Indirect Electrochemical Processes. 14.* Indirect Electrochemical Oxidation of Benzylic Alcohols with Organic Mediators

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Benzylic alcohols can be oxidized with good selectivity, high material yield, and at low potentials to form benzaldehydes, if catalytic amounts of electrogenerated and regenerated triarylamine cation radicals are used as oxidizing agents. The reaction can either take place in acetonitrile or methanol in the presence of 2,6-lutidine or Na_2CO_3 as bases using a divided cell or in an undivided cell, if methanol is used as a solvent. In the latter case the aldehyde is formed as the major product, if small amounts of Na_2CO_3 are present. In the absence of an added base, however, the dimethyl acetal predominates. The cathodic formation of dimeric products from the benzaldehyde can be suppressed by the use of a platinum cathode and by working under neutral conditions. The formation of methyl benzoate as a side product is dependent on the conversion of the substrate.

Anodic oxidation of benzylic alcohols takes place at rather positive potentials¹ and in most cases is accompanied by electrode passivation. In the case of 4-methoxybenzyl alcohol this passivation can be prevented and 4-methoxybenzaldehyde is formed in 72 % yield, if pyridine is present as a base.¹ In other cases Na_2CO_3 in wet acetonitrile was used as base and potential pulsing prevented fouling of the electrode surface.^{2,3} In the case of benzylic alcohol the aldehyde (30 %) was accompanied by benzoic acid (40 %). By application of a nickel gauze anode in aqueous alkali 1,4-bis(hydroxymethyl)benzene can be transformed

to terephthalic acid in high yield.⁴ In a similar way benzylic alcohol forms benzoic acid,⁵ while using a two phase system of water and benzene (1:1) yields benzaldehyde (57 %) and benzoic acid (14 %).⁶ An effective alternative is the use of electrochemically generated hypobromide in a two phase system under phase transfer catalysis conditions leading to benzaldehydes in 70–100 % material yield and 30–80 % current yield.^{7,8}

In previous studies we have shown that benzylic ethers^{9–11} and esters¹² can be oxidized to form benzaldehydes and aliphatic alcohols, respectively acids, with high selectivity under mild conditions, low potentials and without electrode fouling, if electrochemically, respectively chemically generated, triarylammoniumyls are used as oxidizing agents and organic or inorganic bases are present. The electrochemical procedure allows the use of catalytic amounts of the mediator by its continuous regeneration. The purpose of this investigation was the application of this procedure to the oxidation of benzylic alcohols to form benzaldehydes selectively in acetonitrile or methanol as solvents according to eqn. (1).

RESULTS AND DISCUSSION

Electroanalytical studies. The chance of success for the indirect electrochemical reaction can be evaluated by the cyclic voltammetric method (CV) by which not only values of the redox potentials are measured (Table 1) but also the presence of an electrocatalytic mechanism can be

* Part 13. Wienkamp, R. and Steckhan, E. *Angew. Chem.* 94 (1982) 786; *Angew. Chem. Int. Ed. Engl.* 21 (1982) 782; *Angew. Chem. Suppl.* (1982) 1739.

Compound	R ¹	R ²	R ³
1a, 3a	OCH ₃	H	H
1b, 3b	H	H	H
1c, 3c	Br	H	H
1d, 3d	Cl	H	H
1e, 3e	Cl	Cl	H
1f, 3f	Cl	H	Cl
1g, 3g	CH ₂ OH	H	H

Compound	X	Y	Z
2a	H	H	H
2b	Br	H	H
2c	Br	Br	H
2d	Br	Br	Br

indicated by the so-called catalytic effect. In the case of an indirect electrochemical oxidation the anodic peak current for the electron transfer agent (mediator) is increased and the cathodic peak current lowered by the amount of a catalytic current.¹³ The size of the catalytic current is dependent on the potential scan rate, the benzy-

Table 1. Redoxpotentials of compounds 1a-g and 2a-c in acetonitrile/0.2 M LiClO₄ against the normal hydrogen electrode.

Compound	E_{pa}/V^a	E°/V^b
1a	1.72	
1b	2.49	
1c	2.35	
1d	2.44	
1e	2.50	
1f	2.52	
1g	2.23	
2a		1.30
2b		1.42
2c		1.56
2d		1.74
2e		1.72

^a Anodic peak potential, extrapolated for scan rate 0 V/s; first peak. ^b Standard redox potentials; first wave only.

lic alcohol concentration and the overall reaction rate for the regeneration of the mediator in its reduced form. The reaction rate is not only dependent on the difference of the standard redox potentials of the mediator and the benzylic alcohol which determines the equilibrium constant for the homogeneous electron transfer step but also by the rate of the follow-up chemical reaction, the deprotonation of the benzylic alcohol cation radical. Therefore the catalytic effect is expected to show a large influence of the kind and amount of the added base. To examine the size of the catalytic effect cyclic voltammograms have been recorded for different potential scan rates, concentrations of the alcohols and amounts of added bases.

Fig. 1 shows cyclic voltammograms of the triarylamine 2a in acetonitrile in the presence of 4-methoxybenzyl alcohol 1a in the absence and presence of 2,6-lutidine. While in the absence of the base no catalytic effect is observed (Fig. 1B), the electrocatalytic process is initiated by the addition of 2,6-lutidine which is indicated by the strong catalytic current (Fig. 1C, D).

In acetonitrile 4-chlorobenzyl alcohol 1d only shows a very small catalytic effect in the presence of 2d and Na₂CO₃ as a base. The main reason is the low solubility of Na₂CO₃ in the solvent. In

Fig. 1. Cyclic voltammograms of **2a** in the absence and presence of 4-methoxybenzyl alcohol (**1a**) and 2,6-lutidine in acetonitrile. a: 400 mV/s; b: 320 mV/s; c: 240 mV/s; d: 160 mV/s; e: 80 mV/s; f: 40 mV/s; g: 20 mV/s. Platinum anode (0.5 cm²). A: 0.8 mmol/l **2a**; B: 0.8 mmol/l **2a**, 80 mmol/l **1a**; C: 0.8 mmol/l **2a**, 80 mmol/l **1a**, 80 mmol/l 2,6-lutidine; D: 0.8 mmol/l **2a**, 80 mmol/l **1a**, 800 mmol/l 2,6-lutidine.

methanol, however, even in the absence of a base such a strong catalytic current is observed (Fig. 2B) that addition of Na₂CO₃ does not have further influence.

It therefore can be concluded that preparative scale indirect electrochemical oxidations of benzylic alcohols **1b–1g** by triarylamine mediators **2d** and **2e** will be possible in acetonitrile/Na₂CO₃ at a rather slow to moderate rate while **1a** should react much faster with **2a** in acetonitrile/2,6-lutidine.* In methanol/Na₂CO₃, however, also reactions of **1b–1g** with **2d** or **2e** should take place at a fast rate.

* 2,6-Lutidine cannot be used together with **2d**⁺ because it is oxidized.

Preparative oxidation in acetonitrile in a divided cell. Benzylic alcohols **1a–1f** can be oxidized by electrochemically generated and regenerated triarylamine cation radicals **2a**⁺ (**1a**), respectively **2d**⁺ and **2e**⁺ (**1a–1f**), (molar ratio of 1 and 2 = 5:1) in base containing acetonitrile to form benzaldehydes **3a–3f** in high yield (Table 2).

The applied potential for the generation of the oxidizing agent is in all cases considerably lower than the half-wave potentials of the substrates. In this way the oxidation can take place under very mild conditions and high selectivity. The selectivity is demonstrated by the absence of side products, for example acids or esters. The oxidizing power of **2a**⁺ is too low to attack **1b–1f** to any extent while the better oxidizing agents **2d**⁺

Fig. 2. Cyclic voltammograms of *2d* in the absence and presence of 4-chlorobenzyl alcohol *1d* and Na_2CO_3 in acetonitrile/methanol (2:1). a: 1280 mV/s; b: 980 mV/s; c: 720 mV/s; d: 500 mV/s; e: 320 mV/s; f: 180 mV/s. Glassy carbon anode (0.05 cm^2). A: 1 mmol/l *2d*; B: 1 mmol/l *2d*, 10 mmol/l *1d*; C: 1 mmol/l *2d*, 10 mmol/l *1d*, 100 mmol/l Na_2CO_3 ; D: 1 mmol/l *2d*, 20 mmol/l *1d*, 100 mmol/l Na_2CO_3 .

Table 2. Results of the indirect electrochemical oxidation of benzylic alcohols *1a–1f* by electrogenerated triarylamine cation radicals in acetonitrile using a divided cell.

Educt <i>1</i>	Mediator <i>2</i>	Base	Conversion of <i>1</i>	m.y. ^a <i>3</i> (%)	c.y. ^b <i>3</i> (%)
<i>1a</i>	<i>2a</i>	lutidine	100	96	80
<i>1b</i>	<i>2a</i>	lutidine	5	5	<5
<i>1b</i>	<i>2d</i>	Na_2CO_3	77	95	65
<i>1c</i>	<i>2d</i>	Na_2CO_3	92	90	50
<i>1d</i>	<i>2d</i>	Na_2CO_3	85	98	61
<i>1d</i>	<i>2e</i>	Na_2CO_3	85	72	45
<i>1e</i>	<i>2d</i>	Na_2CO_3	78	100	63
<i>1e</i>	<i>2e</i>	Na_2CO_3	86	82	50
<i>1f</i>	<i>2d</i>	Na_2CO_3	90	84	50

^a Material yield of *3* with respect to converted *1*. ^b Current yield of *3*.

and $2e^+$ lead to high material yields. Current densities in these cases are in the order of 3–4 mA/cm² while in the case of *1a/2a* 15 mA/cm² can be reached. The current yields with $2d^+$ and $2e^+$ are lower as compared with $2a^+$ because in a side reaction residual water is oxidized by those mediators. Most electrolyses are stopped after about 85 % conversion. Otherwise the current yield will further decrease.

In the case of 1,4-bis(hydroxymethyl)benzene *1g*, total conversion to form terephthalaldehyde *4g* in 75 % material yield and 46 % current yield can be performed by $2d^+$ according to eqn. (2). By continuous monitoring of the progress of the reaction (see Fig. 3) it was shown that at 50 % conversion the ratio of the monoaldehyde *3g* to dialdehyde *4g* is about 10:1 (44 %:4 %). From 50–70 % conversion the yield of the monoaldehyde still increases faster than for the dialdehyde

indicating a faster oxidation rate for the diol. This is further supported by the indirect electrochemical oxidation of *1g* by *2b* as mediator in acetonitrile/2,6-lutidine leading to a considerably higher selectivity in *3g*.

In correspondence with previously detected similar reactions^{9–11} one could postulate the following mechanism:

Fig. 3. Product distribution during the course of the indirect electrochemical oxidation of 1,4-bis(hydroxymethyl)benzene *1g* by *2d* as mediator in acetonitrile/Na₂CO₃ using a divided cell. Curve 1 (■): Material yield of dialdehyde *4g*; Curve 2 (×): Material yield of monoaldehyde *3g*; Curve 3 (Δ): Unconverted educt *1g*; Curve 4 (●): Current yield of *3g* and *4g*.

An alternative reaction path which possibly could take place by H-atom abstraction from benzylic alcohol by Ar_3N^+ could be excluded in the case of the cleavage of benzylic esters because the reaction rate of benzhydryl esters towards $2d^+$ is lower as compared with 4-methoxybenzyl esters.¹² This is in contradiction to a radical abstraction mechanism but in agreement with the oxidation potentials of the esters (4-(MeO)Ph-CH₂OCOR: $E_{1/2} = +1.89$ vs. NHE; (Ph)₂CHOCOR: $E_{1/2} = 2.70$ V vs. NHE).

A mechanism based on the oxidation of the alcoholate anion by triarylammoniumyls could perhaps better accommodate a "non-bonded" electron transfer.¹⁴ However, in this case an oxyradical would be formed which either could react under hydrogen atom abstraction leading to the same problems as pointed out above, or it must further be oxidized. In both cases the observed potential dependence of the reaction rate indicating that the first electron comes from the benzylic part of the molecule is difficult to explain. Besides that, as the reaction also takes place under neutral conditions only small amounts of PhCH_2O^- would be present.

To accommodate the large potential differences between mediator and substrate also an inner-sphere or "bonded" electron transfer mechanism¹⁴ has to be taken into consideration.

Preparative oxidation in methanol in a divided cell. Preparative oxidation of benzylic alcohols is also possible in methanol/ Na_2CO_3 using a divided cell. In this case, as indicated by the electroanalytical experiments, a higher current density can be obtained as compared with acetonitrile. For example, 4-chlorobenzyl alcohol **1d** is anodically oxidized in the presence of **2d** (**1d**:**2d**=10:1) as a mediator using a $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$ (3:1) solvent system to form 4-chlorobenzaldehyde **3d** and the corresponding methyl 4-chlorobenzoate **5d** in 85 %, respectively 15 %, material yield and 37 %, respectively 14 %, current yield after a conversion of 80 % (eqn. (3)). The current density reaches 5 to 10 mA/cm². Under identical conditions benzyl alcohol **1b** is transformed to yield benzaldehyde **3b** and methyl benzoate **5b** in 63 %, respectively 4 %, material yield and 30 %, respectively 4 %, current yield.

Preparative oxidation in methanol using an undivided cell. The indirect electrochemical oxidation of benzylic alcohols in an undivided cell using methanol as a solvent is complicated by the possibility of the cathodic reduction of the generated benzaldehyde to form the hydrodimer. The hydrodimer is oxidation labile forming benzil and benzoin. The direct cathodic pinacolization of benzaldehydes is favoured in alcoholic KOH at a mercury cathode.¹⁵ The reaction pathways for

Table 3. Results of the indirect electrochemical oxidation of 4-chlorobenzyl alcohol **1d** by electrogenerated $2d^+$ (**1d**:**2d**=10:1) in methanol/methylene chloride (3:1) in an undivided cell.

Exp. No.	Cathode material	Na_2CO_3 (g)	Conversion (%)	Aldehyde 3d (%) ^a	Acetal 6d (%) ^a	Ester 5d (%) ^a	Dimers 7d + 8d + 9d ^b
1	graphite	4	78	47 (18)	—	4.6 (3.5)	30
2	V4A-steel	4	88	39 (13)	—	23 (15)	20
3	platinum	4	59	55 (11)	—	40 (15)	<2
4	platinum	0	73	7 (3)	75 (29)	18 (17)	<0.5
5	graphite	0	82	10 (4)	62 (25)	21 (25)	3
6 ^c	graphite	0.5	79	69	—	10	20
	graphite	0.5	85	67 (28)	—	14 (12)	

^a Material yield with respect to converted educt; current yields in parentheses. ^b Because of uncertainties in the GC-calibration of the dimers only *circa* values are given; the ratio of **7d**:**8d**:**9d** is about 2:1:1; **7d** is produced as *meso*- and *dl*-form in almost equal amounts. ^c Ratio **1d**:**2d**=20:1.

Scheme 1. Reaction scheme for the indirect electrochemical oxidation of 4-chlorobenzyl alcohol **1d** by **2d** as mediator in methanolic solution using an undivided cell.

the indirect electrochemical oxidation in the case of the system **1d/2d** are shown in Scheme 1.

In Table 3 the influence of the reaction parameters on the product distribution is summarized. It could be shown that the dimer formation is influenced by the cathode material and the pH of the solution. Changing the cathode material from graphite to platinum with a lower hydrogen

overvoltage results in drastic reduction of the dimerization (Exp. Nos. 1 and 3). The same is true if one goes from basic to neutral conditions (Exp. Nos. 1 and 5). A different approach is the use of cathodes with a small active area as, for example, a steel rod in connection with a large anode area. Using a carbon felt anode together with a steel rod cathode benzyl alcohol **1b** under

the conditions of experiment No. 5 leads to the formation of only 10 % dimers together with 12 % benzaldehyde, 42 % benzaldehyde dimethyl-acetal and 23 % of methyl benzoate. Under neutral conditions the dimethyl-acetal is the major product (Exp. Nos. 4 and 5) while under basic conditions no acetal formation is observed and the aldehyde predominates. The formation of the methyl benzoates is favoured with increasing conversion (Exp. No. 6). There is also a complex influence of the cathode material and the pH on the ester production which, however, could not be resolved to date.

EXPERIMENTAL

The benzylic alcohols *1a*–*1g* were commercially available and purified by distillation, respectively recrystallization. The triaryl amines *2a*–*2d* and the 9-phenylcarbazole derivative *2e* were synthesized as previously described.¹⁶ Acetonitrile (Merck, for synthesis) was dried over P_2O_5 and K_2CO_3 and further purified by distillation. Methylene chloride was purified by distillation while methanol (Merck, p.a.) was used without further purification.

$LiClO_4$ (Fluka, Buchs) was applied as obtained. Products were identified by mass spectra and NMR spectra which were identical with those reported in the literature.^{17,18} Yields were either determined by isolation or by GLC on a 4 % FFAP/Chromosorb W AWDCMS 100/120 mesh column (2 m $\times$ 2 mm) using methyl *n*-alkanoates as internal standards.

Cyclic voltammetry. As current source a Wenking potentiostat, model PCA 72 L (Bank Elektronik, Göttingen), coupled to a function generator, model 133 LF (Wavetek) was applied. Current/voltage curves were recorded on Hewlett-Packard, model 7045, XY-recorder. A model EA 876–5 (Methrohm, Herisau) analytical cell was used together with a platinum (0.5 cm²) or glassy carbon (0.05 cm²) working electrode, a platinum counter electrode and an Ag/AgNO₃ (0.1 M in CH₃CN) reference electrode. Solvent supporting electrolyte was either CH₃CN (0.1 M $LiClO_4$) or CH₃CN/CH₃OH (2:1) (0.1 M $LiClO_4$).

Equipment for preparative electrolyses. Preparative electrolyses were performed either using a Wenking potentiostat, model ST 72 (Bank Elektronik, Göttingen), or a stabilized current source, model NTN 700M–200 (FUG, Rosenheim), modified as potentiostat together with a digital coulometer based on voltage-to-frequency conversion.*

* Design by H. Luftmann, Münster.

Preparative electrolyses in acetonitrile using a divided cell. General procedure. The mediators *2a*–*2e* (1 mmol) dissolved in 80 ml CH₃CN/CH₂Cl₂ (4:1)/(0.2 M $LiClO_4$) together with the base 2,6-lutidine (20 mmol), respectively Na₂CO₃ (3 g), were transferred to the anode chamber of a two-compartment beaker-type glass cell with cooling mantle. The cathode compartment was formed by a glass cylinder closed by a G-4 glass frit and filled with 20 ml CH₃CN (1 M $LiClO_4$) as catholyte. As electrodes were used a platinum sheet anode (12 cm²), a carbon-felt cathode and an Ag/AgNO₃ (0.1 M) reference electrode together with a salt bridge. The cell was kept at 15 °C by water cooling. After application of the working potential for the oxidation of the mediator a pre-electrolysis was performed until 50 As had been passed and the colour of the triarylamine cation radical had appeared. Subsequent addition of the benzylic alcohols *1a*–*1g* (5 mmol) resulted in the disappearance of the colour and the increase of the current to 35–50 mA, respectively 180 mA in the case of *1a*. Electrolysis was continued until the current dropped to about 15 mA (ca. 1200–1500 As). For separation of the benzaldehydes from unreacted benzylic alcohols after evaporation of most of the solvent, the benzaldehydes were converted into the Schiff base salts of sodium ϵ -aminocaproate according to the literature¹⁹ and extracted into the aqueous phase. After acidification (pH 5–6) the aldehydes could be extracted by ether and further purified by bulb-to-bulb distillation. Yields determined by GLC were nearly identical to the isolated ones. The products were identified by melting points and NMR spectra which in all cases were identical with literature values. The formation of side products could be excluded by GLC analysis of the crude solution. In the case of *1g* the progress of the electrolysis was also followed by GLC.

Preparative electrolysis in methanol in a divided cell. The mediator *2d* (0.5 mmol) dissolved in 80 ml CH₃OH/CH₂Cl₂ (3:1)/0.2 M $LiClO_4$ together with 2 g Na₂CO₃ was transferred to the anode chamber of a divided beaker-type glass cell (see above). The cathode compartment was filled with 20 ml CH₃OH/0.3 M $LiClO_4$. As electrodes were used a glassy carbon anode (12 cm²), platinum cathode (3 cm²) and Ag/AgCl-reference electrode together with a salt bridge. The cell was kept at 15 °C by water cooling. After application of the working potential of +1.56 V a pre-electrolysis was performed until 50 Coulombs had been passed. By addition of 5 mmol *1d* the current increased to about 80–90 mA. After consumption of 2000 Coulombs the electrolysis was worked up as described above.

Preparative electrolysis in methanol in an undivided cell. General procedure. The mediator 2d (1 mmol) (Exp. No. 6: 0.5 mmol) dissolved in 100 ml CH₃OH/CH₂Cl₂ (3:1)/0.2 M LiClO₄ together with the amount of base shown in Table 3 was transferred to an undivided beaker-type glass cell which was equipped with a glassy carbon anode (18 cm²) and Ag/AgCl reference electrode. The material for the cathodes (18 cm²) was varied according to Table 3. The cell was kept at 15 °C by water cooling. After application of the working potential of +1.56 V a pre-electrolysis was performed until 50 Coulombs had been passed. By addition of 10 mmol *Id* the current increased to 100 mA. After consumption of about 4000 Coulombs the electrolyses were worked up. The yields were determined by GLC and the products isolated by HPLC on a 50 cm×1.6 cm Si-60 (7 μm, Merck) column using CH₂Cl₂/ethyl acetate (15:1) as eluent. The products were identified by comparison of their MS spectra, respectively NMR spectra, with literature data.

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