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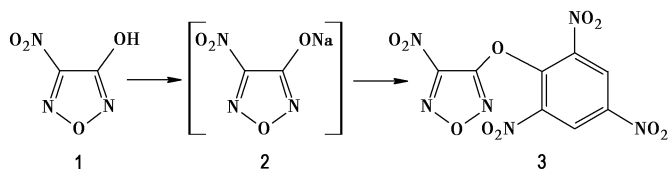
Synthesis of Unsymmetrical Nitrofurazanyl Picryl Ether

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Hydroxyfurazan is a useful building block in the synthesis of oxyfurazanyl modified energetic materials. Some of symmetrical and unsymmetrical difurazanyl ether derivatives were synthesized by S_N2 reaction in which nitro group was as a leaving group.

Picryl group (2, 4, 6-trinitrophenyl-) is also an important building block in energetic materials. In this letter, an unsymmetrical nitrofurazanyl polynitrobenzene ether **3** was synthesized via Williamson reaction (Scheme 1).



Scheme 1

3-Hydroxy-4-nitrofurazan **1** was prepared by literature method. The salt **2** was prepared by adding solution of sodium methoxide in methanol (28% in weight) to ether solution of compound **1** and then stirred at about 35 °C for 1 h. Because salt **2** was explosives, it was not completely dried and used directly for next procedure.

The solutions of 2-chloro-1, 3, 5-trinitrobenzene in acetonitrile was added dropwise to salt **2** suspended in acetonitrile. In order to simplify the post process, salt **2** was over amount (about 20% in molar ratio).

The reaction mixture was stirred at 81 – 82 °C for 14 – 15 h and then poured into ice and the aqueous solution was concentrated in vacuum. Then the residue was dipped by acetone three times and concentrated in vacuum to give yellow powder **3** in 78% yield, m.p.

111.6 °C (DSC, 10 °C min⁻¹, recrystaled from acetone/ether (3/1)).

¹H NMR (500 MHz, C₂D₆CO) δ 8.735; ¹³C NMR (125 MHz, C₂D₆CO) δ 124.015, 126.55, 127.16, 127.97, 142.88, 163.09. FTIR (cm⁻¹) 3613, 3543, 3092, 1635, 1561, 1515, 1494, 1429, 1373, 1344, 1282, 1162, 1085.

Elem. Ana. Calcd. for C₈H₂N₆O₁₀: C 28.07, H 0.06, N 24.56; Found: C 27.88, H 0.12, N 24.61.

The estimated density of compound **3** is calculated as 1.867 g · cm⁻³ using atom/functional group volume additivity methods. The heat of formation of compound **3** is computed as 70.8 kJ · mol⁻¹ using the method ofisodesmic reactions. The enthalpy of reaction is obtained by combining the MP2 (full)/6-311 + + G^{**} energy difference for the reaction, the scaled zero-point energies (B3LYP/6-31 + G^{**}), and other thermal factors. Thus, the heat of formation being investigated can be readily extracted. The oxygen balance of compound **3** is -32.7%. The expected detonation velocity and detonation pressure, 8213 m · s⁻¹ and 30.58 GPa, are calculated using the semiempirical equations suggested by Kamlet and Jacobs.

In conclusion, we reported the synthesis of nitrofurazanyl polynitrobenzene ether. A series of unsymmetrical furazanyl ethers could be prepared by this method. Further studies of other nitrogen-riched heterocyclic nitrofurazanyl ethers are in progress in our laboratory.

Key words: organic chemistry; nitrofurazanyl polynitrobenzene ether; synthesis; property

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