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| <p>The electrophilic nitration of alkanes and cycloalkanes with nitronium salts was studied. Nitration of the cage hydrocarbon adamantane served as a particularly suitable model for these studies. Alkyl and allylsilanes were found to undergo desilylative nitration with nitronium salts providing a mild, selective method to introduce nitro groups into aliphatic compounds. The study of nitrated reactive intermediates, particularly nitrocarbenium ions, was also carried out. The first stable <math>\alpha</math>-nitrocarbenium ion, the diphenylnitrocarbenium ion, was prepared and characterized by <math>^1\text{H}</math>, <math>^{13}\text{C}</math> and <math>^{15}\text{N}</math> nmr spectroscopy. The elusive nitrodiazonium ion was <i>in situ</i> prepared and its nitrating ability studied.</p> |       |   |   |  |                        |
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# Aliphatic Nitrocompounds & Nitrated Reactive Intermediates


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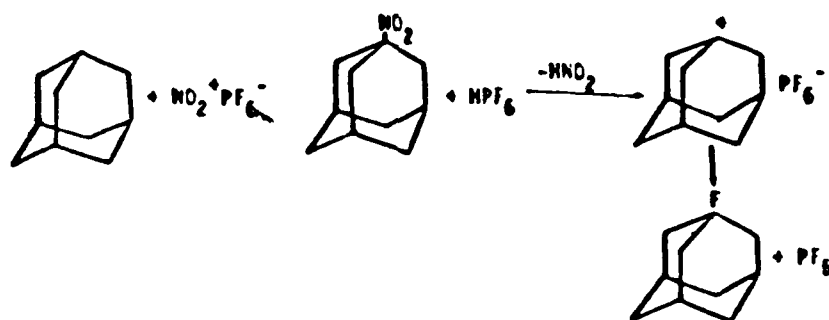
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## Electrophilic nitration of alkanes and cycloalkanes

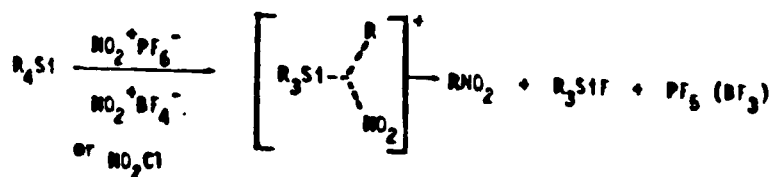
In the last three years our studies were directed to electrophilic aliphatic nitration of alkanes and cycloalkanes.

Initial studies of the electrophilic nitration of alkanes with nitronium salts was extended. Effects arising from the acid catalyzed cleavage reactions of tertiary and secondary nitroalkanes were investigated. This is considered the greatest preparative difficulty to adapt this novel, simple nitration method to practical use. Isobutane, for example, when nitrated with nitronium salts, nitrates predominantly on the tertiary C-H bond. 2-Methyl-2-nitropropane is, however, exceedingly sensitive to acid cleavage giving the *t*-butyl cation, which subsequently can deprotonate to give isobutylene and subsequently a multitude of side products. Whereas when using nitronium salts, the system is initially acid free, the substitution reaction, of course, generates an equimolar amount of strong acid. The same considerations are also valid for the nitration of adamantane although in this case no olefin formation is possible. Tertiary 1-nitroadamantane cleaves, however, very readily with acids to the 1-adamantyl cation, which can be then abstract halide ion from the counter ion or react with other nucleophiles.



The utilization of organometallics in preparing nitrocompounds has received so far little attention, except desilylative nitration of aryltrimethylsilanes.

We have found that tetraalkylsilanes react readily with nitronium salts according



Tetramethylsilane with  $\text{NO}_2^+\text{BF}_4^-$  in sulfolane solution gives according to the reaction



nitromethane in 80% yield.

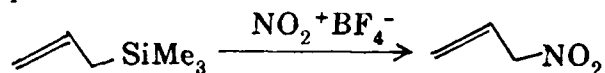
It is possible by using excess nitronium salt to carry further the reaction by reacting  $\text{Me}_3\text{SiF}$  itself



$\text{Me}_2\text{SiF}_2$ , however, does not react further.

Similar nitration of  $\text{Et}_3\text{Si}$  was observed and study was also extended to other alkylsilanes.

The reaction of allyltrimethylsilane with  $\text{NO}_2^+\text{BF}_4^-$  gave a >80% yield of 1-nitropropene-2

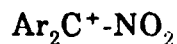


Whereas allylic nitration of the corresponding silanes proceeds well vinylic systems such as  $\text{CH}_2=\text{C}(\text{SiMe}_3)-\text{CH}_2$  gave only polymers.

#### Study of nitrated reactive intermediates

An additional new aspect of our studies of the last three years was directed towards the study of nitrated reactive intermediates, particularly nitrocarbocations.

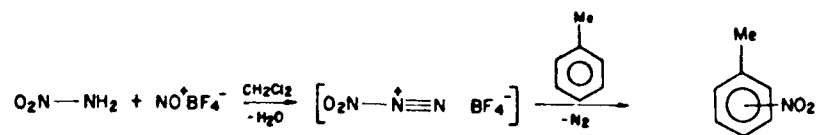
A detailed study of  $\alpha$ -nitrodiarylmethyl cations of the type



was carried out. These ions were successfully prepared from their corresponding gem-dinitro compounds in  $\text{FSO}_3\text{H}/\text{SO}_2\text{ClF}$  solution. Their structure was fully characterized by NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$ ) spectroscopy. Of particular interest was the evaluation of the effect of the  $\alpha$ -nitro group on the carbocationic center.

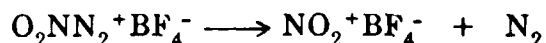
$^{15}\text{N}$  NMR spectroscopic studies of solutions of nitric acid in various superacids were carried out in continued effort to probe the nature of nitrating agents in these media. In the course of our studies directed towards nitrated intermediates we have found that nitrodiazonium tetrafluoroborate  $\text{O}_2\text{N}^+\text{N}\equiv\text{N} \text{BF}_4^-$  can be

generated when nitramide is allowed to react with a molar equivalent of  $\text{NO}^+ \text{BF}_4^-$  in  $\text{CH}_2\text{Cl}_2$  at  $0^\circ\text{C}$ .



Rediazoniative nitration of toluene (4 equiv) gave isomeric nitrotoluenes in 36% overall yield. The observed isomer distribution of nitrotoluenes is 71% ortho, 3.5% meta, and 25.5% para and closely resembles that of electrophilic nitration of toluene with strongly electrophilic nitrating agents, such as nitronium salts.

In a control experiment when nitramide was added to dry toluene in  $\text{CH}_2\text{Cl}_2$  under the experimental condition, no nitrotoluenes were observed after workup and GC analysis, ruling out any possible nitration of toluene by nitramide itself or by nitric acid formed upon hydrolysis. Rediazonation of the nitrodiazonium ion to the nitronium ion is thermodynamically favorable and thus it cannot be excluded that its formation precedes nitration of aromatics.



#### Writing of Comprehensive Review of Nitration

During the last grant period a substantial effort was extended by the senior investigator in cooperation with his former colleagues, Dr. R. Malhotra and Dr. S. C. Narang (both with Stanford Research Institute) in writing a monograph entitled "Nitration: Preparative and Mechanistic Aspects". The book will give a critical review emphasizing both preparative and mechanistic aspects of aromatic and aliphatic nitration. Inevitable delays postponed completion but the manuscript is expected to be completed for publication in 1988.

Scientific Personnel Supported (in part) and Degrees Awarded:

George A. Olah, principal investigator

Judith A. Olah, co-principal investigator

Christophe Rochin, post-doctoral associate

Chandra B. Rao, post-doctoral associate

Judith Handley, graduate fellow

Joseph G. Shih, graduate student (Ph.D. 1985)

List of Publications under ARO Sponsorship: 1984-87

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