Application of a Thermal β-Elimination Reaction to *N*-Alkoxy-3,3-dinitroisoxazolidines: Synthesis of 3-Nitroisoxazolines

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Abstract: A facile general method has been developed for the synthesis of 5-substituted 3-nitroisoxazolines by the application of a thermal β-elimination reaction to *N*-alkoxy-3,3-dinitroisoxazolidines in chlorobenzene.

Key words: β-elimination, [3+2] cycloaddition, isoxazolines, isoxazolidines, heterocycles

Nitroisoxazolines are useful synthetic intermediates[1] and precursors of a wide range of valuable materials such as biocide protecting technical materials,[2] different pharmacological agents,[3] or crop-protecting compositions against phytotoxic secondary effects of herbicides.[4] Their high reactivity provides the following possible functionalizations: 1) the nitro group can be displaced by a variety of nucleophiles such as thiolate, cyanide, hydride, azide ions, ammonia, and alkoxides;[5,6] 2) 3-nitro-Δ^2-isoxazolines can be transformed to 3-nitroisoxazoles by treatment with oxidizing agents;[7] 3) the lability of the N–O bond affords various products via ring cleavage.[1a]

The classical method for the synthesis of isoxazolines is the [3+2] cycloaddition of nitrile oxides to alkenes.[1,8] However, this method is not applicable to 3-nitroisoxazolines since nitronitrile oxide is not yet available.

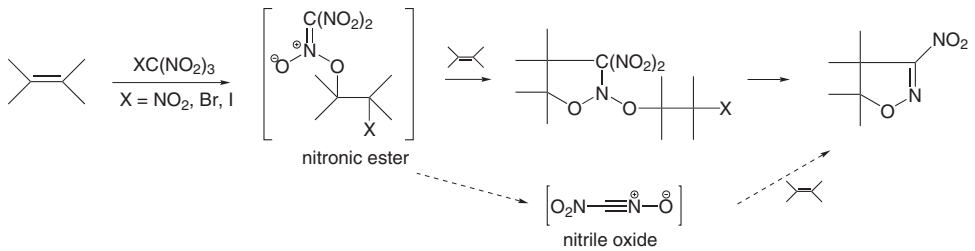
The known approaches to 3-nitroisoxazolines are complex multistep procedures.[6,9–11] At the same time, isoxazolidine derivatives are known to undergo β-elimination forming isoxazolines.[1,8]

Recently, we described the one-pot synthesis of 3,3-dinitroisoxazolidines with various functional groups.[12] This synthetic route is based on the three-component reaction of tetranitro- and halotrinitromethanes with two alkenes, which gives 3,3-dinitroisoxazolidines with electron-withdrawing, aromatic, and heterocyclic substituents in good to excellent yields.[12–15] Interestingly, the three-component reactions of iodotrinitromethane with two alkenes proceed to give iododinitroisoxazolidines, which spontaneously undergo thermal β-elimination at room temperature to form 3-nitroisoxazolines.[15] Therefore the nitroisoxazolines of a target structure can be obtained through this synthetic sequence including the formation of dinitroisoxazolidines followed by β-elimination of nitro and alkoxy groups. In this reaction, in situ generated nitronates can be formally regarded as a synthetic equivalent of nitronitrile oxide (Scheme 1).

From these standpoints, we have developed an effective general method to obtain 3-nitroisoxazolines by β-elimination of available 3,3-dinitroisoxazolidines.

First, we examined the thermal β-elimination from the model isoxazolidine **1a**[12] with heating in various solvents under reflux (Table 1).

Boiling benzene (Table 1, entry 1) resulted in no β-elimination products. In the case of toluene or *o*-xylene their methyl groups underwent radical nitration by the NO_2 radical which formed during the reaction. The formation of side-products substantially complicated the isolation of the target isoxazoline **2**. The same reaction in DMSO at 100 °C or in boiling nitromethane proceeded slower than in pyridine or chlorobenzene. The highest yields were observed when the reaction was performed using chlorobenzene or pyridine as solvents (Table 1, entry 6, 7). Acidic catalysts like hydrochloric acid in benzene or *p*-toluenesulfonic acid as well as basic catalysts like organic bases did not influence the rate of the reaction and the yield of



Scheme 1

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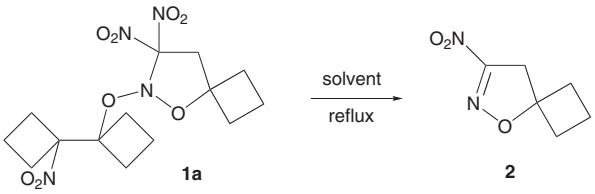
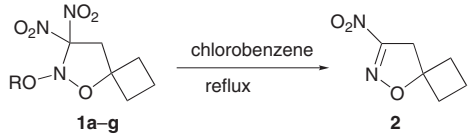
Table 1 Thermal β-Elimination of Isoxazolidine **1a**

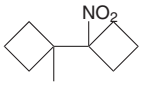
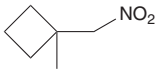
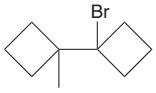
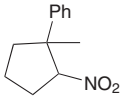
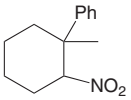


Entry	Solvent	Reaction time (h)	Yield[a] of **2** (%)
1	Benzene	2	–
2	DMSO[b]	9	45
3	Nitromethane	10	68
4	Toluene	4.5	70
5	*o*-Xylene	0.3	traces
6	Pyridine	2	75
7	Chlorobenzene	1.5	77
8	H_2O–$NaHCO_3$	2	–

[a] Yield of isolated product after column chromatography.
[b] Reaction carried out at 100 °C.

Table 2 Thermal β-Elimination of the Model Isoxazolidine **1a–f**



	R	Reaction time (h)	Yield[a] of **2** (%)
1a		1.5	77
1b		1	85
1c		0.5	73
1d		2	75
1e		2	78
1f		1	83
1g	Me	4	–

[a] Yield of isolated product after column chromatography.

isoxazoline **2**. For example, starting isoxazolidine **1a** was isolated unchanged after refluxing in chloroform for two hours in the presence of triethylamine.

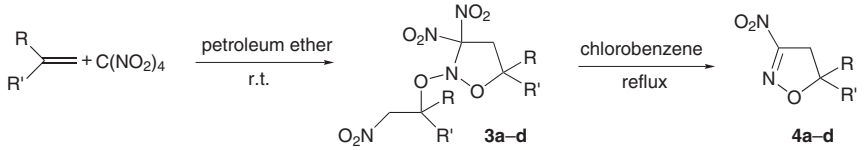
β-Elimination of 3,3-dinitroisoxazolidines **1a–f** bearing various alkoxy substituents in boiling chlorobenzene led to isoxazoline **2** in good yields (Table 2). Therefore, the influence of substituents R on the yields of nitroisoxazoline **2** was minimal.

While nitroisoxazoline **2** was generally formed in good yields (Table 2), in the case of starting isoxazolidine **1g**, a complex mixture of decomposition products was obtained.

In addition, we found that 3-nitroisoxazolines may be obtained by a one-pot synthesis starting from olefins. Thus, for example, nitroisoxazoline **2** was synthesized in 64% yield from bicyclobutylidene, methylenecyclobutane, and tetranitromethane. The one-pot reaction includes the formation of starting isoxazolidine followed by β-elimination without its isolation and may be utilized as a convenient synthesis of 3-nitroisoxazolines.

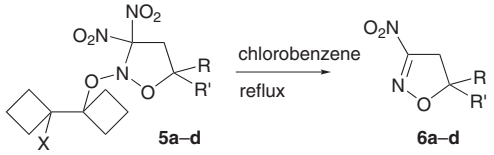
We have screened a number of 3,3-dinitroisoxazolidines to expand the scope of the β-elimination method. Thermolysis of isoxazolidines **3a–d**, obtained by the reaction of commercially available olefins such as styrene, butyl vinyl ether, vinyl acetate, or methylenecyclohexane with tetranitromethane, readily led to nitroisoxazolines **4a–d** in good yields (Table 3). Conversion of isoxazolidine **3a** to isoxazoline **4a** was accompanied by the formation of a small amount of β-nitrostyrene.

Table 3 Thermal β-Elimination 3,3-Dinitroisoxazolidines



Isoxazolidine	R	R′	Reaction time (h)	Isoxazoline	Yield (%)
3a	Ph	H	14	**4a**	71
3b	BuO	H	23	**4b**	73
3c	-$(CH_2)_5$-		10	**4c**	74
3d	$OCOCH_3$	H	15	**4d**	72

Table 4 Thermolysis of Isoxazolidines **5a–d**



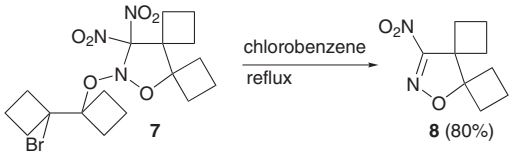
5a–d **6a–d**

Isoxazolidine	X	R	R′	Reaction time (h)	Isoxazoline	Yield (%)
5a	NO_2	$CH(OEt)_2$	H	3.5	**6a**	82
5b	NO_2	CN	H	3	**6b**	72
5c	Br	$COCH_3$	H	4	**6c**	63
5d	NO_2	CO_2CH_3	CH_3	4	**6d**[a]	69

[a] The reaction was performed in refluxing pyridine.

Thermolysis of isoxazolidines **5a–d** synthesized by the three-component reactions of tetranitro- or bromotrinitromethane with alkenes[12–15] allowed us to obtain isoxazolines **6a–d** bearing electron-withdrawing functional groups at C-5 (Table 4).

Thermal β-elimination of isoxazolidine **7**[15] successfully resulted in the synthesis of the unusual 3-nitro-4,4,5,5-tetrasubstituted isoxazoline **8** (Scheme 2).



7 **8** (80%)

Scheme 2

It was observed that the β-elimination of 3,3-dinitroisoxazolidines proceeded via formation of their side-chain rearrangement product. We isolated this product in the reactions with compounds **1a**, **5a–d**, and **7**, containing a bicyclobutyl substituent on the alkoxy fragment. According to these results and literature data, we presume the mechanism of this reaction involves the formation of a stable NO_2 radical, homolytic cleavage of the exocyclic N–O bond, followed by the cleavage of a small ring, and recombination of two radicals to yield nitroketones **9** (Scheme 3).

NMR spectra were recorded on a Bruker DPX-400 spectrometer at r.t.; the chemical shifts were measured in ppm relative to the residual solvent peak (^{1}H: $CDCl_3$, δ = 7.24 ppm, DMSO-d_6, δ = 2.50 ppm; ^{13}C: $CDCl_3$, δ = 77.1 ppm, DMSO-d_6, δ = 39.5 ppm). Mps were recorded on a electrothermal 9100 capillary melting point apparatus and are uncorrected. Column chromatography was performed on silica gel 60 (230–400 mesh, Merck). Petroleum ether (PE) used had the boiling range 40–60 °C. Tetranitromethane and olefins were commercially available. Isoxazolidines **1a**,[12] **1b**,[16] **1c**,[15] **1d**,**e**,[14] **1f**,[15] **3a**,[17] **3b**,[18] **3d**,[18] **5a**,**b**,**d**,[12] **5c**,[15] were prepared according to published procedures.

Caution: Although we have not experienced any problems in the handling of these compounds, full safety precautions should be taken due to their potential explosive nature.

6-Methoxy-7,7-dinitro-5-oxa-6-azaspiro[3.4]octane (1g)

A solution of CH_2N_2 obtained from *N*-methyl-*N*-nitrosourea (2 g, 19 mmol) in benzene (10 mL) was added to a cooled (5 °C) solution of trinitromethane (0.76 g, 5 mmol) and methylenecyclobutane (0.34 g, 5 mmol) in benzene (5 mL). The reaction mixture was warmed to r.t. and kept at that temperature for 1 d. The solvent was evaporated and the residue was dissolved in $CHCl_3$. The product was isolated after column chromatography ($CHCl_3$–PE, 1:2).

Yield: 1.00 g (86%); oil; R_f 0.64 ($CHCl_3$).

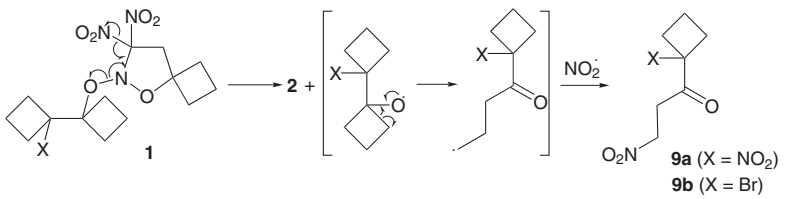
^{1}H NMR ($CDCl_3$): δ = 1.65–1.76 (m, 1 H, *c*-Bu), 1.82–1.92 (m, 1 H, *c*-Bu), 2.16–2.48 (m, 3 H, *c*-Bu), 2.59–2.67 (m, 1 H, *c*-Bu), 3.38 [d, ^2J = 15.2 Hz, 1 H, $CH_2C(NO_2)_2$], 3.66 (s, 3 H, CH_3O), 3.74 [d, ^2J = 15.2 Hz, 1 H, $CH_2C(NO_2)_2$].

^{13}C NMR ($CDCl_3$): δ = 13.2 (CH_2), 34.2 (CH_2), 38.8 (CH_2), 43.2 [$CH_2C(NO_2)_2$], 60.6 (CH_3O), 89.7 (C), 128.0 [$C(NO_2)_2$].

Anal. Calcd for $C_7H_{11}N_3O_6$: C, 36.05; H, 4.72. Found: C, 36.09; H, 4.89.

3,3-Dinitro-2-{[1-(nitromethyl)cyclohexyl]oxy}-1-oxa-2-azaspiro[4.5]decane (3c)

Methylenecyclohexane (0.48 g, 5 mmol) was added to a cooled (0 °C) solution of tetranitromethane (0.49 g, 2.5 mmol) in hexane (5 mL). The reaction mixture was warmed to r.t. and kept at that tem-



1 **9a** (X = NO_2) **9b** (X = Br)

Scheme 3

perature for 7 d. The solvent was evaporated and the residue was dissolved in $CHCl_3$. The product was isolated after column chromatography ($CHCl_3$–PE, 1:2).

Yield: 0.56 g (58%); oil; R_f 0.73 ($CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 1.31–2.05 (m, 20 H, *c*-Hex), 3.11 [d, ^2J = 15.0 Hz, 1 H, $CH_2C(NO_2)_2$], 3.63 [d, ^2J = 15.0 Hz, 1 H, $CH_2C(NO_2)_2$], 4.50 (d, ^2J = 12.0 Hz, 1 H, CH_2NO_2), 4.71 (d, ^2J = 12.0 Hz, 1 H, CH_2NO_2).

^{13}C NMR ($CDCl_3$): δ = 22.4 (2 × CH_2), 23.7 (2 × CH_2), 24.4 (CH_2), 24.5 (CH_2), 31.5 (CH_2), 32.0 (CH_2), 36.3 (CH_2), 39.4 (CH_2), 42.8 [*C*$H_2C(NO_2)_2$], 79.7 (CH_2NO_2), 84.5 (C), 91.1 (C), 128.3 [$C(NO_2)_2$].

Anal. Calcd for $C_{15}H_{24}N_4O_8$: C, 46.39; H, 6.23. Found: C, 46.74; H, 5.97.

Δ²-Isoxazolines 2,[11] 4a–d, 6a–d, and 8 from Isoxazolidines; General Procedure

A solution of isoxazolidine (1 mmol) in chlorobenzene (3 mL) was refluxed until the starting material had disappeared (TLC and ^{1}H NMR). The products were isolated after column chromatography or recrystallization.

3-Nitro-5-phenyl-4,5-dihydroisoxazole (4a)[9,10]

Solid; mp 65 °C (Lit.[9,10] mp 64–65 °C); R_f 0.46 (PE–EtOAc, 4:1).

^{1}H NMR ($CDCl_3$): δ = 3.52 (dd, ^2J = 17.9, ^3J = 6.8 Hz, 1 H, CH_2), 3.90 (dd, ^2J = 17.9, ^3J = 11.7 Hz, 1 H, CH_2), 6.10 (dd, ^3J = 9.8, 11.7 Hz, 1 H, CHO), 7.35–7.51 (m, 5 H, Ph).

^{13}C NMR ($CDCl_3$): δ = 38.0 (CH_2), 89.5 (CH), 126.1 (2 × Ph-CH), 129.3 (2 × Ph-CH), 129.7 (Ph-CH), 137.5 (Ph-C), 163.0 [$C(NO_2)$].

5-Butoxy-3-nitro-4,5-dihydroisoxazole (4b)

Oil; R_f 0.49 (PE–EtOAc, 4:1).

^{1}H NMR ($CDCl_3$): δ = 0.85–1.01 (m, 3 H, CH_3), 1.26–1.48 (m, 2 H, CH_2), 1.51–1.72 (m, 2 H, CH_2), 3.34 [dd, ^2J = 18.4, ^3J = 2.5 Hz, 1 H, $CH_2C(NO_2)$], 3.57 [dd, ^2J = 18.4, ^3J = 7.1 Hz, 1 H, $CH_2C(NO_2)$], 3.63 (dt, ^2J = 9.6, ^3J = 6.6 Hz, 1 H, CH_2), 3.93 (dt, ^2J = 9.6, ^3J = 6.4 Hz, 1 H, CH_2), 5.92 (dd, ^3J = 2.5, 7.1 Hz, 1 H, CHO).

^{13}C NMR ($CDCl_3$): δ = 13.7 (CH_3), 19.1 (CH_2), 31.4 (CH_2), 36.9 [*C*$H_2C(NO_2)$], 69.7 (CH_2O), 109.0 (CHO), 161.5 [$C(NO_2)$].

Anal. Calcd for $C_7H_{12}N_2O_4$: C, 44.68; H, 6.43. Found: C, 44.49; H, 6.81.

3-Nitro-1-oxa-2-azaspiro[4.5]dec-2-ene (4c)

Solid; mp 50–51 °C; R_f 0.50 (PE–EtOAc, 4:1).

^{1}H NMR ($CDCl_3$): δ = 1.39–1.54 (m, 4 H, CH_2), 1.68–1.96 (m, 6 H, CH_2), 3.18 (s, 2 H, CH_2).

^{13}C NMR ($CDCl_3$): δ = 22.7 (2 × CH_2), 24.4 (CH_2), 36.4 (2 × CH_2), 40.3 [*C*$H_2C(NO_2)$], 96.6 (C), 162.5 [$C(NO_2)$].

Anal. Calcd for $C_8H_{12}N_2O_3$: C, 52.17; H, 6.57; N, 15.21. Found: C, 52.69; H, 6.57; N, 15.35.

3-Nitro-4,5-dihydroisoxazol-5-yl Acetate (4d)[9]

Oil; R_f 0.31 ($CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 2.16 (s, 3 H, CH_3), 3.48 [dd, ^2J = 18.9, ^3J = 2.0 Hz, 1 H, $CH_2C(NO_2)$], 3.59 [dd, ^2J = 18.9, ^3J = 7.6 Hz, 1 H, $CH_2C(NO_2)$], 6.98 (dd, ^3J = 2.0, 7.6 Hz, 1 H, CHO).

^{13}C NMR ($CDCl_3$): δ = 19.5 (CH_3), 35.9 [*C*$H_2C(NO_2)$], 99.9 (CHO), 164.2 [$C(NO_2)$], 169.0 (*O*C*O*CH_3).

5-(Diethoxymethyl)-3-nitro-4,5-dihydroisoxazole (6a)

Oil; R_f 0.55 (PE–EtOAc, 4:1).

^{1}H NMR ($CDCl_3$): δ = 1.21 (t, ^3J = 7.1 Hz, 3 H, CH_3), 1.24 (t, ^3J = 7.1 Hz, 3 H, CH_3), 3.42 [dd, ^2J = 17.9, ^3J = 11.7 Hz, 1 H, $CH_2C(NO_2)$], 3.54–3.69 (m, 2 H, O*C*H_2CH_3), 3.59 [dd, ^2J = 17.9, ^3J = 7.3 Hz, 1 H, $CH_2C(NO_2)$], 3.73–3.83 (m, 2 H, O*C*H_2CH_3), 4.61 [d, ^3J = 3.4 Hz, 1 H, C*H*$(OEt)_2$], 5.06 (ddd, ^3J = 3.4, 7.3, 11.7 Hz, 1 H, CHO).

^{13}C NMR ($CDCl_3$): δ = 15.2 (CH_3), 15.9 (CH_3), 30.8 [*C*$H_2C(NO_2)$], 63.9 (CH_2O), 65.6 (CH_2O), 87.5 (CH), 101.1 (CH), 163.8 [$C(NO_2)$].

Anal. Calcd for $C_8H_{14}N_2O_5$: C, 44.03; H, 6.47; N, 12.84. Found: C, 43.92; H, 6.48; N, 12.82.

3-Nitro-4,5-dihydroisoxazole-5-carbonitrile (6b)[9]

Solid; mp 132 °C (Lit.[9] mp 132 °C).

^{1}H NMR (DMSO-d_6): δ = 3.92 [dd, ^2J = 17.4, ^3J = 7.1 Hz, 1 H, $CH_2C(NO_2)$], 4.02 [dd, ^2J = 17.4, ^3J = 11.9 Hz, 1 H, $CH_2C(NO_2)$], 6.10 (dd, ^3J = 7.1, 11.9 Hz, 1 H, CHO).

^{13}C NMR (DMSO-d_6): δ = 36.6 (CH_2), 73.0 (CH), 117.0 (CN), 168.2 [$C(NO_2)$].

1-(3-Nitro-4,5-dihydroisoxazol-5-yl)ethanone (6c)

Solid; mp 60–61 °C (EtOH); R_f 0.31 ($CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 2.26 (s, 3 H, CH_3), 3.50 [dd, ^2J = 18.2, ^3J = 12.6 Hz, 1 H, $CH_2C(NO_2)$], 3.71 [dd, ^2J = 18.2, ^3J = 7.4 Hz, 1 H, $CH_2C(NO_2)$], 5.32 (dd, ^3J = 7.4, 12.7 Hz, 1 H, CHO).

^{13}C NMR ($CDCl_3$): δ = 26.5 (CH_3), 31.7 (CH_2), 89.8 (CH), 163.2 [$C(NO_2)$], 202.0 (CO).

Anal. Calcd for $C_5H_6N_2O_4$: C, 37.98; H, 3.82; N, 17.72. Found: C, C 37.97; H, 3.85; N, 17.55.

Methyl 5-Methyl-3-nitro-4,5-dihydroisoxazole-5-carboxylate (6d)

Oil; R_f 0.19 (PE–EtOAc, 4:1).

^{1}H NMR ($CDCl_3$): δ = 1.80 (s, 3 H, CH_3), 3.38 [d, ^2J = 18.1 Hz, 1 H, $CH_2C(NO_2)$], 3.87 (s, 3 H, CH_3), 4.03 [d, ^2J = 18.1 Hz, 1 H, $CH_2C(NO_2)$].

^{13}C NMR ($CDCl_3$): δ = 23.6 (CH_3), 39.7 [*C*$H_2C(NO_2)$], 53.9 (CH_3O), 92.9 (C), 162.2 [$C(NO_2)$], 169.6 (*C*OOCH_3).

Anal. Calcd for $C_6H_8N_2O_5$: C, 38.30; H, 4.29. Found: C, 38.58; H, 4.45.

11-Nitro-9-oxa-10-azadispiro[3.0.3.3]undec-10-ene (8)

Oil; R_f 0.78 (PE–EtOAc, 4:1).

^{1}H NMR ($CDCl_3$): δ = 1.76–1.87 (m, 1 H, CH_2), 1.92–2.05 (m, 1 H, CH_2), 2.07–2.18 (m, 1 H, CH_2), 2.23–2.33 (m, 1 H, CH_2), 2.35–2.45 (m, 2 H, CH_2), 2.46–2.57 (m, 2 H, CH_2), 2.60–2.73 (m, 4 H, CH_2).

^{13}C NMR ($CDCl_3$): δ = 13.5 (CH_2), 15.7 (CH_2), 26.1 (2 × CH_2), 30.0 (2 × CH_2), 51.6 (CBr), 100.1 (C), 168.0 [$C(NO_2)$].

Anal. Calcd for $C_9H_{12}N_2O_3$: C, 55.09; H, 6.16. Found: C, 54.71; H, 6.51.

4-Nitro(1-nitrocyclobutyl)butan-1-one (9a)

Yield: 0.09 g (42%); oil; R_f 0.40 (PE–EtOAc, 4:1).

^{1}H NMR ($CDCl_3$): δ = 1.80–1.92 (m, 1 H, CH_2), 1.95–2.05 (m, 1 H, CH_2), 2.29 (q, ^3J = 6.8 Hz, 2 H, CH_2), 2.65 (t, ^3J = 6.8 Hz, 2 H, CH_2CO) 2.69–2.84 (m, 4 H, CH_2), 4.41 (t, ^3J = 6.8 Hz, 2 H, CH_2NO_2).

^{13}C NMR ($CDCl_3$): δ = 13.4 (CH_2), 21.0 (CH_2), 30.5 (2 × CH_2), 32.1 (CH_2), 74.0 (CH_2NO_2), 92.9 (C), 198.1 (CO).

Anal. Calcd for $C_8H_{12}N_2O_5$: C, 44.44; H, 5.59. Found: C, 44.46; H, 5.76.

1-(1-Bromocyclobutyl)-4-nitrobutan-1-one (9b)
Yield: 0.08 g (32%); oil; R_f 0.52 (PE–EtOAc, 4:1).

^{1}H NMR ($CDCl_3$): δ = 1.71–1.86 (m, 1 H), 2.17–2.30 (m, 1 H), 2.34 (quint, ^3J = 6.8 Hz, 2 H, CH_2), 2.52–2.61 (m, 2 H), 2.78–2.88 (m, 2 H), 2.91 (t, ^3J = 6.8 Hz, 2 H, CH_2CO), 4.47 (t, ^3J = 6.8 Hz, 2 H, CH_2NO_2).

^{13}C NMR ($CDCl_3$): δ = 16.3 (CH_2), 21.9 (CH_2), 32.0 (CH_2), 35.4 (2 × CH_2), 61.6 (CBr), 74.3 (CH_2NO_2), 203.2 (CO).

Anal. Calcd for $C_8H_{12}BrNO_3$: C, 38.42; H, 4.84; N, 5.60. Found: C, 38.97; H, 5.19; N, 4.95.

7-Nitro-5-oxa-6-azaspiro[2.4]oct-6-ene (2);[11] One-Pot Synthesis
Methylenecyclobutane (2.5 mmol) was added to a cooled (0 °C) solution of tetranitromethane (2.5 mmol) and bicyclobutylidene (**1b**) (2.5 mmol) in chlorobenzene (5 mL). The reaction mixture was warmed to r.t. and kept at this temperature for 48 h. The reaction mixture was refluxed for 1.5 h. The solvent was evaporated and the residue was dissolved in $CHCl_3$. The product was isolated after column chromatography ($CHCl_3$–PE, 1:2).

Solid; mp 52–53 °C; R_f 0.47 ($CHCl_3$).

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