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Ethyl butyrates bearing nitro and difluoroamino groups

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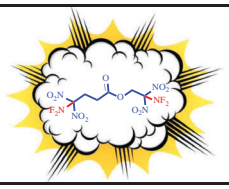
Difluoroamination and esterification reactions were utilized for the preparation of NF_2-analogs of 2,2,2-trinitroethyl 4,4,4-trinitrobutanoate with replacing one or two nitro groups. Difluoroamino products possess promising properties as ingredients of metallized energetic materials.



Keywords: difluoroamino group, difluoroamino(dinitro)methyl group, nitro alcohols, energetic alkyl esters, decomposition temperature, impact sensitivity.

In recent years, significant efforts have been made to synthesize new energetic compounds and to study their chemical, physical, thermochemical and explosive properties for the use as explosives or rocket propellant components. The need for such efforts is evident when the historically changing requirements for energy materials are considered. To create promising materials of the future, an inventory of energetic compounds with a wide range of properties is needed.

An attractive approach to energetic materials is the modification of an old energetic compound. Following this guiding principle, we choose as a starting point 2,2,2-trinitroethyl 4,4,4-trinitrobutanoate **1**, a highly performance melt-castable energetic compound.[1–7] Ester **1** and some of its potentially useful analogs **2**–**4** reported in the literature[8–13] are shown in Figure 1. Attempts to enhance the performance of energetic nitro compounds by further derivatization, leading to an increase in energy output, have formed the basis for a series of papers[14–25] on replacing the nitro group with a difluoroamine (NF_2) group and encouraged us to disclose the results of our research on the modification of ethyl butyrate bearing nitro groups.

We have shown that when readily available salt **5**[26] was treated with *N*,*N*-difluoro-*O*-(fluorosulfonyl)hydroxylamine, F_2NOSO_2F,[17] at a temperature of 0–15 °C in water, difluoroamination of the dinitromethyl anion occurred giving product **6** in moderate yield (Scheme 1). It should be noted that during the reaction, F_2NOSO_2F is partially hydrolyzed, which leads to acidification of the reaction mixture. As a result, part of salt **5** reverts to non-dissociated dinitro compound (it can be isolated from the reaction), which does not react with F_2NOSO_2F. Based on the reacting compound **5**, the yield of **6** is ~50%. Methyl ester **6** is smoothly hydrolyzed to acid **7** when heated in hydrochloric or nitric acid. Heating acid **7** with thionyl chloride gives the corresponding acyl chloride **8** in high yield. Available trinitroethanol[27] and 2-difluoroamino-2,2-dinitroethanol[16] were used to prepare related esters differing in the number of difluoroamino groups. Considering the fact that the electron-withdrawing properties of the NF_2 group are only slightly inferior to the NO_2 group,[28] it can be expected that the above alcohols should have similar reactivity. It was found that the synthesis of both esters **9** and **10** using the esterification reaction with acyl chloride **8** was best performed in 1,2-dichloroethane (DCE) in the presence of $AlCl_3$. Trans-esterification of methyl ester **6** with trinitroethanol in H_2SO_4 also afforded compound **9**, however in the yield not higher than 20%. It is important to note that the difluoroamino(dinitro)methyl group is not affected in the course of the above reactions.

Employing the reaction of acyl chloride **11**[6] with 2-difluoroamino-2,2-dinitroethanol, we synthesized a third analog of compound **1**, ester **12** (Scheme 2).

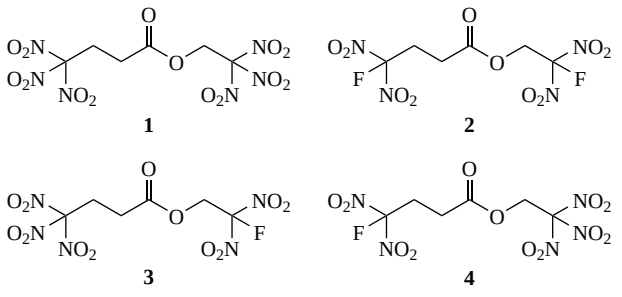
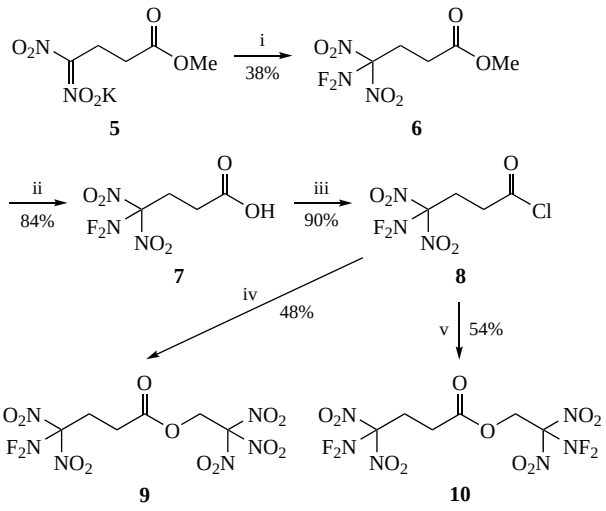


Figure 1 Ethyl butyrates bearing nitro and fluoro groups.

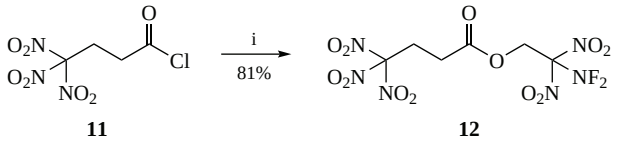


Scheme 1 *Reagents and conditions*: i, H_2O, $MgSO_4$, F_2NOSO_2F, 5 °C; ii, 38% HNO_3, ~70 °C; iii, $SOCl_2$, ~80 °C; iv, $(O_2N)_3CCH_2OH$, DCE, $AlCl_3$, ~80 °C; v, $F_2N(O_2N)_2CCH_2OH$, DCE, $AlCl_3$, ~80 °C.

Table 1 Comparisons between key characteristics of compound **1** and NF_2-analogs.

Compound	Molecular formula/*M*	α^a	F^b (%)	ρ^c/g cm^{-3}	mp^d/°C	Exo. onset/peak DSC (5 °C)^e/°C	IS^f (%)	ΔH_f^{og}/kJ mol^{-1} (kJ g^{-1})
9	$C_6H_6F_2N_6O_{12}$/ 392.14	0.867	9.69	1.84	80	136/163	44	–501.0 (–1.277)
10	$C_6H_6F_4N_6O_{10}$/ 398.14	0.800	19.09	1.85	72	140/162	88	–512.0 (–1.286)
12	$C_6H_6F_2N_6O_{12}$/ 392.14	0.867	9.69	1.83	79.5	135/162	46	–501.5 (–1.279)
1	$C_6H_6N_6O_{14}$/ 386.14	0.933	0	1.84	92	150/167	24	–488.5 (–1.265)

[a] Oxygen coefficient. For a compound with the molecular formula of $C_xH_yN_zO_wF_u$ $\alpha = (2w + u)/(4x + y)$. A compound with $\alpha > 1$ is an oxidizer. [b] Fluorine content. [c] Density measured using a gas pycnometer (25 °C). [d] Melting point. [e] Decomposition temperature measured at a heating rate of 5 K min^{-1}. [f] Impact sensitivity shown as frequency of explosions at the impact to 2 kg/25 cm drop-weight (K-44-II impact machine). [g] Calculated enthalpy of formation for solid state.



11 **12**

Scheme 2 *Reagents and conditions*: i, $F_2N(O_2N)_2CCH_2OH$, DCE, $AlCl_3$, ~80 °C.

All esters bearing difluoroamino(dinitro)methyl unit are white low-melting solids and are stable during long-term storage. Physical characteristics and some key properties of these energetic materials are given in Table 1. To assess the potential of the newly prepared trinitroethyl esters, their energetic characteristics were compared with 2,2,2-trinitroethyl 4,4,4-trinitrobutanoate **1**. The performances of both explosive[†] and rocket propellant[29] ingredients were determined by the ratio between the oxidizing and reducing elements in the molecule (α), the enthalpy of formation (ΔH_f^o) of the energetic compounds and their density. The performance for esters of this study can be evaluated using the data from Table 1. The difluoroamine analogs are similar to compound **1** in terms of density and the enthalpy of formation, but more sensitive to impact. Positional isomers **9** and **12** have similar properties, which is probably due to the same surroundings around the difluoroamino group in both compounds.

The difluoramino group is an explosophoric one[30] that has a number of advantages over other fluorine-containing groups because it makes a significantly more positive contribution to the enthalpy of formation of the molecule. Comparison of the preliminary data on burning rates of **1** (16 mm s^{-1} at 100 MPa), **9** (52 mm s^{-1} at 100 MPa), and **10** (135 mm s^{-1} at 100 MPa) indicates that incorporation of NF_2 group instead of NO_2 group leads to a significant increase in the burning rate; the same trend was observed earlier.[31] The fact that the possibility of achieving full metal combustion/detonation in advanced energetic materials[19–23,25,32,33] can be provided by replacing conventional oxygen-containing energetic oxidizers with oxidizers rich in both oxygen and fluorine makes compounds bearing the difluoroamino(dinitro)methyl unit very promising.

In conclusion, by replacing one or two nitro groups in 2,2,2-trinitroethyl 4,4,4-trinitrobutyrate **1** with a difluoroamino group, we first synthesized its three novel NF_2-analogs. This replacement leads to an increase in impact sensitivity while maintaining the level of density, thermal stability and enthalpy of formation. Nitro–difluoroamino combination is favorable for the complete combustion of metal. These data suggest that the difluoroamines of this study may be useful in future energetic material applications as a potential substitute for conventional nitro compounds. The development of synthetic strategies for the modification of known explosives and rocket propellant components is always in demand to improve the modern organic synthesis toolbox for the construction of energetic compounds.[34–37] Partial replacement of nitro groups by difluoroamine groups in a molecule follows this trend.[19,20,22,25,38]

Dedicated to the memory of Dr. Aleksandr Kh. Shakhnes, ZIOC RAS.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom. 2023.10.034.

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