

The Addition of Nitrogen Tetroxide to Ketene

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Introduction

Nitrogen tetroxide will react with a carbon-carbon double bond to produce various addition products, mostly dinitro and nitro-nitrite derivatives.⁽³⁾ Nitril chloride will react with ketene to produce small amounts of nitro-acetyl chloride. (4) Nitrosyl chloride and ketene produce chloroacetyl chloride. (2) Bolstad (1) reports that ketene and nitrogen dioxide react in the gaseous phase to give a liquid product which has not been identified. He found, moreover, that diketene and liquid nitrogen tetroxide react with explosive violence.

In view of these facts, this investigation undertook to determine if an addition type of reaction would take place between ketene and nitrogen tetroxide. Such an addition product, upon hydrolysis or alcoholysis, should produce nitroacetic acid or an ester of nitroacetic acid.

In an attempt to prepare methyl nitroacetate directly and without the isolation of any intermediate product, methyl alcohol was added directly to the reaction product, the solvent was removed by evaporation, and the product distilled. Such procedures gave products which were unstable to distillation, exploding or fuming off at bath temperatures of 45 to 50°C.

The use of potassium hydroxide in place of methyl alcohol in the above procedure was investigated. If the nitrogen tetroxide-ketene reaction goes as expected, this should produce the dipotassium salt of nitroacetic acid. No evidence of the presence of this salt could be detected.

Since the properties of the nitrogen tetroxide-ketene product suggested those of nitroform, attempts were made to isolate this substance, but no positive results were obtained. In like manner, no nitromethane could be isolated.

The use of ether at -60°C. as a reaction solvent was tried, but gave a product which was unstable at room temperature.

Isolation of the product produced by the reaction of ketene and nitrogen tetroxide was accomplished. It proved to be spontaneously inflammable when dried.

The use of a less active ketene, diphenylketene, was investigated briefly. It was found that the product of this reaction was a yellow brown oil stable at room temperature, but which decomposed on heating to liberate oxides of nitrogen. An unidentified organic residue remained.

Experimental

Attempted Preparation of Methyl Nitroacetate. Twenty-seven g. of nitrogen tetroxide was dissolved in 300 ml. of carbon tetrachloride and cooled to 0°C. Eight ml. of liquid ketene was passed into the reaction chamber by the use of nitrogen as a carrier gas. During the reaction a slow stream of oxygen was passed through the reaction mixture to prevent the reduction of nitrogen tetroxide to nitrogen sesquioxide. After the reaction was complete, 25 ml. of methyl alcohol was added, the solution was allowed to come to room temperature, transferred to a distillation flask, and the solvent removed under reduced pressure. The residue, about 5 ml. of a yellow brown oil, exploded when the bath temperature reached 45°C.

Ether as a Solvent. The procedure used here was similar to that used in the previous experiment except that the solvent used was ether and the reaction was carried out at -60°C. When the reaction was complete no methyl alcohol was added, but the reaction mixture was allowed to warm to room temperature. The solvent was then removed by distillation and the residue amounted to about 10 ml. of a yellow oil. Upon warming to room temperature, the product decomposed rapidly with the evolution of oxides of nitrogen and considerable heat.

Attempted Preparation of the Dipotassium Salt of Nitroacetic Acid. A sample of the reaction product prepared in the manner described in the preceding experiment was dissolved in 100 ml. of water and made basic with 50 per cent potassium hydroxide solution. The resulting red solution was then concentrated by boiling until a solid began to separate out. After cooling, the solid was collected but proved to be an inorganic derivative.

Attempted Identification of Nitroform as the Reaction Product. Another sample of the reaction product obtained in ether solvent was dissolved in ether and a few drops of pyridine was added. No crystalline solid corresponding to the pyridine salt of nitroform was obtained.

Diphenylketene and Nitrogen Tetroxide. A solution of 8 g. of diphenylketene in 50 ml. of ether was added dropwise to a solution of 4 ml. of liquid nitrogen tetroxide in 100 ml. of ether cooled to 0°C. During the addition a slow stream of oxygen was passed through the reaction mixture. No visible reaction took place but removal of the solvent left about 4 ml. of a yellow brown oil. This product appeared to be stable at room temperature but decomposed on heating to give oxides of nitrogen. Analysis of the residue gave no conclusive results.

Summary

The reaction between nitrogen tetroxide and ketene produces a solid which is spontaneously inflammable when freed from the reaction solvent. Its structure has not been determined.

No solid separates out when diphenylketene is added to a solution of Nitrogen tetroxide, but a liquid residue apparently stable at room tem-

perature is left upon removal of the solvent. The structure of this product has not been determined.

Literature Cited

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