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BANIK'S AROMATIC NITRATION

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#Dedicated to the Dr. R. R. Gupta on the Occasion on his 80th Birthday

Abstract:
Bimal Krishna Banik has discovered a new bismuth nitrate-mediated nitration reaction of aromatic compounds. Microwave irradiation has been used successfully to accomplish this goal.

Key Words:
Aromatic nitration, Bismuth nitrate, Microwave irradiation

Introduction:
Bismuth salts are used as medicines because of their low toxicity. The use of bismuth salts in organic synthesis and medicinal chemistry has been increasing very rapidly because of numerous reasons.

Microwave-Assisted Nitration Reaction:
Microwave-mediated organic synthesis is initiated in 1986. Microwaves are non-ionizing radiations that are used for process to occur due to dielectric heating through absorption of energy. It is true that solvents and reactants may undergo numerous molecular conformation and configuration changes because of rapid exposure of microwave irradiation. The most important features of the solvents are that they must be polar in nature and must have a high dipole moment. But, non-polar reactants in the presence of polar solvents produce products in specific examples.

Nitration of Aromatic Hydrocarbons:
Electrophilic aromatic substitution is one of the most crucial reactions in chemistry because of many substantial applications. Aromatic nitration is an example of very important aromatic substitution reaction. This reaction requires concentrated nitric acid and sulfuric acid. Many other reagents have also developed to make nitration a greener method. The aromatic nitro compounds can be converted to aromatic amines. Numerous aromatic nitro and amino compounds and molecules derived from them are medicines. Banik's research culminated in a

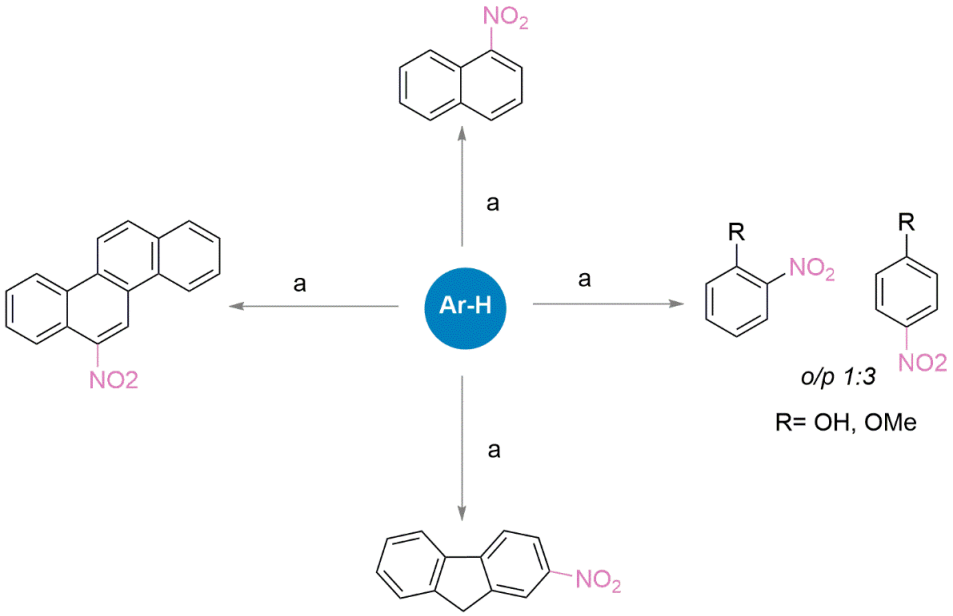
facile method of aromatic nitration with bismuth nitrate impregnated with clay. Microwave irradiation helped the reaction to occur within a few minutes. Various aromatic compounds were nitrated using Banik's nitration reaction. The regioselectivity of bismuth nitrate-mediated reaction was identical with nitric acid-mediated method (Scheme 1)[1].

Nitration of Aromatic Groups Present in β-Lactams:

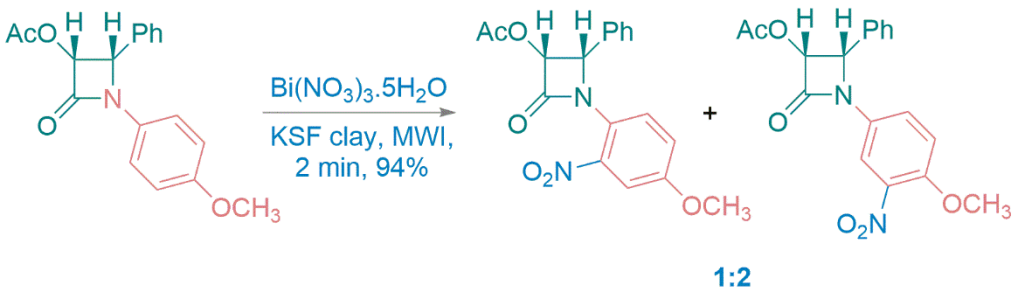
It is known β-lactam rings are very sensitive in the presence of acids. But, nitration of the aromatic group present in these types of systems proceeded smoothly using bismuth nitrate-impregnated with clay under microwave irradiation. There was no ring cleavage observed. However, nitric acid-sulfuric acid mixture cleaved the β-lactam ring. The aromatic ring that has the methoxy group was nitrated through Banik's method (SCHEME 2)[2].

Aromatic Nitration of Eugenol:

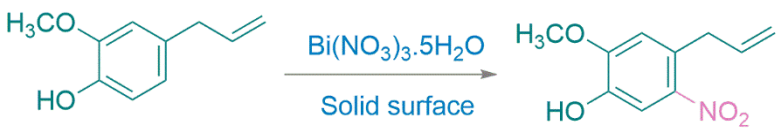
Banik reported a nitration reaction of eugenol with bismuth nitrate impregnated with clay under microwave conditions. The reaction produced a single nitro derivative. The methoxy group controlled



SCHEME 1 Bi $(NO_3)_3.5H_2O$ induced nitration of arenes under microwave condition



SCHEME 2 Bi (NO3).5H2O catalyzed nitration of N-phenyl of β-lactam ring



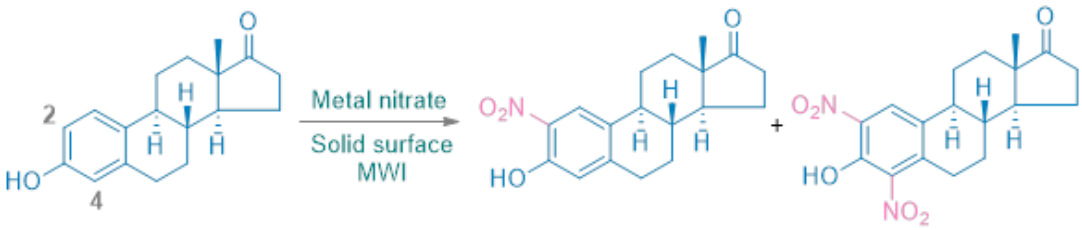
SCHEME 3 Bi (NO3).5H2O catalyzed nitration of eugenol

the distribution of the products (Scheme3) [3]. No isomerization of the unsaturated bond was occurred in this reaction. The regioselectivity remained identical regardless of the solid surfaces used. No oxidation of the molecule was observed.

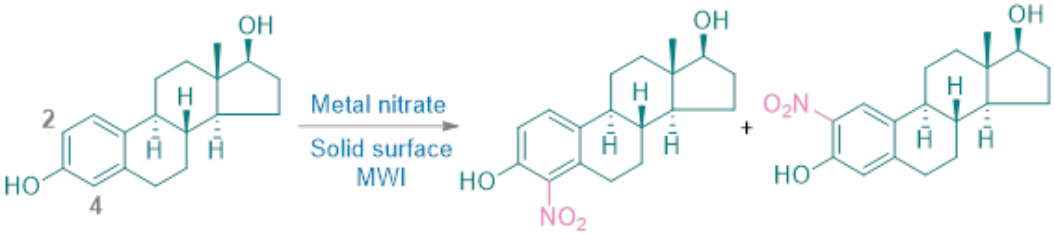
Aromatic Nitration of Estrone and Estradiol:

Hormonal steroids are essential for the growth of fertility in humans and animals. Since estrone and estradiol have a phenolic OH group, Banik's bismuth nitrate-mediated reaction was performed with these two compounds. The reaction of estrone produced two products: 2-nitro and 2, 4-dinitro estrone. Controlled heating of microwave irradiation and limiting the amount of bismuth nitrate, it was possible to obtain the 2-nitro compound as the major product. The ratio and yield of the products depended on the nature of the surfaces used. No oxidation of the aromatic ring was observed.

Banik's reaction was performed with estradiol. Mono-nitro estradiol was the only product from this reaction. No dinitro estradiol was isolated. There was no dehydration and oxidation of the alcoholic OH group and no oxidation of the alcoholic OH group were observed. Estradiol was *O*-alkylated using a strong base like sodium hydride. The nitro estradiol was alkylated with side chains in the presence of potassium carbonate. Numerous amino groups were selected at the terminal site of these side chains (Scheme 4 and 5)[4][5].



SCHEME 4 Nitration estrone



SCHEME 5 Bismuth nitrate-induced nitration of estradiol

Biological application:

Estrogens and Estrogen Receptors (ERs), including ERα and ERβ are crucial in numerous cancers (breast, ovarian, uterine, prostate, and colon) [18, 19]. ERs are the main targets for breast cancer, and the estrogen receptor modulator (SERM). 2-Nitroestradiol is a superior inhibitor of a steroid alcohol sulfotransferase compared with 4-nitroestradiol. However, 4-substituted estrogens inhibit the steroid sulfatase more efficiently than 2-substituted analogues.

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