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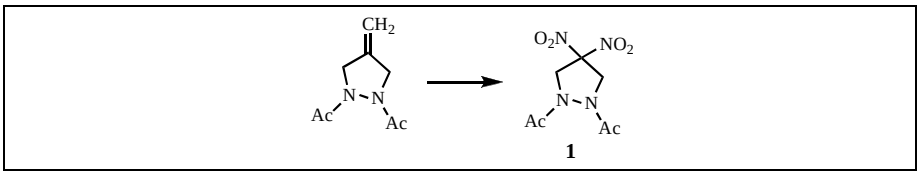

Synthesis of 1, 2-diacetyl-4, 4-dinitropyrazolidine 1 and results of further nitration of the 1,2-diacetyl-4,4-dinitropyrazolidine are described.

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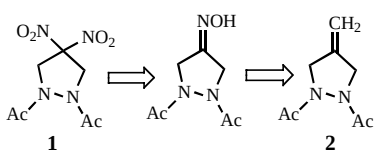
INTRODUCTION

In modern ordnance there is a strong requirement for explosives having good thermal stability, impact insensitivity and explosive performance [1-3]. However, these requirements are somewhat mutually exclusive. Those explosives having good thermal stability and impact insensitivity exhibit poorer explosive performances and *vice versa*. With this background, in the past we have synthesized several gem-dinitro and polynitro energetic compounds [4,5]. In a continuation of the program that is aimed at the development of new, insensitive and yet more powerful energetic formulations and ingredients, we needed to synthesize a gem-dinitropyrazolidine [6] compound bearing electron withdrawing groups such as acetyl, nitro on the nitrogen atoms of the ring. It is in this context that we have chosen 1,2-diacetyl-4,4-dinitropyrazolidine as our target compound and undertaken its synthesis. Herein we describe the results of our synthesis of the target compound **1** and our attempts to further nitrate **1** to the corresponding tetranitro compound **8**.

RESULTS AND DISCUSSION

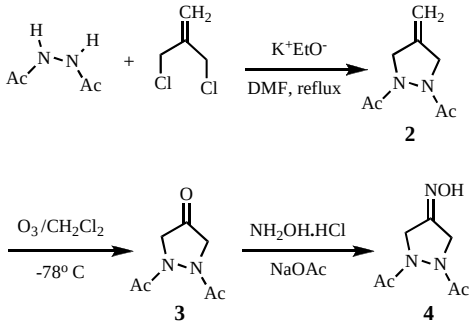
A retro-synthetic analysis of **1** indicated that synthesis of 1,2-diacetylpyrazolidine-4-oxime and its subsequent nitration are the key steps in accomplishing the synthesis of 4,4-dinitropyrazolidine (Scheme 1).

Scheme 1



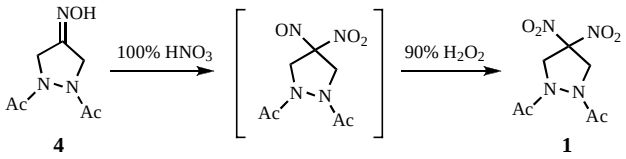
The starting material 4-methylidene-1,2-diacetyl pyrazolidine **2** was prepared using literature reported procedure with modification (Scheme 2) [7]. Thus reaction of the di-potassium salt of a 1,2-diacetylhydrazine with methallyl dichloride in anhydrous DMF under reflux conditions afforded **2**. Ozonolysis of **2** in dichloromethane at -78° C followed by quenching of the reaction mixture with dimethyl sulfide resulted in the formation of the desired pyrazolidinone **3**. The structure of the ketone **3** was confirmed by spectral data as well as single crystal X-ray crystallography. The reaction of **3** with hydroxylamine hydrochloride in aqueous methanol afforded the corresponding oxime **4** as a white solid.

Scheme 2



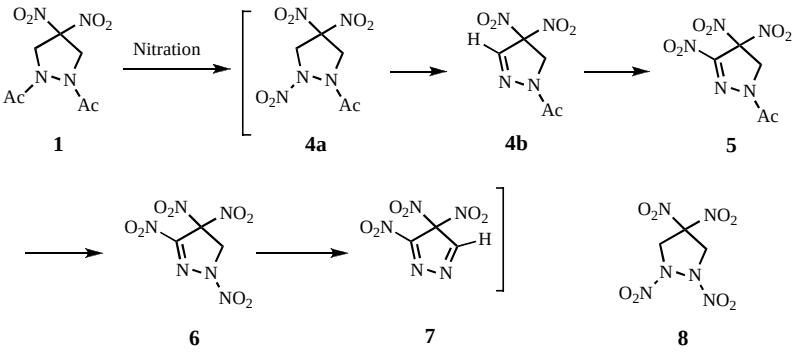
The compound **4** (Scheme 3) was subsequently reacted with 100% nitric acid in refluxing dichloromethane, followed by careful quenching of the reaction mixture at 0°C with 90% H_2O_2, to obtain the target product diacetyl-dinitropyrazolidine **1**. The structure of the diacetylpyrazolidine was established unambiguously *via* single crystal X-ray crystallography.

Scheme 3

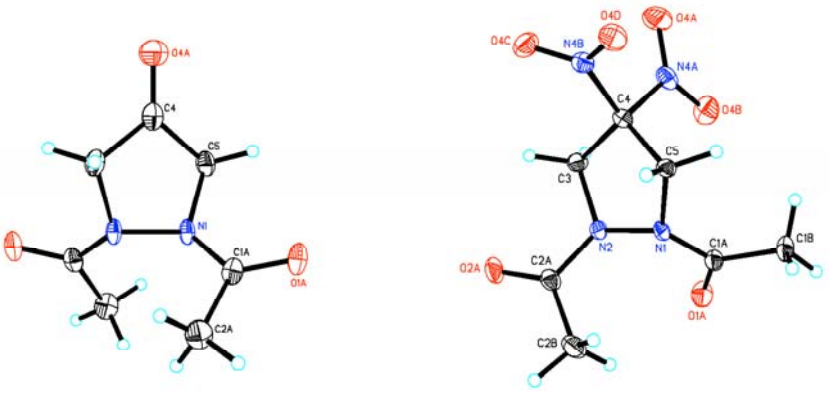


Theoretical calculations by scientists in our labs predicted that 1,2,4,4-tetranitropyrazolidine (**8**), another interesting gem-dinitropyrazolidine with electron with-drawing nitro groups on the ring nitrogen atoms would be a high density and high performance energetic material. Furthermore, cyclic nitramines with 4 and 6 membered rings [5,8] containing gem-dinitro groups at the β-position with respect to the nitramino group are well known. However, the corresponding cyclic nitramines with 5 membered ring are not known to the best of our knowledge. Hence, after successful synthesis of the target compound and in further extension of our work, we made attempts to convert the diacetyl groups of **1** to the corresponding dinitro groups. Our efforts on further nitration to convert the 1,2-diacetyl functionality of **1** to corresponding nitro groups under a variety of conditions (H_2SO_4/HNO_3, 100% HNO_3, $(CF_3CO)_2O$/100% HNO_3, Nafion-HNO_3, NO_2BF_4 and N_2O_4) did not result in the

Scheme 4



An ORTEP view and X-ray crystal structure [10] data for **3** and **1**.



3 **1**

Chemical Formula:	$C_7H_{10}N_2O_3$		$C_7H_{10}N_4O_6$	
MW	170.17		246.19	
Appearance:	Clear colorless prism		Clear colorless prism	
Crystal size(mm):	0.31x0.25x0.20		0.34x0.24x0.16	
Crystal System:	Monoclinic		Orthorhombic	
Temperature:	-180° C		-180° C	
Detector Distance (cm):	5		5	
Frame Time:	10		10	
Space Group:	C2/C		$Pca2_1$	
Unit cell dimensions:	a: 12.72(3)	α: 90	a: 11.1081(5)	α: 90
	b: 8.076(19)	β: 123.54(4)	b: 7.4047(14)	β: 90
	c: 9.41(2)	γ: 90	c: 15.4195(15)	γ: 90
Z:	4		4	
Volume (Å^3)	806 (3)		1034.81(9)	

Density (Mg/m3):	1.402 at -180° C, 1.401 at 21° C	1.580 at -180° C, 1.534 at 21° C 1.492
μ (μμ−1):	0.111	0.139
Goof:	1.058	1.112
T_{min}:	0.966	0.954
T_{max}:	0.978	0.978
R_{int}:	0.0374	0.0276
R1 (I>2σ):	0.0451	0.0324
wR2 (I>2σ):	0.1169	0.0913
R1 (all data):	0.0552	0.0332
wR2 (all data):	0.1227	0.0924
Reflections Collected:	2707	4547
Unique Reflections:	946	1933
Max Resolution Å:	0.75	0.75
% Completeness:	94.4	95.1

formation of desired product. Instead, an unstable pale yellow liquid was isolated. The NMR characteristics of this compound are consistent with argued structure 3,4,4-trinitro-1-acetylpyrazolidene **5** (Scheme 4). However, due to apparent instability of **5**, it could not be sufficiently purified and thoroughly characterized to establish the structure unambiguously.

Further nitration of **5** was carried out in an attempt to synthesize tetranitropyrazolidine. A pale yellow unstable liquid, always containing trace amounts of impurities detected by NMR analysis was isolated from the reaction mixture. Our efforts to purify this crude compound were not successful. The proton NMR of this liquid showed a singlet at 5.26 ppm along with another signal at 7.55 ppm (since the integrations do not correspond to each other, this clearly indicates the mixture of two compounds). The appearance of a signal in the aromatic region and isolation of *N*-acetyl-3,4,4-trinitropyrazoline **5** suggests that the first step in the nitration of 1,2-diacetyl-4,4-dinitropyrazolidine **1** is the formation of 1-acetyl-2,4,4-trinitropyrazolidine **4a**, which readily undergoes a HONO elimination to yield *N*-acetyl-4,4-dinitropyrazoline **4b** which undergoes further nitration [9] to form 1-acetyl-3, 4, 4-trinitropyrazoline **5**. The unstable compound **5** again undergoes nitration leading to the formation of 1,3,4,4-tetranitropyrazolidene **6** which further transforms to **7** again by HONO elimination.

In summary we have synthesized and characterized 1,2-diacetyl-4,4-dinitropyrazolidine by NMR spectra and X-ray analysis. Our attempts of further nitration of **5** led to the formation of unstable polynitropyrazolidine products.

EXPERIMENTAL

4-Methylidene-1,2-diacetylpyrazolidine (**2**). To a solution of elemental potassium (4.2g, 107mmol) in anhydrous ethanol (60 mL) was added diacetylhydrazine (97%, 6.00 g, 50.1 mmol) in warm anhydrous ethanol (60 mL). The resulting mixture was refluxed for 1 hr. The reaction mixture was evaporated to dryness on a rotary evaporator under vacuum. Anhydrous dimethylformamide (85 mL) was added to the residual translucent solid and the reaction mixture was heated at 155 °C for l hr. 3-Chloro-2-chloromethyl-1-propene (96%, 6.56g, 50.4 mmol) was added, drop-wise, over a period of 15 min and heating under reflux was continued for another 5 hr. The cooled reaction mixture was filtered and the filtrate was evaporated under reduced pressure. The residual oil was distilled under vacuum- fractionated in a bulb-to-bulb apparatus (170 to 185°) - to obtain 2.33 grams of pure product. ^{1}H ($CDCl_3$): 2.16 (s, 6H), 3.64 (br s, 2H), 4.82 (br s, 2H), 5.13 (s, 2H). *Anal*. Calcd. for $C_8H_{12}O_2N_2$: C, 57.13; H, 7.19; N, 16.65. Found: C, 57.10; H, 7.18; N, 16.64.

1-2-Diacetyl pyrazolidine-4-one (**3**). A solution of 4-methylidine-1,2-diacetyl pyrazolidine (500 mg, 2.97 mmol) in anhydrous CH_2Cl_2 (25 mL) was cooled to -78°C using a dry ice-acetone bath. Ozone gas was bubbled into this cold solution until the blue color persisted. The reaction mixture was then purged with N_2 gas to remove excess of ozone and quenched with dimethylsulfide (1.5 mL). The reaction mixture was allowed to warm gradually to room temperature and stirred for another 2 hr. The resulting turbid solution was then evaporated under reduced pressure to yield a white solid. This solid was triturated with CH_2Cl_2 and filtered to obtain pure product as a white solid in 79% (400 mg) yield. m.p: 179-181°; ir (potassium bromide): 3017 (m), 2932 (w), 1778 (s), 1677 (s), 1417 (s), 1381 (s), 1272 (m), 1217 9m), 1192 (m), 1152 (m), 1033 (m) cm^{-1}; ^{1}H-nmr ($CDCl_3$): 2.25 (s, 6H, 2xCH_3), 3.48 (d, ABq, *J*= 17.88Hz, 2H), 4.62 (d, ABq, *J*=17.88Hz, 2H); ^{13}C-nmr ($CDCl_3$): 20.45, 51,94, 175.13; 205.88. *Anal*. Calcd. for $C_7H_{10}O_3N_2$: C, 49.41; H, 5.92; N, 16.46. Found: C, 49.41; H, 5.91; N, 16.44

1-2-Diacetylpyrazolidine-4-one-oxime (**4**). To a suspension of ketone **3** (380 mg, 2.23 mmol) in water (1 mL) was added sodium acetate (478 mg, 3.52 mmol) and hydroxylamine hydrochloride (242 mg, 3.52 mmol) sequentially. The reaction mixture was heated in a pre-heated oil bath at 60°C for 45 min. The solid that formed was collected by filtration and washed with a few drops of ice-cold water. The resulting solid was air dried to give the pure product **4** in 55% (220 mg) yield. m.p 197-198°; ir (potassium bromide): 3431 (br, s), 1678 (s), 1442 (s), 1376 (s), 1224 (s), 1045 (m) cm^{-1}; ^{1}H-nmr (acetone-d_6): 2.15 (s, 6H, 2xCH_3), 3.85 (br S, 2H), 4.78 (dd, *J*=60.1, 20.1 Hz, 2H); ^{13}C-nmr (acetone-d_6): 20.7, 46.1, 47.1, 157.2, 175.6. *Anal*. Calcd. for $C_7H_{11}O_3N_3$: C, 45.40; H, 5.99; N, 22.69. Found: C, 45.41; H, 5.97; N, 22.67

1,2-Diacetyl 4,4-dinitropyrazolidine (**1**). To a suspension of the oxime **4** (200 mg, 1.08 mmol) in anhydrous CH_2Cl_2 under reflux was added drop-wise 99% HNO_3 (1.5 mL). The resulting blue reaction mixture was refluxed for 20 min, gradually allowed to cool to room temperature and then cooled to 0°C in an ice-salt bath. To this cooled reaction mixture was added

carefully and drop-wise 90% H_2O_2 (1.5 mL). The resulting heterogeneous mixture was stirred for 45 min. The reaction mixture was diluted with water (5 mL) and extracted with CH_2Cl_2 (3x5 mL). The organic layers were combined, washed with water (1x10 mL), brine (1x10 mL), dried (Na_2SO_4) and evaporated under reduced pressure to yield the crude product as pale yellow syrup. This crude product was subjected to column purification (Si-gel, 15 % EtOAc-Hexanes) to give the pure product in 11% yield (31 mg). m.p 123-125°; ir (potassium bromide): 3133(s), 1731 (m), 1505 (s), 1410 (s), 1359 (s), 1288 (s), 1190 (m), 1160 (m), 1028 (m), 997 (s) cm^{-1}; ^{1}H-nmr ($CDCl_3$): 2.23 (s, 6H, 2xCH_3), 4.06 (d, J = 14.5 Hz, 2H), 5.38 (d, J = 14.5 Hz, 2H); ^{13}C-nmr ($CDCl_3$): 20.1, 53.8, 120.6, 174.4. *Anal*. Calcd. for $C_7H_{10}O_6N_4$: C, 34.15 ; H, 4.09; N, 22.76. Found: C, 34.15; H, 4.10; N, 22.74

Nitration of 1,2-diacetyl-4,4-dinitropyrazolidine. To a refluxing solution of diacetyl dinitropyrazolidine **1** (25 mg) in dichloromethane (5 mL) under nitrogen was added drop wise a mixture of sulphuric acid and nitric acid (15:85, 0.5 mL) *via* an addition funnel. The reaction mixture was refluxed for 1 h and then cooled to room temperature, poured over crushed ice (10 g) and extracted with dichloromethane (3x5 mL). The combined organic layer was washed with water (1x10 mL), and brine (1x10 mL) and dried (Na_2SO_4). The solvent was evaporated to yield a pale yellow syrup (8 mg) which was then subjected to preparative TLC (25 % EtOAc: Hexanes as eluent). The products isolated were found to be unstable and the NMR spectra of the isolated products tentatively indicated the formation of products **5**, and **6**. However, the instability of the products did not allow for a complete and thorough characterization to prove tentatively assigned structures unambiguously.

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[10] Complete crystallographic information files for 1, and 3 have been deposited with the Cambridge Crystallographic Data Center as supplementary publications CCDC 600980 & 600981 Copies of this data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ (UK); Tel.: (+44) 1223-336-408, Fax: (+44) 1223-336-033, or E-mail: **deposit@ccdc.cam.ac.uk.**