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THE SPECIFICITY OF BISMUTH NITRATE AND CERIC AMMONIUM NITRATE IN THE REACTION WITH N-ANISYL B-LACTAMS

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Abstract:
Bismuth nitrate and ceric ammonium nitrate act as a nitrating agent in a reaction with N-anisyl β-lactams at high temperature (60^0C) or under microwave irradiation method. In contrast, their actions become different at ice-cold conditions (^{0}C). Ceric ammonium nitrate acts as an oxidizing agent whereas bismuth nitrate has no effect at ^{0}C.

Key Words
Bismuth nitrate, Ceric ammonium nitrate, Beta Lactam, Nitration, Oxidation

Introduction:
Banik's aromatic nitration reaction describes a facile method by which nitro groups are introduced in aromatic compounds of diverse structures including hydrocarbon, β-lactam, natural product and hormone [1, 2]. Bismuth nitrate produces nitro products through acid-induced reactions. The interaction of bismuth with the nitrate anion on which it is bonded is not high due to the big size of bismuth. Under the reaction conditions, bismuth nitrate generates nitric acid in the presence of solvents and under microwave irradiation. Ceric ammonium nitrate (CAN) can also generate nitric acid in media under forcing conditions. This paper describes the precise differences of the reactivity of bismuth nitrate and ceric ammonium nitrate in the nitration of N-p-anisyl β-lactam.

Results and Discussions:
Aromatic nitration is a crucial reaction in organic chemistry. Therefore, many methods are developed for this purpose. A simple method of aromatic nitration with bismuth nitrate impregnated with clay was developed and it is called Banik's nitration [1a]. This reaction proceeded well at high temperature or under microwave. The nitration was then extended to nitrate the aromatic rings present in the nitrogen of the β-lactams ring. Nitration of the aromatic group present at the N- of the β-lactam ring proceeded well using bismuth nitrate-impregnated

with clay under the influence of microwave. No products were formed at cold conditions in the presence of solvent with bismuth nitrate. No oxidation of the *p*-anisyl group was occured.
The reaction of the same β-lactam with ceric ammonium nitrate produced –NH β-lactam at 0^0C in acetonitrile-water. However, ceric ammonium nitrate produced nitro β-lactam at high temperature or under microwave irradiation.
The reactions described above are interesting. Ceric ammnonim nitrate works as an oxidizing agent at cold conditions in the presence of solvents and as a nitrating agent at high temperature in the absence of a solvent. Bismuth nitrate works as a nitrating agent at high temperature. Bismuth nitrate at cold conditions is in the presence of solvent is not capable of removing the N-aromatic group from the β-lactam ring.
Subjecting the nitro derivative with CAN at cold conditions in the presence of acetonitrile and water failed to give the –NH product. Therefore, the nitro derivative is not an intermediate. Obviously, CAN gives two products following two different pathways. Mild oxidation pathway with CAN is favored at cold condition whereas electrophilic nitronium ion attack is the pathway under drastic condition. Bismuth nitrate follows only electrophilic reaction with nitronium ion. The oxidizing ability of bismuth nitrate at cold condition in the presence of solvent is not seen.

Conclusions:
The selectivity between CAN and bismuth nitrate in two types of reactions is found. It seems nitration follows a more drastic condition than oxidation.

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