INDIRECT ELECTROCHEMICAL α -METHOXYLATION OF ALIPHATIC ETHERS AND ACETALS -REACTIVITY AND REGIOSELECTIVITY OF THE ANODIC OXIDATION USING TRIS(2,4-DIBROMOPHENYL)AMINE AS REDOX CATALYST

KLAUS-DIETER GINZEL and EBERHARD STECKHAN*

INSTITUT FÜR ORGANISCHE CHEMIE UND BIOCHEMIE; RHEINISCHE FRIEDRICH-WILHELMS-UNIVERSITÄT, GERHARD-DOMAGK-STR. 1, D-5300 BONN 1, F.R.G.

DIETER DEGNER

BASF AKTIENGESELLSCHAFT, HAUPTLABORATORIUM, D-6700 LUDWIGSHAFEN, F.R.G.

(Received in Germany 17 July 1987)

Abstract - The technically important α -methoxylation of aliphatic ethers and acetals to form mixed acetals respectively aldehydes or ortho-esters can be performed electrochemically at low potentials in methanol solution using an undivided cell and tris(2,4-dibromophenyl)amine as redox catalyst. The regioselectivity is usually considerably higher as compared with direct electrolysis in the absence of a catalyst. Especially valuable is the method for the regioselective methoxylation of secondary carbon atoms in presence of primary or tertiary ones and of the acetal carbon in 1,3-dioxolanes. The redox catalyst is stable under the reaction conditions so that more than thousand turnovers could be obtained.

Because of their very positive potential the oxidation of aliphatic ethers and acetals is very difficult. This is also true for the anodic oxidation. Therefore, using graphite anodes and methanol/sodium methoxide as electrolyte only very poor current yields (2-methoxy tetrahydrofuran = 16.3 \%^{1} could be obtained. Current yields could be improved using platinum or glassy carbon anodes and methanol/tetramethylammonium methosulfate as electrolyte, however, the regioselectivity in the methoxylation of unsymmetrical ethers is still very low². The methoxylation of 1,3-dioxolanes can be performed at a platinum anode using an electrolyte of methanol/potassium hydroxide yielding the orthoesters in good material yields. The current yield for 2-methoxy 1,3-dioxolane, however, is only 15 x^3 . Similar results could be obtained for 1,3-benzodioxols⁴. α -Hydroylation of tetrahydrofuran can be performed in a 1 M H₂SO₄ electrolyte at platinum anodes using a quasi divided cell in current yields of up to 70 x^5 . The selectivity of this procedure, however, seems to be low, if cycloaliphatic diethers are employed. Under similar conditions B-cyanoethyl ethers are oxidized to form cyanoacetic acid⁶.

Very often it is possible to perform electrolyses at much lower potentials and with considerably higher selectivities, if a redox catalyst (mediator) is inserted between the electrode reaction and the substrate oxidation step⁷. Recently we were able to perform selective anodic oxidations at low potentials of benzylic alcohols to benzaldehydes⁸ and alkyl aromatic compounds to benzoic esters of orthobenzoic esters⁹ in methanol solution using an undivided cell by applying tris(2,4-dibromophenyl)amine as a mediator. We are now reporting the results of the indirect electrochemical α -methoxylation of aliphatic ethers and acetals under similar conditions. The principle of the reaction is shown in Scheme 1 and 2 including all products which possibly may be formed.



SCHEME I



SCHEME II

Compounds 2, 3 and 9, 10 are regioisomers which may be obtained from the unsymmetrical ethers 1,2-dimethoxy ethane (1g), ally1-<u>n</u>-penty1 ether (1h), <u>t</u>-buty1-methy1 ether (1i), cyclohexy1-<u>n</u>-buty1 ether (1k), and the acetals 1,3-dioxolane (8a), 2-<u>n</u>-propy1-1,3-dioxolane (8b), n-butanaldimethy1 acetal (8c), 2-methoxy tetrahydrofuran (8d). In the case of the symmetrical ethers di-<u>n</u>-buty1 ether (1a), di-<u>i</u>-propy1 ether (1b), dially1 ether (1c), tetrahydrofuran (1d), tetrahydro-pyran (1e), and 1,4-dioxane (1f) as substrates compounds 2 and 3, 4 and 5, as well as 6 and 7 are identical. Dimethylacetals 4 and 5, and orthoester 11 are transacetalation products of 2, 3 and 9, respectively. The esters 6, 7 and 12 are follow-up products of the respective orthoesters.

The reaction has first been studied be cyclovoltammetric measurements in MeOH/LiClO₄ (0.2 M). If only the mediator tris(2,4-dibromophenyl)amine $(2x10^{-3}M)$ was present, the peak current ratio i_{pred}/i_{pox} for the mediatior redox pair at +1.74 V vs. NHE was about 0.9 at a sweeprate of 0.225 V/sec indicating a slow reaction between the mediator cation radical presumably with methanol or residual water. In the presence of larger concentrations of THF (1d) and sodium carbonate as a base the peak current ratio dropped to 0.72 (THF concentration $5x10^{-2}M$) or to 0.6 (THF concentration $10x10^{-2}M$). This is evidence for a rather slow reaction between the mediator cation radical and THF. In the presence of the more easily oxidizable diallyl ether (1c) even with a 1:1 ratio of mediator and substrate the peak current ratio is lowered considerably indicating a much faster reaction. These results can be explained by the following mechanism (eq. 1 - 5).

$$AR_{3}N \xrightarrow{ANODE} AR_{3}N^{+} (1)$$

$$AR_{3}N^{+} + R^{-}O^{-}CH_{2}R^{+} \xrightarrow{} (AR_{3}N^{+} \cdots R^{-}O^{-}CH_{2}R^{+}) (2)$$

$$R_{3}N^{+} \cdots R^{-}O^{-}CH_{2}R^{+} + B \xrightarrow{} AR_{3}N^{+} R^{-}O^{-}CH_{2}R^{+} + HB^{+} (3)$$

$$R^{-}O^{-}CH_{1}R^{+} + AR_{3}N^{+} \xrightarrow{} R^{-}O^{-}CH_{1}R^{+} + AR_{3}N (4)$$

$$R^{-}O^{-}CH_{1}R^{+} + CH_{3}OH \xrightarrow{} R^{-}O^{-}CH_{1}R^{+} + H^{+} (5)$$

$$OCH_{3}$$

Because of the large potential differences between substrate and mediator a "bonded" electrontransfer mechanism^{9,10} via a complex formation (eq. 2) is assumed. The driving force for the reaction is the deprotonation (eq. 3) yielding the alkoxy alkyl radical. Therefore, in the absence of a base like NaOMe or Na₂CO₃ the reaction takes place only at a very slow speed or not at all.

The preparative application of this method was optimized using tetrahydrofuran (1d) as the substrate. Figures 1 and 2 show that the current yield increases with increasing substrate concentration and with decreasing base (NaOMe) concentration.



using 20 ml THF in 90 ml solution

concentration in 90 ml solution

٢A

The optimum conditions are as follows: To prevent predominant methanol oxidation the concentration of the substrate should be as high as possible, preferentially the substrate should be used as co-solvent. The concentration of the mediator tris(2,4-dibromophenyl)amine usually is ca. 1 mmol in 100 ml electrolyte solution. The substrate to mediator ratio can reach 300 to 200:1. The concentration of the base optimally is 1 to 3 mmol NaOMe in 100 ml solution. High concentration will cause predominant oxidation of methanol giving low current yields, while lower concentrations will result in larger electrolysis duration because of lower current densities. KOH and Na₂CO₃ can also be used as bases. KOH causes faster transacetalation, while Na₂CO₃ results in slower reactions (Table 1: entries 3, 6, 7, and Table 2: entry 2). As solvent supporting electrolyte either LiClO₄ or sodium benzoate in methanol are used. All types of carbon can be used as electrodes in the undivided cells. The optimum temperature is about 40°C. The electrolysis is performed under potential control at 1.55 V vs. a Ag/AgCl reference electrode which is considerably lower than the electrode potentials of the ethers and acetals. Losses in current yields are due to the fact that methanol is oxidized by triarylamine cation radicals to form formaldehyde dimethylacetal in a parallel reaction. The mediator is stable over several thousand cycles⁹. Tables 1 and 2 give the results of the indirect electrochemical α -methoxylation of ethers and acetals respectively.

Table l.	Results of the indirect electrochemical oxidation of aliphatic ethers 1	
	in methanol with tris(2,4-dibromophenyl)amine as mediator	

Entry	Comp.	Substrate 1 mmol	Base (mmol)	Ar ₃ N mmol	Prod	uct Se	lecti	vity ^a	Product Yield in mmol (current yield in $\%^{b}$) 3 4 5 7			
					3	4	5	7				
1	a	119.4	NaOMe (4.0)	1.5	61	с	17	8.6	55 (26)	с	16 (7.5)	8 (7.5)
2	b	200	NaOMe (10.0)	1.0	69	с	10		3.2 (3.0)	с	0.5 (0.5)	
3	b	200	КОН (3.0)	1.0	78	с	۱		0.03 (0.03)	с	3.4 (3.6)	
4	с	250	Na0Me (12.5)	1.7	79	с	16		24 (35)	с	6.5 (9.0)	
5	d	113	NaOMe (1.8)	1.0	95	с			18 (35)	С		
6	d	76	KOH (3.0)	1.0	95	с			19 (25)	С		
7	d	113	Na ₂ CO ₃ (1.8)	1.0	9 5	c			16 (32)	с		
8	e	154	NaOMe (3.0)	1.0	95	C			7.1 (7.2)	С		
9	f	100	NaOMe (5.0)	1.0	90	С			7.0 (6.5)	c		
10	g	250	NaOMe (10.0)	1.7	84				51 (23)			
11	h	31	NaOMe (1.5)	0.7	56		3 9		17 (37)		12 (25)	
12	i	400	NaOMe (10.0)	1.5	90				9 (9)			
13	k	29	NaOMe (1.5)	0.7		20 ^d	60	9		1.6 ^d (3.6)	4.9 (11)	0.5 (2.3)

^a Product selectivity is defined as mol percent for a certain product based on the sum of all products. It should not be mixed up with the term "regioselectivity which means the

5800

sum of those products obtained by attack at a certain carbon atom in percent based upon the amount of all products.

- ^b The current yield of a product is determined as percentage of that amount of product which could be obtained, if 100 % of consumed charge would only give this one product.
- ^C In case of symmetrical ethers products **4** and **5** are identical.
- $^{\rm d}$ Also obtained are 0.4 mmol (product selectivity 5 %) of cyclohexanone.

Entry	Comp.	Substrate 8 mmol	Base (mmol)	Ar ₃ N mmol	Product Selectivity				Product Yield in mmol (current vield in %)			
					9	10	[~] 11	12	9	10	11	12
1	a	382	NaOMe (3.8)	1.0	89.9	5.7	4.4		71.2 (70.8)	4.5 (4.4)	3.5 (7)	
2	a	382	KOH (3.8)	1.0	68.6	9.7	21.7		43.4 (55.8)	6.1 (7.9)	13.7 (17.7)	
3	b	67.5	NaOMe (1.5)	1.0				95 ^a				8.03 ^a (12.2)
4	с	108	NaOMe (5.0)	0.7				60				11.1 (4. 4)
5	d	60	NaOMe (1.5)	1.0				no	reaction	1		

Table 2. Results of the indirect electrochemical oxidation of acetals 8 in methanol with tris(2,4-dibromophenyl)amine as mediator

^a 9.5 mmol of starting material were recovered as n-butanal dimethoxyacetal by transacetalation during electrolysis. Oxidation of this transacetalation product proceeds at a much slower rate than that of the starting dioxolane **8b**.

The regioselectivity of the methoxylation can be represented in the following way.

Regioselectivity of the methoxylation in %



This demonstrates the superiority of the indirect electrochemical method with respect to the regioselectivity of the reaction over all other previously reported electrochemical ether and acetal oxidations.

Reactivity and current yields are changing parallel to each other as shown below: Reactivity and CurrentYields in %



Highest reactivity and therefore highest current yields (up to 75 %) are obtained in the α -methoxylation of allylic methylene groups (Table 1: entries 4 and 11) and of the methylenedioxy group in 1,3-dioxolane (Table 2: entries 1 and 2). The reactivity of an aliphatic CH₂-group in α -position to oxygen is much higher (current yield up to 40 %) than those of either a CH- or a CH₃group. Thus 1,2-dimethoxy ethane (1g) is selectively methoxylated at the CH₂-group (Table 1: entry 10), and in cyclohexyl-<u>n</u>-butyl ether (1k) the secondary carbon is preferentially oxidized over the tertiary one (ratio 69: 25; Table 1: entry 13). The reduced reactivity of tertiary carbons which also shows up, if 1,3-dioxolane (8a) and 2-<u>n</u>-propyl-1,3-dioxolane (8b) (Table 2: entries 1 and 3) are compared, can be rationalized by a steric effect. The formation of a complex between substrate and mediator cation radical, which seems to be a prerequisite for the success of this reaction (eq. 2)^{9,10}, is hindered in these cases. Five-membered cyclic ethers are much more reactive than six-membered rings (Table 1: entries 5,8,9). This may be due to the ring strain of fivemembered rings which results in a higher standard heat of formation.

The results show that the indirect electrochemical α -methoxylation of aliphatic ethers and acetals using tris(2,4-dibromophenyl)amine as a mediator is especially useful for the selective oxidation of aliphatic or allylic methylene groups in unsymmetrical ethers. Therefore large scale electrolyses of 1,2-dimethoxy ethane was performed using an undivided capillary gap cell with 6 bipolar graphite disc electrodes at a fixed current density of 3.3 A/dm^2 . The electrolysis of 1225 g (13.01 mol) 1,2-dimethoxy ethane (1g) in the presence of 1188 g methanol, 12.3 g sodium benzenesulfonate, 12.3 g sodium methoxide, an 12.3 g (17 mmol) tris(2,4-dibromophenyl)amine as mediator after consumption of 30 Faraday resulted in the formation of 2.24 mol methoxyacetaldehyde dimethylacetal (3g) together with 0.51 mol 1-methoxymethoxy-2-methoxy ethane (2g). 938 g (10.4 mol) of starting material could be recovered. Because this reaction was performed without potential control at a relatively high current density the selectivity in the formation of 3g dropped to 70 % and the regioisomer 2g was obtained with 16 % selectivity, while under potential control 3g was obtained as sole product (Table 1; entry 10). If the reaction was performed under identical conditions, however in the absence of the mediator, compounds 3g and 2g were isolated in a one to one ratio (selectivity 43 % : 42 %) and methyl orthoformate was formed with 15 % selectiviy. Current yields were comparable with the indirect method.

To compare the indirect electrochemical oxidation of 1,3-dioxolane ($\mathbf{8a}$) (entry 1, Table 2) with the direct anodic transformation, 1,3-dioxolane was electrolyzed under identical conditions only in the absence of the mediator at the same potential as in its presence (+ 1.5 V vs. Ag/-AgCl). As a result the obtainable current density was between two and ten times lower than in the mediated reaction and after consumption of 8300 As it became so small that no further reaction was possible. Only 9.1 mmol of product $\mathbf{9a}$ were formed in a current yield of 21 %. Instead in the indirect case after consumption of 19400 As 71 mmol $\mathbf{9a}$ were formed in a current yield of 71 % in one third of the time.

EXPERIMENTAL

M.p.s. were determined with a Reichert hot-stage microscope and are uncorrected. NMR Spectra were measured with Varian EM-360 and Bruker WH-90 instruments (solutions in deuteriochloroform, tetramethylsilane as internal standard). Mass spectra were obtained by GC/MS coupling using a Varian MAT 111 or a Finnigan MAT 1020 B instrument at 70 eV.

5802

Materials

Starting materials 1a, 1b, 1d-1g, 1i, and 2a were commercialy available. Their purity was controlled by g.l.c. and, if necessary, they were purified by distillation. 1c, 1h, 1k, 2b and 2c were prepared by standard procedures 11,12 . Tris(2,4-dibromophenyl)amine was synthesized by direct bromination of triphenylamine 13 . The purity was determined by g.l.c. on an OV 101 (1 % on Chromosorb W) column and by cyclic voltammetry. Acetonitrile (Merck, Aldrich, p.a.) was used as obtained, methanol (Merck, p.a.) was stored over molecular sieve (4 Å). Ethanol was distilled from tartaric acid while diethyl ether was stored over KOH and distilled from KOH and iron sulfate.

Equipment for Cyclovoltammetry

Cyclovoltammograms were obtained using a Wenking-Potentioscan POS-73 (Bank, Göttingen) together with a Hewlett Packard XY-recorder, model 7045 A. The analytical cell with cooling mantle, type EA 876-20, was obtained from Metrohom (Herisau, Switzerland). A glassy carbon disc ($\phi = 0.3$ cm) was used as working electrode while the counter electrode was a Pt-foil (0.3 cm^2). As reference electrodes either a Ag/AgNO₃ (0.1 M) system was used in acetonitrile electrolytes while in methanol a Ag/AgCl-electrode was applied.

Equipment for Preparative Electrolyses

Preparative electrolyses were performed with a Wenking-Potentiostat ST 72 (Bank, Göttingen) in combination with a digital coulometer based on votage to frequency conversion.

Electrochemical Cells

Cell A: Undivided beaker type cell (120 ml) with cooling mantle equipped with glassy carbon cylinder anode (Sigradur K, Sigri Elektrographit, Meitingen, inner ø 26 mm, height 50 mm), Pt-wire cathode, and Ag/AgCl-reference electrode. Temperature 40°C.

Cell B: Undivided capillary gap cell (ca. 4 1) equipped with 6 or 11 graphite disc electrodes with a gap of 0.5 mm. Flow of electrolyte maintained by pumping it at a rate of 200 1/h. Temperature 25 - 27 °C.

General Procedure for the Indirect Electrolysis of Ethers 1 and Acetals 8 in Methanol/Sodium Methoxide

Using cell A amounts in the range of 1.7 and 0.7 mmmol (1.17 g to 0.5 g) of the mediator tris (2,4-dibromo phenyl)amine are dissolved in a 90 ml mixture of methanol and the substrate (see Table 1 and 2) containing 1.5 g LiClO_4 as solvent supporting electrolyte. In several cases decaline (10 mmol) is added as internal standard for g.l.c. control during electrolysis. After application of 1.55 V vs. the Ag/AgCl-reference electrode it is electrolyzed at a current of 100 to 150 mA until the desired amount of charge (10000 to 50000 As) is consumed. For work-up of those products which do not easily undergo transacetalation methanol is evaporated from the electrolysis mixture, then 40 - 50 ml of dilute aqueous KOH (2 %) are added and continously extracted with <u>n</u>-pentane. In an optimized procedure ether is added to the electrolysis solution and water soluble components are extracted with a saturated K_2CO_3 aqueous solution.

After drying over K_2CO_3 the pentane or ether phases are distilled over a Fischer Micro-Spaltrohr column, and the purity of the fractions controlled by g.l.c.. In other cases the 2,4-dinitrophenyl hydrazones of the corresponding aldehydes or ketones are isolated and identified. Determination of the exact regioselectivity is performed by g.l.c. quantification using decaline as internal

standard. The quantities of employed substrates and reagents and the yield of the products are reported in Tables 1 and 2.

General Procedure for the Large Scale Indirect Electrolysis of 1g in Methanol/Sodium Methoxide

Using cell B amounts in the range of 17 and 20 mmol (12.3 - 14.5 g) of the mediator tris (2,4-dibromophenyl)amine are dissolved in a mixture of 1500 g lg, 1500 g methanol, 15 g sodium methoxide, and 15 g sodium benzene sulphonate. The electrolysis is performed at a fixed current density of 3.3 A/dm^2 under circulation of the electrolyte at a rate of 200 l/h and at a temperature of 25 -27°C. Work-up is performed as described above. The product distribution is determined by g.l.c.

The physical and spectroscopic data of the methyl carboxylate 7 respectively 12 and the trimethyl orthoformate 11a and products 3d and 9a compared well with those of the commercially available reference compounds. Dimethyl acetals 4 and 5 and methoxyacetalaldehyde dimethylacetal 3g are well known compounds. They were identified by comparison of their spectroscopic data and their g.l.c. retention times with those of authentical samples which are prepared by acetalation of the carbonyl compounds with trimethyl orthoformate using standard procedures.

Mixed acetals **3a**, **3b**, **3c**, **3e**, **3f**, **3h**, **3i** were identified by their ¹H-NMR and/or their MS-spectra. In addition, the acetals **3a**, **3b**, **3c**, **3h** and **3i** were transformed to the 2,4-dinitrophenyl hydrazones of the corresponding carbonyl compounds and compared with authentical samples.

 $1-\underline{n}-Butoxy-1-methoxybutane (3a): {}^{1}H-NMR (CDCl_3, 90 MHz); 5 = 0.77-1.1 (2 t, 6H, 2 CH_3), 1.14-1.78 (m, 8H, 4 CH_2), 3.32 (s, 3H, 0CH_3), 3.46 (t, 1H, 0CH_2), 3.56 (t, 1H, 0CH_2), 4.44 (t, 1H, 0-CH-0) ppm. - MS (70 eV): m/e = 159 (0.2 %, M⁺-1), 129 (7), 117 (24), 103 (2), 87 (51), 73 (16), 61 (100), 57 (31), 55 (19), 45 (37), 41 (17).$

2-Methoxy-2- $\frac{1}{2}$ -propyloxypropane (**3b**): MS (70 eV): m/e = 100 (1 %, M⁺- CH₃OH), 99 (2.5), 73 (100), 59 (8), 55 (11), 43 (21).

3-Allyloxy-3-methoxy-1-propene (3c): ¹H-NMR (CDCl₃, 90 MHz): $\delta = 3.32$ (s, 3H, OCH₃), 3.98-4.14 (m, 2H, CH₂0), 4.83-4.94 (dt, 1H, 0-CH-0), 5.06-5.57 (m, 4H, 2 CH₂=), 5.46-6.22 (m, 2H, 2 CH=) ppm. - MS (70 eV): m/e = 128 (0.03 %, M⁺), 127 (0.27), 101 (8), 97 (20), 87 (6), 71 (92), 59 (7), 55 (18), 41 (100).

2-Methoxytetrahydropyran (3e): 1 H-NMR (CDCl₃, 90 MHz): δ = 1.36-2.11 (m, 6H, 3 CH₂), 3.40 (s, 3H, OCH₃), 3.44-4.11 (m, 2H, CH₂O), 4.51 (m, 1H, O-CH-O) ppm. - MS (70 eV): m/e = 116 (6 %, M⁺), 115 (20), 88 (10), 85 (100), 71 (6), 67 (10), 61 (98), 58 (52), 56 (78), 55 (22), 43 (22).

2-Methoxy-1,4-dioxane (3f): ¹H-NMR (CDCl₃, 90 MHz): $\delta = 3.47$ (s, 3H, OCH₃), 3.56-4.2 (m, 6H, 3 CH₂), 4.48 (t, 1H, 0-CH-0) ppm. - MS (70 eV): m/e = 118 (24 %, M⁺), 88 (62), 87 (19), 61 (100), 559 (8), 58 (35), 57 (11), 45 (12), 43 (44).

 $3-\underline{n}-Butyloxy-3-methoxy-1-propene$ (**3h**): MS (70 eV): m/e = 131 (3 %, M⁺-C₂H₃), 127 (8), 101 (15), 71 (100), 61 (10), 57 (20), 55 (5), 43 (24).

<u>t</u>-Butoxy-methoxy-methane(31): ¹H-NMR (CDCl₃, 90 MHz): $\delta = 2.30$ (s, 9H, C(CH₃)₃), 3.55 (s, 3H, OCH₃), 3.85 (s, 2H, O-CH₂-O) ppm. - MS (70 eV): m/e = 103 (25 %, M⁺-CH₃), 87 (2), 73 (19), 57 (44), 45 (100), 43 (5), 41 (16).

4-Methoxy-1,3-dioxolane (10a) was only identified by its MS spectrum which was obtained by GC/MS coupling: MS (70 eV): m/e = 104 (15 %, M^+), 103 (16), 75 (9), 73 (12), 45 (60), 44 (100), 43 (31).

<u>Acknowledgements</u>. Financial support by the Arbeitsgemeinschaft industrieller Forschungsvereinigungen, by the Fonds der Chemischen Industrie, and by BASF Aktiengesellschaft is gratefully acknowledged.

REFERENCES

- 1. T. Shono, Y. Matsumura, J.Am.Chem.Soc. 91, 2803 (1969).
- 2. J. Cramer (Hoechst AG), Ger.Offen. 3000243 (1981); Chem.Abstr. 95, 140904j (1982).
- 3. J.W. Sheeren, H.J.M. Goossens, A.W.H. Top, Synthesis 1978, 283.
- 4. H.G. Thomas, A. Schmitz, Synthesis 1985, 31.
- 5. B. Wermeckes, F. Beck, H. Schulz, Tetrahedron 43, 577 (1987).
- 6. B. Wermeckes, F. Beck, Electrochim. Acta 30, 1491 (1985).
- E. Steckhan, <u>Angew.Chem.</u> 98 681 (1986); <u>Angew.Chem., Int.Ed. Engl.</u> 25, 683 (1986); <u>Top.Curr.</u> <u>Chem.</u> 142 (in press).
- 8. K.H. Grosse Brinkhaus, E. Steckhan, W. Schmidt, Acta Chem. Scand. B 37, 499 (1983).
- 9. K.H. Grosse Brinkhaus, E. Steckhan, D. Degner, <u>Tetrahedron</u> 42, 553 (1986).
- 10. L. Eberson, Adv. Phys. Org. Chem. 18, 79 (1982).
- 11. H. Meerwein, in <u>Methoden der organischen Chemie</u> (Houben-Weyl-Müller, Ed.), 4 th ed., Vol. VI/3, p. 31, Thieme, Stuttgart 1965.
- 12. Organikum, 15th ed., p. 490, VEB Deutscher Verlag der Wissenschaften, Berlin 1977.
- 13. W. Schmidt, E. Steckhan, Chem.Ber. 113, 577 (1980).