing hypervalent hydrogen are not as widely spread in organic chemistry as in the chemistry of inorganic and organometallic compounds.⁹⁰ Nonetheless, some examples of such bonds are known (Scheme 110).

Scheme 107^{303b}

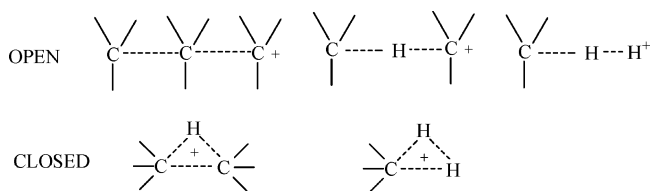
Scheme 108



Scheme 109

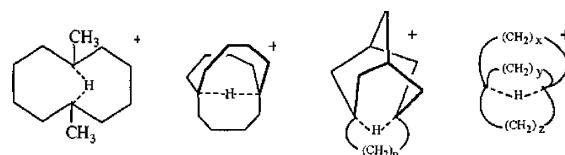


Scheme 110



“Closed”, that is, cyclic $3c-2e$ bonds have triangular geometry with bonding interaction involving all three atoms, as in Scheme 110, whereas “open” $3c-2e$ bonds are roughly linear, with bonding interaction between the terminal atoms being negligible. Neither $(C-C-C)^+$ nor $(C-C-H)^+$ open $3c-2e$ bonds are known.³¹³ The existence of open C-H-C bonds was proposed by Prelog et al. more than 40 years ago.^{314a} First Prelog, and soon after that Cope et al.,^{314b} demonstrated that derivatives of medium-sized cycloalkanes undergo direct transannular shifts upon solvolysis. These transformations occur *via* TSS, which resemble μ -hydrido-bridged carbocation structures. Sorensen was the first to

Scheme 111

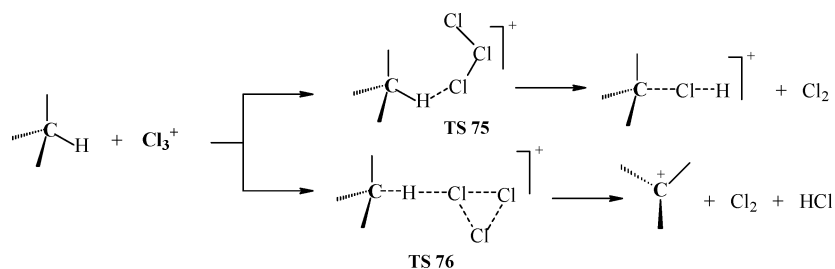


prove, in 1978, the existence of μ -hydrido-bridged carbocations containing $3c-2e$ bonds.³¹⁵ In their meticulous NMR studies, Sorensen and coauthors have demonstrated the presence of stable C-H-C bonds in the 1,6-dimethyl-1-cyclodecyl cation and several related ions generated from the corresponding alcohols upon treatment with fluorosulfonic acid at -120 °C.³¹⁵ Since then, other open $3c-2e$ cations, including some that are stable under normal conditions, have been prepared and studied both experimentally and theoretically by several research groups.^{316,317} Selected examples of μ -hydrido-bridged carbocations containing $3c-2e$ bonds are presented in Scheme 111.

MO calculations have been carried out on a series of model μ -hydrido-bridged carbocations such as $H_3C-H-CH_3^+$, $Et-H-Et^+$, and $Pr-H-Pr^+$ (MINDO and STO-4G *ab initio*), and *tert*-Bu-H-*tert*-Bu⁺ (MNDO/3).³¹⁷ These calculations have shown that in all cases the C-H-C angle is close to 180° , that the hybridization of the bridged carbons is intermediate between sp^2 and sp^3 , and that the μ -hydrogen has a slight negative charge and sits in a very “loose” potential. This hydrogen can move easily and substantially up, down, or sideways with little overall change in the total energy. After 16 years of DFT and *ab initio* MP2 studies, M. Boronat et al.³¹⁸ came to a similar conclusion about the reactions between alkanes and carbocations. All these reactions were found to proceed *via* the same two-step mechanism consisting of the formation of a stable tight cationic intermediate $[R\cdots H\cdots R']^+$ from R^+ and $R'H$ and its decomposition to products, R^+ and $R'H$ or R'^+ and RH . The formation of the cationic intermediate from either set of partners occurs without an activation barrier. It was shown that, while both methods produced similar results for the geometry of the intermediates, the DFT calculations failed to describe the energetics of the complex formation. Stable carbenium ions having a nonclassical ($3c-2e$) C-H-C bond have been shown to mediate in the conventional way a number of acid-catalyzed reactions of hydrocarbons, such as hydride transfer, alkylation, dehydrogenation, and disproportionation.³¹⁸

Recently, Siehl et al. reported a detailed quantum chemical study of the mechanism of degenerate 1,2-, 1,3-, and 1,4-hydride shifts in a series of acyclic tertiary C_6-C_8 carbocations by using DFT-hybrid and Moller-Plesset perturbation

Scheme 112



theory methods.³¹⁹ It was shown that the B3LYP level of theory does not correctly describe systems with hypercoordinated hydrogens involved in $3c-2e$ C–H–C bonds. In contrast, the MP2 method with basis sets of 6-311 G(d, p) turned out to be workable. A comparative study revealed similar potential energy profiles for the 1,2-, 1,3-, and 1,4-hydride shifts. Two global minima corresponding to equivalent open-chain carbocation intermediates, as well as a local minimum corresponding to a symmetrical hydrido-bridged high-lying intermediate, and two maxima corresponding to unsymmetrical hydrido-bridged TSs were found on the PES. The energy barriers for the 1,2-, 1,3-, and 1,4-hydride shifts were calculated at 3.9, 4.2, and 7.5 kcal/mol, respectively, in good agreement with the experimental data.³¹⁹

4.1.4.1. Reactions of Saturated Hydrocarbons with Br^+ and Polyhalogen Electrophiles. The reaction of methane with “naked” Br^+ has been studied using the MNDO/PM3 method as a model for a mono-positively charged bromine-containing species.³²⁰ The reaction starts with barrierless addition of the electrophile to methane to form $\text{H}_3\text{C}-\text{H}-\text{Br}^+$, which contains a hypervalent hydrogen. The involvement of such a powerful electrophile as “naked” Br^+ results in immediate activation of the C–H bond *via* hydride abstraction from the methane molecule. Nonempirical, *ab initio* HF/6-31G, 6-31G**, DZV, and DZV** calculations³²¹ led to the same conclusion. However, the *ab initio* HF methods pointed to a more significant elongation of the C–H bond and enhanced transfer of the positive charge to the methyl group in the almost linear transition state, as compared with the pathway calculated by the MNDO/PM3 method. The *ab initio* HF calculations with an increased basis showed that in the system $\text{CH}_4 + \text{Br}^+$ the potential barrier is very small, *ca.* 1 kcal/mol, and the transformation into the bromonium ion HBr^+CH_3 is virtually barrierless. In other words, the high level *ab initio* calculations of the reactions of CH_4 and C_3H_8 with the Br^+ indicate that the Br atom in the Br^+HR species “sits in a very “loose” potential; it can be moved substantially up, down, or sideways with little overall change in the total energy”.³¹⁷

Linear C–H–X bonds have been found in the TSs of reactions of isobutane and adamantane with weaker electrophiles which are nonetheless strong oxidizers, such as HX_2^+ and X_n^+ ($n = 3-7$, X = Cl, Br).¹⁶³ Two distinctly different types of TSs involving the attack of the polyhalogen electrophiles at the H atom of isobutane were calculated at the MP2 and B3LYP level of theory with the 6-31G** and 3-21G* basis sets. The first type of TS is the early nonlinear structure $\text{R}-\text{H}-\text{E}^+$ such as **75** in Scheme 112. It contains only a slightly elongated C–H bond and has a negligible electron-transfer contribution because there is little charge transfer from isobutane to the electrophile. The second type is exemplified by a linear TS such as **76**, in which the C–H bond is considerably elongated and there is significant charge

transfer from the alkane to the electrophile. The transformations *via* TSs such as **75** are viewed as electrophilic reactions, while the processes involving TSs similar to **76** have been classified as inner electron-transfer reactions.

The H-coupled electron-transfer mechanism has been supported by computation as well as by experiment for adamantane halogenation by polyhalogen electrophiles.¹⁶³ The TSs were characterized by the virtually linear structure of the $\text{Ad}-\text{H}-\text{X}$ moiety and significant charge transfer from AdH to the electrophile, as is indicated by the structures of the hydrocarbon fragment in the TS which are similar to those of the radical cation Ad^+ . The large observed kinetic isotope effect supports this mechanism.

As seen from the above, hydrido-bridged cations can exist as TSs and even stable intermediates. Moreover, in some cases, such cations are lower in energy than their nonbridged isomers. We conclude, therefore, that electrophilic reactions of alkanes can occur *via* $[\text{R}-\text{H}-\text{E}]^+$ TSs or intermediates.

4.2. The Nature of Complexes Responsible for the Super-electrophilicity of Polyhalomethanes in the Presence of Aluminum Halides or Protic Superacids

The nature of the reactive species derived from polyhalomethanes in the presence of protic or aprotic superacid is intriguing. Unlike the tetrahalomethane– SbF_5 systems (Section 2) their aluminum halide counterparts have not been studied by spectral methods. Polyhalomethyl cations are likely generated from polyhalomethanes in the presence of strong Lewis acids, as is suggested by the spectroscopy data for the polyhalomethane– SbF_5 systems in solution¹²² and in the solid state,¹²³ as well as by the established fact of aluminum halide-induced polyhalomethane ionization.^{120,121} Both semiempirical and nonempirical calculations of the $\text{CCl}_4 \cdot n\text{AlCl}_3$ and $\text{CBr}_4 \cdot n\text{AlBr}_3$ ($n = 1-3$) complexes and related CX_3^+ , CHX_2^+ , CHX^{2+} , CX_2^{2+} ions have been carried out. These studies indicated that the polyhalomethyl cations (X = Cl, Br, I, but not F), both free and incorporated in cationic CX_3^+Y^- and dicationic $\text{CX}_2^{2+}\text{Y}_2^-$ ($\text{Y} = \text{AlBr}_4$ or Al_2Br_7) complexes, are not carbenium ions but rather are halonium cations or cationic complexes containing positively charged halogen atoms directly bonded to the carbon, that is, $\text{X}_2\text{C}=\text{X}^+$ or $\text{X}^+=\text{C}=\text{X}^+$.^{296,322} In other words, electron density transfer from the lone electron pairs of the halogen to the carbocation center (Scheme 4) is significant to the extent that a large positive charge is localized on the halogen atoms, with the C-atom being electroneutral or negatively charged. Similar results have been obtained by DFT and *ab initio* calculations.^{122b,323-327} Selected data on the charge distribution and bond lengths in the polyhalomethyl cations are presented in Tables 4 and 5. These halonium cations differ fundamentally from the classical carbenium (e.g., CF_3^+ , CHF_2^+ , CF_2^{2+}) and halonium ions.³²⁸

Table 4. Calculated Atomic Mulliken Charges of CX₃⁺, CX₂²⁺, and Related Ions^b

species	q, au		species	q, au		
	X	C		X	C	H
CF ₃ ⁺	-0.04 ÷ -0.18	1.12 ÷ 1.55	HCF ₂ ⁺	0.07	0.54	0.31
CCl ₃ ⁺	0.34 ÷ 0.39	-0.02 ÷ -0.17	HCCl ₂ ⁺	0.35	0.04	0.25
CBr ₃ ⁺	0.43 ÷ 0.51	-0.29 ÷ -0.53	HCBR ₂ ⁺	0.46	-0.17	0.25
CI ₃ ⁺	0.51 ÷ 0.63	-0.52 ÷ -0.90	HCI ₂ ⁺	0.53	-0.29	0.23
CF ₂ ²⁺	0.47	1.06				
CCl ₂ ²⁺	0.94	0.12				
CBr ₂ ²⁺	1.04	-0.07				
CI ₂ ²⁺	1.04	-0.08				

^aMP2/6-31G*, MP2/LANL2DZ^{122b}, MP2/VDZ+P,³²⁵ DFT,^{326,327} SCF-RHF/6-31G,³²³ AM1.³²² ^bSCF-RHF/6-31G,³²³ AM1.³²²

Table 5. Calculated Bond Lengths (Å) of HCX₃^a, CX₃⁺ Cations^b, and CX₂²⁺ Dications^c

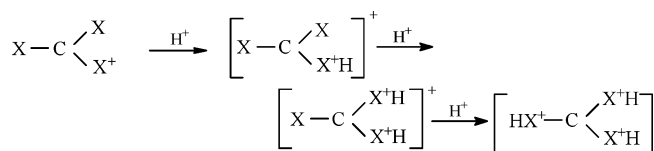
bond lengths	HCX ₃	CX ₃ ⁺	CX ₂ ²⁺
C–F	1.35	1.24 ÷ 1.30	1.21
C–Cl	1.78	1.65 ÷ 1.72	1.50
C–Br	1.94	1.81 ÷ 1.89	1.65
C–I	2.17	1.96 ÷ 2.07	1.84

^aMP2/VDZ+P,³²⁵ ^bMP2/VDZ+P,³²⁵ MP2/6-31G*, MP2/LANL2DZ,^{122b,324} SCF-RHF/6-31G,³²³ DFT,^{122b,324,326,327} AM1.³²² ^cSCF-RHF/6-31G,³²³ AM1.³²²

Calculations at the MP2/VDZ+P and MP2/VTZ+D+P levels have been reported for the cations AX₃⁺ and AXH₂⁺ (A = C, Si, Ge, Sn, Pb; X = F, Cl, Br, I).³²⁵ In contrast with other data,^{122b} the π -donating ability of the halogens was shown to increase in the order F < Cl < Br < I for all of the cations. The heavy-atom homologues of the C⁺ (Si⁺, Ge⁺, Sn⁺, Pb⁺) and those of the boron atom (Al, Ga, In, Tl) displayed the same trends for the halogens, except the π -donation and the thermodynamic stabilization/destabilization were markedly less pronounced than for the C⁺ and B. Stabilization of the carbenium ions by adjacent heteroatoms has been considered for mono- and polysubstituted carbocations.^{329–332} Grutzmacher and co-workers have shown that the homologous ions C(XH)₃⁺ (X = S, Se, Te) also differ greatly and fundamentally from carbocations, in that the carbon atom is negatively charged as a result of effective X to C donation in the σ - and π -systems. For example, in the trithiocarbenium ions, the C-atoms are indeed electron-deficient, but the sum of the SH group charges, at +0.750 each, far exceeds unity. It was therefore concluded that “A negative charge $q_C = -1.248$ a.u. is revealed for the “electron-deficient” carbon!”³³²

The question arises as to whether the superelectrophilicity of the systems under consideration is due to the formation of the CX₃⁺Y⁻ cationic complexes or if there are other, even more electrophilic, cations that determine the specific reactivity of these systems. One might expect that protonation of polyhalomethyl cations or the formation of donor–acceptor complexes of these cations with Lewis acids would enhance the electrophilicity. Such multicharged cations might be responsible for the superelectrophilic properties of polyhalomethanes in the presence of protic and aprotic superacids (Scheme 113), as has been proposed for the systems containing acylium salts in the presence of strong protic and Lewis acids.^{99,100,135–144}

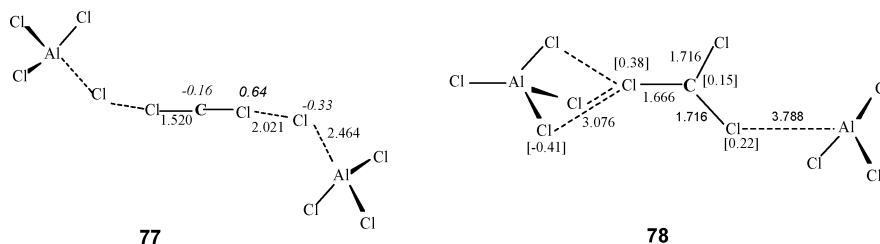
Protonated halomethyl cations have been studied computationally.³²⁴ Nonempirical calculations did not contradict the assumption that polyhalomethanes are converted to multi-

Scheme 113

charged ions in protic superacids. For example, monoprotation of CCl₃⁺ required only 4.0 kcal/mol, and the diprotonated dications CBr₃H₂²⁺ and CCl₃H₂²⁺ appeared more stable than the corresponding monocations CBr₃⁺ and CCl₃⁺ by 15.5 and 44.7 kcal/mol, respectively. Furthermore, the high barriers to deprotonation of the thermodynamically very unstable multiprotonated polyhalomethanes suggested that, once formed, they should be kinetically stable. For instance, the barriers to deprotonation of CBr₃H₂³⁺ and CBr₃H₃⁴⁺ were calculated at 74.3 and 37.1 kcal/mol, respectively.

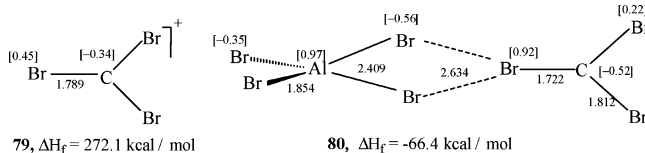
In contrast, theoretical studies of the systems CCl₄•2AlCl₃ and CCl₃⁺ → AlCl₃ led to a different conclusion. For the systems CCl₄•2AlCl₃, two local minima were found on the PES by both AM1 and *ab initio* calculations at the STO-3G basis,³²³ corresponding to complexes **77** and **78** in Scheme 114.

Intermediate **77** contains a linear fragment Cl⁻–Cl⁺–C–Cl⁺–Cl⁻ whose terminal Cl atoms are bonded to two molecules of AlCl₃ via donor–acceptor bonds. The local minimum of **77** lies higher by 90 kcal/mol than the major one corresponding to CCl₄. The linear fragment of **77** may be considered as an isomer of CCl₄ with extremely polarized C–Cl bonds. The positive charges on the chlorine of the CCl₂²⁺ moiety in complex **77** were the highest among all complexes found for the systems CCl₄•*n*AlCl₃, though its formation from CCl₄ and Al₂Cl₆ is strongly endothermic (97.7 kcal/mol, AM1). An *ab initio* study produced similar results. Intermediate **78** represents a cationic complex with one Cl atom of the CCl₃⁺ bonded tridentatively to the AlCl₄⁻, and another Cl coordinated to a molecule of AlCl₃ via a very weak donor–acceptor bond. The maximal charge on the chlorine in complex **78** is only 0.03 au larger than the one determined for the Cl atom in the cationic complex CCl₃⁺AlCl₄⁻. Attempts to find complex **78** by *ab initio* calculations at the STO-3G basis were unsuccessful. Recent DFT calculations of the system CBr₄•2AlBr₃ led to similar results.³²⁷ Therefore, quantum-chemical calculations have not confirmed the assumption that the reactivity of polyhalomethanes in the presence of aluminum halides is due to the formation of dicationic species. The calculations suggest that both systems CX₄•*n*AlX₃ with *n* = 1 or 2 might be precursors to similar systems such as nonpolar donor–acceptor complexes CX₄ → E (E = AlCl₃ and Al₂Cl₆) or ionic complexes of the CX₃⁺Y⁻ (Y = AlX₄⁻, Al₂X₇⁻) containing positively charged X. Importantly, the charges at the superelectrophilic center of the halomethyl cations are very close for both systems. But if CX₄•*n*AlX₃ and related systems generate similar complexes of the halomethyl cations CX₃⁺ for both *n* = 1 and *n* = 2, then why do the complexes arising from different *n* values differ so sharply in reactivity? We propose that the dissimilarity is due to a different content of donor–acceptor and ionic complexes in these systems in a solvent. Indeed, DFT/B3LYP/6-31G* calculations have shown that, at *n* = 1, the donor–acceptor complexes are more stable than the ionic complexes by 7 kcal/mol, whereas for *n* = 2, the energy difference is only 0.3 kcal/mol. If the CH₂Cl₂

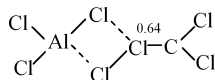
Scheme 114^a

^a The numbers were calculated by the AM1 (atomic charges italicized) and *ab initio* methods at the STO-3G basis. The atomic charges were calculated by the Mulliken method.

Scheme 115



solvent effect is included, these calculations have shown that, at $n = 2$, ionic complexes become even more stable than donor–acceptor complexes, while at $n = 1$, such substantial changes do not occur.³³³ These results suggest that only the donor–acceptor complexes with a small positive charge on the halogen atom are present in the equimolar systems, whereas in the systems with excess aluminum halide, polar complexes with high positive charges on the halogens are produced. Similarly, the $\text{RCOX} \cdot n\text{AlX}_3$ exist in solution as donor–acceptor complexes that are unreactive toward alkanes ($n = 1$) or mixtures of such complexes with much more reactive acylium salts ($n = 2$).^{99,100,135} The bidentate complex, which has a large positive charge on the nodal chlorine atom, has been considered³²³ as the most likely candidate for the role of a key superelectrophile in the $\text{CCl}_4 \cdot n\text{AlCl}_3$ systems.



The charge on the tricoordinate chlorine atom amounts to +0.64 (*ab initio*) or +0.54 au (AM1), which is greater than in the CCl_3^+ cation by 0.13 (*ab initio*) and 0.21 au (AM1). Similarly, two isomeric bidentate complexes containing very large positive charges of 0.92 and 0.87 au on the bromine atom have been found on the PES for the $\text{CBr}_4 \cdot n\text{AlBr}_3$ system^{325,326} (see section 4.3).

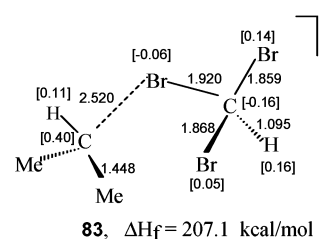
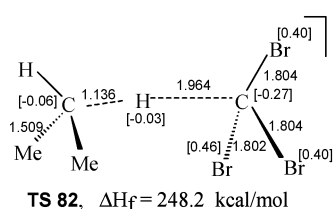
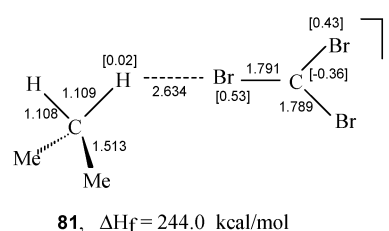
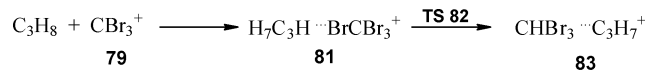
4.3. Mechanisms of Reactions of Alkanes with Bromine-Centered Superelectrophiles

4.3.1. Reactions of Propane with CBr_3^+ and $\text{CBr}_3^+ \text{AlBr}_4^-$

The results of mechanistic studies of reactions of alkanes with tribromomethyl cationic complexes and the parent “naked” cations are particularly important for the understanding of electrophilic reactions of alkanes. As mentioned above (section 4.2), the CBr_3^+ cation and the $\text{CBr}_3^+ \text{AlBr}_4^-$ cationic complexes generated from the $\text{CBr}_4 \cdot \text{AlBr}_3$ systems contain strongly positively charged bromine atoms. The calculated structures of the CBr_3^+ cation (**79**) and one of the two rotamers of $\text{CBr}_4 \cdot \text{AlBr}_3$ (**80**) with the bridging Br atoms carrying large positive charges^{296,334} are shown in Scheme 115.

Both semiempirical (MNDO/PM3)³³⁴ and nonempirical (DFT-B3LYP/LANL2DZ, DFT-PBE)³²¹ calculations pointed

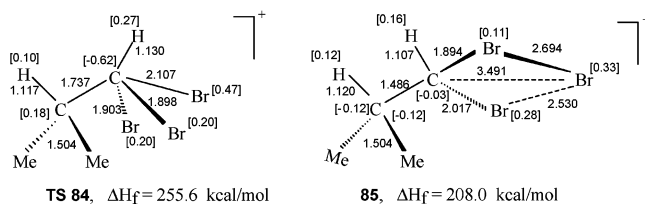
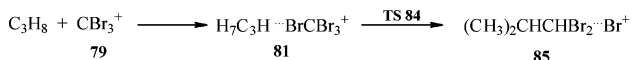
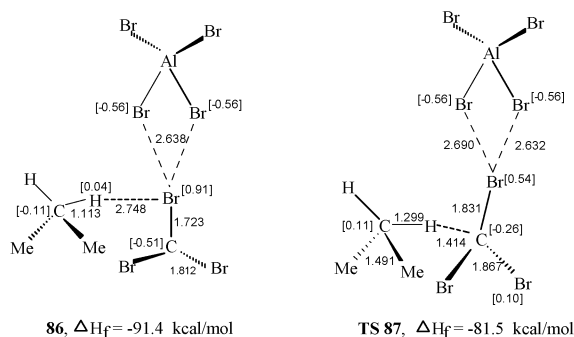
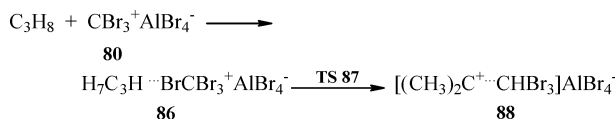
Scheme 116. Results of the MNDO/PM3 Calculations³³⁴ for the Reaction of Propane with CBr_3^+



to the same mechanistic scheme for the reactions of propane with “naked” CBr_3^+ (**79**) and the cationic complex $\text{CBr}_3^+ \text{AlBr}_4^-$ (**80**). In both cases, the propane molecule forms weak adducts with the CBr_3^+ cation or a molecular complex, $\text{CBr}_3^+ \text{AlBr}_4^-$. In some of these adducts, the H atoms of the methylene group coordinate with the Br atom carrying the largest positive charge. The $\text{H} \cdots \text{Br}$ distance shortens, and at a certain point, the hydrogen migrates to the C-atom of the CBr_3^+ fragment. The TSs are linear for both reactions.

For the reaction of propane with CBr_3^+ , all of the above computational methods led to very similar structures for the initial solvate and for the TS for the transformation of the initial solvate to the final product. The structure of the latter, however, is predicted to be different by different types of calculations. The MNDO/PM3 calculation³³⁴ suggests that the final product is a solvate, ${}^i\text{Pr}^+ \cdot \text{Br}_3\text{CH}$ (**83**), whereas the DFT-B3LYP/LANL2DZ and DFT-PBE methods point to the formation of a bromonium ion, ${}^i\text{PrBr}^+ \text{CHBr}_2$.³²¹ Scheme 116 shows the results of the MNDO/PM3 calculations for the reaction of propane with CBr_3^+ .

In addition to the mechanism shown in Scheme 116, another pathway for the reaction of propane with the CBr_3^+ cation (reductive alkylation; Scheme 117) has been demon-

Scheme 117. Results of the MNDO/PM3 Calculations for Reductive Alkylation of the CBr_3^+ Cation by Propane³³⁴**Scheme 118**

strated.³³⁴ The reductive alkylation pathway results in complex **85**, in which the Br^+ is coordinated to two geminal Br atoms of dibromoisobutane in a bidentate fashion. TS **84**, containing a pentacoordinate carbon, is formed as a secondary H atom of propane migrates to the electrophile and the emerging Pr^+ cation approaches the CBr_3H . The potential barrier for this pathway (Scheme 117) is 10.2 kcal/mol higher than for the one shown in Scheme 116.

Scheme 118 illustrates the results of MNDO/PM3 calculations for the reaction of propane with $\text{CBr}_3^+\text{AlBr}_4^-$. Similarly to the reaction presented in Scheme 116, the activation starts with the formation of solvate **86**, in which one hydrogen atom of the methylene group is weakly bound to the $\text{CBr}_3^+\text{AlBr}_4^-$ complex *via* the Br atom carrying the largest positive charge. As the fragments of the solvate are brought closer together, the coordinated H atom migrates to the carbon of the CBr_3^+ moiety. TS **87** is almost linear. The final product (**88**) is an electrostatically bonded complex of Br_3CH , $^i\text{Pr}^+$, and AlBr_4^- with the bonding energy calculated at 82.7 kcal/mol. Similar results were obtained by DFT-PBE calculations.³²¹

In both reactions (Schemes 116 and 118), the initial slight energy increase is due to the repulsion of the fragments in the “solvates”, which is caused by bringing the two together. A sharp decrease in energy (up to 40 kcal/mol) then follows, which corresponds to the transformation of the initial “solvates” (**81** and **86**) into much more energetically favorable complexes **83** and **88**. The barriers for these migrations were found to be low for both systems with the values for the pathways shown in Schemes 116 and 118 being approximately 3 and 6 kcal/mol, respectively. Both overall processes are exothermic, with that corresponding to Scheme 116 being exothermic by 41.3 kcal/mol, and that corresponding to Scheme 118 by 31.4 kcal/mol. Thus, the reaction

mechanism remains unchanged upon replacement of “naked” CBr_3^+ with the neutral complex $\text{CBr}_3^+\text{AlBr}_4^-$. In both cases, H-migration from the secondary carbon to the C-atom of the electrophile occurs without the formation of cyclic *3c-2e* transition states or intermediates.

4.3.2. Reaction of Methane with CBr_3^+

Mechanisms of the reactions of methane with “naked” CBr_3^+ and the $\text{CBr}_3^+\text{AlBr}_4^-$ cationic complex are of special interest. Computational studies of these reactions have been carried out by PM3,²⁹⁶ DFT-B3LYP/6-31G (d), and DFT-PBE/3z methods,^{321,326,327} all of which lead to similar results. Both reactions were found to proceed *via* a novel and unprecedented mechanism. The model reaction of methane with CBr_3^+ involves the formation of solvate **89** in Scheme 119, which transforms to $\text{CH}_3\text{Br}^+\text{CBr}_2\text{H}$, a bromonium cation (**91**). TS **90** on the way to **91** from **89** provides the pathway for hydride transfer from methane to CBr_3^+ , which is facilitated by interaction of a lone pair on the Br atom with the emerging methyl cation. This nucleophilic assistance is confirmed by the Br–C distance in **90**, which is shorter by 0.72 Å than the sum of the van der Waals radii.³³⁵ The structure of cyclic *4c-4e* TS **90** is shown in Scheme 119.

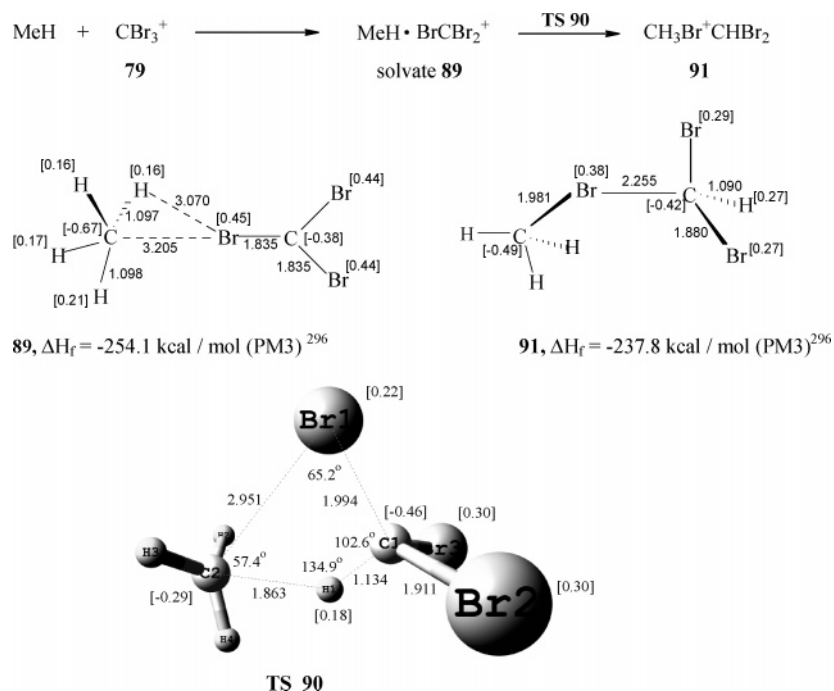
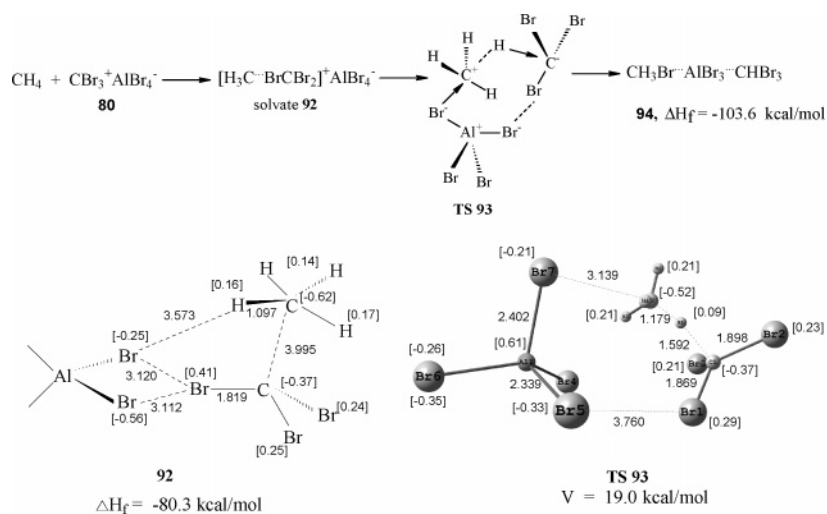
This is the first example of an alkane reaction involving hydride abstraction with nucleophilic aid. The peculiarity here is that the process involves a cation providing nucleophilic assistance. Note that the alternative Olah mechanism for methane bromination with such a powerful electrophile as “naked” CBr_3^+ displays, according to the calculations, a very high barrier of 63.3 kcal/mol. The nucleophilic assistance apparently brings the barrier down by approximately 20 kcal/mol.²⁹⁶

4.3.3. Reactions of Methane with the $\text{CBr}_3^+\text{AlBr}_4^-$ Cationic Complex

The formation of solvate **92** in Scheme 120 is the first step of the reaction of methane with $\text{CBr}_3^+\text{AlBr}_4^-$. TS **93** for the conversion of **92** to the final complex $\text{CH}_3\text{Br}\bullet\text{AlBr}_3\bullet\text{CHBr}_3$ (**94**) exhibits a cyclic planar structure.^{296,326,334} One might view **93** as a transition state that is electrostatically stabilized by charge transfer. Although well-known in organic and organometallic chemistry,^{264,336} such transition states had no precedent in early reports on electrophilic reactions of alkanes.

The reaction of methane with $\text{CBr}_3^+\text{AlBr}_4^-$ also involves nucleophilic assistance for electrophilic cleavage of the C–H bond. In this case, however, it is the Br atom of the AlBr_4^- anion that provides the required nucleophilic assistance. As a result, the reaction of methane with the complex $\text{CBr}_3^+\text{AlBr}_4^-$ is more facile than with “naked” CBr_3^+ .

Electrophilic reactions of alkanes with nucleophilic assistance (see sections 4.3.2 and 4.3.3) fit well in the general context of widespread electrophilic reactions with nucleophilic aid. One should distinguish two types of electrophilic reactions of alkanes with nucleophilic assistance. The first type is realized in some reactions involving electrophilic attack on a C-atom of an alkane. In the resulting pentacoordinate carbon complex, the hydrogen of the C–H bond is more acidic and therefore can interact with a heteroatom of the electrophile bearing a lone electron pair. The nucleophilic assistance is hence provided to the H-atom. The second type is observed when the H-atom is more hydridic in nature and the nucleophilic interaction involves the C-atom.

Scheme 119. Model Reaction of Methane with CBr_3^+ According to the DFT-PBE/TZ Method^{326,327}Scheme 120. Reaction of Methane with $\text{CBr}_3^+\text{AlBr}_4^-$ According to the DFT-PBE/TZ Method^{326,334}

The brilliant postulate of Olah and Hogeveen treats alkane C–H and C–C σ -bonds as two-electron donors with the tetracoordinate carbon hence being able to expand its coordination number. This idea was groundbreaking for fundamental organic chemistry. Olah has written:

“More importantly, the concept of pentacoordinated carbonium ion formation *via* electron sharing of single bonds with electrophilic reagents in three-center bond formation promises to open up a whole new important area of chemistry. Whereas the concept of tetravalency of carbon is not affected, carbon penta-coordination as a general phenomenon must be recognized.”

“The realization of the electron donor ability of shared (bonded) electron pairs (single bonds) could one day rank equal in importance with G.N. Lewis realization of the importance of the electron donor unshared (non-bonded) electron pairs.”³³⁷ In 1989, repeating these words, Olah has written: “It seems that the intervening years have justified that prediction in a significant degree. The electrophilic

chemistry of alkanes has rapidly expanded and has started to occupy a significant role even in the conversion of methane.”^{302a}

Olah’s prediction has come true. New superelectrophilic systems that are highly reactive toward alkanes have been found. The existence of species with hypervalent carbon atom has been well-documented. The classical $3c-2e$ mechanism of electrophilic cleavage of alkanes has indeed been established for some reactions. However, as we show in this review article, the $3c-2e$ mechanism is not universal. The electron donor ability of C–H σ -bonds can bring about other pathways for hydrogen transfer. The reactions of alkanes involving electrophilic attack on C- or H-atoms are now widely known. Other, also unprecedented, mechanistic schemes have been found for reactions of the most inert alkane, methane. These reactions proceed *via* a cyclic TS, involve nucleophilic assistance, and may be regarded as $4c-4e$ with alternating charges.

5. Conclusions

Although the hypothesis about multicharged species, which can be generated from molecules with several nucleophilic centers upon the action of several aluminum halide molecules (such as $CX_4 \bullet 2AlX_3$, $Br_2 \bullet 2AlBr_3$, $SOCl_2 \bullet 2AlCl_3$, $BX_3 \bullet 2AlX_3$, and $PX_3 \bullet 2AlX_3$ ¹⁴⁵ systems with X = Cl, Br) has not been confirmed, this approach has resulted in the development of a new generation of superelectrophiles which are capable of effectively reacting with alkanes. It is especially important that many transformations of alkanes and cycloalkanes induced by these superelectrophiles can be carried out selectively. Of prime interest among such superelectrophiles are polyhalomethanes in combination with aluminum halides. These systems, which have been known for more than a century, have been lately experiencing a second birth. The fact that in an organic medium under a CO atmosphere they effectively initiate the generation of acylium salts from linear alkanes and also from mono-, bi-, and tricyclanes, as well as the evidence that these reactions are often selective, opens unique prospects for the extensive use of saturated hydrocarbons and CO as reagents in organic synthesis. It is important that these acylations with $RH + CO$ can be carried out as one-pot procedures. Obviously, this approach is most promising for the synthesis of those carbonyl-containing products that can hardly be prepared in a traditional way because the corresponding carboxylic acids or their derivatives are inaccessible. Finding an easy method for the regeneration of aluminum halides which are not spent in the course of the reactions would be a significant achievement for the development of large-scale organic synthesis based on alkanes and cycloalkanes.

Theoretical studies of methane and propane reactions with CBr_3^+ and $CBr_3^+ AlBr_4^-$ have revealed novel reaction mechanisms which do not obey the classical *3c-2e* scheme. Thus, the results of these theoretical studies have enriched our knowledge of electrophilic alkane reactions.

It can also be argued that polyhalomethanes in combination with aluminum halides may be of use in the creation of new highly active electrophilic complexes of transition metals for catalytic functionalization of low alkanes, as well as beyond the field of alkane chemistry.

Alkane chemistry has developed vigorously over the last decades, and one can predict that this process will accelerate. We also believe that various approaches to alkane functionalization will be fruitful, and many of them will find new exciting areas of application.

6. Abbreviations

AcAc	acetylacetonato
Amyl	pentyl
AIM analysis	atom in molecule
AM1	Austin model 1
B3LYP	Becke's three-parameter exchange with Lee-Yang-Parr correlation functional
DFT	density functional theory
DMD	dimethyldecalin
HF	Hartree-Fock
HOMO	highest occupied molecular orbital
IPSO	substitution other than hydrogen atom in aromatic ring
KIE	kinetic isotope effect
MMO	methane monooxygenase
MNDO	Modified neglect of differential overlap
MP#	Moller-Plesset (order)

MP4SDTQ	MP4 with singles, doubles, triples, and quadruples
PES	potential energy surface
SET	single electron transfer
TMNB	trimethylenenorbornane
TOF	turnover frequency
TS	transition structure
TZ	triple- ζ
TZ2P	triple- ζ with double polarization
TZV	triple- ζ valence
cc-pVTZ	correlation consistent valence, polarized triple- ζ
cc-VTZ2P	correlation consistent valence, triple- ζ with double polarization
Wheland δ complex	cation generated by addition of electrophile to arene
ZPVE	zero-point vibrational energy

7. Acknowledgments

We are deeply grateful to our late teacher, Mark Vol'pin, with whom we started to work in the field of alkane chemistry and who was a great enthusiast of these studies. We would like to express our thanks to Dr. Nina Gambarian for fruitful discussion and helpful advice in writing Part 4 of this review. Her help is difficult to overestimate. Support of our work by the Russian Foundation for Basic Research (Grants Nos. 06-03-32924 and 04-03-32430) is gratefully acknowledged.

8. References

- (1) Gol'dshleger, N. F.; Tyabin, M. B.; Shilov, A. E.; Shteinman, A. A. *Zh. Fiz. Khim.* **1969**, *41*, 2147.
- (2) (a) Olah, G. A.; Lukas, J. *J. Am. Chem. Soc.* **1967**, *89*, 2227. (b) Olah, G. A.; Lukas, J. *J. Am. Chem. Soc.* **1967**, *89*, 4739. (c) Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 173.
- (3) (a) Bickel, A. F.; Gaasbeek, C. J.; Hogeveen, H.; Oelderik, J. M.; Platteeuw, J. C. *J. Chem. Soc., Chem. Commun.* **1967**, 634. (b) Hogeveen, H.; Bickel, A. F. *J. Chem. Soc. Chem. Commun.* **1967**, 635. (c) Hogeveen, H.; Lukas, J.; Roobeek, C. F. *J. Chem. Soc. Chem. Commun.* **1969**, 920. (d) Brouwer, D. M.; Hogeveen, H. In *Progress in Physical Organic Chemistry*; Taft, R. W., Streitwieser, A., Jr, Eds.; Interscience: New York, 1972; Vol. 9, pp 179.
- (4) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; Wiley-Interscience: New York, 1985.
- (5) Olah, G. A.; Prakash, G. K. S. *Electrophile Reactions of Alkanes. The Chemistry of Alkanes and Cycloalkanes*; Patai, S., Rappoport, Z., Eds.; Wiley-Interscience: Chichester-New York, 1992; Chapter 13.
- (6) Olah, G. A. *Nobel Lecture. Angew. Chem., Int. Ed. Engl.* **1995**, *13/14*, 1393.
- (7) (a) Sommer, J.; Bukala, J. *Acc. Chem. Res.* **1993**, *26*, 370. (b) Culmann, J.-C.; Cherry, G.; Jost, R.; Sommer, J. *Tetrahedron Lett.* **1989**, *30*, 701. (c) Sommer, J.; Jost, R. *Pure Appl. Chem.* **2000**, *72*, 2309.
- (8) Paatz, R.; Weisgerber, G. *Chem. Ber.* **1967**, *100*, 984.
- (9) (a) Asinger, F. *Paraffines. Chemistry and Technology*; Pergamon Press: New York, 1965. (b) Pines, H. *The Chemistry of Catalytic Hydrocarbon Conversions*; Academic Press: New York, 1981. (c) Davis, J. A.; Watson, P. L.; Liebman, J. F.; Greenberg, A. *Selective Hydrocarbon Activation, Principles and Progress*; VCH: Weinheim, Germany, 1990. (d) Olah, G. A.; Molnar, A. *Hydrocarbon Chemistry*; Wiley-Interscience: New York, 1995.
- (10) (a) Hill, C. L. *Activation and Functionalization of Alkanes*; Wiley-Interscience: New York, 1989. (b) A special issue dedicated to the topic. *Alkane Activation and Functionalization. New J. Chem.* **1989**, *13*, 645.
- (11) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; Riedel Publishing Co.: Dordrecht, Netherlands, 1985.
- (12) Schafer, H. J. *The Chemistry of Alkanes and Cycloalkanes*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester-New York, 1992; p 781.
- (13) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245.
- (14) Crabtree, R. H.; Brown, S. H.; Muedas, C. A.; Boogarma, G.; Ferguson, R. R. *CHEMTECH* **1991**, *21*, 634.

- (15) (a) Crabtree, R. H. *Chem. Alkanes Cycloalkanes* **1992**, 653. (b) Crabtree, R. H. *Chem. Rev.* **1995**, *95*, 987. (c) Crabtree, R. H. *J. Chem. Soc. Dalton. Trans.* **2001**, 2437.
- (16) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154.
- (17) A special issue dedicated to aspects of C-H activation. *J. Organomet. Chem.* **1995**, *504*, 1.
- (18) Lersch, M.; Tilset, M. *Chem. Rev.* **2005**, *105*, 2471.
- (19) Arndtsen, B. A.; Bergman, R. G. *Science* **1995**, *270*, 1970.
- (20) Bromberg, S. E.; Yang, W.; Asplund, M. C.; Lian, T.; McNamara, B. K.; Kotz, K. T.; Yeston, J. S.; Wilkens, M.; Frei, H.; Bergman, R. G.; Harris, C. B. *Science* **1997**, *278*, 260.
- (21) (a) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879. (b) Jones, W. D. Activation of C-H Bonds: Stoichiometric Reactions. In *Activation of Unreactive Bonds and Organic Synthesis*; Murai, S., Ed.; Springer: New York, 1999; p. 9. (c) Kakiuchi, F.; Murai, S. Activation of C-H Bonds: Catalytic Reactions. In *Activation of Unreactive Bonds and Organic Synthesis*; Murai, S., Ed.; Springer: New York, 1999; p. 47.
- (22) Huyser, E. S. *Free Radical Chain Reactions*; Wiley: New York, 1970.
- (23) Poutsma, M. L. *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 2, p 204.
- (24) Giese, B. *Radicals in Organic Synthesis*; Pergamon: Oxford, U.K., 1986.
- (25) Fossey, J.; Lefort, D.; Sorba, J. *Free Radicals in Organic Chemistry*; Wiley: Chichester, U.K., 1995.
- (26) Ferguson, R. R.; Crabtree, R. H. *J. Org. Chem.* **1991**, *56*, 5503.
- (27) Barton, D. H. R.; Doller, D. *Acc. Chem. Res.* **1992**, *25*, 504.
- (28) Lin, M.; Sen, A. J. *Chem. Soc. Chem. Commun.* **1992**, 892.
- (29) Boese, W. T.; Goldman, A. S. *J. Am. Chem. Soc.* **1992**, *114*, 350.
- (30) Mella, M.; Freccero, M.; Albini, A. *J. Chem. Soc. Chem. Commun.* **1995**, 41.
- (31) Hill, C. L. *Synlett* **1995**, 127.
- (32) Ryu, I.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1050.
- (33) MacFaul, P. A.; Wayner, D. D. M.; Ingold, K. U. *Acc. Chem. Res.* **1998**, *31*, 159.
- (34) Gozzo, F. J. *Mol. Catal.* **2001**, *171*, 1.
- (35) Sakaguchi, S.; Nishiwaki, Y.; Kitamura, T.; Ishii, Y. *Angew. Chem., Int. Ed.* **2001**, *40*, 222.
- (36) Fokin, A. A.; Schreiner, P. R. *Adv. Synth. Catal.* **2003**, *345*, 1035.
- (37) Fokin, A. A.; Schreiner, P. R. *Chem. Rev.* **2002**, *102*, 1555.
- (38) Groves, J. T.; Nemo, T. E.; Myers, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 1032.
- (39) Meunier, B. *Chem. Rev.* **1992**, *92*, 1411.
- (40) *Active Oxygen in Biochemistry*; Valentine, J. S.; Foote, C. S.; Greenberg, A.; Liebman, J. F., Eds.; Chapman and Hall: London, 1995.
- (41) (a) Bailey, P. D.; Higgins, S. D.; Ridyard, C. H.; Roberts, S. M.; Rossair, G. M.; Whittaker, R. A.; Willets, A. J. *Chem. Soc. Chem. Commun.* **1996**, 1833. (b) Ridyard, C. H.; Whittaker, R. A.; Higgins, S. D.; Roberts, S. M.; Willets, A. J.; Bailey, P. D.; Rossair, G. M. *J. Chem. Soc. Perkin. Trans. II* **1996**, 1811.
- (42) Shilov, A. E. *Metal Complexes in Biometric Chemical Reactions*; CRC Press: New York, 1997.
- (43) Shilov, A. E.; Shteinman, A. A. *Acc. Chem. Res.* **1999**, *32*, 763.
- (44) Solomon, E. I.; Brunold, T. C.; Davis, M. I.; Kemsley, J. N.; Lee, S.-K.; Lehnert, N.; Neese, F.; Skulan, A. J.; Yang, Y.-S.; Zhou, J. *Chem. Rev.* **2000**, *100*, 235.
- (45) Loew, G. H.; Harris, D. L. *Chem. Rev.* **2000**, *100*, 407.
- (46) Armentrout, P. B.; Beauchamp, J. L. *Acc. Chem. Res.* **1989**, *22*, 315.
- (47) Schroder, D.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1433.
- (48) Eller, K.; Schwarz, H. *Chem. Rev.* **1991**, *91*, 1121.
- (49) Weisshaar, J. C. *Acc. Chem. Res.* **1993**, *26*, 213.
- (50) Schroder, D.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1973.
- (51) *Organometallic Ion Chemistry*; Freiser, B.S., Ed.; Kluwer Academic Publishers: Dordrecht, Netherlands, 1996.
- (52) Schwarz, H.; Schroder, D. *Pure Appl. Chem.* **2000**, *72*, 2319.
- (53) (a) Masters, C. D.; Root, D. H.; Attanasi, E. D. *Science* **1991**, *253*, 146. (b) Starr, C.; Searl, M. F.; Alpert, S. *Science* **1992**, *256*, 981.
- (54) (a) Somorjai, G. A. *Science* (Washington DC) **1978**, *201*, 489. (b) Somorjai, G. A. *Pure Appl. Chem.* **1988**, *60*, 1499. (c) Somorjai, G. A. *IUPAC Series Chemistry for the 21st Century*; Thomas, J., Zamaraev, K., Eds.; Blackwell Science Publ.: London, 1992, 147.
- (55) (a) Maire, G. L. C.; Garin, F. G. *Catalysis—Science and Technology*; Anderson, J. R., Boudart, M., Eds.; Springer-Verlag: Berlin, 1984; Vol. 6, p 161. (b) Thomas, J. M. *Pure Appl. Chem.* **1988**, *60*, 1517.
- (56) *Metal Clusters*; Moskovits, M. Ed.; Wiley-Interscience: New York, Chichester, U.K., 1986.
- (57) (a) Dyer, A. *Introduction to Zeolite Molecular Sieves*; Wiley: New York, 1988. (b) *Catalysis on Zeolites*; Kallo, D.; Minachev, K. M. Eds.; Akademia: Budapest, Hungary, 1988. (c) Kung, H. H. *Transition Metal Oxides*; Elsevier: Amsterdam, 1989. (d) Schenk, M.; Smit, B.; Vligt, T. J. H.; Maesen, T. L. M. *Angew. Chem., Int. Ed.* **2001**, *40*, 736. (e) Dugal, M.; Sankar, G.; Raja, R.; Thomas, J. M. *Angew. Chem., Int. Ed.* **2000**, *39*, 2310.
- (58) Cosma, A. *Chem. Rev.* **1995**, *95*, 559.
- (59) (a) *Acid-Base Catalysis. Catal. Today* **1997**, *38* (a special issue of *Catal. Today*). (b) Coulson, G. M.; Bare, S. R.; Kung, H.; Birkeland, K.; Bethke, G. K.; Harlow, R.; Herron, N.; Lee, P. L. *Science* **1997**, *275*, 191. (c) Batamack, P.; Bucsi, I.; Molnar, A.; Olah, G. A. *Catal. Lett.* **1994**, *25*, 11. (d) Waycuilis, J. J. CA Patent 2561133, 2005.
- (60) (a) Cronstedt, A. F. *Svenska Vetenskaps Akademiens*; Handigar: Stockholm, Sweden, **1756**, *17*, 120. (b) Cronstedt, A. F.; Kuhl, G. H. In *Proceedings from the Ninth International Zeolite Conference*, Montreal, Canada, 1992; von Ballmoos, R.; Higgins, J. B.; Treacy, M. M. J. Eds.; Butterworth-Heinemann: Stoneham, MA, 1993; Vol. 1, p 3; translated by Shlenker, J. L.
- (61) Billups, W. E.; Konarski, M. M.; Hauge, R. H.; Margrave, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 7393.
- (62) (a) Ozin, G. A.; McIntosh, D. F.; Mitchell, S. A. *J. Am. Chem. Soc.* **1981**, *103*, 1574. (b) Ozin, G. A.; McCaffrey, J. G. *J. Am. Chem. Soc.* **1982**, *104*, 7351. (c) Ozin, G. A.; McCaffrey, J. G.; McIntosh, D. F. *Pure Appl. Chem.* **1984**, *56*, 111. (d) Ozin, G. A.; McCaffrey, J. G.; Parnis, J. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1072.
- (63) (a) Green, M. L. H.; Parker, G. J. *Chem. Soc., Chem. Commun.* **1984**, 1467. (b) Bandy, J. A.; Cloke, F. G. N.; Green, M. L. H.; O'Hare, D.; Prout, K. J. *Chem. Soc., Chem. Commun.* **1984**, 240. (c) Green, M. L. H.; O'Hare, D.; Parker, G. J. *Chem. Soc., Chem. Commun.* **1985**, 356. (d) Green, M. L. H. *Pure Appl. Chem.* **1984**, *56*, 47. (e) Green, M. L. H.; O'Hare, D. *High Energy Processes in Organometallic Chemistry*; Suslick, K. S. Ed.; American Chemical Society: Washington DC, 1987; p 260.
- (64) (a) Davis, S. C.; Klabunde, K. J. *J. Am. Chem. Soc.* **1978**, *100*, 5973. (b) Klabunde, K. J. *Chemistry of Free Atoms and Particle*; Academic Press: New York, 1980. (c) Davis, S. C.; Severson, S.; Klabunde, K. J. *J. Am. Chem. Soc.* **1981**, *103*, 3024. (d) Matsuo, K.; Klabunde, K. J. *J. Catal.* **1982**, *73*, 216. (e) Davis, S.; Klabunde, K. J. *Chem. Rev.* **1982**, *82*, 153. (f) Klabunde, K. J.; Imizu, Y. *J. Am. Chem. Soc.* **1984**, *106*, 2721.
- (65) Remick, R. J.; Asunta, T. A.; Skell, P. S. *J. Am. Chem. Soc.* **1979**, *101*, 1320.
- (66) Kharatyan, S. L.; Chatilyan, A. A.; Merzhanov, A. G. *Khim. Fiz.* **1989**, *8*, 521.
- (67) Davis, S. C.; Zaera, F.; Somorjai, G. A. *J. Catal.* **1982**, *77*, 439.
- (68) Barret, P. H.; Pasternak, M.; Pearson, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 222.
- (69) Perutz, R. N. *Chem. Rev.* **1985**, *85*, 77.
- (70) Lefcourt, M. A.; Merritt, C. L.; Peterson, M. R.; Csizmadia, I. G. *J. Mol. Struct.* **1988**, *181*, 315.
- (71) Kolbanovkiy, Yu. A.; Gagarin, S. G. *Kinet. Catal.* **1988**, *29*, 88..
- (72) Xiao, Z. L.; Hauge, R. H.; Margrave, J. L. *Inorg. Chem.* **1993**, *32*, 642.
- (73) (a) Akhrem, I. S.; Vol'pin, M. E. *Russ. Chem. Rev.* **1990**, *59*, 1906. (b) Vol'pin, M. E.; Akhrem, I. S.; Reznichenko, S. V.; Grushin, V. V. *J. Organomet. Chem.* **1987**, *334*, 109. (c) Akhrem, I. S.; Reznichenko, S. V.; Chistovalova, N. M.; Grushin, V. V.; Vol'pin, M. E. *Catal. Lett.* **1993**, *20*, 275.
- (74) (a) Khcheyan, K. E.; Revenko, O. M.; Tikhonova, M. P.; Borisoglebskaya, A. V. *Otkryitiya, Izobret., Prom. Obraztsy, Tovarnye Znaki* **1980**, *38*, 113; *Chem. Abstr.* **1981**, *84*, 191871h. (b) Khcheyan, K. E.; Revenko, O. M.; Shatalova, A. N. *Proc. Would Petrol. Congr.* **1983**, *4*, 465.
- (75) (a) Amenomiya, Y.; Birss, V. I.; Goledzinowski, M.; Galuszka, J.; Sanger, A. R. *Catal. Rev. Sci. Eng.* **1990**, *32*, 163. (b) Krylov, O. V. *Usp. Khim.* **1992**, *61*, 1550. (c) Osada, Y.; Okino, N.; Ogasawara, S.; Fukushima, T.; Shikada, T.; Ikariya, T. *J. Chem. Soc., Chem. Commun.* **1990**, 1434. (d) Osada, Y.; Okino, N.; Ogasawara, S.; Fukushima, T.; Shikada, T.; Ikariya, T. *Chem. Lett.* **1990**, 281. (e) Suzuki, T.; Wada, K.; Watanabe, Y. *Ind. Eng. Chem. Res.* **1991**, *30*, 1719. (f) Otsuka, M.; Hatano, T.; Amaya, T. *J. Catal.* **1992**, *137*, 487. (g) Kim, H.; Suh, H.; Paik, H. *Appl. Catal.* **1992**, *87*, 115. (h) Khan, A. Z.; Ruckenstein, E. *J. Chem. Soc., Chem. Commun.* **1993**, 587.
- (76) (a) Olah, G. A.; Prakash, G. K. S.; Williams, R. E.; Field, L. D.; Wade, K. *Hypercarbon Chemistry*; Wiley-Interscience, John Wiley & Son: New York, 1987. (b) Meerwein, H.; van Emster, K. *Chem. Ber.* **1922**, *55*, 2500.
- (77) Schleyer, P. v. R.; Carneiro, J. W. M. *J. Comput. Chem.* **1992**, *13*, 997.
- (78) (a) Schreiner, P. R.; Kim, S.-J.; Schaefer, H. F., III; Schleyer, P. v. R. *J. Chem. Phys.* **1993**, *99*, 3716. (b) Schreiner, P. R. *Angew. Chem., Int. Ed.* **2000**, *39*, 3239.

- (79) Muller, H.; Kutzelnigg, W.; Noga, J.; Klopper, W. *J. Chem. Phys.* **1997**, *106*, 1863.
- (80) (a) Scuseria, G. E. *Nature* **1993**, *366*, 512. (b) Collins, S. J.; O'Malley, P. J. *J. Chem. Phys. Lett.* **1994**, 246. (c) Okulik, N. B.; Diez, R. P.; Jubert, A. H.; Esteves, P. M.; Mota, C. J. A. *J. Phys. Chem. A* **2001**, *105*, 7079.
- (81) (a) Ahlberg, P.; Karlsson, A.; Goepfert, A.; Nilsson Lill, S. O.; Diner, P.; Sommer, J. *Chem.—Eur. J.* **2001**, *7/9*, 1936 (see corrigenda *Chem.—Eur. J.* **2001**, *7/12*, 2501).
- (82) (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352. (b) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929. (c) Periana, R. A.; Bergman, R. G. *Organometallics* **1984**, *3*, 508. (d) Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 8731. (e) Bergman, R. G. *J. Organomet. Chem.* **1990**, *400*, 273. (f) Bengali, A. A.; Schultz, R. H.; Moore, C. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 9585. (g) Schultz, R. H.; Bengali, A. A.; Tauber, M. J.; Weiller, B. H.; Wasserman, E. P.; Kyle, K. R.; Moore, C. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 7369.
- (83) (a) Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 3723. (b) Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 7190.
- (84) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1982**, *104*, 4240; **1984**, *106*, 1650; **1986**, *108*, 4814.
- (85) (a) Perutz, R. N.; Belt, S. T.; McCamley, A.; Whittlesey, M. K. *Pure Appl. Chem.* **1990**, *62*, 1539. (b) Koola, J. D.; Roddick, D. M. *J. Am. Chem. Soc.* **1991**, *113*, 1450. (c) Whittlesey, M. K.; Mawby, R. J.; Osman, R.; Perutz, R. N.; Field, L. D.; Wilkinson, M. P.; George, M. W. *J. Am. Chem. Soc.* **1993**, *115*, 8627. (d) Bennett, J. L.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1994**, *116*, 2179. (e) Buys, I. E.; Field, L. D.; Hambley, T. W.; McQueen, A. E. D. *J. Chem. Soc., Chem. Commun.* **1994**, 557. (f) Squires, M. E.; Sardella, D. J.; Kool, L. B. *Organometallics* **1994**, *13*, 2970.
- (86) (a) Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006. (b) Low, J. J.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1984**, *106*, 8321. (c) Ziegler, T.; Tschinke, V.; Fan, L.; Becke, A. D. *J. Am. Chem. Soc.* **1989**, *111*, 9177. (d) Koga, N.; Morokuma, K. *J. Phys. Chem.* **1990**, *94*, 5454. (e) Blomberg, M. R. A.; Siegbahn, P. E. M.; Svensson, M. *J. Am. Chem. Soc.* **1992**, *114*, 6095. (f) Margl, P.; Ziegler, T.; Blochl, P. E. *J. Am. Chem. Soc.* **1995**, *117*, 12625. (g) Song, J.; Hall, M. B. *Organometallics* **1993**, *12*, 3118. (h) Su, M.-D.; Chu, S.-Y. *J. Am. Chem. Soc.* **1997**, *119*, 5373.
- (87) (a) Yoshizawa, K.; Yamaba, T.; Hoffmann, R. *New J. Chem.* **1997**, *21*, 151. (b) Espinosa-Garcia, J.; Corchado, J. C.; Truhlar, D. G. *J. Am. Chem. Soc.* **1997**, *119*, 9891.
- (88) (a) Holthausen, M. C.; Koch, W. *J. Am. Chem. Soc.* **1996**, *118*, 9932. (b) Mamaev, V. M.; Gloriov, I. P.; Prisyajnyuk, A.; Ustynyuk, Yu. A. *Mendeleev Commun.* **1996**, 203.
- (89) Jia, C.; Kitamura, T.; Fujiwara, Y. *Acc. Chem. Res.* **2001**, *34*, 633.
- (90) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.
- (91) (a) Schneider, J. I. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1068. (b) Hall, C.; Perutz, R. N. *Chem. Rev.* **1996**, *96*, 3125. (c) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789. (d) Evans, D. R.; Drovetskaya, T.; Bau, R.; Reed, C. A.; Boyd, P. D. W. *J. Am. Chem. Soc.* **1997**, *119*, 3633. (e) Sun, X.-Z.; Grills, D. C.; Nikiforov, S. M.; Poliakov, M.; George, M. W. *J. Am. Chem. Soc.* **1997**, *119*, 7521. (f) Geftakis, S.; Ball, G. E. *J. Am. Chem. Soc.* **1998**, *120*, 9953. (g) Castro-Rodriguez, I.; Nakai, H.; Gantzel, P.; Zakharov, L. N.; Rheingold, A. L.; Meyer, K. *J. Am. Chem. Soc.* **2003**, *125*, 15734.
- (92) (a) Siegbahn, P. E. M.; Crabtree, R. H. *Struct. Bonding* **2000**, *97*, 125. (b) Friesner, R. A.; Dunietz, B. D. *Acc. Chem. Res.* **2001**, *34*, 351.
- (93) (a) Farcasiu, D.; Lukinskas, P. *J. Chem. Soc., Chem. Commun.* **2001**, 77. (b) Farcasiu, D.; Lukinskas, P. *J. Phys. Chem.* **2002**, *106*, 1619. (c) Farcasiu, D.; Lukinskas, P. *Rev. Roum. Chim.* **1999**, *44*, 1091. (d) Senger, S.; Radom, L. *J. Am. Chem. Soc.* **2000**, *122*, 2613. (e) Schoofs, B.; Schuermans, J.; Schoonheydt, R. A. *Microporous Mesoporous Mater.* **2000**, *35–36*, 99. (f) Sokolovskii, V. D.; Mamedov, E. A. *Catal. Today* **1992**, *14*, 331. (g) Capitan, M. J.; Odriozola, J. A.; Marquez, A.; Sanz, J. F. *J. Catal.* **1995**, *156*, 273. (h) Kazansky, V. B.; Frash, M. V.; van Santen, R. A. *Cat. Lett.* **1994**, *28*, 21.
- (94) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1987.
- (95) (a) Fujiwara, Y.; Takaki, K.; Taniguchi, Y. *Synlett* **1996**, 591. (b) Taniguchi, Y.; Hayashida, T.; Shibasaki, H.; Piao, D.; Kitamura, T.; Yamaji, T.; Fujiwara, Y. *Org. Lett.* **1999**, *1*, 557. (c) Asadullah, M.; Kitamura, T.; Fujiwara, Y. *Angew. Chem., Int. Ed.* **2000**, *39*, 2475. (d) Reis, P. M.; Silva, J. A. L.; Palavra, A. F.; Frausto da Silva, J. J. R.; Kitamura, T.; Fujiwara, Y.; Pombeiro, A. J. L. *Angew. Chem., Int. Ed.* **2003**, *42*, 821.
- (96) (a) Kao, L.-C.; Hutson, A. C.; Sen, A. *J. Am. Chem. Soc.* **1991**, *113*, 700. (b) Sen, A. *Acc. Chem. Res.* **1998**, *31*, 550. (c) Seki, Y.; Mizuno, N.; Mizono, M. *App. Cat., A* **1997**, *158*, 147. (d) Piao, D.; Inoue, K.; Shibasaki, H.; Taniguchi, Y.; Kitamura, T.; Fujiwara, Y. *J. Organomet. Chem.* **1999**, *574*, 116. (e) Yin, G.; Piao, D.; Kitamura, T.; Fujiwara, Y. *Appl. Organomet. Chem.* **2000**, *14*, 438.
- (97) (a) Periana, R. A.; Taube, D. J.; Evitt, E. R.; Loffler, D. G.; Wentreek, P. R.; Voss, J.; Masada, T. A. *Science* **1993**, *259*, 340. (b) Periana, R. A.; Taube, D. J.; Gamble, S.; Taube, H.; Satoh, T.; Fujii, H. *Science* **1998**, *280*, 560.
- (98) Akhrem, I. S.; Orlinkov, A. V.; Mysov, E. I.; Vol'pin, M. E. *Tetrahedron Lett.* **1981**, *22*, 3891.
- (99) Vol'pin, M. E.; Akhrem, I. S.; Orlinkov, A. V. *New J. Chem.* **1989**, *13*, 771.
- (100) Akhrem, I. S.; Orlinkov, A. V.; Vol'pin, M. E. *Russ. Chem. Rev.* **1996**, *65*, 849.
- (101) (a) Nenitzescu, C. D. *Usp. Khim.* **1957**, *27*, 399. (b) Gore, P. H. *Chem. Rev.* **1955**, *55*, 229.
- (102) *Friedel-Crafts and Related Reactions*; Olah, G. A. Ed.; Wiley-Interscience: New York, 1964; Vol. 3.
- (103) *The Chemistry of Acyl Halides*; Patai, S. Ed.; Wiley-Interscience: London, 1972; Chapters 4 and 8.
- (104) (a) Chevriar, B.; Weiss, R. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 1. (b) Chevriar, B.; White, A. M. *Carbonium Ions*; Wiley-Interscience: New York, 1976; p 2049.
- (105) Seyferth, D. *Organometallic Chemical Reviews. Library 9*; Elsevier: Amsterdam, 1980.
- (106) Orlinkov, A. V.; Akhrem, I. S.; Vol'pin, M. E. *Russ. Chem. Rev.* **1991**, *60*, 524.
- (107) Akhrem, I. S.; Orlinkov, A. V.; Afanas'eva, L. V.; Vol'pin, M. E. *Dokl. Akad. Nauk SSSR* **1988**, *298*, 107.
- (108) Orlinkov, A. V.; Akhrem, I. S.; Afanas'eva, L. V.; Vol'pin, M. E. *Bull. Acad. Sci. USSR Div. Chem. Sci.* **1986**, *35*, 1286.
- (109) Orlinkov, A. V.; Akhrem, I. S.; Afanas'eva, L. V.; Vol'pin, M. E. *Dokl. Akad. Nauk SSSR* **1988**, *299*, 890.
- (110) Orlinkov, A. V.; Akhrem, I. S.; Vitt, S. V.; Afanas'eva, L. V.; Vol'pin, M. E. *Bull. Acad. Sci. USSR Div. Chem. Sci.* **1990**, *39*, 290.
- (111) Akhrem, I. S.; Orlinkov, A. V.; Vitt, S. V.; Vol'pin, M. E. *Dokl. Akad. Nauk SSSR* **1986**, *288*, 130.
- (112) (a) Akhrem, I. S.; Orlinkov, A. V.; Vitt, S. V.; Dulova, V. G.; Vol'pin, M. E. USSR Patent 1452073; *Byull. Izobret.* **1989**, *2*, 264. (b) Akhrem, I. S.; Orlinkov, A. V.; Vitt, S. V.; Dulova, V. G.; Afanas'eva, L. V.; Pavlov, V. A.; Vol'pin, M. E. USSR Patent 1452074; *Byull. Izobret.* **1989**, *2*, 264.
- (113) Orlinkov, A. V.; Akhrem, I. S.; Afanas'eva, L. V.; Vol'pin, M. E. *Bull. Acad. Sci. USSR Div. Chem. Sci.* **1986**, *37*, 1965.
- (114) Akhrem, I. S.; Orlinkov, A. V.; Vitt, S. V.; Afanas'eva, L. V.; Vol'pin, M. E. *Bull. Acad. Sci. USSR Div. Chem. Sci.* **1989**, *38*, 1864.
- (115) Orlinkov, A. V.; Akhrem, I. S.; Vitt, S. V.; Afanas'eva, L. V.; Vol'pin, M. E. *Bull. Acad. Sci. USSR Div. Chem. Sci.* **1991**, *40*, 90.
- (116) Akhrem, I. S.; Orlinkov, A. V.; Vitt, S. V.; Afanas'eva, L. V.; Vol'pin, M. E. *Russ. Chem. Bull.* **1993**, *42*, 1196.
- (117) Akhrem, I.; Orlinkov, A.; Vol'pin, M. *J. Chem. Soc., Chem. Commun.* **1993**, 257.
- (118) Akhrem, I. S.; Bernadyuk, S. Z.; Vol'pin, M. E. *Mendeleev Commun.* **1993**, 188.
- (119) Orlinkov, A. V. Ph.D. Thesis Moscow, Russia, 1989.
- (120) Pouret, C. *Bull. Soc. Chim. Fr.* **1901**, *3*, 25, 191.
- (121) Wallace, C. H.; Willard, J. E. *J. Am. Chem. Soc.* **1950**, *72*, 5275.
- (122) (a) Olah, G. A.; Heiliger, L.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1989**, *111*, 8020. (b) Olah, G. A.; Rasul, G.; Heiliger, L.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1996**, *118*, 3580.
- (123) Vancik, H.; Percac, K.; Sunko, D. E. *J. Am. Chem. Soc.* **1990**, *112*, 7418.
- (124) (a) Culmann, J.-C.; Simon, M.; Sommer, J. *J. Chem. Soc., Chem. Commun.* **1990**, 1098. (b) Culmann, J.-C.; Sommer, J. *J. Am. Chem. Soc.* **1990**, *112*, 4057.
- (125) Akhrem, I. S.; Orlinkov, A. V.; Vol'pin, M. E. *J. Chem. Soc., Chem. Commun.* **1993**, 671.
- (126) Ault, B. S.; Andrews, L. *J. Chem. Phys.* **1975**, *63*, 1411.
- (127) Kelsall, B. J.; Andrews, L. *J. Mol. Spectros.* **1983**, *97*, 362.
- (128) Andrews, L.; Dyke, J. M.; Jonathan, N.; Keddar, N.; Morris, A. *J. Chem. Phys.* **1983**, *79*, 4650.
- (129) Jacox, M.; Milligan, D. E. *J. Chem. Phys.* **1971**, *54*, 3935.
- (130) Jacox, M. *Chem. Phys.* **1976**, *12*, 51.
- (131) Kafafi, S. A.; Hudgens, J. W. *J. Phys. Chem.* **1989**, *93*, 3474.
- (132) Levy, G. C.; Lichter, R. L.; Nelson, G. L. *Carbon-13 NMR Spectroscopy*; Wiley-Interscience: New York, 1980.
- (133) Olah, G. A.; Wu, A.; Farooq, O. *J. Org. Chem.* **1989**, *54*, 1463.
- (134) Olah, G. A.; Bruce, M. R. *J. Am. Chem. Soc.* **1979**, *101*, 4765.
- (135) (a) Amiantov, I. Yu.; Khotsyanova, T. L.; Akhrem, I. S.; Orlinkov, A. V.; Vol'pin, M. E. *Zh. Strukt. Khim.* **1984**, *25*, 46. [*J. Struct. Chem. (USSR)* **1984**, *26* (Engl. Trans.)]. (b) Akhrem, I. S.; Orlinkov,

- A. V.; Bakhmutov, V. I.; Petrovskii, P. V.; Pekhk, E. T.; Lipmaa, E. T.; Vol'pin, M. E. *Dokl. Akad. Nauk SSSR* **1985**, *284*, 627. (c) Akhrem, I. S.; Orlinkov, A. V.; Bakhmutov, V. I.; Afanas'eva, L. V.; Vol'pin, M. E. *Bull. Acad. Sci. USSR Div. Chem. Sci.* **1990**, *39*, 2252.
- (136) Stankevich, I. V.; Chistyakov, A. L.; Akhrem, I. S.; Orlinkov, A. V.; Gambaryan, N. P.; Vol'pin, M. E. *Russ. Chem. Bull.* **1993**, *42*, 805.
- (137) Brouwer, D. M.; Kiffen, A. A. *Recl. Trav. Chim., Pays-Bas* **1973**, *92*, 689, 809, 906.
- (138) Olah, G. A.; Germain, A.; Lin, H. C.; Forsyth, D. A. *J. Am. Chem. Soc.* **1975**, *97*, 2928.
- (139) Lammertsma, K. *J. Am. Chem. Soc.* **1984**, *106*, 4619.
- (140) Olah, G. A.; Burrichter, A.; Rasul, G.; Prakash, G. K. S.; Hachoumy, M.; Sommer, J. J. *J. Am. Chem. Soc.* **1996**, *118*, 10423.
- (141) Sato, Y.; Yato, M.; Ohwada, T.; Saito, S.; Shudo, K. *J. Am. Chem. Soc.* **1995**, *117*, 3037.
- (142) Brown, H. C.; Marino, G. *J. Am. Chem. Soc.* **1959**, *81*, 3308.
- (143) Ohwada, T.; Yamagata, N.; Shudo, K. *J. Am. Chem. Soc.* **1991**, *113*, 1364.
- (144) Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 767.
- (145) (a) Akhrem, I. S.; Orlinkov, A. V. *Russ. Chem. Bull.* **1998**, *47*, 740. (b) Akhrem, I. *Russ. Chem. Bull.* **2003**, *52*, 2606.
- (146) (a) Akhrem, I. S.; Afanas'eva, L. V.; Orlinkov, A. V.; Vol'pin, M. E. *Mendeleev Commun.* **1994**, 131. (b) Chistyakov, A. L.; Stankevich, I. V.; Akhrem, I. S.; Gambaryan, N. P.; Vol'pin, M. E. *Mendeleev Commun.* **1996**, 175.
- (147) Akhrem, I.; Gudima, S.; Vol'pin, M. *Chem.—Eur. J.* **1996**, *2*, 812.
- (148) Pinyaskin, V. V.; Stankevich, I. V.; Chistyakov, A. L.; Akhrem, I.; Gudima, S. *Russ. Chem. Bull.* **1996**, *45*, 1056.
- (149) Akhrem, I. S.; Churilova, I. M.; Vitt, S. V. *Russ. Chem. Bull.* **2001**, *50*, 81.
- (150) (a) Fort, R. C. In *Adamantane. The Chemistry of Diamond Molecules*; Marcel Dekker: New York, 1976. (b) Kurisaki, K. *Chem. Econ. Eng. Rev.* **1976**, *8*, 12. (c) Bagrii, E. I. *Adamantanes: Production, Properties, Application*; Nauka: Moscow, 1989. (d) Kovtun, V. Yu.; Plakhotnic, V. M. *Chem. Pharmacol. J.* **1987**, *28*, 931 and patents cited therein. (e) Shvakhgeimer, M.-G. A. *Usp. Khim.* **1996**, *65*, 603. [*Russ. Chem. Rev.* **1996**, *65* (Engl. Transl.)]. (f) Borchert, J. U.S. Patents 3536732, 1970.
- (151) Akhrem, I. S.; Vitt, S. V.; Churilova, I. M.; Orlinkov, A. V. *Russ. Chem. Bull.* **1999**, *48*, 2279.
- (152) Gavrilov, R. G.; Luksha, V. G.; Averyanov, S. F. *Zh. Prikl. Khim.* **1978**, *51*, 671.
- (153) Gavrilov, R. G.; Luksha, V. G.; Tropinova, L. N. *Zh. Org. Khim. USSR* **1976**, *12*, 1599.
- (154) Eidus, J. T.; Pirozhkov, S. D.; Puzitskii, K. V. *Zh. Org. Khim. USSR* **1968**, *4*, 1214.
- (155) (a) Koch, H.; Haaf, W. *Liebigs Ann. Chem.* **1958**, *618*, 251. (b) Bahrman, H. In *New Syntheses with Carbon Monoxide*; Falbe, J. Ed.; Springer-Verlag: Berlin, 1980; p 372.
- (156) Olah, G. A.; Lukas, J. *J. Am. Chem. Soc.* **1968**, *90*, 933.
- (157) Grignard, V.; Stratford, R. *Compt. Rend.* **1924**, *178*, 2149.
- (158) Nenitzescu, C. D.; Ionescu, C. N. *Ann.* **1931**, *491*, 189.
- (159) (a) Doering, W. E.; Schoenewaldt, E. F. *J. Am. Chem. Soc.* **1951**, *73*, 2333. (b) Conn, W. K.; Schneider, A. *J. Am. Chem. Soc.* **1954**, *76*, 4578.
- (160) Gavrilov, R. G.; Luksha, V. G.; Slobodin, Yu. M.; Kovyazin, V. E. *Zh. Org. Khim. USSR* **1975**, *11*, 597.
- (161) (a) Omae, I.; Urasaki, T.; Shima, T. Japan, Patent 7401548, *Chem. Abst.* **1974**, *80*, 145591. (b) Omae, I.; Urasaki, T. Shima, T. Japan, Patent 7401549, *Chem. Abst.* **1974**, *80*, 145592.
- (162) Thoret-Bauchet, J. P.; Mortreux, A.; Petit, F. *J. Mol. Catal.* **1993**, *83*, 323.
- (163) (a) Fokin, A. A.; Schreiner, P. R.; Gunchenko, P. A.; Peleshanko, S. A.; Shubina, T. E.; Isaev, S. D.; Tarasenko, P. V.; Kulik, N. I.; Schiebel, H.-M.; Yurchenko, A. G. *J. Am. Chem. Soc.* **2000**, *122*, 7317. (b) Fokin, A. A.; Shubina, T. E.; Gunchenko, P. A.; Isaev, S. D.; Yurchenko, A. G.; Schreiner, P. R. *J. Am. Chem. Soc.* **2002**, *124*, 10719.
- (164) Orlinkov, A. V.; Akhrem, I. S.; Vitt, S. V.; Vol'pin, M. E. *Tetrahedron Lett.* **1996**, *37*, 3363.
- (165) Akhrem, I. S.; Orlinkov, A. V.; Afanas'eva, L. V.; Mysov, E. I.; Vol'pin, M. E. *Tetrahedron Lett.* **1995**, *36*, 9365.
- (166) Akhrem, I. S.; Orlinkov, A. V.; Afanas'eva, L. V.; Vol'pin, M. E. *Russ. Chem. Bull.* **1996**, *45*, 1140.
- (167) (a) Bach, R. D.; Badger, R. C. *Synthesis* **1979**, 528. (b) Schreiner, P. R.; Lauenstein, O.; Kolomitsyn, I. V.; Nadi, S.; Fokin, A. A. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1895. (c) Fokin, A. A.; Lauenstein, O.; Gunchenko, P. A.; Schreiner, P. R. *J. Am. Chem. Soc.* **2001**, *123*, 1842. (d) Smirnov, V. V.; Zelikman, V. M.; Beletskaya, I. P.; Levitskii, M.; Kazankova, M. A. *Mendeleev Commun.* **2000**, 175.
- (168) (a) Landa, S.; Hala, S. *Chem. Listy* **1954**, *51*, 2325. (b) Stetter, H.; Schwarz, M.; Hirschhorn, A. *Chem. Ber.* **1959**, *92*, 1629.
- (169) (a) Olah, G. A.; Schilling, P. *J. Am. Chem. Soc.* **1973**, *95*, 7680. (b) Halpern, Y. *Isr. J. Chem.* **1975**, *13*, 99.
- (170) (a) Akhrem, I. S.; Orlinkov, A. V.; Vol'pin, M. E. In *Green Industrial Application of Ionic Liquids*; Mamantov, G.; Seddon, K. R.; Volkov, S. Eds.; Nato Science Series-Kluwer Academic Publishers: Dordrecht-Boston-London, 2003; p 483. (b) Hussey, C. L. *Adv. Molten Salt Chem.* **1983**, *5*, 185. (c) Carlin, R. T.; Wilkes, J. S. In *Advances in Nonaqueous Chemistry*; Mamantov, G.; Popov, A. Eds.; VCH Publishing: New York, 1994. (d) Seddon, K. R. *Kinet. Catal.* **1996**, *37*, 693. (e) Olivier-Bourbigou, H. In *Aqueous-Phase Organometallic Catalysis: Concepts and Applications*; Cornils, B.; Herrmann, W. A. Eds.; Wiley-VCH: Weinheim, Germany, 1998. (f) Welton, T. *Chem. Rev.* **1999**, *99*, 2071.
- (171) Liquori, L. H.; Bjorsvik, H.-R.; Bravo, A. R.; Fontana, R.; Miniski, F. *J. Chem. Soc. Chem. Commun.* **1997**, 1501.
- (172) (a) Tanner, D. D.; Gidley, G. C. *J. Am. Chem. Soc.* **1968**, *90*, 808. (b) Tanner, D. D.; Rowe, J. E.; Potter, A. *J. Org. Chem.* **1986**, *51*, 457.
- (173) Schreiner, P. R.; Lauenstein, O.; Butova, E. D.; Fokin, A. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 2786.
- (174) Akhrem, I. S.; Orlinkov, A. V.; Vitt, S. V.; Chistyakov, A. L. *Tetrahedron Lett.* **2002**, *43*, 1333.
- (175) (a) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *11*, 3865. (b) Laikov, D. DFT 2000. Satellite Symposium of the 10th International Congress of Quantum Chemistry, Menton, France, 2000. (c) Laikov, D. N. *Chem. Phys. Lett.* **1997**, *281*, 151.
- (176) (a) Merkushev, E. B. *Russ. Chem. Rev.* **1984**, *53*, 343. (b) Merkushev, E. B. *Synthesis* **1988**, 923.
- (177) Wirth, H. O.; Konigstein, O.; Kern, W. *Liebigs Ann. Chem.* **1960**, *634*, 84.
- (178) Radner, F. *J. Org. Chem.* **1988**, *53*, 3548.
- (179) Sugiyama, T. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2847.
- (180) Galli, G. *J. Org. Chem.* **1991**, *56*, 3238.
- (181) Seevers, R. H.; Counsell, R. E. *Chem. Rev.* **1982**, *82*, 575.
- (182) Olah, G. A.; Wang, Q.; Sandford, G.; Prakash, G. K. S. *J. Org. Chem.* **1993**, *58*, 3194.
- (183) (a) Pianfetti, J. A.; Quin, L. D. *J. Am. Chem. Soc.* **1962**, *84*, 851. (b) Pianfetti, J. A. U.S. Patent 3210418, 1965; *Chem. Abstr.* **1965**, *64*, 2188.
- (184) Gehrman, K.; Ohorodnik, A.; Steil, K. H.; Schafer, S. DE Patent 2629299; *Chem. Abstr.* **1978**, *89*, 24531.
- (185) Uhing, E. H. *Ger. Offen.* 20463114; *Chem. Abstr.* **1971**, *74*, 142063.
- (186) Stetter, H.; Last, W. D. *Chem. Ber.* **1969**, *102*, 3364.
- (187) Olah, G. A.; Farooq, O.; Wang, Q.; Wu, A.-h. *J. Org. Chem.* **1990**, *55*, 1224.
- (188) (a) Clay, J. P. *J. Org. Chem.* **1951**, *16*, 892. (b) Kosolapoff, G. M. Reactions in Organophosphorous Chem. In *Friedel-Crafts and Related Reactions*; Olah, G. A. Ed.; Wiley-Interscience: New York, 1965.
- (189) Maryanoff, B. E.; Hutchins, R. O. *J. Org. Chem.* **1972**, *37*, 3475.
- (190) Thomas, M. G.; Schults, C. W.; Parry, R. W. *Inorg. Chem.* **1977**, *16*, 994.
- (191) Cowley, A. H.; Kemp, R. A. *Chem. Rev.* **1985**, *85*, 367.
- (192) Olah, G. A.; Gupta, B. G. B. *J. Org. Chem.* **1980**, *45*, 3532.
- (193) Ritter, J. J.; Minieri, P. P. *J. Am. Chem. Soc.* **1948**, *70*, 4045.
- (194) Koch, V. R.; Miller, L. L. *J. Am. Chem. Soc.* **1973**, *95*, 8631.
- (195) Akhrem, I. S.; Orlinkov, A. V.; Vitt, S. V. *Inorg. Chim. Acta* **1998**, *280*, 355.
- (196) (a) Gillespie, R. J.; Passmore, J. *Acc. Chem. Res.* **1971**, *4*, 413. (b) Gillespie, R. J.; Passmore, J. *Adv. Inorg. Chem.* **1975**, *17*, 49. (c) Burns, R. C.; Gillespie, R. J.; Sawyer, J. *Inorg. Chem.* **1971**, *10*, 2781.
- (197) Corbett, C. F. *Prog. Inorg. Chem.* **1976**, *21*, 129.
- (198) (a) Gillespie, R. J. *Inorg. Synth.* **1974**, *XV*, 213. (b) Oae, S. *Khimiya Organicheskikh soedinenii seri (Chemistry of Organosulfur Compounds)*; Khimiya: Moscow, 1975 (in Russian).
- (199) Rosan, A. M. *J. Chem. Soc., Chem. Commun.* **1985**, 377.
- (200) Olah, G. A.; Wang, Q.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1990**, *112*, 3697.
- (201) (a) Hopff, H.; Roggero, R.; Valkanes, G. *Rev. Chim. (Bucharest, Rom.)* **A1962**, *7*, 921.
- (202) Gejgy, J. R.; Brit, A. G. British Patent 783037, 1957; *Chem. Abstr.* **1958**, *52*, 3860.
- (203) Schmerling, L.; Vesely, J. A. *J. Org. Chem.* **1973**, *38*, 312.
- (204) Orlinkov, A. V.; Akhrem, I. S.; Afanas'eva, L. V.; Mysov, E. I.; Vol'pin, M. E. *Mendeleev Commun.* **1997**, 61.
- (205) Beckert, W. F.; Lowe, J. U. *J. Org. Chem.* **1967**, *32*, 582.
- (206) Akhrem, I. S.; Churilova, I. M.; Orlinkov, A. V.; Afanas'eva, L. V.; Vitt, S. V.; Petrovskii, P. V. *Russ. Chem. Bull.* **1998**, *47*, 918.
- (207) Angelini, G.; Fornarini, S.; Speranza, M. *J. Am. Chem. Soc.* **1982**, *104*, 4773.

- (208) Wasserman, E.; Hutton, R. S.; Kuck, V. J.; Chandross, E. A. *J. Am. Chem. Soc.* **1974**, *96*, 1965.
- (209) Morrison, R. T.; Boyd, R. N. *Organic Chemistry*; Allyn and Bacon, Inc.: Boston, MA, 1970; Chapter 12.8.
- (210) (a) Hopff, H. *Ber. Dtsch. Chem. Ges.* **1931**, *64*, 2739. (b) Hopff, H. *Ber. Dtsch. Chem. Ges.* **1932**, *65*, 482.
- (211) Hopff, H.; Nenitzescu, C. D.; Isacescu, D. A.; Cantuniar, I. P. *Ber. Dtsch. Chem. Ges.* **1936**, *69*, 2244.
- (212) Pines, H.; Ipatieff, V. N. *J. Am. Chem. Soc.* **1947**, *69*, 1337.
- (213) Hopff, H. *Angew. Chem.* **1948**, *60*, 245.
- (214) (a) Sakakura, T.; Tanaka, M. *Chem. Phys. Lett.* **1987**, *249*, 1113. (b) Sakakura, T.; Sodeyama, T.; Sasaki, K.; Wada, K.; Tanaka, M. *J. Am. Chem. Soc.* **1990**, *112*, 7221. (c) Tanaka, M.; Sakakura, T. In *Advances in Chemistry Series*; Moser, W. R.; Slocum, D. W. Eds.; American Chemical Society: Washington, DC, 1992; Vol. 230, p 181.
- (215) Margl, P.; Ziegler, T.; Blochl, P. E. *J. Am. Chem. Soc.* **1996**, *118*, 5412.
- (216) Lin, M.; Hogan, T. E.; Sen, A. *J. Am. Chem. Soc.* **1996**, *118*, 4574.
- (217) Barton, D. H. R. *Synlett* **1997**, 229.
- (218) Jaynes, B. S.; Hill, C. L. *J. Am. Chem. Soc.* **1995**, *117*, 4704.
- (219) (a) Boese, W. T.; Goldman, A. S. *Tetrahedron Lett.* **1992**, *33*, 2119. (b) Boese, W. T.; Goldman, A. S. *J. Am. Chem. Soc.* **1992**, *114*, 350.
- (220) Koch, W.; Haaf, H. *Angew. Chem.* **1960**, *72*, 628.
- (221) Hogeveen, H. *Advances in Physical Organic Chemistry*; Gold, V., Ed.; Academic Press: London, 1973; Vol. 10, p 29.
- (222) (a) Yoneda, N.; Fukuhara, T.; Takahashi, Y.; Suzuki, A. *Chem. Lett.* **1983**, *17*. (b) Yoneda, N.; Takahashi, Y.; Fukuhara, T.; Suzuki, A. *Bull. Soc. Chem. Jpn.* **1986**, *59*, 2819.
- (223) Xu, Q.; Souma, Y. *Top. Catal.* **1998**, *6*, 17.
- (224) Olah, G. A.; Schlosberg, R. H. *J. Am. Chem. Soc.* **1968**, *90*, 2726.
- (225) Olah, G. A.; Klopman, G.; Schlosberg, R. H. *J. Am. Chem. Soc.* **1969**, *91*, 3261.
- (226) (a) Balaban, A. T.; Nenitzescu, C. D. *Liebigs Ann.* **1959**, *66*, 625. (b) Nenitzescu, C. D.; Balaban, A. T. In *Friedel-Crafts and Related Reactions*; Olah, G. A., Ed.; Wiley: New York, 1964; Vol. 3, p 1033.
- (227) Orlinkov, A. V.; Akhrem, I. S.; Vitt, S. V. *Mendeleev Commun.* **1999**, 198.
- (228) Akhrem, I. S.; Orlinkov, A. V.; Afanas'eva, L. V.; Vol'pin, M. E. *Russ. Chem. Bull.* **1996**, *45*, 1154.
- (229) (a) Delavarenne, S.; Simon, M.; Fauconet, M.; Sommer, J. *J. Chem. Soc., Chem. Commun.* **1989**, 1049. (b) Delavarenne, S.; Simon, M.; Fauconet, M.; Sommer, J. *J. Am. Chem. Soc.* **1989**, *111*, 383. (c) Culmann, J.-C.; Simon, M.; Sommer, J. *J. Chem. Soc., Chem. Commun.* **1990**, 1098. (d) Bukala, J.; Culmann, J.-C.; Sommer, J. *J. Chem. Soc., Chem. Commun.* **1992**, 481.
- (230) Prakash, G. K. S.; Bausch, J. W.; Olah, G. A. *J. Am. Chem. Soc.* **1991**, *113*, 3203.
- (231) Gillespie, R. J.; Morton, M. J. *J. Chem. Soc., Chem. Commun.* **1968**, 1565.
- (232) Akhrem, I.; Orlinkov, A.; Afanas'eva, L.; Petrovskii, P.; Vitt, S. *Tetrahedron Lett.* **1999**, *40*, 5897.
- (233) Akhrem, I. S. *Top. Catal.* **1998**, *6*, 27.
- (234) Zhorov, Yu. M. *Termodinamika khimicheskikh protsessov [Thermodynamics of Chemical Processes]*; Khimiya: Moscow, 1985; p 182 (in Russian).
- (235) Akhrem, I.; Afanas'eva, L.; Vitt, S.; Petrovskii, P. *Mendeleev Commun.* **2002**, 180.
- (236) Haaf, W.; Koch, H. *Liebigs Ann.* **1960**, *638*, 122.
- (237) Souma, Y.; Sano, H. *Bull. Soc. Chim. Jpn.* **1974**, *47*, 1717.
- (238) (a) Egorov, S. V.; Kuchma, V. I.; Freidlina, R. Kh.; Terent'ev, A. B. *Chem. Abstr.* **1972**, *77*, 105202k. (b) Aslanov, N. N.; Barysheva, K. F.; Freidlina, R. Kh.; Terent'ev, A. B. *Chem. Abstr.* **1974**, *81*, 28080x. (c) Bogatyrev, P. M.; Smilga, H.; Belyaeva, K. R. Ivanov, B. I.; Freidlina, R. Kh.; Terent'ev, A. B. *Chem. Abstr.* **1975**, *83*, 81407b. (d) Freidlina, R. Kh.; Terent'ev, A. B.; Povolotskii, D. I.; Mihailov, V. M. *Chem. Abstr.* **1978**, *89*, 108166k.
- (239) Bernadyuk, S. Z.; Akhrem, I. S.; Vol'pin, M. E. *Mendeleev Commun.* **1994**, 183.
- (240) Culmann, J.-C.; Cherry, G.; Jost, R.; Sommer, J. *Tetrahedron Lett.* **1989**, *30*, 701.
- (241) Akhrem, I. S.; Afanas'eva, L. V.; Petrovskii, P. V.; Vitt, S. V.; Orlinkov, A. V. *Tetrahedron Lett.* **2000**, *41*, 9903.
- (242) Akhrem, I. S.; Afanas'eva, L. V.; Petrovskii, P. V.; Vitt, S. V.; Orlinkov, A. V. *Russ. Chem. Bull.* **2001**, *50*, 2394.
- (243) (a) Turova-Polyak, M. B.; Sidel'kovskaya, F. P. *Zh. Obsh. Khim.* **1941**, *11*, 817 [*J. Gen. Chem. USSR* **1941**, *11* (Engl. Trans.)]. (b) Guschin, P. P.; Lebedev, E. V.; Pivovarova, T. E. *Neftekhimiya* **1972**, *12*, 383.
- (244) Petrov, A. A. *Khimiya naftenov (The Chemistry of Naphthenes)*; Nauka: Moscow, 1971; p 191 (in Russian).
- (245) (a) Souma, Y.; Sano, H. *J. Org. Chem.* **1973**, *38*, 3633. (b) Souma, Y.; Sano, H. *Bull. Soc. Chim. Jpn.* **1976**, *49*, 3296.
- (246) Stull, D. R.; Westrum, E. F.; Sinke, G. R. *Chemical Thermodynamics of Organic Compounds*; Wiley-Interscience: New York, 1969.
- (247) Koch, H.; Haaf, W. *Org. Syntheses*; J. Wiley and Sons: New York, 1964; Vol. 44, p 1.
- (248) Kato, S.; Iwahama, T.; Sakaguchi, S.; Ishii, Y. *J. Org. Chem.* **1998**, *63*, 222.
- (249) Akhrem, I. S.; Afanas'eva, L. V.; Avetisyan, D. V.; Vitt, S. V.; Petrovskii, P. V., to be submitted for publication.
- (250) (a) Abboud, J.-L. M.; Castano, O.; Della, E. W.; Herreros, M.; Muller, P.; Notario, R.; Rossier, J.-C. *J. Am. Chem. Soc.* **1997**, *119*, 2262. (b) Schreiner, P. R.; Severance, D. L.; Jorgensen, W. L.; Schleyer, P. v. R.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1995**, *117*, 2663.
- (251) Olah, G. A.; Prakash, G. K. S.; Saunders, M. *Acc. Chem. Res.* **1983**, *15*, 440.
- (252) Grob, C. A. *Acc. Chem. Res.* **1983**, *16*, 426.
- (253) (a) Brown, H. C. (with comments by P. v. R. Schleyer) *The Non-Classical Ion Problem*; Plenum Press: New York, 1977. (b) Brown, H. C. *Acc. Chem. Res.* **1983**, *16*, 432.
- (254) (a) Koch, W.; Haaf, H. *Organic Synth.*, Coll. vol. V, 1973, p. 20. (b) Nazarova, M. P.; Morozov, V. A.; Podkhaluzin, A. T. *Zh. Org. Khim.*, **1983**, *19*, 565. (c) Barton, Derek H. R.; Bech, A. H.; Delanghe, N. C. *Tetrahedron Lett.*, **1996**, *37*, 1555. (d) Kovalev, V. V.; Fedorova, O. A.; Shokova, E. A. *Zh. Org. Khim.*, **1987**, *23*, 1672.
- (255) Akhrem, I.; Churilova, I.; Bernadyuk, S.; Vol'pin, M. *Tetrahedron Lett.* **1996**, *37*, 5775.
- (256) Akhrem, I. S.; Churilova, I. M.; Vitt, S. V.; Orlinkov, A. V.; Vol'pin, M. E. *Russ. Chem. Bull.* **1997**, *46*, 491.
- (257) (a) Olah, G. A.; Pelizza, F.; Kobayashi, S.; Olah, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 296. (b) Olah, G. A.; Laali, K.; Farooq, O. *J. Org. Chem.* **1985**, *50*, 483.
- (258) Farooq, O.; Marcelli, M.; Prakash, G. K. S.; Olah, G. A. *J. Am. Chem. Soc.* **1988**, *110*, 864.
- (259) Olah, G. A.; Wang, Q. *Synthesis* **1992**, 1090.
- (260) (a) Cremaschin, P.; Simonetta, M. *Theor. Chem. Acta* **1973**, *43*, 351. (b) Summers, N. L.; Tyrrell, J. *J. Am. Chem. Soc.* **1977**, *99*, 3960. (c) Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1983**, *105*, 5484. (d) Wong, M. W.; Yates, B. F.; Nobes, R. H.; Radom, L. *J. Am. Chem. Soc.* **1987**, *109*, 3181. (e) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986.
- (261) Harland, P. W.; Kim, N. D.; Petrie, S. A. *Austral. J. Chem.* **1989**, *42*, 9.
- (262) Takeuchi, K.; Miyazaki, T.; Katagawa, I.; Okamoto, K. *Tetrahedron Lett.* **1985**, *26*, 661.
- (263) Takeuchi, K.; Akiyama, F.; Miyazaki, T.; Katagawa, I.; Okamoto, K. *Tetrahedron Lett.* **1987**, *28*, 701.
- (264) Bassindale, A. R.; Taylor, R. P. G. In *The Chemistry of Organosilicon Compounds*; Patai, S.; Rappoport, J., Eds.; Wiley: Chichester, New York, Brisbane, 1989; Vol. 2, p 909.
- (265) Dey, K.; Eaborn, C.; Walton, D. R. M. *Organomet. Chem. Synthesis* **1970/71**, *1*, 151.
- (266) Yakubovich, A. Yu.; Motsarev, G. V. *Dokl. Akad. Nauk SSSR* **1953**, *88*, 87.
- (267) Olah, G. A.; Ho, T.-L.; Prakash, G. K. S.; Gupta, B. G. B. *Synthesis* **1977**, *10*, 677.
- (268) Akhrem, I. S.; Avetisyan, D. V.; Afanas'eva, L. V.; Vitt, S. V.; Petrovskii, P. V., to be submitted for publication.
- (269) Gorelik, M. V.; Efros, L. S. *Osnovy khimii i tekhnologii aromaticheskikh soedinenii (Foundations of the Chemistry and Technology of Aromatic Compounds)*; Khimiya: Moscow, 1992; p 270 (in Russian).
- (270) Ercoli, R.; Mantica, E.; Claudia, G.; Chiozzotto, S.; Santambrogio, E. *J. Org. Chem.* **1967**, *32*, 2917.
- (271) (a) Gronowitz, S. *Advances in Heterocyclic Chemistry*; Katritzky, A. R., Ed.; Acad. Press: New York, 1963; Vol. 1. (b) Meyers, A. J. *Heterocycles in Organic Syntheses*; Wiley-Interscience: New York, 1974; p 202. (c) Barton, D.; Ollis, W. D. *Comprehensive Organic Chemistry*; Sammes, P. G., Ed.; Pergamon Press: Oxford, New York, 1979; Vol. 4, Part 17.
- (272) Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*; Wiley: New York, 1999; p 494.
- (273) Mulzer, J. In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I., Eds.; Pergamon Press: Oxford, U.K., 1991; Vol. 6, p 323.
- (274) (a) Kontonasstos, D.; Sandres, C.; Tsatsas, G.; Casadio, S.; Lumachi, B.; Turba, C. *J. Med. Chem.* **1969**, *12*, 170. (b) Honna, K.; Ichikawa, H.; Fujimoto, Y. Japan Patent 77144680, 1977; *Chem. Abstr.* **1978**, *88*, 136676g.
- (275) Akhrem, I. S.; Avetisyan, D. V.; Afanas'eva, L. V.; Vitt, S. V.; Petrovskii, P. V.; Kagramanov, N. D.; Orlinkov, A. V. *Mendeleev Commun.* **2007**.

- (276) Akhrem, I. S.; Avetisyan, D. V.; Vitt, S. V.; Petrovskii, P. V., to be submitted for publication.
- (277) (a) Bourguignon, A. *Bull. Soc. Chim. Belg.* **1908**, 22, 87. (b) Gol'dfarb, Y. L.; Smorgonskii, L. M. *J. Gen. Chem.* **1938**, 8, 1516. (c) Cloke, J. B.; Pilgrim, F. J. *J. Am. Chem. Soc.* **1939**, 61, 2667. (d) British Patent 642489; *Chem. Abstr.* **1952**, 46, 132. (e) Burwell, R. L., Jr. *Chem. Rev.* **1954**, 54, 615. (f) Inoue, S.; Aide, T. In *Ring-Opening Polymerization*; Ivin, K. J.; Saegusa, T. Eds.; Elsevier Applied Science Publishers: London, New York, 1984; Vol. 1, p 186. (g) Pischmassade, B. F.; Nabiew, N. N. *Azerb. Khim. Zh.* **1971**, 92, 94; *Chem. Abstr.* **1972**, 76, 85 338.
- (278) Akhrem, I. S.; Avetisyan, D. V.; Vitt, S. V.; Petrovskii, P. V. *Mendeleev Commun.* **2005**, 5, 185.
- (279) (a) Oka, T. *Phys. Rev. Lett.* **1980**, 43, 531. (b) Oka, T. *Molecular Iones: Spectroscopy, Structure and Chemistry*; Miller, T. A.; Bondyby, V. E., Eds.; North Holland Publishing Company: Amsterdam, 1983; p 73.
- (280) Hogeveen, H.; Bickel, A. F. *Recl. Trav. Chim. Pays-Bas.* **1967**, 86, 1313.
- (281) (a) Tal'roze, V. L.; Lyubimova, A. L. *Dokl. Akad. Nauk SSSR* **1952**, 86, 909. (b) Jennings, K. R. *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, p 123.
- (282) (a) Gamba, A.; Morin, G.; Simonetta, M. *Chem. Phys. Lett.* **1969**, 3, 20. (b) Lathan, W. A.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1971**, 93, 808. (c) Dycymons, V.; Kutzeinigg, W. *Theor. Chem. Acta* **1974**, 33, 239.
- (283) Boo, D. W.; Lee, Y. T. *Chem. Phys. Lett.* **1993**, 221, 358.
- (284) (a) Ast, F. *Adv. Mass. Spectrum.* **1980**, 8A, 555. (b) Prakash, G. K. S.; Rawdah, T. N.; Olah, G. A. *Angew. Chem. Int. Ed.* **1983**, 95, 356. (c) Stahl, D.; Maquin, F. *Chimia* **1983**, 37, 87. (d) Lammertsma, K.; Barzaghi, M.; Olah, G. A.; Pople, J. A.; Schleyer, P. v. R.; Simonetta, M. *J. Am. Chem. Soc.* **1983**, 105, 5258. (e) Lammertsma, K.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1983**, 105, 1049. (f) Guihas, M.; Brenton, A. G.; Beynon, H. J.; Raberenivic, M.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1985**, 210.
- (285) Olah, G. A.; Rasul, G. *J. Am. Chem. Soc.* **1996**, 118, 12922.
- (286) Olah, G. A.; Rasul, G. *J. Am. Chem. Soc.* **1996**, 118, 8503.
- (287) Wexler, S.; Jesse, N. *J. Am. Chem. Soc.* **1962**, 84, 3425.
- (288) Hiraoka, K.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, 98, 6119.
- (289) Yeh, L. I.; Price, J. M.; Lee, Y. T. *J. Am. Chem. Soc.* **1989**, 111, 5597.
- (290) Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, 103, 5649.
- (291) Carneiro, J. W. M.; Schleyer, P. v. R.; Saunders, M.; Remington, R.; Schaefer, H. F., III; Rauk, A.; Sorensen, T. S. *J. Am. Chem. Soc.* **1994**, 116, 3483.
- (292) (a) Radom, L.; Poppinger, D.; Hadon, R. C. In *Carbonium Ions*, 5; Olah, G. A.; Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1976; p 2329. (b) Okulik, N. B.; Sosa, L. G.; Esteves, P. M.; Mota, C. J. A.; Jubert, A. H.; Peruchena, N. M. *J. Phys. Chem. A* **2002**, 106, 1584. (c) Bader, R. F. W. *Atoms in Molecules. A Quantum Theory*; Charendon: Oxford, U.K., 1990.
- (293) Wang, Z.-X.; Huang, M.-B. *J. Am. Chem. Soc.* **1998**, 120, 6758.
- (294) Chistyakov, A. L.; Stankevich, I. V.; Gambaryan, N. P.; Akhrem, I. S. *Russ. Chem. Bull.* **2000**, 49, 799.
- (295) Chistyakov, A. L.; Stankevich, I. V.; Gambaryan, N. P.; Akhrem, I. S. *Zh. Org. Khim.* **2001**, 37, 1755. [*J. Org. Chem. Russ.* **2001**, 37 (Engl. Transl.)].
- (296) Chistyakov, A. L.; Stankevich, I. V.; Gambaryan, N. P.; Akhrem, I. S. *Zh. Org. Khim.* **2003**, 39, 659 [*J. Org. Chem. Russ.* **2003**, 39 (Engl. Transl.)].
- (297) (a) Olah, G. A.; Hartz, N.; Rasul, G.; Wang, Q.; Prakash, G. K. S.; Casanova, J.; Christie, K. O. *J. Am. Chem. Soc.* **1994**, 116, 5671. (b) Schreiner, P. R.; Fokin, A.; Schleyer, P. v. R.; Schaefer, H. F., III. In *Conceptual Trend in Quantum Chemistry*; Kryachko E., Ed.; Kluwer Academic Publ.: Dordrecht, Netherlands, 2003; p 369.
- (298) Schreiner, P. R.; Schleyer, P. v. R.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1993**, 115, 9659.
- (299) Schreiner, P. R.; Schleyer, P. v. R.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1995**, 117, 453.
- (300) Olah, G. A.; Hartz, N.; Rasul, G.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1995**, 117, 1336.
- (301) De Puy, C. H.; Gareyev, R.; Hankin, J.; Davico, G. E.; Krempp, M.; Damrauer, R. *J. Am. Chem. Soc.* **1998**, 120, 5086.
- (302) (a) Olah, G. A.; Farooq, O.; Prakash, G. K. S. *Activation and Functionalization of Alkanes*; Hill, C. L., Ed.; John Wiley and Sons: New York, 1989; p 27. (b) Olah, G. A.; Parker, D. G.; Yoneda, N. *Angew. Chem., Int. Ed.* **1978**, 17, 909.
- (303) (a) Bach, R. D.; Andres, J. L.; Su, M.-D.; McDouall, J. J. W. *J. Am. Chem. Soc.* **1993**, 115, 5768. (b) Bach, R. D.; Su, M.-D. *J. Am. Chem. Soc.* **1994**, 116, 10103.
- (304) Bach, R. D.; Su, M.-D.; Aldabbagh, E.; Andres, J. L.; Schlegel, H. B. *J. Am. Chem. Soc.* **1993**, 115, 10237.
- (305) For discussion see: Jorgensen, W. L.; Salem, L. *The Organic Chemist's Book of Orbitals*; Academic Press: New York, 1993.
- (306) (a) Groves, J. T.; McClunsky, G. A. *J. Am. Chem. Soc.* **1976**, 98, 859. (b) Groves, J. T. *J. Chem. Educ.* **1985**, 62, 928.
- (307) Sono, M.; Roach, M. P.; Coulter, E. D.; Dawson, J. H. *Chem. Rev.* **1996**, 96, 2841.
- (308) (a) Atkinson, J. K.; Hollenberg, P. F.; Ingold, K. U.; Johnson, C. C.; Le Tadic, M.-H.; Newcomb, M.; Putt, D. A. *Biochemistry* **1994**, 33, 10630. (b) Newcomb, M.; Le Tadic, M.-H.; Putt, D. A.; Hollenberg, P. F. *J. Am. Chem. Soc.* **1995**, 117, 3312. (c) Newcomb, M.; Shen, R.; Choi, S.-Y.; Toy, P. H.; Hollenberg, P. F.; Vaz, A. D. N.; Coon, M. J. *J. Am. Chem. Soc.* **2000**, 122, 2677. (d) Collman, J. P.; Chien, A. S.; Eberspacher, T. A.; Brauman, J. I. *J. Am. Chem. Soc.* **2000**, 122, 11098.
- (309) (a) Shestakov, A. F.; Shilov, A. E. *J. Mol. Catal. A* **1996**, 105, 559. (b) Karasevich, E. I.; Shestakov, A. F.; Shilov, A. E. *Kinet. Catal.* **1997**, 38, 782.
- (310) Liu, K. E.; Johnson, C. C.; Newcomb, M.; Lippard, S. J. *J. Am. Chem. Soc.* **1993**, 115, 939.
- (311) Choi, S.-Y.; Eaton, P. E.; Kopp, D. A.; Lippard, S. J.; Newcomb, M.; Shen, R. *J. Am. Chem. Soc.* **1999**, 121, 12198.
- (312) Yoshizara, K.; Shiota, Y.; Yamabe, T. *Organometallics* **1998**, 17, 2825.
- (313) (a) Bau, R.; Teller, R. G.; Kirtley, S. W.; Koetzle, T. F. *Acc. Chem. Res.* **1979**, 12, 176. (b) McMurry, J. E.; Lectka, T. *Acc. Chem. Res.* **1992**, 25, 47.
- (314) (a) Prelog, V.; Traynham, J. G. *Molecular Rearrangements*, de Mayo, P., Ed.; Interscience: New York, 1963; Vol. 1, p 593. (b) Cope, A. C.; Martin, M. M.; McKervey, M. A. *Q. Rev. Chem. Soc.* **1966**, 20, 119.
- (315) Kirchen, R. P.; Sorensen, T. S. *J. Chem. Soc., Chem. Commun.* **1978**, 769.
- (316) (a) Kirchen, R. P.; Sorensen, T. S.; Wagstaff, K. *J. Am. Chem. Soc.* **1978**, 100, 6761. (b) Kirchen, R. P.; Sorensen, T. S. *J. Am. Chem. Soc.* **1979**, 101, 3240. (c) Kirchen, R. P.; Okazawa, N.; Ranganayakulu, K.; Rauk, A.; Sorensen, T. S. *J. Am. Chem. Soc.* **1981**, 103, 597. (d) Sorensen, T. S.; Whitworth, S. M. *J. Am. Chem. Soc.* **1990**, 112, 8135. (e) Sun, F.; Sorensen, T. S. *J. Am. Chem. Soc.* **1993**, 115, 77. (f) Galasso V. *Int. Quantum Chem.* **1998**, 70, 313. (g) Galasso V. *Chem. Phys.* **1999**, 241, 247.
- (317) Kirchen, R. P.; Ranganayakulu, K.; Rauk, A.; Singh, B. P.; Sorensen, T. S. *J. Am. Chem. Soc.* **1981**, 103, 588.
- (318) (a) Boronat, M.; Viruela, P.; Corma, A. *J. Phys. Chem. B* **1997**, 101, 10069. (b) Boronat, M.; Viruela, P.; Corma, A. *J. Phys. Chem. B* **1999**, 103, 7809.
- (319) Vrcek, I. V.; Vrcek, V.; Siehl, H.-U. *J. Phys. Chem. A* **2002**, 106, 1604.
- (320) Chistyakov, A. L.; Stankevich, I. V.; Gambaryan, N. P.; Akhrem, I. S.; Vol'pin, M. E. *Russ. Chem. Bull.* **1998**, 47, 1666.
- (321) (a) Chistyakov, A. L.; Stankevich, I. V.; Gambaryan, N. P.; Akhrem, I. S. Presented at the VIIIth Russian Conference on Organometallic Chemistry, Moscow, Russia, 1999; book of abstracts, p 220. (b) Gambaryan, N. P.; Chistyakov, A. L.; Stankevich, I. V.; Akhrem, I. S. Presented at the Modern Trends in Organoelement and Polymer Chemistry, International Conference, Moscow, Russia, 2004; p 182.
- (322) Chistyakov, A. L.; Stankevich, I. V.; Akhrem, I. S.; Gambaryan, N. P.; Vol'pin, M. E. *Russ. Chem. Bull.* **1996**, 45, 514.
- (323) Akhrem, I. S.; Chistyakov, A. L.; Gambaryan, N. P.; Vol'pin, M. E. *J. Organomet. Chem.* **1997**, 536, 489.
- (324) Olah, G. A.; Rasul, G.; Yudin, A.; Burrichter, A.; Prakash, G. K. S.; Chistyakov, A. L.; Stankevich, I. V.; Akhrem, I. S.; Gambaryan, N. P.; Vol'pin, M. E. *J. Am. Chem. Soc.* **1996**, 118, 1446.
- (325) Frenking, G.; Fau, S.; Marchand, C. M.; Grutzmacher, H. *J. Am. Chem. Soc.* **1997**, 119, 6648.
- (326) Chistyakov, A. L.; Stankevich, I. V.; Gambaryan, N. P.; Akhrem, I. S. *Dokl. Acad. Nauk* **2003**, 390, 205.
- (327) Chistyakov, A. L.; Stankevich, I. V.; Gambaryan, N. P.; Akhrem, I. S. *Zh. Org. Khim.* **2006**, 42, 1621.
- (328) (a) Olah, G. A. *Halonium Iones*; Wiley-Interscience: New York, 1975. (b) Koser, G. F. *The Chemistry of Functional Groups*, Supplement, D.; Patai, S.; Rappoport, Z., Eds.; J. Wiley & Sons: New York, 1983; Chapter 25.
- (329) Creary, X. *Chem. Rev.* **1991**, 91, 1625.
- (330) (a) Schleyer, P. v. R. *Pure Appl. Chem.* **1987**, 59, 1647. (b) Bernardi, F.; Bottoni, A.; Venturini, A. *J. Am. Chem. Soc.* **1986**, 108, 5395. (c) Rodriguez, C. F.; Hopkinson, A. C. *J. Mol. Struct.: THEOCHEM* **1987**, 152, 55.
- (331) (a) Gonzalez, A. I.; Mo, O.; Yanez, M.; Leon, E.; Tortajada, J.; Morizur, J. P.; Leito, I.; Maria, P.-C.; Gal, J. F. *J. Phys. Chem.* **1996**, 100, 10490. (b) Gobbi, A.; Frenking, G. *J. Am. Chem. Soc.* **1993**, 115, 2362. (c) Jordan, M. J.; Gready, J. E. *J. Comput. Chem.* **1989**, 10, 186. (d) Ohlmann, D.; Marchand, C. M.; Grutzmacher, H.; Chen, G. S.; Farmer, D.; Glaser, R.; Currao, A.; Nesper, R.; Pritzkow, H. *Angew. Chem., Int. Ed.* **1996**, 35, 300.

- (332) Glaser, R.; Choy, G. S.-C.; Chen, G. S.; Grutzmacher, H. *J. Am. Chem. Soc.* **1996**, *118*, 11617.
- (333) Chistyakov, A. L.; Stankevich, I. V.; Gambaryan, N. P.; Chistyakov, A. L.; Stankevich, I. V.; Akhrem, I. S. Presented at the IVth Russian Conference "Molecular Modelling", Moscow, Russia, 2005; book of abstracts, p 57.
- (334) Chistyakov, A. L.; Stankevich, I. V.; Akhrem, I. S.; Gambaryan, N. P.; Vol'pin, M. E. *Russ. Chem. Bull. Int. Ed.* **2001**, *50*, 28.
- (335) Zefirov, Yu. V.; Zorkii, P. M. *Russ. Chem. Rev.* **1995**, *64*, 446.
- (336) Reutov, O. A.; Beletzkaya, I. P.; Sokolov, V. I. *Mechanisms of Organometallic Compounds*; Chemistry: Moscow, 1972 (in Russian).
- (337) Olah, G. A. *Carbocations and Electrophilic Reactions*; Verlag Chemie, Wiley: New York, 1974.

CR970005N