

Improved Preparation of 3-Oximinooxetane – An Important Precursor to Energetic Oxetanes

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Abstract: Oximes represent an extremely versatile building block in energetic materials chemistry. While oxidation with peroxy acids affords the corresponding mononitro compounds, tandem oxidation-nitration reactions such as the Scholl reaction lead to geminal dinitro compounds. Furthermore, the corresponding amines can be obtained by reduction of the oxime group. Accordingly, 3-oximinooxetane represents a suitable precursor for 3-nitro- and 3,3-dinitrooxetane as well as 3-aminooxetane. 3-Oximinooxetane, which is poorly described in the literature, has now

been extensively characterized by vibrational-, mass- and NMR spectroscopy, as well as elemental and thermal analysis. In addition, its synthesis has been significantly improved compared to literature. The molecular structure was elucidated by single-crystal X-ray diffraction. Since 3-oximinooxetane is energetic by itself, its performance was calculated using the EXPLO5 V6.04 thermochemical code, and its sensitivity towards external stimuli such as impact, friction, and electrostatic discharge was determined by BAM standard procedures.

Keywords: 3-Oximinooxetane · oxetan-3-one oxime · energetic monomer · energetic oxetanes

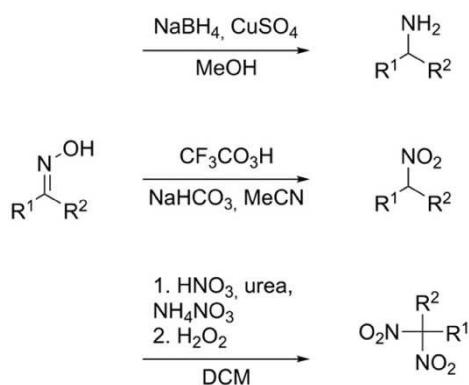
1 Introduction

Oximes play an important role in the chemistry of energetic materials. They can be easily obtained from corresponding keto compounds and offer great synthetic potential. Their reduction allows the synthesis of amines [1], which can be converted to nitramines or nitro compounds by oxidation of the amino group [2]. Direct oxidation of oximes with peroxy acids such as peroxytrifluoroacetic acid allows conversion into the corresponding mononitro compounds [2]. Tandem nitration-oxidation reactions such as the *Scholl* or *Ponzo* reaction even directly afford the respective geminal dinitro compounds (Scheme 1) [2].

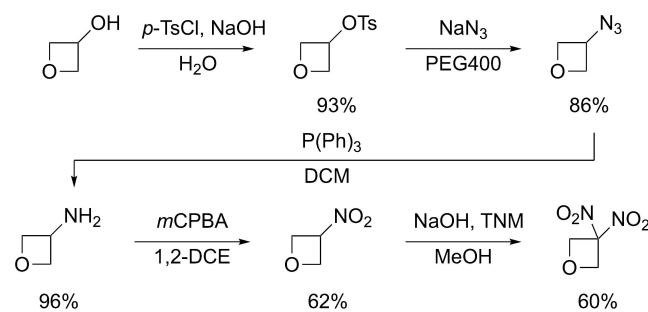
Accordingly, 3-oximinooxetane is an important and general precursor for 3-nitrooxetane, 3,3-dinitrooxetane, and 3-

aminooxetane, which are currently only accessible via multiple steps starting from oxetan-3-ol (Scheme 2) [3].

The utility of 3-oximinooxetane as valuable starting material is further supported by the commercial availability of



Scheme 1. Typical functional group transformations of oximes and exemplary reagents [1,2].



Scheme 2. Literature procedure for the preparation of 3-amino-, 3-nitro- and 3,3-dinitrooxetane.

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oxetan-3-one in the meantime. Despite this, the synthesis of 3-oximinooxetane is only poorly described in the literature, and its physicochemical and energetic properties are scarcely known or not known at all. A synthetic procedure for 3-oximinooxetane is disclosed in a patent by DuPont describing it as a useful polymer intermediate [4]. Unfortunately, the reported yield of 82% is obtained after an overall reaction time of three days. A more recent and perhaps faster synthesis is indicated by Chen et al. in a general procedure for the preparation of cyclobutanone oxime esters [5]. However, 3-oximinooxetane is only used here as an intermediate and the required reaction time, as well as the yield and further characterization of the compound, are not reported. Thus, a straightforward synthesis of 3-oximinooxetane in high yield is still highly desirable.

Herein, we report an improved synthesis of 3-oximinooxetane with high yield and purity starting from the corresponding carbonyl compound oxetane-3-one. Its crystal and molecular structure was elucidated by single-crystal X-ray diffraction for the first time. The compound was also studied in detail by thermal analysis and spectroscopic methods. First indications about its energetic performance were obtained applying the EXPLO5 V6.04 thermochemical code [6] and its sensitivity to external stimuli such as impact and friction was determined.

2 Experimental Section

2.1 Methods and Materials

All reagents and solvents were used as received (Sigma-Aldrich, ABCR, TCI). FT-IR spectra were measured with a Perkin Elmer Spectrum One FT-IR instrument using neat compounds. Raman spectra were recorded with a Bruker MultiRam FT Raman spectrometer using a neodymium-doped yttrium aluminum garnet (Nd: YAG) laser ($\lambda=1064$ nm) and 1074 mW output. NMR spectra were measured with a Bruker Avance 400 instrument operating at 400.1 MHz (^1H), 100.6 MHz (^{13}C), and 40.5 MHz (^{15}N) using TMS (^1H and ^{13}C) or nitromethane (^{15}N) as reference. X-ray data were collected using an Oxford Xcalibur3 diffractometer equipped with a CCD area detector and operating with Mo $K\alpha$ radiation ($\lambda=0.7107$ Å). Thermal behavior was assessed using a Mettler Toledo DSC822e instrument at a heating rate of 5°Cmin^{-1} using 40 μL aluminum crucibles with a lid hole and nitrogen purge gas at a flow rate of 30 mLmin^{-1} . Elemental analysis was performed with an Elementar Vario EL device by sample pyrolysis and subsequent analysis of formed gases. The density of 3-oximinooxetane was calculated from the obtained X-ray density using a thermal correction factor ($\rho_{298\text{K}}=\rho_{143\text{K}}/1.028$). The sensitivity data was assessed using a BAM (Bundesanstalt für Materialforschung) drop hammer according to STANAG 4489 modified instruction [7] and a BAM friction tester according to STANAG 4487 modified instruction [8].

2.2 Synthesis of 3-Oximinooxetane

Oxetan-3-one (2.00 g, 27.8 mmol) was dissolved in methanol (25.0 mL) and the solution was added to a mixture of hydroxylammonium chloride (2.89 g, 41.6 mmol, 1.5 eq.) and sodium hydroxide (1.67 g, 41.6 mmol, 1.5 eq.) in a 50 mL round bottom flask. An instantaneous exothermic reaction was observed causing a mild boiling. The flask was quickly equipped with a reflux condenser and the obtained suspension was vigorously refluxed for two hours using an oil bath. Subsequently, the mixture was evaporated to dryness, and dichloromethane (40 mL) was added. Afterward, all inorganic salts were removed by filtration through a Celite plug which was thoroughly rinsed with additional dichloromethane (2×30 mL). The solvent was removed by rotary evaporation to afford 2.22 g (25.5 mmol, 92%) of 3-oximinooxetane as a colorless solid.

$^1\text{H NMR}$ (400 MHz, CDCl_3 , 25°C): $\delta=8.67$ (s, 1H, NOH), 5.33 (A-part of AA'BB', 2H, CH_2), 5.27 (B-part of AA'BB', 2H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3 , 25°C): $\delta=153.61$, 79.07, 79.06. $^{15}\text{N NMR}$ (41 MHz, CDCl_3 , 25°C): $\delta=-66.9$. FT-IR (ATR, cm^{-1}): $\tilde{\nu}=3298$ (m), 3184 (m), 2983 (w), 2940 (m), 2884 (m), 1462 (m), 1443 (m), 1433 (m), 1304 (w), 1184 (m), 1114 (w), 1049 (w), 964 (s), 939 (vs), 920 (s), 863 (s), 737 (s), 666 (vs), 535 (s), 420 (m). Raman (1075 nm, 1000 mW, cm^{-1}): $\tilde{\nu}=3310$ (8), 2982 (37), 2946 (67), 2915 (12), 2851 (10), 1746 (12), 1731 (10), 1453 (45), 1432 (18), 1308 (12), 1279 (16), 1183 (10), 1139 (24), 1106 (8), 965 (100), 938 (47), 927 (63), 871 (10), 738 (18), 543 (80), 421 (37). EA calcd. for $\text{C}_3\text{H}_5\text{NO}_2$ (87.08 g mol^{-1}): C 41.38, H 5.79, N 16.09. Found: C 41.10, H 5.81, N 15.81. HRMS (EI) m/z : $[\text{M}]^+$ calcd. for $\text{C}_3\text{H}_5\text{NO}_2$ 87.0320. Found 88.0394 $[\text{M}+\text{H}]^+$, 70.0288 $[\text{C}_3\text{H}_4\text{NO}]^+$, 59.0366 $[\text{C}_2\text{H}_5\text{NO}]^+$, 57.0210 $[\text{C}_2\text{H}_3\text{NO}]^+$, 56.0132 $[\text{C}_2\text{H}_2\text{NO}]^+$, 43.0178 $[\text{C}_2\text{H}_3\text{O}]^+$, 41.0258 $[\text{C}_3\text{H}_5\text{NO}_2]^+$. DSC (5°Cmin^{-1}): 88.9°C (mp) 178.6°C (dec). IS: >40 J. FS: >360 N. ESD: 1.0 J.

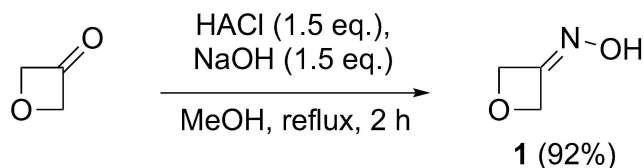
3 Results and Discussion

3.1 Synthesis

First, a short comparative screening was performed (0.5 g scale) to assess optimum conditions for the preparation of 3-oximinooxetane. In all cases, hydroxylammonium chloride (1.5 eq.) was employed and sodium hydroxide (1.5 eq.) was used as base to form hydroxylamine *in situ*. Water, acetonitrile, and methanol were chosen as suitable, polar solvents. In addition to ambient conditions, reflux conditions and sonication were investigated. According to literature, silica gel acts as a catalyst in the solvent-free synthesis of oximes [9]. Although a solvent-free synthesis was not attempted, silica was added to reference batches to study a potential influence on the reaction. However, no apparent effect could be found in this case. The results of the respective trials are summarized in Table 1.

Table 1. Preparation of 3-oximinooxetane using different conditions.

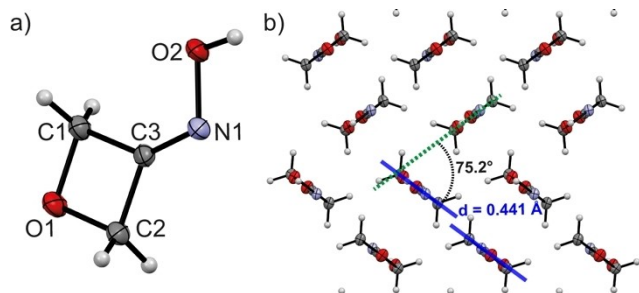
Condition	rt	Ultrasound		Reflux		MeOH	
Solvent	Water	MeCN		MeCN		MeOH	
Silica gel	no	no		no	yes	no	yes
Time [h]	48	2	4	3	3	1.5	1.5
Yield [%]	38	66	44	75	82	93	78

**Scheme 3.** Improved preparation of 3-oximinooxetane.

The best result was obtained using methanol as solvent and reflux conditions without any catalyst. Upscaling by a factor of four required a slightly prolonged reaction time to afford a similar yield (Scheme 3).

3.2 Crystallography

Single crystals of 3-oximinooxetane were obtained by slow evaporation of a saturated chloroform solution. The compound crystallizes in the monoclinic space group $P2_1/n$ with four formula units per unit cell and a density of $1.486 \text{ g}\cdot\text{cm}^{-3}$ (143 K) corresponding to a room temperature density of $1.450 \text{ g}\cdot\text{cm}^{-3}$. As expected, all bond angles of the oxetane ring show significant deviations from the ideal tetrahedral angle of sp^3 -hybridized carbon atoms. Within the oxetane ring, angles range from $88.8(8)^\circ$ (O1–C2–C3) and $89.1(8)^\circ$ (O1–C1–C3) up to $89.6(8)^\circ$ (C2–C3–C1), while the largest angle is found at the oxygen atom (C1–O1–C2, $92.4(7)^\circ$). The shortest bond within the ring is found between O1 and C1 ($1.462(1) \text{ \AA}$) and the longest between C2 and C3 ($1.501(1) \text{ \AA}$) (Figure 1 a).

**Figure 1.** a) Molecular structure of 3-oximinooxetane in the crystal. b) Arrangement of the 3-oximinooxetane molecules in the crystal, view along the c axis.

The oxetane ring is essentially planar with a puckering angle of only 1.38° , which is much smaller than in the unsubstituted parent compound oxetane ($8.7(2)^\circ$, 140 K) [10]. The oximino group is slightly bent out of the oxetane plane (C1–C3–C3) by 0.9° . Both the C–N bond length ($1.263(2) \text{ \AA}$) and N–O bond length ($1.416(1) \text{ \AA}$) are in the expected range [11]. The view along the c axis (Figure 1 b) reveals an arrangement of the molecular entities in two types of parallel layers which intersect at an angle of 75.2° . Between parallel layers, an interlayer distance of 0.441 \AA is found.

3.3 Physicochemical and Energetic Properties

The thermal behavior of 3-oximinooxetane was analyzed by differential scanning calorimetry (DSC) at a heating rate of 5°C min^{-1} revealing a melting point of 88.9°C and a decomposition temperature of 178.6°C . When heated on a copper plate using a Bunsen burner (hot plate test), the material deflagrates quite violently with a bright orange flame and a hissing noise (see Supporting Information). The heat of formation was calculated by *ab-initio* methods using Gaussian16 on the CBS-4M level of theory making use of the obtained crystal structure [12]. A heat of formation of $-84.5 \text{ kJ mol}^{-1}$ was calculated. Subsequently, the EXPLO5 V6.04 thermochemical code was used to assess the energetic performance of 3-oximinooxetane [6]. Although it has not previously been described in the literature as an energetic or sensitive compound, the oxime exhibits a detonation velocity of 6488 ms^{-1} and a detonation pressure of 14.7 GPa and shows sensitivity towards mechanical stimuli and electrostatic discharge (Table 2). Based on calculated values, it outperforms the well-known oxetane monomer NIMMO and even competes with the highly performant BAMO. Thus, it represents a considerably energetic, but “insensitive” compound [13].

4 Conclusion

Due to the significantly improved synthetic procedure in comparison to literature methods, 3-oximinooxetane can now be obtained in very high yield and purity after a short reaction time starting from commercially available materials. It has been extensively characterized for the first time, its crystal and molecular structure has been elucidated and its energetic properties investigated and demonstrated. As a result, 3-oximinooxetane is likely to be employed as a precursor for the synthesis of the energetic derivatives 3-nitrooxetane and 3,3-dinitrooxetane in the future. These can be used to prepare useful energetic binders by cationic ring-opening polymerization. Furthermore, the described oxime is capable to provide 3-aminooxetane by reduction, which can also serve as a versatile precursor to various energetic oxetane derivatives.

Table 2. Important physicochemical and energetic properties of 3-oximinoxetane in comparison to NIMMO and BAMO.

	1	NIMMO	BAMO
Formula	C ₃ H ₅ NO ₂	C ₅ H ₉ NO ₄	C ₅ H ₈ N ₆ O
FW [g·mol ⁻¹]	87.08	147.13	168.16
IS ^a [J]	40	40	40
FS ^b [N]	360	360	360
Ω ^c [%]	−64.3	−59.8	−76.12
T _m ^d /T _{dec} ^e [°C]	88.9, 178.6	−13.8, 170.3	−207.3
ρ ^f [g·cm ⁻³]	1.45	1.19	1.23
ΔH _f ^g [kJ·mol ⁻¹]	84.5	−268.9	510.5
EXPLO5V6.04			
−Δ _E U ^{oh} [kJ·kg ⁻¹]	3833	3949	4479
T _{C-J} ⁱ [K]	2453	2507	2786
p _{C-J} ^j [GPa]	14.7	10.6	12.4
D _{C-J} ^k [m·s ⁻¹]	6488	5906	6548
V ₀ ^l [dm ³ ·kg ⁻¹]	772	827	797

^a Impact sensitivity (BAM drophammer, method 1 of 6). ^b Friction sensitivity (BAM friction apparatus, method 1 of 6). ^c Oxygen balance based on CO formation. ^d Melting point (DSC, β = 5 °C·min⁻¹). ^e Decomposition temperature (DSC, β = 5 °C·min⁻¹). ^f Density at 298 K – weighing of 100 μL (NIMMO, BAMO). ^g Standard molar enthalpy of formation. ^h Detonation energy. ⁱ Detonation temperature. ^j Detonation pressure. ^k Detonation velocity. ^l Volume of detonation gases at standard temperature and pressure.

Abbreviations

BAMO	3,3-bis(azidomethyl)oxetane
1,2-DCE	1,2-dichloroethane
DCM	dichloromethane
HACl	hydroxylammonium chloride
mCPBA	meta-chloroperoxybenzoic acid
NIMMO	3-nitatomethyl-3-methyloxetane
p-TsCl	para-toluenesulfonyl chloride
TNM	tetranitromethane.

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