HIGH ENERGY NITROGEN COMPOUNDS

FINAL REPORT

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The fundamental mechanistic aspects of the nitration of toluene to 2,4,6-trinitrotoluene(TNT) and benzene to 1,3,5-trinitrobenzene(TNB) were studied. Studies included rate studies (based on product analysis)and studies of reactive intermediates,including Fourier transfer ^{13}C nuclear magnetic resonance and X-ray photo electron spectroscopic (ESCA) studies. An effective preparation method for the direct trinitration of benzene was achieved to prepare TNB in good yield and high purity. New selective nitration methods were found for preparation of nitroaromatic compounds.The nitration of aliphatic compounds was also studied.

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FORWARD

The objective of the work was to extend our knowledge of electrophilic nitration, including the new area of aliphatic electrophilic nitration, to prepare new high energy nitrogen compounds and/or to substantially improve preparative route to known high energy compounds such as TNT and TNB (1,3,5-trinitrobenzene)

Results and Conclusions

All objectives of the research project were met. The mechanism of the electrophilic nitration of toluene to trinitrotoluene (TNT) as well that of benzene to trinitrobenzene (TNB) was studied. Results disclosed a basic mechanistic difference between the mononitration step, and the di-and trinitration steps. Studies included rate studies via product analysis and study of reactive intermediates including the application of ^{13}C Fourier transform nmr and X-ray Induced Photoelectron spectroscopic methods. Comparison of solution nitration with gaseous molecule ion reactions, where no solvation effects are operative, was also carried out using the ion cyclotron resonance spectroscopic method. A highly efficient preparation method for the preparation of TNB was worked out.

A new selective nitration method was found in the boron trifluoride catalyzed nitration of aromatic with alkyl nitrates, particularly methyl nitrate. The method was found very selective in the mononitration of polyalkylbenzenes. It also allowed a detailed mechanistic study of the nitration of benzene, alkylbenzenes and halobenzenes in homogeneous, easy to handle systems where diffusion controll of the reactions can be excluded.

The use of hydrogen fluoride and hydrogen fluoride like aminopolyhydrogen fluoride solutions was evaluated in electrophilic nitrations. These solvents have no oxidizing ability and show promise in minimizing oxidative side reactions.

The nitration of aliphatic and cycloaliphatic hydrocarbons was studied under electrophilic conditions. Preparative methods for nitroaliphatic compounds including nitroalkanes, nitroalkenes and nitroadamantane were developed.

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