Asian Journal of Chemistry; Vol. 24, No. 4 (2012), 1453-1455

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Synthesis of Unsymmetrical Nitrofurazanyl Ethers

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(*Received*: 11 January 2011; *Accepted*: 17 November 2011) AJC-10689

Three novel unsymmetrical nitrofurazanyl ethers were synthesized *via* Williamson reaction. Some properties of the product, such as density, heat of formation, oxygen balance, detonation pressures and detonation velocities were calculated.

Key Words: Unsymmetrical nitrofurazanyl ethers, Hydroxynitrofurazan, Properties.

INTRODUCTION

Nowadays, nitrogen-riched heterocyclic compounds have been considered as potential energetic materials due to their high heats of formation and highly endothermic in nature[1-3].

Hydroxyfurazan (**3**) is a useful building block in the synthesis of oxyfurazanyl modified energetic materials[4]. And some symmetrical and unsymmetrical difurazanyl ether derivatives have been developed as highly energetic materials having good explosive performance[5]. Normally, these compounds were found to be quite dense and have high thermal stability and performance as insensitive high explosives (IHEs). The symmetrical and unsymmetrical difurazanyl ethers could be prepared by SN_2 reaction from hydroxyfurazan in which nitro group was as a leaving group[5,6].

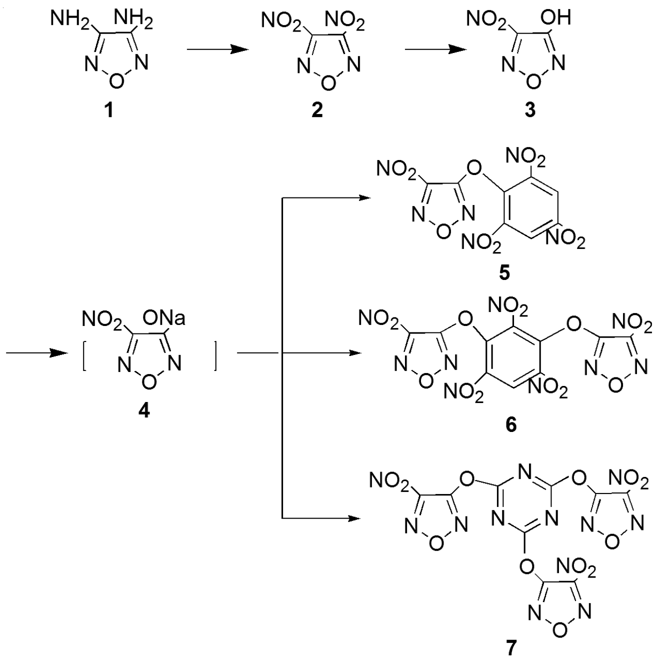
Picryl groups (2,4,6-trinitrophenyl-) and triazine are also important building blocks in energetic materials. In this study, novel unsymmetrical nitrofurazane picryl ether derivatives and nitrofurazane triazine ether derivative were synthesized *via* Williamson reaction (**Scheme-I**).

EXPERIMENTAL

3,4-Diaminofurazan (**1**) was synthesized followed in literature[7]. 3,4-Dinitrofurazan (**2**) was prepared by oxidation of 3,4-diaminofurazan in H_2SO_4/H_2O_2 system[8]. 3,4-Dinitrofurazan (**2**) was transformed to 3-hydroxy-4-nitrofurazan (**3**) with weak base K_2CO_3 in dry acetonitrile[9].

Compound **2**. Yellow liquid, 62 % yield. (KBr, ν_{max}, cm^{-1}) :1576, 1541, 1452, 1353, 1139, 1031, 842, 806; ^{13}C NMR (125 MHz, DMSO-d_6) δ 153.9.

Compound **3**: Yellow liquid, 72 % yield. (KBr, ν_{max}, cm^{-1}): 3569-3200, 1615, 1548, 1448, 1382, 1206, 1030; ^{13}C NMR (125 MHz, DMSO-d_6) δ 153.84, 158.57.



Scheme-I Synthesis of unsymmetrical nitrofurazanyl ethers

3-Nitro-4-(2,4,6-trinitrophenoxy)furazan (5): To a solution of compound **4** (0.65 g, 4.25 mmol) suspended in 50 mL acetonitrile, 1-chloro-2,4,6-trinitrobenzene (0.94 g, 3.80 mmol) was added. The reaction mixture was stirred at 81-82 ºC for 14-15 h and poured into ice overnight. The filtered aqueous solution was concentrated in vacuum. Then the product was dipped by acetone three times and concentrated in vacuum. Saturated aqueous NaCl solution was added to the crude product and extracted three times with acetonitrile. The combined extracts were then washed with saturated aqueous NaCl solution, dried,

TABLE-1
PROPERTIES OF UNSYMMETRICAL NITROFURAZANYL ETHERS

Compound	m.f.	T_m[a]	ρ[b]	OB[c]	ΔH_f[d]	D[e]	P[f]
5	$C_8H_2N_6O_{10}$	111.6	1.867	-32.7	70.8	8213	30.6
6	$C_{10}HN_9O_{14}$	82.5	2.003	-22.1	169.9	8969	43.2
7	$C_9N_{12}O_{12}$	132.3	1.992	-21.2	248.1	8583	34.6

[a]Melting point (°C, DSC, 10 °C min^{-1}). [b]Density (g cm^{-3}). [c]Oxygen balance (OB)—index of the deficiency or excess of oxygen in a compound required to convert all C into CO_2 and all H into H_2O. For a compound with the molecular formula of $C_aH_bN_cO_d$, OB (%) = 1600[(d-2a-b/2)/MW]. [d]Molar enthalpy of formation (kJ mol^{-1}). [e]Detonation velocity (m s^{-1}). [f]Detonation pressure (GPa)

filtered and evaporated in vacuum to dryness. Recrystallization from acetone-ether (3:1) afforded product **5** (0.40 g, 31 %). (KBr, ν_{max}, cm^{-1}) : 3613, 3543, 3092, 1635, 1615, 1561, 1515, 1494, 1429, 1373, 1344, 1282, 1162, 1085; ^{1}H NMR (500 MHz, C_2D_6CO) δ 8.735; ^{13}C NMR (125 MHz, C_2D_6CO) δ 163.09, 142.88, 127.97, 127.16, 126.55, 124.015. Anal. calcd. for $C_8H_2N_6O_{10}$: C, 28.07; H, 0.06; N, 24.56. Found: C, 28.17; H, 0.05; N, 24.75.

4,4'-(2,4,6-Trinitro-1,3-phenylene)-*bis*(oxy)-bis(3-nitrofurazan) (6): Compound **4** (1.02 g, 6.67 mmol) and 1,3-dichloro-2,4,6-trinitrobenzene (0.71 g, 2.52 mmol) in 50 mL acetonitrile were kept at 81-82 °C for 2 h. Same procedure as compound **5** afforded white powder **6** (0.50 g, 42 %). (KBr, ν_{max}, cm^{-1}): 3633, 3518, 3093, 1655, 1613, 1565, 1535, 1497, 1435, 1336, 1307, 1255, 1161; ^{1}H NMR (500 MHz, C_2D_6CO) δ 8.976; ^{13}C NMR (125 MHz, C_2D_6CO) δ 163.24, 142.14, 127.92, 127.60, 126.94, 125.25. Anal. calcd. for $C_{10}HN_9O_{14}$: C, 25.48; H, 0.002; N, 26.75. Found: C, 25.06; H, 0.01; N, 26.34.

2,4,6-Tri(3-nitro-furazanyl-4'-el-)-1,3,5-triazine (7). To a solution of compound **4** (0.64 g, 4.18 mmol) suspended in 50 mL acetonitrile and cooled to 3-5 °C, the solution of 2,4,6-trichloro-1,3,5-triazine (0.23 g, 1.25 mmol) in 5 mL acetonitrile was added dropwise and kept at this temperature for 7.5 h. Same procedure as compound **5** afforded yellow powder **7** (0.47 g, 80%). (KBr, ν_{max}, cm^{-1}): 1772, 1703, 1621, 1559, 1278, 1046, 1539, 1384; ^{13}C NMR (125 MHz, C_2D_6CO) δ 162.14, 158.85, 152.12. Anal. calcd. for $C_9N_{12}O_{12}$: C, 22.86; N, 35.18. Found: C, 23.08; N, 34.90.

RESULTS AND DISCUSSION

Compound **3** was white crystals and hygroscopic. Normally, **3** was in ether solution and kept in refrigerator. The content of **3** was conducted by weighening after drying its ether solution in vacuum three times. Compound **4** was prepared by adding solution of sodium methoxide in methanol (28 % in weight) to the ether solution of **3** and then stirred at about 35 °C for 1 h. The white crystals were filtered and washed by cold dry ether three times. Because **4** was explosives, it was not complete dry and used directly for next procedure.

The solution of 2-chloro-1,3,5-trinitrobenzene, 2,4-dichloro-1,3,5-trinitrobenzene or 2,4,6-trichloro-1,3,5-triazine in acetonitrile was added dropwise to **4** suspended in acetonitrile. In order to simplify the post process, **4** was over amount (about 20 % in mol ratio).

The reactions were monitored by HPLC. For 2-chloro-1,3,5-trinitrobenzene, the reaction was transformed 50 % in 0.5 h at 81-82 °C while it remained about 9 % even after 35 h at this temperature. Though the amount of the starting material changed unconspicuously after 16 h, the HPLC area of the impurity was gradually increased. For 2,4-dichloro-1,3,5-trinitrobenzene, the reaction was more faster that it transformed completely in 2 h. when **4** reacted with 2,4,6-trichloro-1,3,5-triazine at 3-5 °C, the starting material consumed completely in 7.5 h.

For the synthesis of salt **4**, sodium methoxide should be excess more than 100 % (in molar ratio). The yield of salt **4** was low as about 30-45 % when sodium methoxide was equal to **3**. The unreacted sodium methoxide was concomitant with salt **4** and could produce methyloxyl derived polynitrobenzene. However these byproducts could be easily separated by filtered from the reaction mixture aqueous solution.

The estimated densities of compounds **5**, **6** and **7** were calculated using atom/functional group volume additivity methods[10,11]. The heats of formation of compounds **5**, **6** and **7** are computed using the method of isodesmic reactions[12]. The enthalpy of reaction (ΔHr^o_{298}) 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 expected detonation pressures (P) and detonation velocities (D) were calculated using the semiempirical equations suggested by Kamlet *et al.*[13-15] and Zhang[16]. All these data were listed in Table-1.

The geometric optimization (Fig. 1) and total atom charge (Table-2) of compound **5** were carried out by using B3LYP functional with 6-31+ G** basis set. The O9 atom carries the largest negative charge in the structure. Compound **5** was decomposed at O9 atom when it was heated. TGA result (Fig. 2) of **5** shows two steps of mass loss, in which the first mass loss process is attributed to the formation of picric acid derived from the cleavage of O9-C2.

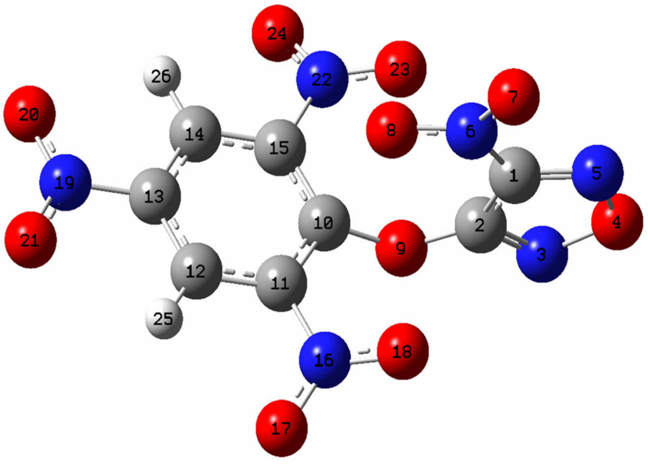


Fig. 1. Molecular structure of compound (**5**)

TABLE-2
TOTAL ATOM CHARGE DISTRIBUTION OF COMPOUND **5**

Atom	Charge	Atom	Charge	Atom	Charge
C1	0.52	C10	0.35	N19	0.06
C2	0.53	C11	0.30	O20	-0.26
N3	-0.10	C12	-0.05	O21	-0.26
O4	-0.21	C13	0.29	N22	0.06
N5	-0.05	C14	-0.05	O23	-0.28
N6	0.09	C15	0.31	O24	-0.24
O7	-0.21	N16	0.06	H25	0.25
O8	-0.30	O17	-0.24	H26	0.25
O9	-0.54	O18	-0.28	–	–

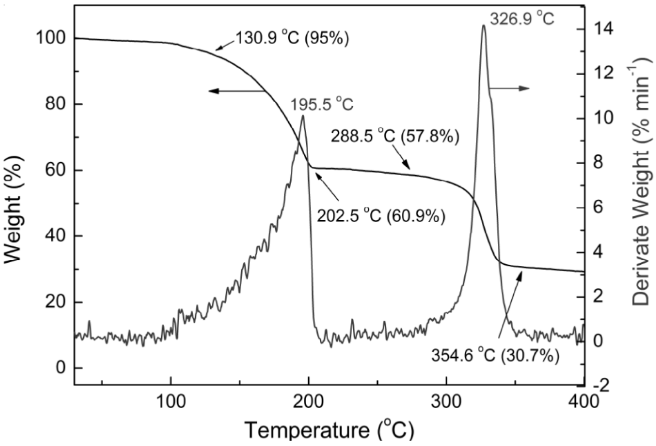


Fig. 2. TGA curve of compound **5**

Conclusion

In conclusion, we reported here the synthesis of nitrofurazanyl polynitrobenzene ethers and nitrofurazanyl triazine ether derivatives. 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.

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