Review of N, N-Difluorohydroyxlamine-O-flourosulfonate (NF_2OSO_2F): Preparation, Characteristic and Appliance to Produce Difluoroamino-dinitromethyl [-C (NO_2)$_2NF_2$] Moiety

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Abstract

NF2OSO2F (N, N - Difluorohydroyxlamine -O – flourosulfonate), recently discovered by scientists, serves as an efficient reagent for difluoramination to product difluoroamino-dinitromethyl explosophore. It can be produced by tetrafluorohydrazine (N2F4) and peroxydisulfuryl difluoride (S2O6F2). This paper review its preparation, characteristic and appliance to product – C (NO2) 2NF2 moiety.

Keywords

NF2OSO2F, Difluoroamino-dinitromethyl, Difluoramination.

1. Introduction

High energy density materials (HEDMs) have a huge potential more in peaceful applications than in armed conflict. They work as explosive, propellants and pyrotechnic agents by storing relatively large amounts of energy [1-3]. Traditional energetic compounds include TNT (2,4,6-trinitrotoluene), RDX (1,3,5-trinitro-1,3,5-triazacyclohexane), HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane), CL-20 (hexanitrohexaazaisowurtzitane) and so on.

New energetic materials have been investigated to replace the traditional one by many groups [4-6]. Many functional groups, such as nitro (-NO2), amino (-NH2), azido (-N3), and other explosophores, can be introduced to nitrogen-rich frameworks to enhance detonation performance of energetic compounds. One of the groups is difluoramino (-NF2), in which structure, two fluorine atoms link to directly nitrogen atom. The difluoramino compound is an interesting one in the field of energetic compounds chemistry because it can decompose to produce HF, a gas that has not only relatively low molecular mass, but also high heat of generation. What`s more, fluorine is an oxidizer that can be combined with metal fuel ingredients (e.g., aluminum or boron) in propellants. Besides, difluoramino group can provides higher density than nitro, contributing favorably to explosive performance and to propellant property [7].

Some reagents are need in introducing difluoramino group to organic or inorganic compounds by difluoramination. In 2001, Shreeve group[8] reported that electfluor™, whose full name is 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2] octane bis (tetrafluoroborate), can fluorinate secondary or tertiary amine. In 2002, G. K. Surya et al.[9] clarified that F2NCPh3 is a convenient reagent for the conversion of ketones into gem-bis (difluoramines). In 2006, Haiges et al.[10] found that acetone can produce the corresponding gem-bis(difluoramino) counterpart by NF2SO3Na. In 2011, Belter [11] used benzene, alkanes and ethers of volatile chains and rings to react with excess NF3 to produce the corresponding difluoroamino-substituted compounds. These compounds are known as the difluoramination reagent.

The title compound is also a good difluoramination reagent which is widely used recently. This paper summarizes preparation and characteristic of NF2OSO2F, then reviews its appliance to product –C (NO2)2NF2 moiety.

2. Preparation and Characteristics

NF_2OSO_2F was prepared first by Lustig [12] in 1962. Tetrafluorohydrazine, N_2F_4, and peroxydisulfuryl difluoride, $S_2O_6F_2$ are used to prepare NF_2OSO_2F at room temperature, shown in Scheme 1. Product is characterized by some methods. Infrared spectrum reveals absorption at 1492 and 1250 cm^{-1} due to S=O bond; 1032 and 913 cm^{-1} due to N-F stretching; 840 cm^{-1} due to S-F stretching; 778 cm^{-1} due to S-O stretch. The mass spectrum of NF_2OSO_2F reveals that the particle of the highest concentration is the NF_2^+ ion with a mass number of 52. The ^{19}F NMR spectrum of 43.5 p.p.m supports that result.

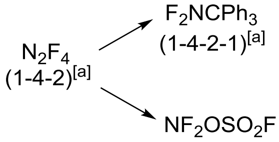
$$S_2O_6F_2 + N_2F_4 \longrightarrow NF_2OSO_2F$$

Scheme 1 Preparation of NF_2OSO_2F

In the reaction, N_2F_4 break to a radical, shown in Scheme 2. $S_2O_6F_2$ is also a radical, therefore also chemically extremely reactive. As a difluoramination reagent, that NF_2OSO_2F comes from N_2F_4 consistents with the Difluoramination System predicted by Chen [13]. In the Difluoramination System, compounds after the arrow are synthesized by ones before the arrow. New compounds derived given compounds of the system may be used as novel difluoramination reagent. According to Chen, N_2F_4 is a given compound in the system whose code is 1-4-2. It can product F_2NCPh_3 reported in 1961 [14], which is a reagent leading to difluoramino products. Also, tetrafluorohydrazine can produce other new difluoramination reagent, which may be the title compound. Therefore, there will be a new compound NF_2OSO_2F adding to the Difluoramination System found by Chen, shown in Scheme 3.

$$N_2F_4 \rightleftharpoons \cdot NF_2$$

Scheme 2 N_2F_4 break to a radical



Scheme 3 Part of the new Difluoramination System

[a] It is a code made by Chen in the system

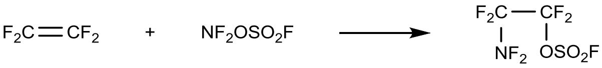
NF_2OSO_2F has a density of $1.498 g/cm^3$ under standardized temperature and pressure. It has a freezing point at -128.8°C and a boiling point at -2.5 °C, so it is usually gaseous. The title compound is readily neither reacted with base nor with Lewis acid. It is slow that NF_2OSO_2F reacted with an excess NaOH solution at 70 °C. And it is not observed to reaction between NF_2OSO_2F with BF_3. However, title compound is readily attacked by chloride and fluoride anions either in solution or in the dry state [15], shown in Scheme 4.

$$NF_2OSO_2F + Cl^- \longrightarrow FSO_3^- + ClNF_2$$

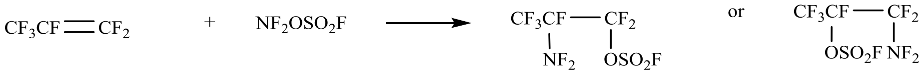
$$NF_2OSO_2F \xrightarrow{F^-} FSO_2F + NOF$$

Scheme 4 Reaction between NF_2OSO_2F with anions

The most important feature of NF_2OSO_2F is used as a source leading to difluoramino products. In 1965 [16], title compound was used to react with the unsaturated fluorocarbons CF_2CF_2 and CF_3CFCF_2 to product $CF_2NF_2CF_2OSO_2F$, in the first and the isomeric mixture $CF_3CF(OSO_2F)CF_2NF_2$ and $CF_3CFNF_2CF_2(OSO_2F)$, in the other. They are show in Scheme 5 and 6, respectively.



Scheme 5 Reaction between NF_2OSO_2F with CF_2CF_2

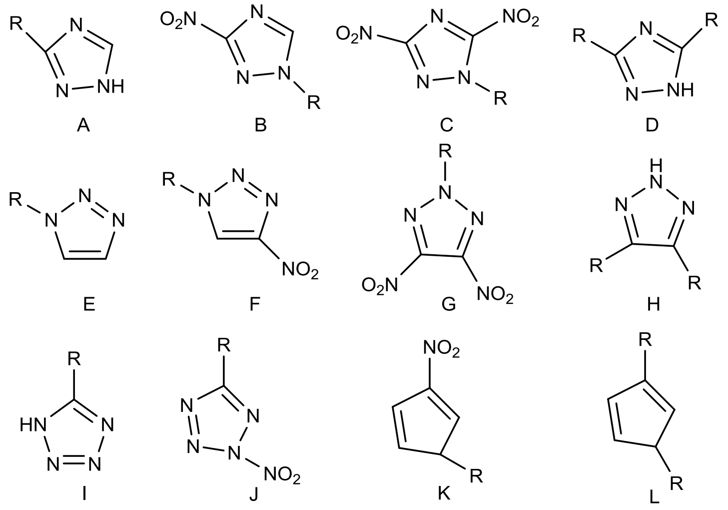


Scheme 6 Reaction between NF_2OSO_2F with CF_3CFCF_2

3. Difluoramination

The title compound has aroused interest of many research groups for using as an effective reagent to produce difluoroamino-dinitromethyl [-$C(NO_2)_2NF_2$] moiety, which is typically prepared from -$C(NO_2)_2$ salts.

In the moiety, NF_2 and multi-nitro functional groups can significantly improve oxygen balance, increase density and obtain highly positive heat of formation. This moiety can be introduced to carbon or nitrogen atom in rich nitrogen skeleton. Fei [17] calculated detonation performance of twelve triazole or tetrazole derivatives with density function theory, and their structures were shown in Scheme 7. Results reveled that B, F, H, and I displayed excellent integrated performance, with higher density (≥ 1.95 g/cm^3), oxygen balance (≥ 2.97%), detonation velocity (>8900 m/s), and detonation pressure values (>40.0 GPa) than RDX.



R=C(NO$_2$)NF$_2$

Scheme 7 Structure of twelve triazole or tetrazole derivatives

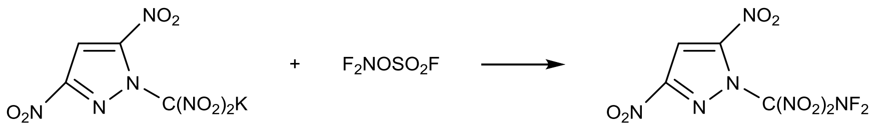
In 1996, Fokin et al [18]. first developed a novel method to synthesize difluoroamino- dinitromethyl compounds by NF_2OSO_2F. The yields depended on the reaction conditions, the structure of salts, and the properties of solvents. When the substrate was lithium, sodium, and potassium salt, the yield decreased in turn. Besides, the yield depended on stability of anion, and α carbon linking carbonyl, cyano or other conjugated groups can enhance the stability, shown in Scheme 8. Acetonitrile solvent would result in reaction completion immediately.

$$F_2NOSO_2F + XC(NO_2)_2R \longrightarrow F_2NC(NO_2)_2R$$

X=Li , Na or K

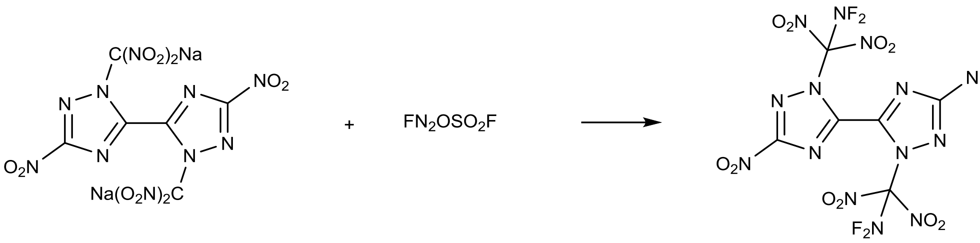
Scheme 8 Reaction introducing difluoroamino-dinitromethyl moiety

Recently, there are many compounds containing [-$C(NO_2)_2NF_2$] moiety being studied as new high-energy density material. In 2015, Dalinger [19] reported the synthesis of the first stable monocyclic azoles with $C(NO_2)_2NF_2$ attached at the nitrogen atom position of pyrazole ring. In the experiments, potassium 1,1-dinitro-1- (3,5-dinitropyrazol-1-yl)methanide reacted with a slight excess of F_2NOSO_2F in MeCN at -15 °C leading to difluoroamino derivative in 75% yield, shown in Scheme 9.

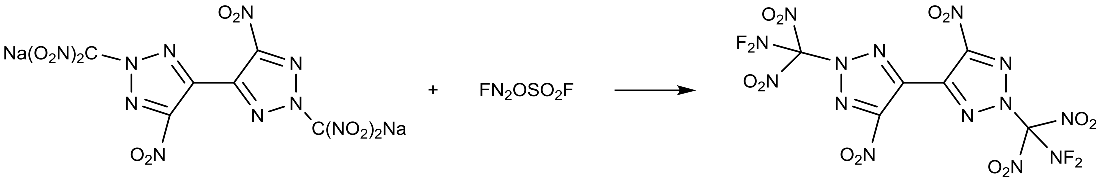


Scheme 9 Reaction between potassium 1,1-dinitro-1- (3,5-dinitropyrazol-1-yl)methanide with F_2NOSO_2F

In 2017, Semenov [20] reported a modification of 2,2'-bis(dinitromethyl)-5,5'- dinitro- 2H,2'H-3,3'-bi(1,2,4-triazole) and 2,2'-bis(dinitromethyl)-5,5'-dinitro-2H,2'H-4,4'-bi(1,2,3- triazole) by introduction of difluoroamino group. The two starting materials easily formed stable disodium salts due to the high acidity of N-dinitromethyl groups, and then difluoroaminate at dinitromethyl groups to synthesize the counterparts at –30 to –40°C in methanol or acetonitrile, shown in Scheme 10 and 11, respectively.

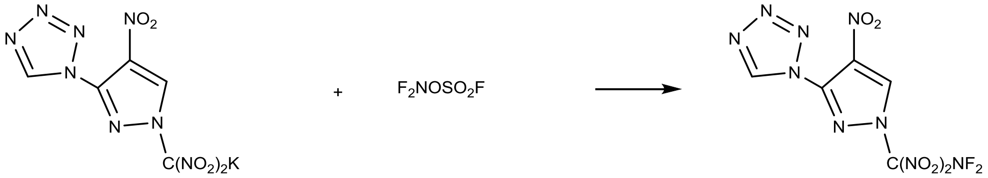


Scheme 10 Reaction between disodium 2,2'-bis(dinitromethyl)-5,5'-dinitro- 2H,2'H-3,3'-bi(1,2,4-triazole) with F_2NOSO_2F



Scheme 11 Reaction between disodium 2,2'-bis(dinitromethyl)-5,5'-dinitro- 2H,2'H-4,4'-bi(1,2,3-triazole) with F_2NOSO_2F

In 2018, Dalinger [21] focused on combination of nitropyrazole unit and tetrazole ring linearly bonded [$-C(NO_2)_2NF_2$] energetic modules. (dinitro(4-nitro-3-(1H- tetrazol-1-yl)-1H- pyrazol-1-yl)methyl) potassium is used to react with F_2NOSO_2F in acetonitrile at -33ºC in good yield, shown in Scheme 12.



Scheme 12 Reaction between (dinitro(4-nitro-3-(1H- tetrazol-1-yl)-1H-pyrazol-1-yl)methyl) potassium with F_2NOSO_2F

4. Conclusion

High energetic compounds are components of explosive, rocket propellants, various special compositions, such as entertainment pyrotechnic, gas generators and so on. Rich nitrogen compounds bearing difluoroamino-dinitromethyl explosophore is a potential high energetic material and is studied widely in recent years. NF_2OSO_2F is an efficient reagent for difluoraminating $-C(NO_2)_2$ salts to product difluoroamino- dinitromethyl explosophore. Tetrafluorohydrazine and peroxydisulfuryl difluoride can be used to prepare NF_2OSO_2F. This paper reviews its preparation, characteristic and appliance to product $-C(NO_2)_2NF_2$ moiety.

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