

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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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 Kononov³ 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. Kononov, *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).

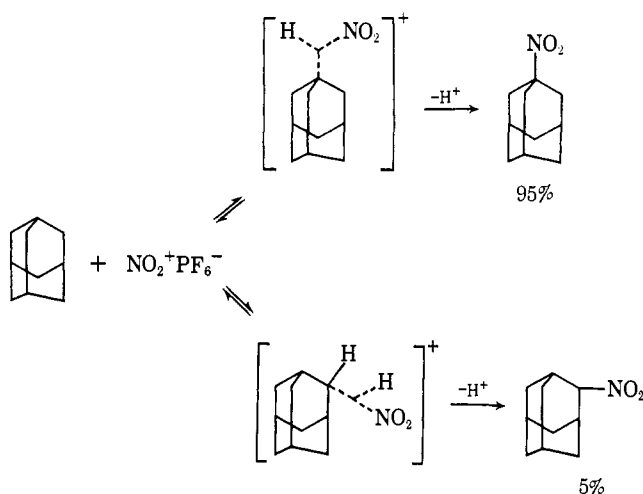
(7) For summaries on aliphatic nitration see (a) F. Asinger, "Paraffins," Pergamon Press, New York, N. Y., 1968, Chapter 4, pp 365–482; (b) A. V. Topchiev, "Nitration of Hydrocarbons and Other Organic Compounds," Pergamon Press, New York, N. Y., 1960; (c) A. I. Titov, *Tetrahedron*, **19**, 557 (1963); (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.

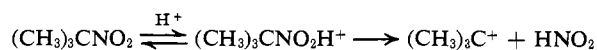
the cleaved alkylcarbenium ions) or secondary alkylation products, themselves capable of undergoing reaction with the nitronium salt.

Frontside attack by the electrophile, as suggested, should result in retention of optical activity, if reaction was carried out on an optically active hydrocarbon. Our studies in this regard are in progress and will be reported later. We have, however, already been able to carry out NO_2^+ nitration of rigid systems, like adamantane.

The ease and predominant formation of the tertiary bridgehead 1-nitroadamantane clearly indicates the suggested mechanism since no "backside" attack is possible through the cage compound.

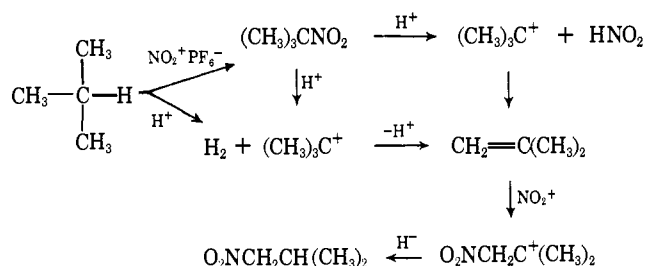


Contrasted with electrophilic aromatic nitration, electrophilic aliphatic nitrations are much affected by protolytic denitrations, which particularly with tertiary and secondary nitro compounds are of major importance. The fact that denitration affects electrophilic aliphatic nitration can be best demonstrated in the case of 2-nitro-2-methylpropane which was found to undergo protolytic cleavage in $\text{FSO}_3\text{H}-\text{SbF}_5$, $\text{HF}-\text{SbF}_5$, and also in $\text{HF}-\text{PF}_5$ solution even at -80° . The protolytic cleavage reaction yields *tert*-butyl cation and nitrous acid (or subsequently, nitrosonium ion). No nitronium ion is formed, as indicated by absence of any aromatic nitration product found when *tert*- $\text{C}_4\text{H}_9\text{NO}_2$ was treated with benzene and toluene in the presence of strong acids; *i.e.*, only *tert*-butylated products were obtained.



Whereas our studies centered so far primarily on the feasibility of the nitration of alkanes (cycloalkanes) with nitronium salts in aprotic solvent systems, once reactions are demonstrated they can, of course, also be carried out under more conventional conditions. Mixed acid ($\text{HNO}_3-\text{H}_2\text{SO}_4$) nitration of isobutane at 50° gave the following nitroalkane composition: CH_3NO_2 , 28%; $\text{CH}_3\text{CH}_2\text{NO}_2$, 4.9%; $(\text{CH}_3)_2\text{CHNO}_2$, 0.5%; $(\text{CH}_3)_3\text{CNO}_2$, 66.6%. Mixed acid nitration can be complicated by protolytic cleavage of product nitroalkanes, by isomerization of the hydrocarbon, oxidative side reactions, and, if higher reaction temperatures are applied, by free-radical nitration products. Nitroethane and 2-nitropropane formed in small amounts in the mixed acid nitration of isobutane can

result from nitration of propane, formed *via* subsequent hydride transfer in the nitrolysis yielding nitromethane. In principle, however, there seems to be no reason why electrophilic aliphatic nitration should not become a general reaction, with a variety of nitrating agents capable to act as precursors to the nitronium ion. Anhydrous hydrogen fluoride and fluorosulfuric acid were found as improved solvents for the nitration of methane with nitronium salts. In these strong acid solvents even under the mild reaction conditions (room temperature) at least tenfold increased yields ($\sim 1\%$) could be obtained. As no protolytic reactions of methane take place in HF under the reaction conditions, side reactions are not observed. This is not the case in the nitration of isobutane in HF solution, where 90% of the nitroalkanes obtained consisted of 1-nitro-2-methylpropane. Since only traces of this isomer were found in nitronium salt nitration in aprotic CH_2Cl_2 -sulfolane solution, the formation of 1-nitro-2-methylpropane must be considered due to formation of isobutylene (either from isobutane itself in HF containing PF_5 or more probably from the protolytic cleavage of 2-nitro-2-methylpropane).



The polar nitro group with its unshared electron pair donor oxygen atoms can act as a strong internal nucleophile and facilitates nitrous acid cleavage. If this effect is indeed of importance, it could also suggest that in the reverse step, *i.e.*, the NO_2^+ nitration of isobutane, the proton is removed internally by the oxygen atom of the polar nitro group.

The ease of protolysis of tertiary (and to a lesser degree secondary) aliphatic nitro compounds explains in part the complex reaction mixtures obtained in mixed acid nitrations of alkanes.

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Organometallic Chemistry. I. The Ethylene- and Norbornylenemercurinium Ions

Sir:

Mercurinium ions have been postulated as intermediates in the electrophilic addition of mercuric salts to olefins, in hydroxymercuration reactions, in oxidation reactions involving mercuric salts, and in certain Friedel-Crafts reactions.¹ Although there is extensive

(1) For a recent review of the role of mercurinium ions in these reactions see W. Kitching, *Organometal. Chem. Rev.*, 3, 61 (1968).