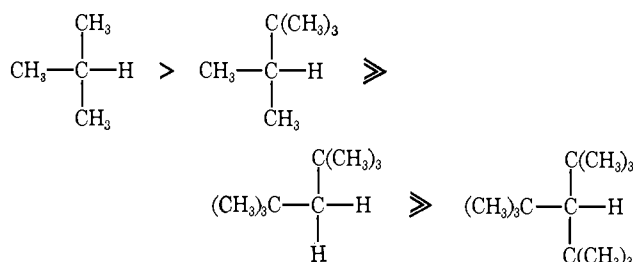


kinetic studies (in progress) and must always be related to specific systems studied. Isoalkanes containing a tertiary C-H bond show preference of reactivity of this bond. (This can also include hydride transfer to alkyl-carbenium ions formed in C-C bond protolysis.) Increased branching and steric crowding can cause a shift of reactivity in favor of C-C bond protolysis. Comparison of isobutane, triptane, di-*tert*-butylmethane, and tri-*tert*-butylmethane²¹ demonstrates well this point. The decreasing order of tertiary C-H bond reactivity is



In isobutane, C-H over C-C reactivity at -78° is 50:1 and at 25° it is about 9:1. In triptane under similar conditions the reactivity ratio is 20:1 and 3:1, respectively. In di-*tert*-butylmethane, C-C bond reactivity is nearly exclusive and in tri-*tert*-butylmethane²¹ there is absolutely no observable reactivity on the highly shielded C-H bond. Similar to the well-studied steric factors of n - or π -donor bases,²² steric strain thus effects σ bond basicities of alkanes.

The concept of triangular three-center bond formation in pentacoordinated carbonium ion type transition states (or even probable intermediates in some favorable cases) satisfactorily explains the mechanism of acid-catalyzed saturated hydrocarbon transformation reactions. These include isomerizations (involving hydrogen and alkyl shifts), fragmentations, and alkylations (see subsequent communication). This concept supplements Whitmore's and Bartlett's mechanisms where trivalent carbenium ion processes (frequently associated with subsequent deprotonation leading to olefin formation) are involved. At the same time our work substantially extends the scope and understanding of electrophilic reactions, based on the realization of the general electron pair donor ability of single bonds (shared electron pairs) which eventually may equal the importance of lone electron pairs (unshared electron pairs, Lewis bases).

Acknowledgment. Support of our work by the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation is gratefully acknowledged.

(21) Professor M. Stiles is thanked for a sample of tri-*tert*-butylmethane and information on the synthesis of the compound prior to publication.

(22) H. C. Brown and R. D. Johanessen, *J. Amer. Chem. Soc.*, **75**, 16 (1953), and earlier papers referred to therein.

George A. Olah,* Yuval Halpern, Jacob Shen, Y. K. Mo

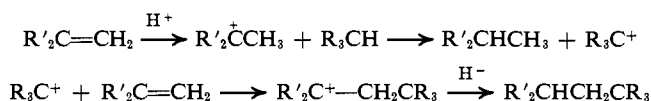
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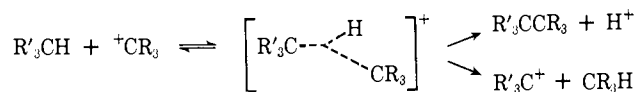
Electrophilic Reactions at Single Bonds. IV.^{1a} Hydrogen Transfer from, Alkylation of, and Alkylolysis of Alkanes by Alkylcarbenium Fluoroantimonates^{1b}

Sir:

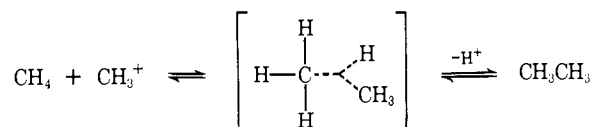
Despite frequent literature references to electrophilic alkylation of alkanes by olefins, from a mechanistic point of view these reactions must be considered as alkylations of the olefin by the carbenium ion derived from the isoalkane by intermolecular hydride transfer.² The suggested reaction pathway is reflected by the



products formed in the reaction of propylene and isobutylene with isobutane. Products do not contain 2,2,3-trimethylbutane or 2,2,3,3-tetramethylbutane, which would be expected primary alkylation products in direct alkylation of isobutane with propylene and isobutylene, respectively. In the Bartlett-Nenitzescu intermolecular hydride abstraction from a tertiary isoalkane by a carbenium ion, the transition state either could be considered linear or triangular (from frontside attack on the C-H bond). The latter would not be symmetrical due to a steric effect between the carbenium ion and the tertiary isoalkane. With an even strongly distorted triangular transition state (*i.e.* the reaction taking place on the C-H bond and not at the hydrogen atom), it becomes obvious that cleavage can result not only in intermolecular hydride transfer, but also, *via* proton elimination, in direct alkylation



For simplicity we are depicting the triangular three-center bonds with dotted lines. To study the reaction of alkanes with alkylcarbenium ions with the hope of carrying out "direct" alkane alkylations, it was necessary to find carbocation reaction conditions unfavorable for olefin formation in order to eliminate the previously discussed reaction pathway for olefin-isoalkane alkylation. To our knowledge the only alkane alkylation reported so far in the literature fulfilling these conditions was our recently discovered methane and methyl fluoride condensation reaction.³ The methyl cation (CH_3^+) formed in the course of the reactions methylates excess methane (or methyl fluoride) in the key step.



We report now the first systematic study of the direct alkylation of alkanes (both isoalkanes and *n*-alkanes)

(1) (a) Part III: G. A. Olah, Y. Halpern, J. Shen, and Y. K. Mo, *J. Amer. Chem. Soc.*, **93**, 1251 (1971). (b) For a general definition of carbocations and differentiation of trivalent carbenium ions from penta- or tetraordinated carbonium ions see G. A. Olah, *ibid.*, in press.

(2) For a summary, see L. Schermerling in "Friedel-Crafts and Related Reactions," G. A. Olah, Ed., Vol. II, Wiley-Interscience, New York, N. Y., 1964, pp 1075-1131, and references given therein.

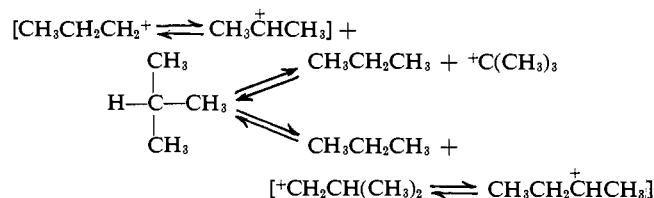
(3) G. A. Olah and R. H. Schlosberg, *J. Amer. Chem. Soc.*, **90**, 2726 (1968); **91**, 3261 (1969).

by alkylcarbenium ion salts using the aprotic solvent, SO_2ClF . Whereas the system is aprotic initially, as the alkylation reaction proceeds proton elimination produces fluoroantimonic acid. Protolytic side reactions are thus possible, but in the relatively low concentrations of acid formed and at low temperatures used they are not of major importance.

We achieved alkylations by using stable alkylcarbenium fluoroantimonate salts⁴ (like isopropyl, *sec*-butyl, and *tert*-butyl fluoroantimonates) prepared from the corresponding halides and antimony pentafluoride in sulfur chloride fluoride solution⁵ and treating them in the same solvent system with alkanes. Reagents were mixed at -78° , warmed up to -20° (1 min), and then quenched with cold methanol or ice water. Products were analyzed by capillary gas-liquid chromatography and comparison with pure hydrocarbons.

Intermolecular hydride transfer between tertiary and secondary carbenium ion reagents and alkanes is always the fast reaction in the systems, with alkylation reactions being generally much slower. Consequently, alkylation products are also those derived from the new alkanes and carbenium ions formed in the hydride transfer reaction (*i.e.*, secondary alkylation products). Relative rates of hydrogen transfer and alkylation determine product compositions. Furthermore, isomerization of the carbenium ions and to some degree the alkanes, through usual intramolecular processes, causes further diversification of the alkylation mixture. Products result from all hydrocarbons and carbenium ions present in the system. Isomerization of alkanes can be depressed, although not completely eliminated, by carrying out the alkylation at low temperatures (generally -78 to -20°) and for only short reaction times (<30 sec).

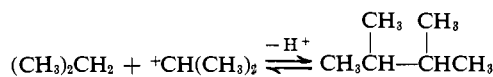
Typical examples of alkylation of alkanes are those of propane, isobutane, or *n*-butane by isopropyl cation, or the alkylation of propane and butanes by *tert*-butyl or *sec*-butyl cation, systems made somewhat interchangeable by competing hydrogen transfer and rearrangement of carbenium ions (although product compositions very much depend on relative rates of all competing processes).



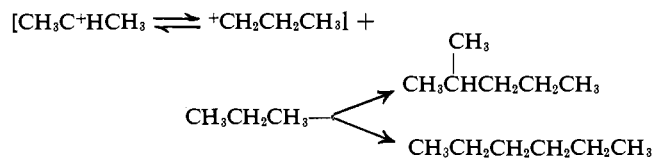
Propylation of propane by isopropyl fluoroantimonate gave typical hexane isomer distributions like 26% 2,3-dimethylbutane, 28% 2-methylpentane, 14% 3-methylpentane, and 32% *n*-hexane. (It must be emphasized that product compositions in all alkylations are dependent on reaction conditions; therefore, only results of typical experiments can be given.) 2,3-Dimethylbutane is clearly a primary alkylation product

(4) For a summary see G. A. Olah and J. A. Olah in "Carbonium Ions," G. A. Olah and P. v. R. Schleyer, Ed., Vol. II, Wiley-Interscience, New York, N. Y., 1970, Chapter 17, pp 715-782.

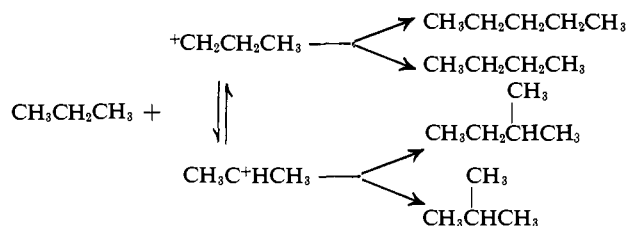
(5) This extremely useful solvent was introduced into carbocation chemistry in our previous work (for example, G. A. Olah and J. Lukas, *J. Amer. Chem. Soc.*, **89**, 4739 (1967).



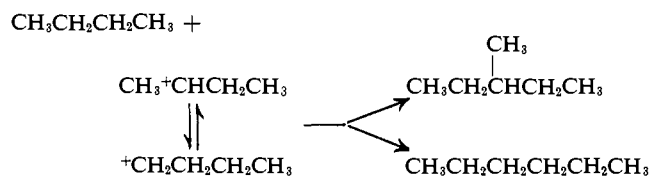
The high amount of *n*-hexane formed indicates that not only the isopropyl cation, but also the *n*-propyl cation (as shown by $\text{C}_2 \rightarrow \text{C}_1$ scrambling in the long-lived isopropyl cation⁶) is also involved in alkylation.



The absence of 2,2-dimethylbutane from the alkylate hexanes indicates substantially nonisomerizing conditions, as this isomer is important in acid-catalyzed isomerization of hexanes. The alkylation products also show the presence of *n*-butane, isobutane, *n*-pentane, and isopentane and small amounts of C_7 and C_8 alkylates (obviously formed through hydrogen transfer and alkylation involving butanes and pentanes). Formation of *n*-butane and *n*-pentane as well as isobutane and isopentane is rationalized by *C-C bond alkylation* in propane (*alkylolysis*).⁷



Very different hexane isomer distributions were obtained in the C_6 fractions of alkylation of butanes with butyl cations (or in $\text{C}_4 + \text{C}_3$ systems). For example when *n*-butane is allowed to react with *sec*-butylcarbenium fluoroantimonate, the hexane fraction, depending on reaction conditions, contains from 57 to 88% of 3-methylpentane and 38 to 7% *n*-hexane, with only 3 or 4% 2,3-dimethylbutane and about 1% 2-methylpentane. Data strongly indicate alkylolysis of *C-C* bonds of *n*-butane by *sec*-butyl cation.



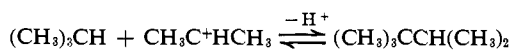
Alkylations of propane by butyl fluoroantimonates or of butanes by isopropyl fluoroantimonate yield the expected more complex product mixtures. Hexanes (C_6 fraction), heptanes (C_7 fraction), and octanes (C_8 fraction) are the major alkylates formed in varying ratios, reflecting relative rates of alkylation and hydrogen transfer.

The relative amount of C_7 alkylates in the $\text{C}_4 + \text{C}_3$ systems is relatively low (10-25% of combined C_6 - C_8 alkylates), reflecting the faster intermolecular hydride

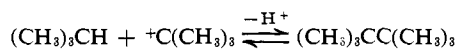
(6) G. A. Olah and A. M. White, *ibid.*, **92**, 2546 (1970).

(7) We define *C-H* bond substitution (*i.e.*, replacement of hydrogen) as *alkylation* and *C-C* bond substitution (involving *C-C* bond cleavage) as *alkylolysis* (similarly to protolysis, nitrolysis, chlorolysis, etc.).

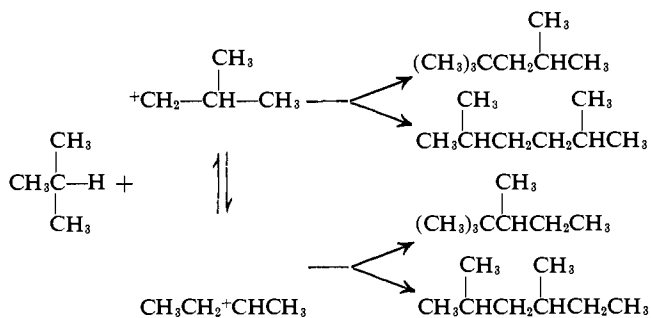
transfer compared to alkylation. This point is particularly emphasized in the reaction of propane with *tert*-butyl cation. Only 10% of heptanes are formed, due to the particularly fast hydride transfer reaction between propane and the *tert*-butyl cation, which gives isopropyl cation. The isopropyl cation then reacts with propane giving 70% hexanes. Under the reaction conditions 2,3-dimethylbutane and 2-methylpentane are the main products in 41 and 54% yield, respectively, and only 2% *n*-hexane is formed. In the C₇ fraction there is 5–12% 2,2,3-trimethylbutane (triptane), depending on reaction conditions, indicating direct primary alkylation of the tertiary C–H bond by the isopropyl cation.



Regardless of whether starting from isobutane or *n*-butane, both butanes are always present in equilibrium due to hydrogen transfer and carbenium ion rearrangement taking place in the systems. Alkylation products, consequently, are also derived from *sec*-butyl and isobutyl cations (protonated methylcyclopropane can be involved in the ion rearrangement). Indeed we feel that direct alkylation by the bulkier *tert*-alkylcarbenium ions (like the *tert*-butyl cation) is limited because of steric reasons and due to the much faster intermolecular hydrogen transfer reactions, giving more reactive and sterically less hindered secondary and even (through rearrangements involving protonated cyclopropanes) incipient primary carbenium ions. That tertiary carbenium ions themselves can act as alkylating agents is proven, however, by the formation of small, but important amounts (1–2% of the C₈ fractions) of 2,2,3,3-tetramethylbutane in the alkylation of isobutane with *tert*-butyl fluoroantimonate. We can visualize no other way than direct alkylation of the C–H bond in isobutane for its formation.



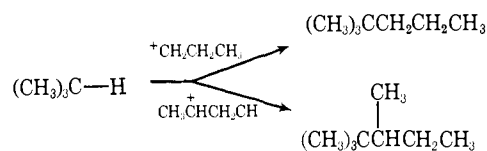
It is interesting to note that the reverse reactions, *i.e.*, the protolytic cleavage of 2,2,3,3-tetramethylbutane (as well as those of other discussed alkylation reactions), were also observed,¹ indicating related three-center bound pentacoordinated carbonium ion transition states. The major C₈ products of the reaction of isobutane and *tert*-butyl fluoroantimonate are 2,2,4-trimethylpentane (18%), 2,5-dimethylhexane (43%), as well as 2,4-dimethylhexane (7.5%) and 2,2,3-trimethylpentane (3%), indicating alkylation by the *sec*-butyl and isobutyl cation (protonated methylcyclopropane).



Propane and 2-methylbutane are also formed in the system indicating C–C bond alkylation (alkylolysis) of isobutane with subsequent hydride transfer to the

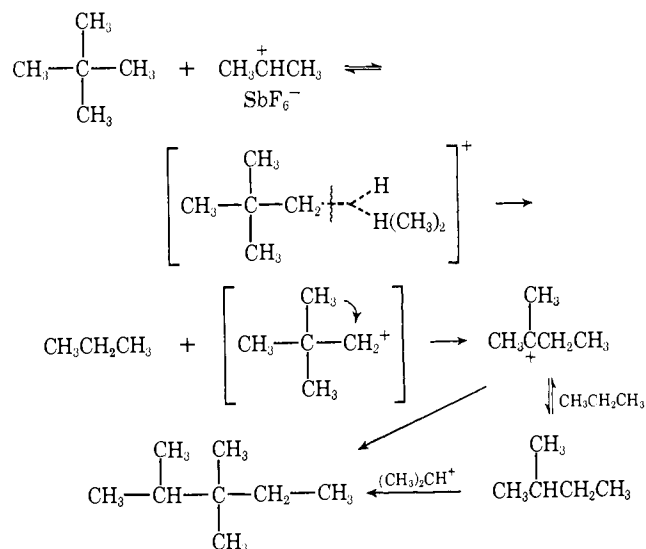
isopropyl cation. The formation of C₇ (as well C₆) alkylates is also indicative of initial alkylolysis followed by alkylation in the C₄ + C₃ system. Additional alkylation products also include those derived from *n*-butane (formed *via* hydride transfer in the system), like 3-methylhexane. When *tert*-butyl fluoroantimonate is treated with *n*-butane, the fast reaction is hydride transfer, giving *sec*-butyl cation which then alkylates isobutane to give as the main product (70%) 2,2,3-trimethylpentane.

The bulky *tert*-butyl cation thus plays only a minor role in direct alkylations of alkanes, but produces secondary cations with ease in intramolecular hydrogen transfer reactions. Consequently, we interpret formation of 2,2-dimethylpentane (a major product in C₄ + C₃ alkylation) and of 2,2,3-trimethylpentane (in C₄ + C₄ alkylation) not as tertiary butylation by the *tert*-butyl cation, but as propylation or butylation of isobutane by the more reactive and less bulky secondary or incipient primary ions.



In all these reactions C–C bond alkylation (alkylolysis) by the secondary alkylcarbenium ions is always observed and thus plays an important role.

The *tert*-butyl cation does not alkylate methane and ethane under the reaction conditions used (in SO₂ClF solution at low temperature). In contrast the isopropyl cation reacts with ethane showing hydride transfer and alkylation (products being propane with some isobutane and 2-methylbutane also formed). At higher reaction temperatures there is even indication of reaction of the isopropyl cation with methane (indicated by the formation of propane and some isobutane). Neopentane reacts with isopropyl cation showing predominant hydride transfer and some alkylation. However, the latter is not necessarily direct alkylation of neopentane (C–C alkylation is indicated by formation of isobutane), but of isopentane (formed *via* rearrangement of the primary neopentyl cation and hydride transfer), as the main C₈ alkylation product is 2,2,3-trimethylpentane. The *sec*-butyl cation



generally shows reactivity similar to that of the isopropyl cation.

As alkylcarbenium ions are readily formed when alkanes themselves are treated with superacids, it is not surprising that we observed polycondensation (self-alkylation) when treating an excess of simple alkanes (including methane, ethane, propane, and butanes) with $\text{FSO}_3\text{H-SbF}_5$ ("magic acid") to form highly branched polyalkanes of low molecular weight.

In conclusion, the major reactions in the alkylation of alkanes by alkylcarbenium ions are: (1) fast intermolecular hydrogen transfer, (2) direct alkylation and/or alkylolysis, (3) secondary alkylation and/or alkylolysis. The nature of the transition state in all of these reactions is considered to involve electrophilic frontside attack on covalent C-H or C-C bonds by the carbenium ions. The three-center bonds in the triangular transition states are not considered symmetrical, particularly when steric hindrance, like in tertiary-tertiary systems, makes this difficult. In the transition states, however, attack by the electrophile still is on the covalent bonds, where the electron density resides (the back lobes of the orbitals are considered poor electron donors, since probably less than 10% of the overall electron density is to be found in them). The role of steric hindrance is well demonstrated by the relatively small amount of 2,2,3,3-tetramethylbutane formed in the reaction of isobutane with *tert*-butyl cation. The sterically less hindered isopropyl cation with isobutane gives higher yields of 2,2,3-trimethylbutane, as does the reaction of *sec*-butyl cation with isobutane.

It can be concluded that aliphatic electrophilic alkylation of alkanes by alkylcarbenium ions is a general reaction which can proceed without involvement of olefins and represents a significant example of electrophilic reactions at single bonds.

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Received September 12, 1970

Electrophilic Reactions at Single Bonds. V.¹ Nitration and Nitrolysis of Alkanes and Cycloalkanes with Nitronium Salts

Sir:

Whereas electrophilic aromatic nitration is one of the most thoroughly studied substitution reactions, electrophilic aliphatic nitration remains virtually unrecognized. Nitration of paraffins was first carried out by Beilstein and Kurbatov² in 1880 and subsequently by Konovalov³ and Markovnikov.⁴ It was shown that generally higher temperatures and dilute nitric acid is needed to achieve nitration of saturated aliphatic hydrocarbons. Hass⁵ in the 1930's developed a

(1) Part IV: G. A. Olah and J. A. Olah, *J. Amer. Chem. Soc.*, **93**, 1256 (1971).

(2) F. Beilstein and A. Kurbatov, *Ber.*, **13**, 1818, 2029 (1880).

(3) M. Konovalov, *ibid.*, **26**, 878 (1893); **28**, 1852 (1895).

(4) V. Markovnikov, *ibid.*, **32**, 1441, 1445 (1899); **33**, 1905 (1900); **35**, 1584 (1902).

practical gas-phase nitration of paraffins like propane, *n*-butane and isobutane, and *n*-pentane and isopentane with nitric acid vapor at 350–400°. Grundmann⁶ was able to extend the scope of the reaction to higher molecular weight hydrocarbons by carrying out the reaction at 160–180° in the liquid phase, with superheated nitric acid vapor or with nitrogen dioxide. From all these studies it was generally concluded that aliphatic hydrocarbon nitrations are free-radical reactions, with nitrogen dioxide acting as the nitrating agent.⁷

We now report our observations that electrophilic nitration and nitrolysis⁸ of alkanes and cycloalkanes with stable nitronium salts can be carried out under well-controlled conditions, excluding the probability of free-radical formation.

A colorless solution of a stable nitronium salt (generally the hexafluorophosphate $\text{NO}_2^+\text{PF}_6^-$ but also the hexafluoroantimonate $\text{NO}_2^+\text{SbF}_6^-$ or tetrafluoroborate $\text{NO}_2^+\text{BF}_4^-$) in methylene chloride-tetramethylene sulfone solution was treated with the alkane (cycloalkane), with usual precautions taken to avoid moisture and other impurities. Reactions were carried out at room temperature (25°) and in the dark in order to avoid or minimize the possibility of radical side reactions and/or protolytic cleavage reactions (tertiary nitroalkanes particularly undergo ready protolytic cleavage reactions). No attempt was made to optimize conditions or increase yields by raising reaction temperatures.

Product analyses were carried out by gas-liquid chromatography and comparison (ir, nmr) of isolated products with authentic materials. Data obtained are summarized in Table I.

Table I. Nitration and Nitrolysis of Alkanes and Cycloalkanes with $\text{NO}_2^+\text{PF}_6^-$ in CH_2Cl_2 -Sulfolane Solution at 25°

Hydrocarbon	Nitroalkane products and their mol ratio
Methane	CH_3NO_2
Ethane	$\text{CH}_3\text{NO}_2 > \text{CH}_3\text{CH}_2\text{NO}_2$, 2.9:1
Propane	$\text{CH}_3\text{NO}_2 > \text{CH}_3\text{CH}_2\text{NO}_2 > 2\text{-NO}_2\text{C}_3\text{H}_7 > 1\text{-NO}_2\text{C}_3\text{H}_7$, 2.8:1:0.5:0.1
Isobutane	<i>tert</i> - $\text{NO}_2\text{C}_4\text{H}_9 > \text{CH}_3\text{NO}_2$, 3:1
<i>n</i> -Butane	$\text{CH}_3\text{NO}_2 > \text{CH}_3\text{CH}_2\text{NO}_2 > 2\text{-NO}_2\text{C}_4\text{H}_9 \sim 1\text{-NO}_2\text{C}_4\text{H}_9$, 5:4:1.5:1
Neopentane	$\text{CH}_3\text{NO}_2 > \textit{tert}-\text{C}_4\text{H}_9\text{NO}_2, 3.3:1$
Cyclohexane	Nitrocyclohexane
Adamantane	1-Nitroadamantane > 2-nitroadamantane, 17.5:1

The σ basicity of alkanes obviously is lower than the n basicity of lone-pair donor molecules used as solvent systems. This represents a major difficulty in achieving practical aliphatic nitrations with nitronium ions.

(5) H. B. Hass, *et al*, *Ind. Eng. Chem.*, **28**, 339 (1936); **30**, 67 (1938); **31**, 648 (1939); **32**, 427 (1940); **33**, 1138 (1941).

(6) C. Grundmann, *Chemie*, **56**, 159 (1943).

(7) For summaries on aliphatic nitration see (a) F. Asinger, "Paraffins," Pergamon Press, New York, N. Y., 1968, Chapter 4, pp 365–482; (b) A. V. Topchiev, "Nitration of Hydrocarbons and Other Organic Compounds," Pergamon Press, New York, N. Y., 1960; (c) A. I. Titov, *Tetrahedron*, **19**, 557 (1963); (d) N. Kornblum, *Org. React.*, **12**, 101 (1962); (e) H. O. Larson in "The Chemistry of the Nitro and Nitroso Group," Vol. I, H. Feuer, Ed., Wiley-Interscience, New York, N. Y., 1969, Chapter 6; (f) for a mechanism of gas-phase nitration, see G. B. Bachman, L. M. Addison, J. V. Hewett, L. Kohn, and A. Millikan, *J. Org. Chem.*, **17**, 906 (1952).

(8) The terms are defined as substitution (of hydrogen for the nitro group) and nitrolytic cleavage (of C-C bonds), respectively.