

Nitrosonium Tetrafluoroborate¹



[14635-75-7] BF_4NO (MW 116.82)

InChI = 1/BF4.NO/c2-1(3,4)5;1-2/q-1;+1

InChIKey = KGCNVGDHOSFKFT-UHFFFAOYAW

(efficient nitrosating and diazotizing agent;¹ mild oxidant;² hydride- and halide-abstracting agent²)

Physical Data: d 2.185 g cm⁻³.³

Solubility: soluble in acetonitrile.

Form Supplied in: colorless crystalline compound; commercially available.

Purification: commercial NO^+BF_4^- frequently contains some $\text{NO}_2^+\text{BF}_4^-$; NO_2^+ can be removed from NO^+BF_4^- by washing with dry benzene; sublimation (200–250 °C/0.01 mmHg) can be used if highly pure NO^+BF_4^- is needed.³

Handling, Storage, and Precautions: due to its hygroscopic nature, NO^+BF_4^- should be stored and used under anhyd conditions; use in a fume hood.

Original Commentary

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Nitrosation. NO^+BF_4^- is a highly efficient nitrosating agent, and has been used widely for synthetic purposes. Alcohols and secondary amines react readily with NO^+BF_4^- to form alkyl nitrites and nitrosamines, respectively, in high yields (eqs 1 and 2).⁴ Nitrosation of less reactive *N*-alkylamides and sulfonamides can also be achieved without difficulty, where other nitrosating agents are not effective.^{5,6} Reaction of NO^+BF_4^- with pyridine yields *N*-nitrosopyridinium tetrafluoroborate.⁷ Aziridines react with NO^+BF_4^- to yield nitrosoaziridines. Extrusion of N_2O from the products under thermal decomposition conditions led to formation of carbon–carbon double bonds.⁸ This reaction has been employed for the synthesis of *cis*-diazabis- σ -homobenzene.^{8a}



$\text{R}^1 = \text{alkyl}; \text{R}^2 = \text{alkyl, acyl}$

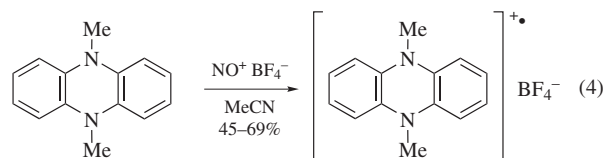
Diazotization and Related Reactions. When primary amines react with NO^+BF_4^- , diazonium tetrafluoroborates are generated.¹ This reaction has been extensively studied with arylamines, since it is particularly useful for the isolation of the corresponding diazonium tetrafluoroborates (eq 3).⁹ Decomposition of these salts produces fluoroarenes.¹⁰ Isocyanates also react with NO^+BF_4^- to yield diazonium salts.^{2a,11} Primary amides can be converted to acids by NO^+BF_4^- via diazotization and subsequent hydrolysis.¹²



Treatment of alkyl azides with NO^+BF_4^- led to the formation of carbenium ions, which can be intercepted with various nucleophiles such as fluoride, hydroxide, carboxides, and nitriles.¹³ The reaction using nitriles has been utilized to prepare dihydroisoquinolines and oxazoles. Vinyl azides react with NO^+BF_4^- to form 1,2,5-oxadiazoles and/or 1,2,4-oxadiazoles, depending on the structures of the substrates.¹⁴ When 1,2-dialkylvinyl azides are used, 1,2,5-oxadiazoles were obtained as the only heterocyclic compounds in 75–80% yields.

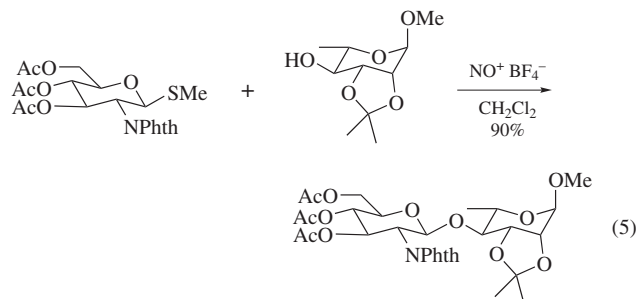
Various substituted hydrazines react with NO^+BF_4^- to form azides.¹⁵

Oxidation. NO^+BF_4^- is a mild oxidant, with NO/NO^+ having 1.5 V standard oxidation–reduction potential in acetonitrile.¹⁶ It has been widely used as a single electron transfer oxidant. Many arene- and sulfur-containing radical cations have been prepared by treatment of corresponding precursors with NO^+BF_4^- (eq 4).^{17,18} The easy removal of the side-product NO makes the procedure especially convenient. These radical cations have played a significant role in the development of organic ferromagnets and conductors.



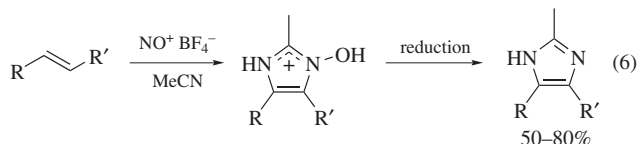
The oxidative property of NO^+BF_4^- has also been synthetically utilized to regenerate carbonyl groups from masked derivatives such as 1,3-dithioacetals, oximes, and dimethylhydrazones.¹⁹

The same principle was applied to stereospecific construction of *O*-glycosidic linkages.²⁰ Treatment of readily available methyl *S*-glycosides with an equimolar amount of NO^+BF_4^- in dry methylene chloride at temperatures between 0 and 25 °C gives high yields of *O*-glycosides in the presence of a hydroxylic component (eq 5). The stereospecificity and lack of complications compared with earlier methods make this procedure very attractive.



Noteworthy is the oxidative iodination of aromatic compounds with NO^+BF_4^- as catalyst.²¹ A wide range of arenes were iodinated with the system $\text{I}^-/\text{O}_2/\text{NO}^+\text{BF}_4^-$.^{21b} This method is not as effective as I_2/Ag^+ , but much more efficient than the use of other oxidative iodination systems such as $\text{I}_2/\text{Ce}^{\text{IV}}$ salts and $\text{I}_2/(\text{NH}_4)_2\text{S}_2\text{O}_8$. The more important feature of this transformation is the suppression of side-chain oxidation of alkylarenes.^{21c}

Electrophilic Addition to Unsaturated Carbon–Carbon Bonds. As an electrophilic agent, NO^+BF_4^- is able to initiate electrophilic addition to unsaturated carbon–carbon bonds. Reaction of alkenes with NO^+BF_4^- in the presence of acetonitrile yields imidazoles after reduction (eq 6).^{22a} Changing acetonitrile to dimethyl sulfide led to formation of nitrososulfonium tetrafluoroborate (in dimer form).^{22b} The dimer can be depolymerized, tautomerized, and hydrolyzed to give oxosulfonium salt, which can be utilized synthetically. NO^+BF_4^- was reported to dimerize certain alkenes and alkynes.^{22c,d} In the latter case, the true identity of the reagent that initiates the reaction (whether it is NO^+ or NO_2^+) is unclear. $\text{NO}_2^+\text{BF}_4^-$ is known to induce the same reaction.^{22d}

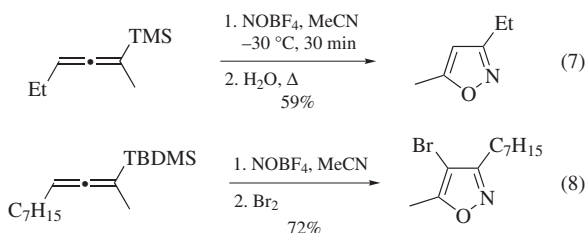


NO^+ can also insert into the cyclopropane ring, offering a new route to 2-isoxazolines.²³

Hydride and Halide Abstraction. NO^+BF_4^- is able to abstract a hydride from a tertiary C–H bond, generating a carbocation. The carbocationic intermediate can be trapped by a fluoride or alkyl nitriles, forming alkyl fluorides or *N*-alkylamides respectively.²⁴ Silanes also react with NO^+BF_4^- to form fluorosilanes.²⁵

In a similar fashion, NO^+ can also abstract a halogen atom from alkyl halides. In the presence of alkyl nitriles, *N*-alkylamides were obtained as a consequence of the Ritter reaction.²⁶

Addition to Allenylsilanes. Allenylsilanes react with nitrosonium tetrafluoroborate in acetonitrile at -30°C to form 4-trialkylsilyloxadiazole derivatives in good yield.²⁷ This method provides a regioselective [3 + 2] annulation route to unsymmetrically substituted isoxazoles. The silyloxadiazole products can be further elaborated by electrophilic substitution in the same operation (eqs 7 and 8). In these [3 + 2] annulations, NOBF_4 is distinctly superior to other nitrosating agents such as *Nitrosyl Chloride* and *Nitrosylsulfuric Acid*.

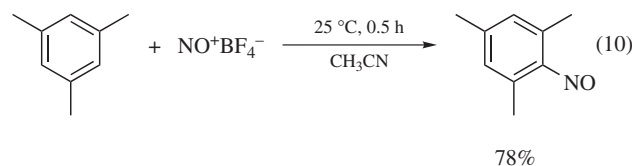
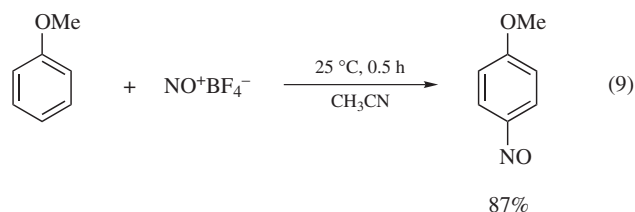


First Update

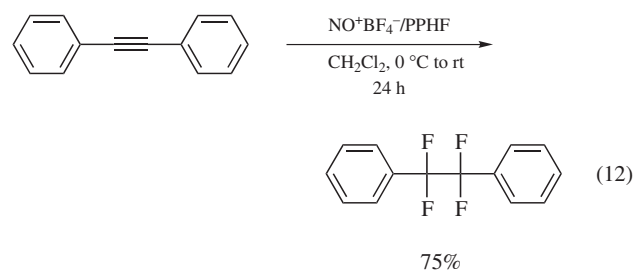
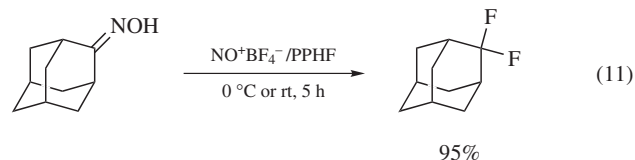
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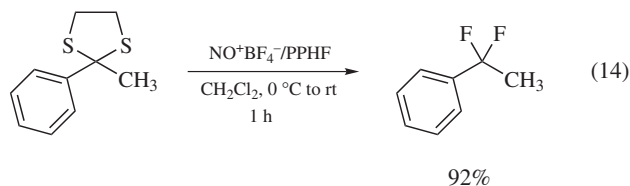
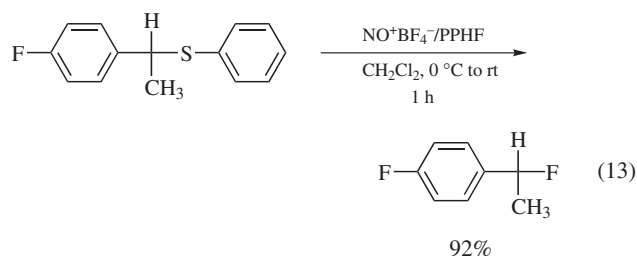
Electrophilic Aromatic Nitrosations. NO^+BF_4^- can be used for the direct electrophilic nitrosation of electron-rich aromatic compounds (such as anisoles and polymethylbenzenes) in

good yields under mild conditions in which the conventional procedure (based on the nitrite with strong acid) is ineffective (eqs 9 and 10).²⁸ The reaction rates of nitrosation are much slower than those of aromatic nitration, which is ascribed to a rate-limiting deprotonation of the reversibly formed Wheland intermediate $[\text{Ar}^+(\text{H})\text{NO}]$. Moreover, nitrosoaromatic products are better electron donors than the aromatic precursors from which they are derived.²⁸ The highly disparate rates of electrophilic aromatic nitrosation and nitration have also been explained by a charge-transfer mechanism.²⁹

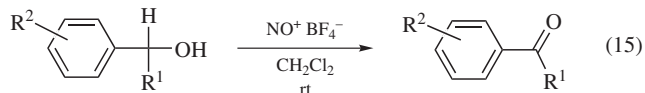


Selective Fluorinations with NO^+BF_4^- /Pyridinium Poly(hydrogen fluoride). NO^+BF_4^- /pyridinium poly(hydrogen fluoride) (PPHF with 60 wt % HF) is a useful nucleophilic fluorinating agent, which can be employed for the selective fluorination of ketoximes,³⁰ diarylacetylenes,³¹ aryl sulfides, and aryl dithiolane derivatives³² to give the corresponding fluorinated products under mild reaction conditions (eqs 11–14). The mechanism of these fluorinations is based on the electrophilic activation by nitrosonium ion (NO^+) and/or acid (H^+) on the substrates, followed by nucleophilic fluorination with fluoride ions (F^-).^{30–32} The NO^+BF_4^- /PPHF method provides a convenient and mild alternative way to the conventional fluorination with SF_4 , SeF_4 , DAST, or elemental fluorine (F_2).

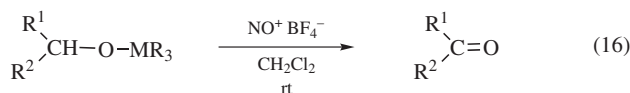




Oxidations of Alcohols and Related Compounds. Although many alcohols react readily with NO^+BF_4^- to form alkyl nitrites,⁴ benzylic alcohols can be oxidized by NO^+BF_4^- under mild conditions to give satisfactory yields of aldehydes or ketones (eq 15).³³ This is ascribed to the benzylic hydride abstraction by NO^+BF_4^- to generate a carbocation that in fact is a protonated carbonyl compound.³³ *exo*-Bicyclo[2.2.1]-heptan-2-ol can also be oxidized with NO^+BF_4^- to give bicyclo[2.2.1]heptan-2-one.³⁴ Simple aliphatic alcohols do not undergo clean oxidation with NO^+BF_4^- , however, their *O*-tributylstannyl and *O*-trimethylsilyl derivatives can be readily oxidized by NO^+BF_4^- to give corresponding carbonyl compounds in good yields (eq 16).³³



$\text{R}^1 = \text{H, alkyl, aryl}$
 $\text{R}^2 = \text{H, F, alkyl}$

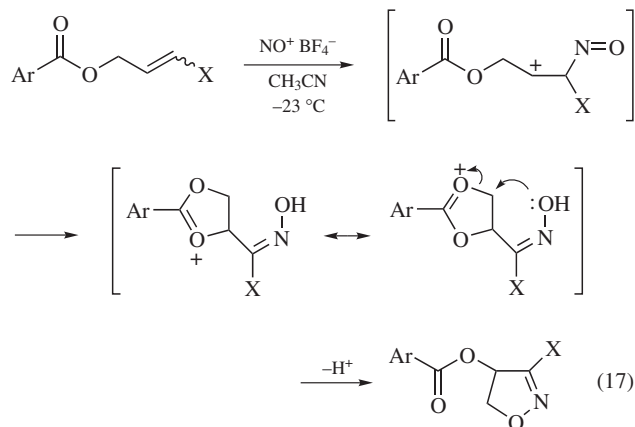


$\text{R}^1, \text{R}^2 = \text{H, alkyl, aryl, cyclic}$
 $\text{MR}_3 = -\text{Sn}(n\text{-C}_4\text{H}_9)_3, -\text{Si}(\text{CH}_3)_3$

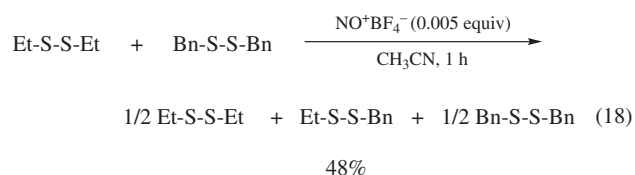
Additions to Allylic Esters. NO^+BF_4^- can also undergo electrophilic addition to allylic esters such as allyl benzoate, allyl phenylacetate, allyl 3-phenylpropionate, crotyl esters, 4-bromo-2-butenyl esters, and 1,4-bis(aryloxy)-2-butenes in acetonitrile at $-23\text{ }^\circ\text{C}$ to give the corresponding 2-isoxazolines (eq 17).³⁵

Disproportion Reactions of Disulfides. A catalytic amount (0.005 equiv) of NO^+BF_4^- can promote the disproportion reactions of disulfides in acetonitrile at room temperature (eq 18).³⁶ A possible mechanism involves cleavage of the disulfide S-S bond following attack by NO^+ to afford the *S*-nitrosothiol and a sulfenium cation. The sulfenium cation can then attack another molecule of disulfide to give an unsymmetrical disulfide and a

new sulfenium cation, which propagates the reaction and drives it to the statistically most probable 1:2:1 mixture of three disulfides (eq 18).³⁶



Ar = aryl; X = H, CH₃, CH₂O₂CAr



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