



BANIK'S OXIDATION REACTION BY SODIUM BISMUTHATE

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

Abstract:

Bimal Krishna Banik has discovered a new reaction (Banik's Oxidation Reaction) of benzylic methylenes to benzylic ketones with sodium bismuthate in acetic acid. Some of the compounds derived from this study have demonstrated selective anticancer activities against several human cancer cell lines.

Definition:

Oxidation of benzylic methylene is performed successfully with sodium bismuthate for the first time. This method has been applied in structurally complex biologically active organic molecules.

New Discoveries in this Method:

Sodium bismuthate in the benzylic methylene oxidation; Sodium bismuthate in the benzylic and allylic alcohol oxidation

Solvents: Acetic acid

Temperature:

Room temperature-100^oC

Time of the Reaction:

2h-10h

Use of the Products:

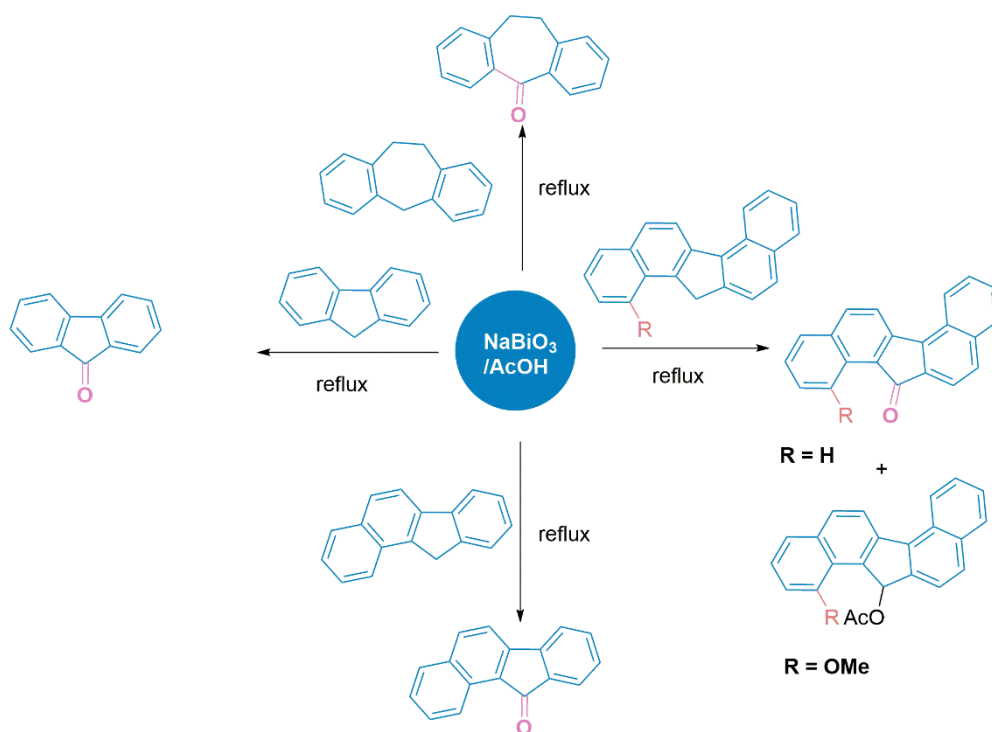
Some of the products prepared by Banik's oxidation reaction have demonstrated selective anticancer activities against breast, blood, skin, ovary, pancreas, prostate, and colon cancer cells.

Description:

Commercially available tetralin, diphenylmethane, 9-10 dihydroanthracene, dibenzofuran, fluorene, and 2-nitrofluorene were readily converted to the respective ketone by sodium bismuthate in acetic acid. The presence of acetic acid was needed for the completion of the reaction. The progress of the reaction became very slow when carried out without acetic acid.

It is important to note that substituents in the aromatic ring lead to the formation of the ketone and acetate derivatives with a high proportion of ketone (2:1). The reactivity of benzylic oxidation with sodium bismuthate in acetic acid with an electron-donating group accelerates the reaction significantly compared to the substrate lack of this type of substituent[1,2]

In the general experimental procedure, to hydrocarbon (20 mmol) in aqueous acetic acid (4 mL, 50%, v/v) and acetone (2 mL), was added sodium bismuthate (80 mmol), and the mixture was heated to reflux. At the end of the reactions, as indicated by TLC, the mixture was filtered through a pad of Celite and diluted with water (10 mL). The mixture was extracted with methylene chloride (3 x 20 mL). The combined organic layer was washed with sodium bicarbonate solution (3 x 10 mL, 10%), brine (10 mL), dried over anhydrous sodium sulfate, and concentrated under reduced



SCHEME 1 Sodium Bismuthate mediated benzylic oxidation of polyaromatic hydrocarbons

pressure. The resultant crude product was purified by column chromatography over silica gel using ethyl acetate-hexanes.

This reaction was extended for the oxidation of benzylic and allylic alcohols to the carbonyl compounds.

Mechanism:

To understand the reaction course, Banik proposed the plausible mechanism of the oxidation reaction. We envisioned that the reaction proceeds through the formation of carbocation

intermediate (INT1) by attack of the reagent. The carbocation formed by the attack of bismuthate anion can produce the ketone, or by a nucleophilic attack by acetic acid it can give the acetate derivative. The acetate derivative of corresponding hydrocarbons was expected to be formed by the direct attack of acetic acid to the resulting carbocation intermediate (PATH B). However, the formation of ketone can be explained by following the PATH A in which the bismuthate anion initially attacks the carbocation intermediate to form the corresponding borate ester. Consequently, the elimination via path A of a benzylic proton leads the formation of oxidized product exclusively[3].

It worthy to be note that at higher temperature, the reaction takes the path A and favours the formation of ketone as the major or exclusive product. During the investigation of the oxidation reaction, we haven't noticed the formation of side products like hydroxy, quinone or dicarboxylic acid.

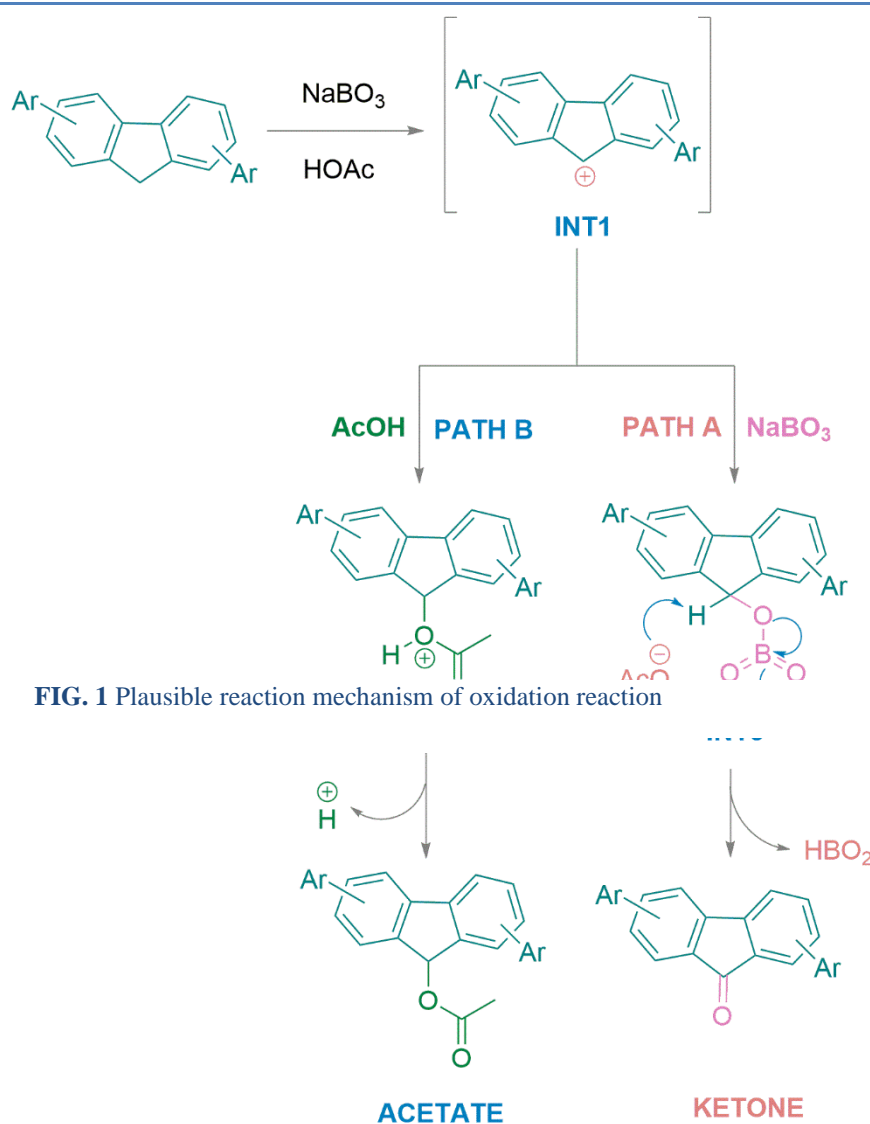


FIG. 1 Plausible reaction mechanism of oxidation reaction

In conclusion, Banik's oxidation reaction involves a conversion of benzylic methylene to benzylic ketone and benzylic acetate with sodium bismuthate in acetic acid. This reaction is extended for the oxidation of benzylic and allylic alcohols to the carbonyl compounds. Many

of these ketones are converted to diverse heterocycles that have demonstrated anticancer activities (4).

Reference:

- [1] B. K. Banik, A. Ghatak, C. Mukhopadhyay, F. F. Becker, Sodium bismuthate mediated oxidation study of hydrofluorenes, *J. Chem. Res. - Part S.* (2000) 108–109. <https://doi.org/10.3184/030823400103166797>.
- [2] D. Bandyopadhyay, B. K. Banik, Versatile Bismuth Salts-induced Reactions From Our Laboratory: A Perspective, *Heterocycl. Lett.* 10 (2020) 341.
- [3] B. K. Banik, A.T. Reddy, A. Datta, C. Mukhopadhyay, Microwave-induced bismuth nitrate-catalyzed synthesis of dihydropyrimidones via Biginelli condensation under solventless conditions, *Tetrahedron Lett.* (2007). <https://doi.org/10.1016/j.tetlet.2007.08.007>.
- [4] F. F. Becker, B. K. Banik, Synthesis and biological evaluation of novel dibenzofluorenes, *Frontiers in Med. & Pharm. Chem.* (2014) 2:55; DOI: 10.3389/fchem.2014.00055.

Received on March 17, 2021.