

Anodic Oxidation of Norcamphor in Aqueous Electrolytes

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Abstract. Norcamphor (**1**) was anodically oxidized at Pb/PbO₂ anodes in 1 M · H₂SO₄, MeCN/H₂O (V/V = 1/1). 3-Oxocyclopentaneacetic acid (**3**) and oxabicyclo[3.3.0]octan-3-one (**4**) were obtained with

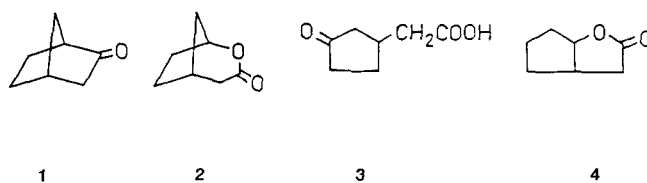
material yields up to 76 % and 42 %, respectively. The effects of electrode materials, current densities and concentrations were studied. A possible anodic oxidation mechanism was proposed.

Since Baeyer and Villiger reported the first example of the peracid oxidation of ketones to esters or lactones in 1899 [1], this type of oxidation has found a wide variety of important synthetic and degradative applications [2, 3]. Thus, peracids have been used to synthesize steroid and terpene lactones, as well as lactones involving medium and larger rings which are virtually unobtainable by any other means till now. Recently, we were able to demonstrate the direct anodic oxidation of camphor to 1,2-campholide with high material yields [4].

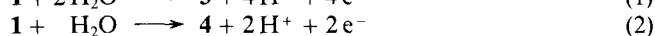
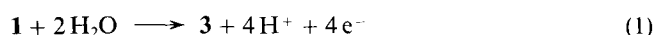
In analogy to this finding, we tried to prepare 2-oxabicyclo[3.2.1]octan-3-one (**2**), via anodic oxidation of norcamphor (bicyclo[2.2.1]heptan-2-one) (**1**).

The Baeyer-Villiger oxidation of **1** has received extensive researches [5–11], and the bridgehead migrated lactone **2** was obtained both in acids and buffer solutions with high yields. However, the direct

electrochemical oxidation under the same conditions [4] afforded quite different main products, **3** and **4**, both to be follow up products of **2**. We like to report on the electrosynthesis of 3-oxocyclopentane-acetic acid (**3**) and 2-oxabicyclo[3.3.0]octan-3-one (**4**).



The main products for the anodic oxidation of **1** under our conditions are **3** and **4**, and the overall reactions are as following:



The preparative results are compiled in Table 1. It can be seen that **3** formed at the PbO₂ anode with material yields MY of up to 76 % and current efficiencies CE

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Table 1 Anodic oxidation of norcamphor in 1 M H₂SO₄, MeCN/H₂O (V/V = 1/1) at 15 °C. Quasidivided cell, V = 250 ml. The theoretical electrochemical conversion β₀ was 100 %, corresponding to 4 F per mol norcamphor. MY = material yields. CE = current efficiencies

No.	Anode	j (A m ⁻²)	n ₀ (mmol)	β (%) (analyt.)	3		4	
					MY	CE	MY	CE
1	PbO ₂	100	12.5	36	58	21	22	2
2	PbO ₂	300	12.5	22	48	11	1	1
3	PbO ₂	100	40.0	50	76	38	8	2
4	Pt	100	12.5	74	52	38	9	3
5	Pt	300	12.5	45	46	21	42	10
6	Pt	750	12.5	26	15	4	—	—
7	Pt	300	40.0	76	33	25	40	15

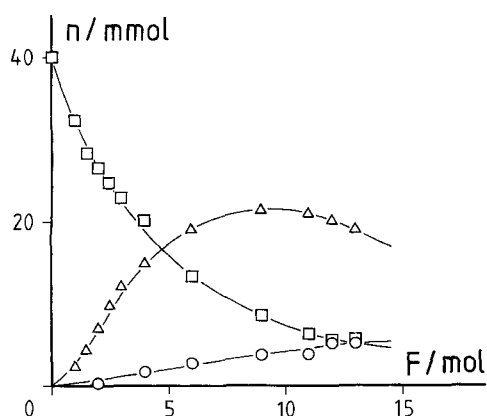


Fig. 1 Kinetic curves for the anodic oxidation of Norcamphor **1** at PbO_2 anode, cf. No. 3 in Table 1

- 1 □ — □
 3 △ — △
 4 ○ — ○

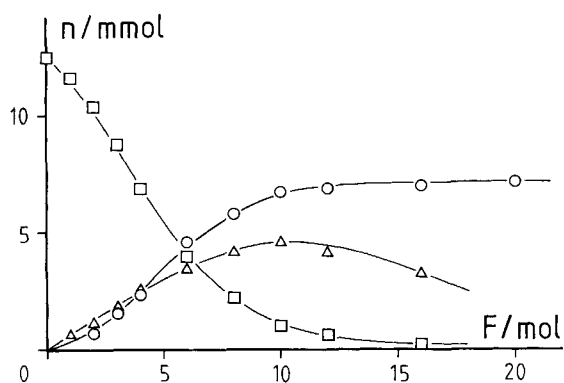


Fig. 2 Kinetic curves for the anodic oxidation of Norcamphor **1** at Pt anode, cf. No. 4 in Table 1

- 1 □ — □
 3 △ — △
 4 ○ — ○

of up to 38%, while **4** formed at the Pt anode with MY of up to 42% and CE of up to 15%. The actual conversions of the starting material **1** are low in the case of low concentrations of **1** except No. 4. With regard to the practical anode material PbO_2 , high concentrations of the starting material and low current densities seem to be optimum.

The kinetic curves for the anodic oxidation of **1** are displayed in Figs. 1 and 2. In the case of PbO_2 anode

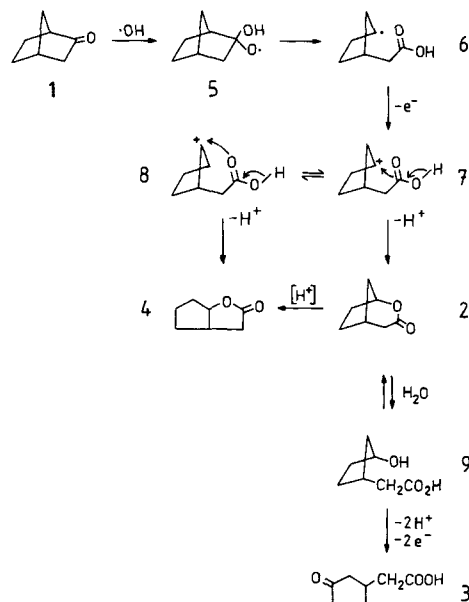


Fig. 3 Reaction mechanism for the anodic oxidation of Norcamphor **1**

(Fig. 1), the formation of **3** as main product and **4** as side product is clearly shown. However, in the case of Pt anode (Fig. 2), **3** and **4** were generated in parallel. This shows that the product selectivity is significantly influenced by the anode material. From the product analysis, an oxidation mechanism according to Fig. 3 follows immediately. At the anode, an OH-radical is added to the carbonyl of **1**. The intermediate **5** is formed, which can be oxidized to **2** through a bridgehead migration, or to **4** when one of the hydrogens in **7** migrates to position 1. The hydrolysis of **2** leads to the hydroxy carboxylic acid **9**, which is further oxidized to product **3**.

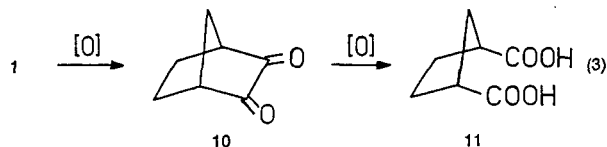
It should be noted that **2** is able to convert to **4** under acid catalysis.

The above mentioned situation is different from that of Baeyer-Villiger oxidation of **1** [5–11]. In that case lactone **2** was obtained in 88–100% yields, its hydrolysis was considered to be difficult due to a severe congestion for the tetrahedral intermediate [12], and no conversion of **2** to **4** was found. However, hydrolysis of **2** with dilute alkali could give the corresponding hydroxy acid **9**, which could be oxidized by the chromic acid-pyridine reagent to **3** [7].

The anodic oxidation of norcamphor **1** also shows different results from that of camphor. In the case of camphor, 1,2-campholide was obtained with high MY of up to 96% at the PbO_2 anode [4]. No hydrolysis and further oxidation of this lactone were found. The different reaction routes for the anodic oxidation of camphor and norcamphor can be understood from steric reasons. For the former, the endo-adsorption of the starting material onto anode leads to the exo-prod-

uct [4]. For the latter, the exo-adsorption of **1** leads to endo-product of **2** which is still susceptible to react with the electrode, and tends to form the further oxidized product **3** or rearranges to form **4**. The same situation holds for the electroreduction of camphor oxime and norcamphor oxime to the corresponding amines, where 99% exo- and 100% endo-products were obtained, respectively [13].

We have previously investigated the anodic oxidation of cyclic 1,3-diketones [14, 15]. The final products at PbO₂ anodes were dicarboxylic acids with one C less. A reaction mechanism via the intermediate 1,2,3-triketones, which could be obtained with good MY and CE at Pt anodes [15], was derived. However, we did not find any trace of the corresponding intermediate, bicyclo[2.2.1]heptane-2,3-dione (**10**), in the anodic oxidation of **1**. Its further oxidation product, norcamphoric acid **11**, was not detected either. The same situation holds for the anodic oxidation of camphor [4]. The reason may be the different degree of enolization between monoketone and 1,3-diketone. This deduction can be further supported by our previous findings for the anodic oxidation of cyclohexanone, where an oxygen insertion mechanism was concluded [16].



In summary, we have obtained the keto acid **3** and lactone **4** by direct anodic oxidation of norcamphor **1** with good yields. Till now **3** can only be obtained by chemical multi step oxidation [7]. **3** is the important intermediate for the synthesis of one of the constituents of jamine oil, methyl jamate [7].

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Experimental

IR: Perkin-Elmer 283 spectrophotometer. — ¹H NMR: 60 MHz JEOL PMX 60 SI spectrometer, internal TMS. — GC/MS: Varian Mat 311 A spectrometer, connected to a Varian aerograph 1400. — HPLC: ERC pump 64, Hewlett Packard 1050 Variable Wavelength detector, Hewlett Packard 3396A integrator, Grilson FC 2300 fraction collector, and Nucleosil-5C18 (0.8 × 25 cm) column.

Norcamphor **1**, 98% from Heraeus was used as starting material. The electrolyte was 1 M H₂SO₄ in MeCN/H₂O (V/V = 1/1), made from AnalR grade 97% H₂SO₄ (Merck), "Zur Synthese" acetonitrile (Merck) and tridistilled water. Anode materials were conventional. Smooth platinum sheet of 0.1 mm thickness and Pb/PbO₂ anode with 1–2 mm lead sheet. The electrode area was 2 × 25 cm² (two face). Pt anode was cleaned with chromic acid, 100 °C, 10 minutes, and

successive treatment in boiling HCl for 15 minutes [17]. The anodic formation of PbO₂ proceeded in 1.0 M H₂SO₄ at 100 A m⁻² for 3 hours [4, 14]. The counter electrodes were two stainless steel (V2A) wires (A = 2 × 0.3 cm²). The quasi-divided cylindrical cell was made of glass (250 ml), with cooling jacket and planar ground cover. The direct current sources were galvanostates of Philips (PE 1512) and of Hewlett Packard (6269B) for I = 0–3 A and 0–50 A, respectively.

A representative electrolysis (cf. No. 3 in Table 1) is described as following: The quasidivided cell was filled with 4.4 g (40 mmol) **1** in 250 ml 1 M H₂SO₄, MeCN/H₂O (V/V = 1/1). The electrolyte was stirred with a magnetic stirrer. Nitrogen was introduced to the top of the cell to dilute hydrogen and oxygen generated during electrolysis. The current of 0.5 A, corresponding to a current density of 100 A m⁻² was kept constant. The temperature was held at 15 °C. After 8 hours and 35 minutes, corresponding to a theoretical **1** conversion of β = 100% (cf. definition in Table 1), the electrolysis was interrupted. 20 mmol nonconverted **1** was found, hence the effective conversion was 50%.

The electrolyte was extracted with ether (5 × 25 ml). The combined extracts were washed with 5 wt % NaHCO₃ solution and then with water. The extracts were dried over anhydrous Na₂SO₄ for 1 day. After ether stripping, 3.2 g yellow oil was obtained.

The product analysis was mainly performed via HPLC (eluent MeOH/H₂O (V/V = 1/2, flow rate 1.5 ml min⁻¹). The main peaks of the electrolyte and the crude product appeared at 8.6 and 6.6 min. The retention time t_R of **1** was 31.6 min. The crude product was separated by preparative HPLC (column: Nucleosil 100-5C18 (2 × 25 cm), eluent: MeOH/H₂O (V/V = 1/1, flow rate 20 ml min⁻¹). The collected samples were extracted with ether, the combined extracts were dried over anhydrous Na₂SO₄. After work up, the samples were analyzed by ¹H NMR and IR, and the results show that the products with t_R = 8.6 and 6.6 min. are 3-oxocyclopentaneacetic acid **3** and 2-oxabicyclo[3.3.0]octan-3-one **4**, respectively. GC/MS-coupling measurement of the crude product gave the identical results.

3: ¹H NMR (CDCl₃), δ = 1.0–1.5 (m, 2H, -CH₂), 2.1–2.9 (m, 7H, -CH, -CH₂CO₂, 2-CH₂CO). GC/MS (EI): m/z (%) = 142 (25, M⁺), 100 (37), 83 (100), 60 (30), 55 (70), 45 (29).

In order to increase the solubility, **3** was esterified to methyl 3-oxocyclopentaneacetate with MeOH. ¹H NMR (CDCl₃): δ = 1.0–1.5 (m, 2H), 2.1–2.9 (m, 7H), 3.7 (s, 3H, -COOCH₃). GC/MS (EI): m/z % = 156 (9, M⁺), 125 (12), 99 (26), 83 (100), 74 (37), 69 (24), 59 (37), 55 (40).

4: IR (neat): ν = 1720 cm⁻¹ (s), 1390 (s), 1277 (s). GC/MS (EI): m/z (%) = 126 (9, M⁺), 97 (55), 80 (48), 67 (100), 55 (94), 54 (98).

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