

# Synthesis and properties of 4,4,5,5-tetrafluoro-3-trifluoromethyl-1,3-oxazolidin-2-one

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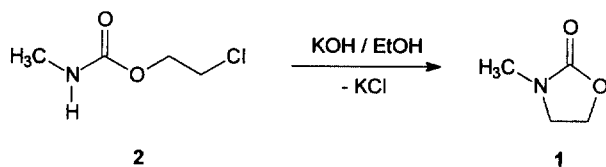
## Abstract

The electrochemical fluorination (ECF) of 3-methyl-1,3-oxazolidin-2-one (**1**) in anhydrous HF leads to the hitherto unknown 4,4,5,5-tetrafluoro-3-trifluoromethyl-1,3-oxazolidin-2-one (**4**) in 14% yield. Spectral data ( $^{13}\text{C}$ -NMR,  $^{19}\text{F}$ -NMR, IR and mass spectra) were recorded and other physical properties (viscosity, melting point, boiling point and density) were determined. In addition the oxidation and reduction stability was measured using cyclic voltammetry (CV). © 1998 Elsevier Science S.A. All rights reserved.

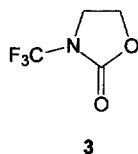
**Keywords:** Electrochemical fluorination (ECF); 3-Methyl-1,3-oxazolidin-2-one; 4,4,5,5-tetrafluoro-3-trifluoromethyl-1,3-oxazolidin-2-one

## 1. Introduction

*N*-methyloxazolidinone (NMO) or better 3-methyl-1,3-oxazolidin-2-one (**1**) was first prepared by Aeschlimann in 1936 by the reaction of methylcarbamidacid-(2-chloro-ethyl-ester) (**2**) with strong bases [1,2].



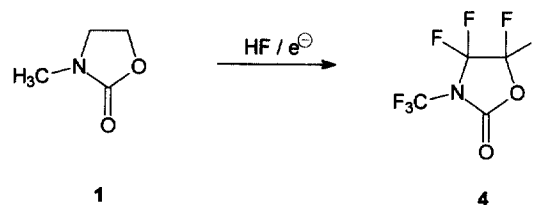
NMO **1** is mainly used as an electrolyte solvent in primary [3,4], and secondary batteries [5–8] as well as in photoelectrochemical cells (Graetzelle) [9]. The only known fluorine-containing derivative is 3-trifluoromethyl-1,3-oxazolidin-2-one (**3**).



**3** is used as a synthetic building block for the preparation of organophosphorus compounds, which have insecticide, miticide or nematocidal effects [10]. The complete perfluorination of **1** should increase the thermal and electrochemical stability and on the other hand decrease the melting and boiling points as well as the viscosity.

## 2. Results and discussion

Electrochemical fluorination (ECF) of **1** in anhydrous hydrogen fluoride leads to 4,4,5,5-tetrafluoro-3-trifluoromethyl-1,3-oxazolidin-2-one (**4**).



The yield follows the amount of current consumed (Fig. 1). The maximum yield of 14% (current yield is 11%) **4** is obtained using 126% of theoretical current. During the ECF of **1** the HF solution turns dark red. The colour disappears at the end of the ECF when approaching 90–110% of theoretical current.

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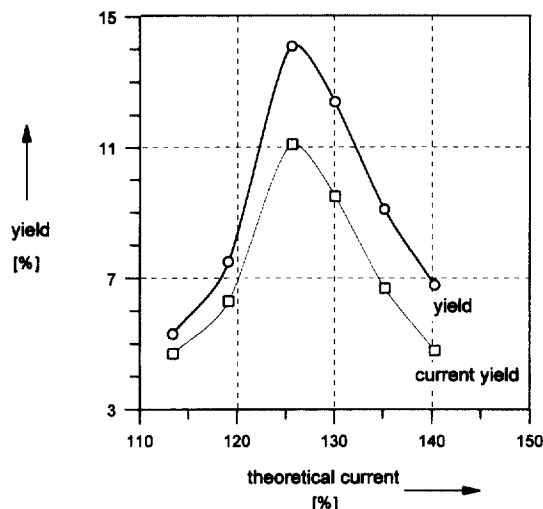


Fig. 1. Yield and current yield (dotted line) in relation to the theoretical current.

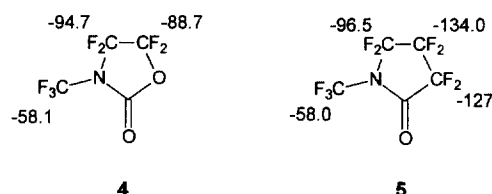
Table 1  
Comparison of the physical properties of **1** and **4**

	<b>1</b>	<b>4</b>
FW	101.11 g mol <sup>-1</sup>	227.03 g mol <sup>-1</sup>
m.p.	15.9°C	-53.3°C
bp	270°C	52°C
density	1.170 g ml <sup>-1</sup>	1.641 g ml <sup>-1</sup>
refractive index $n_D^{20}$	1.4522	1.2904
Viscosity (25°C)	2.45 mPa s	0.79 mPa s

The perfluorinated NMO **4** can be isolated as a clear colourless and very volatile liquid. **4** is characterised by <sup>13</sup>C-NMR, <sup>19</sup>F-NMR, IR and mass-spectroscopy. Additionally the melting-point is determined using DSC (Differential Scanning Calorimetry). Perfluorination of **1** causes completely different physical properties and chemical behaviour for **4**. Density and formula weight increase and viscosity, melting and boiling point decrease. The perfluorinated NMO **4** no

longer shows basicity or nucleophilicity. It appears, in contrast to NMO **1**, as an hydrophobic liquid, which is only soluble in coordinating solvents like THF and acetonitrile (Table 1).

The IR-spectra of **4** show a remarkable high C=O vibration at 1891 cm<sup>-1</sup>. This is 83 cm<sup>-1</sup> higher than unfluorinated **1**. C=O vibrations of other cyclic urethanes are found between 1740 and 1690 cm<sup>-1</sup> [11]. Perfluorinated ring systems like the lactam **5** [12] with 1834 cm<sup>-1</sup> show lower frequencies than **4**. Comparison of <sup>19</sup>F-NMR data of **4** with the cyclic lactone **5** shows no significant deviations for the chemical shift of the chemically identical CF<sub>3</sub>- and N-CF<sub>2</sub>-groups.



To determine the electrochemical stability of **4**, cyclic voltammograms (CV) were recorded.<sup>1</sup> As a reference system lithium bis(trifluoromethylsulfonyl)imide (**6**) in dimethylcarbonate (DMC) was used. The residual currents of the system **6**/DMC (Fig. 2a) and **4**/**6**/DMC (Fig. 2b) show no significant differences.

This means that **4** should be stable to reduction over the investigated potential range. Comparing the oxidation stability of **4** with the reference system one can find a more structured shape of the curve.

There is a slow increase of the anodic current above 3 V and in addition there is a weak cathodic peak at 3.3 V against Li/Li<sup>+</sup>. Therefore the electrolyte was kept for 48 h at 4 V against Li/Li<sup>+</sup> to see if there is any decomposition of the perfluorinated NMO **4**. In this case the current decreases

<sup>1</sup> Recorded at the University of Regensburg by J. Barthel, M. Schmidt.

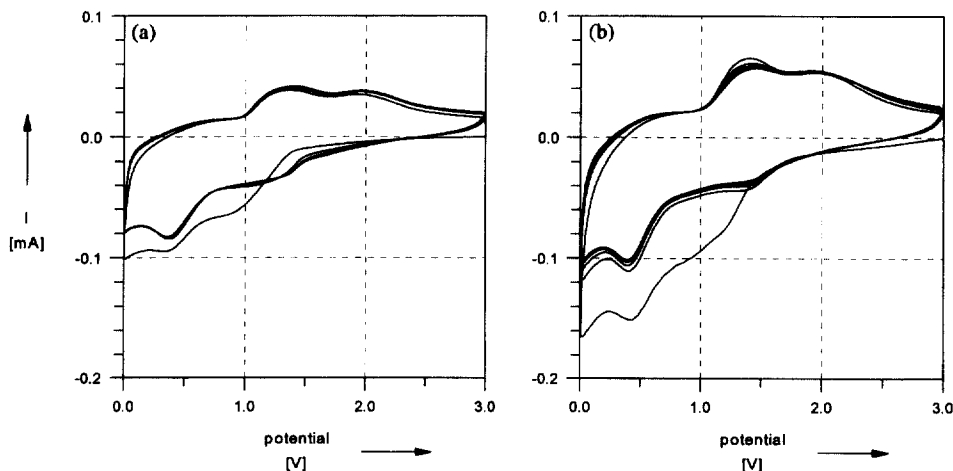


Fig. 2. Residual current of A LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> (**6**)/DMC and B LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> (**6**)/DMC/4,4,5,5-tetrafluoro-3-trifluoromethyl-1,3-oxazolidin-2-one (**4**), as obtained from five sweeps of a CV.

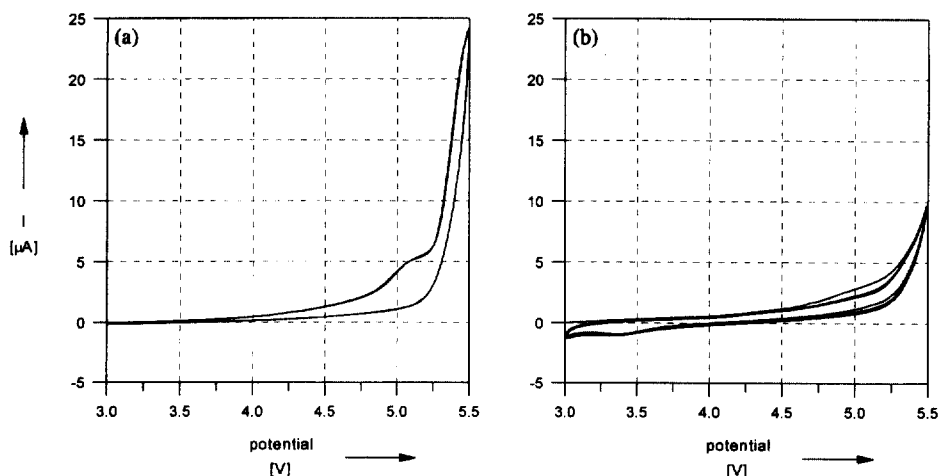


Fig. 3. CV of **A**  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$  (**6**)/DMC and **B**  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$  (**6**)/DMC/4,4,5,5-tetrafluoro-3-trifluoromethyl-1,3-oxazolidin-2-one (**4**) against  $\text{Li}/\text{Li}^+$  showing the stability of **4**.

within 1 h below  $1 \mu\text{A cm}^{-2}$ . This implies that the differences in Fig. 3 are mainly caused by water impurities in the electrolyte and not by a decomposition of **4**.

### 3. Experimental details

#### 3.1. Apparatus

The electrochemical fluorination cell and its techniques were described in previous papers [13].

#### 3.2. Analytical procedures

IR spectra were recorded from  $4000\text{--}225 \text{ cm}^{-1}$  on a Nicolet 20 DXB instrument. NMR-spectra were taken on Bruker DRX 500 ( $125.8 \text{ MHz } ^{13}\text{C}$ ,  $470.6 \text{ MHz } ^{19}\text{F}$ ) in acetonitrile- $d_3$  with  $\text{CD}_3\text{CN}$  as internal (for  $^{13}\text{C}$ ) and  $\text{C}_6\text{F}_6$  (for  $^{19}\text{F}$ ) as external standard, respectively. Mass spectral data were determined with a Varian MAT 311A (EI, 70 eV) and AMD Intektra DP10 V 0.86 as data system. The viscosity was measured on a Low Shear 30 (Contraves) and DSC-experiments were recorded on a DSC-2C (Perkin-Elmer). CV-measurements were conducted at the University of Regensburg, Institute of Physical and Theoretical Chemistry.

#### 3.3. Chemicals

3-Methyl-1,3-oxazolidin-2-one (**1**) was supplied from Aldrich.

#### 3.4. Synthesis of 4,4,5,5-tetrafluoro-3-trifluoromethyl-1,3-oxazolidin-2-one (**2**)

Two-hundred g anhydrous hydrogen fluoride were introduced into the ECF cell (volume 280 ml) and dried for about 30 h by passing current to remove moisture and to condition the Ni-electrodes. A cell voltage of 4.5–4.8 V was maintained

for this drying process. The temperature of the cell was held at  $0^\circ\text{C}$  and the temperature of the condenser was maintained at  $-30^\circ\text{C}$  in this experiment. A 15% (w/w) solution of **1** in anhydrous hydrogen fluoride was transferred into the cell.

Electrolysis was carried out under galvanostatic conditions (current density:  $0.80 \text{ A dm}^{-2}$ ). The cell voltage was maintained between 4.8–5.3 V. Subsequent addition of the starting material (33.3 g portions) was made after passing the corresponding current. The electrofluorination was stopped after nearly 100 g of compound had been electrofluorinated. The perfluorinated materials obtained were separated from the hydrogen fluoride phase, washed with cold water, 2% sodium hydrogen carbonate solution and again with water and finally dried using anhydrous sodium sulfate. After filtration the clear and colourless liquid was distilled.

Yield: 31.80 g 14%; current yield: 11%; m.p.:  $-53.3^\circ\text{C}$ ; bp:  $52^\circ\text{C}$ , density:  $1.641 \text{ g ml}^{-1}$ ;  $n_{\text{D}}^{20} = 1.2904$ ; viscosity ( $25^\circ\text{C}$ , m Pa) = 0.79;  $^{13}\text{C}$ -NMR ( $\text{CD}_3\text{CN}$ , 75.5 MHz):  $\delta = 114.31$  (tt,  $^1J_{\text{CF}} = 270.3 \text{ Hz}$ ,  $^2J_{\text{CF}} = 33.25 \text{ Hz}$ ,  $\text{CF}_2\text{-N}$ ), 118.45 (qua,  $^1J_{\text{CF}} = 268.0 \text{ Hz}$ ,  $\text{CF}_3\text{-N}$ ), 118.48 (tt,  $^1J_{\text{CF}} = 274.1 \text{ Hz}$ ,  $^2J_{\text{CF}} = 19.51 \text{ Hz}$ ,  $\text{CF}_2\text{-O}$ ), 142.09 (s,  $\text{C=O}$ );  $^{19}\text{F}$ -NMR ( $\text{CD}_3\text{CN}$ , 75.4 MHz):  $\delta = -94.70$  (qa,  $^4J_{\text{FF}} = 6.7 \text{ Hz}$ , 2F),  $-88.71$  (s, 2F),  $-58.06$  (t,  $^4J_{\text{FF}} = 6.8 \text{ Hz}$ , 3F); IR (KBr-Film):  $\tilde{\nu} = 1891\text{sst}$ ,  $1397\text{sst}$ ,  $1338\text{sst}$ ,  $1300\text{sst}$ ,  $1263\text{sst}$ ,  $1224\text{sst}$ ,  $1219\text{sst}$ ,  $1091\text{st}$ ,  $1020\text{sst}$ ,  $922\text{sst}$ ,  $753\text{st}$ ,  $682\text{m}$ ,  $672\text{m}$ ,  $575\text{s}$ ,  $524\text{s}$ ,  $483\text{m}$ ; MS (EI, 70 eV,  $120^\circ\text{C}$ ): m/e = 227 (1.8%,  $\text{M}^+$ ), 208 (2.9%,  $\text{M} - \text{F}^+$ ), 164 (24.1%,  $\text{F}_3\text{C-N-CF}_2\text{-CF}^+$ ), 161 (24.6%,  $\text{F}_3\text{C-N}(\text{CF}_2)\text{-CO}^+$ ), 133 (31.8%,  $\text{F}_3\text{C-N-CF}_2^+$ ), 114 (100%,  $\text{CF}_2\text{-CF}_2\text{-N}^+$ ), 92 (26.0%,  $\text{O=C-N-CF}_2^+$ ), 69 (83.5%,  $\text{CF}_3^+$ ), 50 (5.8%,  $\text{CF}_2^+$ ) and other fragments.

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