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Catalytic Electrochemical Reduction of 1,2-Dibromocyclohexane Derivatives at Carbon Electrodes Modified with Cobalt Porphyrin Siloxane Films

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Dedicated to Professor Henning Lund on the occasion of his 70th birthday.

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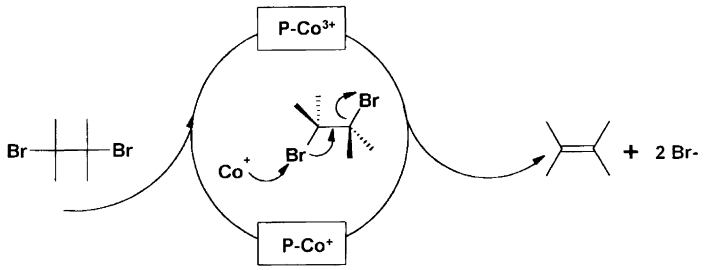
The electrochemical reduction of *trans*-1,2-dibromocylohexanes is catalyzed effectively by Co(II) porphyrins at potentials ≥ 1 V positive of the uncatalyzed case. With siloxane films on carbon electrodes containing a specially designed, diethylene glycol spacered Co-porphyrin, high catalytic currents are observed. Preparative current yields of 65% on a mmol scale are obtained with average calculated catalyst turnover numbers of ca. 5000.

Mediator-catalyzed electrochemistry can reduce overpotentials and enhance selectivity and many preparative electrochemical reactions using mediators have been described.[1,2] It seems reasonable to confine mediator systems at the electrode surface, but surprisingly few examples have been published[3–5] although theories[6,7] predict that appreciable current densities are possible with mediators attached to polymer films at electrodes. It is necessary, however, that a number of parameters is valid; i, the mediator system must be chemically stable in both oxidation states; ii, the mediator concentration in the film must allow rapid electron hopping between next neighbours; iii, the polymer film must allow free motion of mediator sites, supporting electrolyte ions, substrates and products.

Several examples of redox polymer electrochemistry employing nitroxides at tailored polyacrylates have recently been published.[4,8] In our laboratory a siloxane-based nitroxide redox polymer at carbon electrodes has been developed.[9,10] Here we report a covalently bound porphyrin siloxane film as a redox mediator. Cobalt(II) octaethylporphyrin has been shown to be an excellent catalyst for the reductive debromination of vicinal bromides (Scheme 1) and it turns out that the catalytic step is an *inner-sphere* process.[11] This type of catalysis is particularly valuable because such reactions are often specific for a class of compounds, and large reductions of overpotentials can be expected due to rapid kinetics.[12]

Assembly of the siloxane-porphyrin films. The basic unit of the siloxane film is the oligomeric structure Me_3Si–$(SiHMe)_{\approx 60}$–$SiMe_3$.[9] The attachment of side chains is



Scheme 1.

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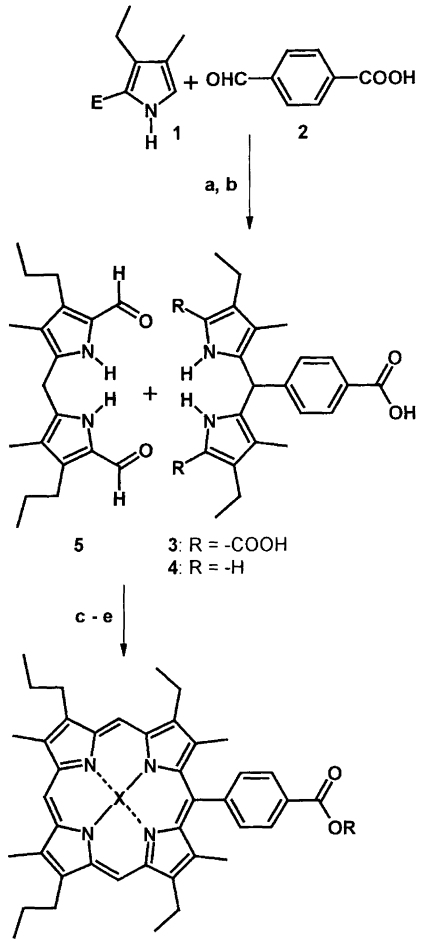
very easy by Pt-catalyzed addition of the oligomer Si–H bonds to allyl terminated reagents.[13,14] In order to achieve easy diffusion in the polymer it is necessary to bind the catalytic centers by means of spacers, preferably with an oligothylene bridge. In our earlier work we found that up to 10% of mediator functions are sufficient but an additional number of pendant oligoethylene glycol chains with terminal methoxy groups is useful in order to enhance the diffusivity of the films. The remaining free SiH sites do not interfere with the electrochemistry. They may, however, serve as linkers to –OH groups at the carbon surface and for some cross-linking of the oligomers.

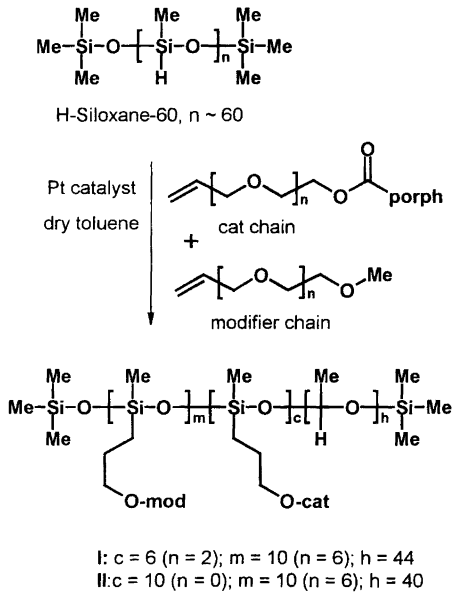
The porphyrin to be attached to the silicon film was synthesized by a dipyrrolylmethane condensation in analogy to a protocol of Sessler *et al.* (Scheme 2).[15] The dipyrrolylmethane **3** was obtained by condensation of **1**[16] with terephthalaldehyde followed by bis-decarboxylation and cyclocondensation with the known dipyrrolylmethane dialdehyde **5**[17] and oxidation of the tetrahydroporphyrin. The esterification of the porphyrin-carboxylic acid **7** with allylic alcohol and monoallyl diethylene glycol using various coupling reactions turned out to be difficult owing to rapid formation of the anhydride, which itself was unreactive towards the alcohol. However the esters **9a** and **9b** were available in acceptable yield by the method of Mukaiyama.[18]

Of the many possible variations of the modified siloxane[9] only two variants **I** and **II** are described here which gave the best results (Scheme 3). A spacer length of two ethylene glycol units is sufficient for good performance. Toluene solutions of **I** or **II** were used directly to coat the carbon materials. As representative substrates for the study of the performance of the porphyrin-modified electrodes 1,2-dibromocyclohexane (DBCH) and (±)-4-phenyl-*trans*-1,2-dibromocyclohexane **11** were chosen, the latter being obtained by bromination of 4-phenylcyclohexene with pyridinium tribromide (Scheme 4).[19] The phenyl group of **11** is equatorial and the two bromine substituents are in a diaxial disposition as shown by small coupling of the two of the CHBr protons. This is very similar to the stereochemical relationship of the bromination of the corresponding *tert*-butylcyclohexane derivative.[20]



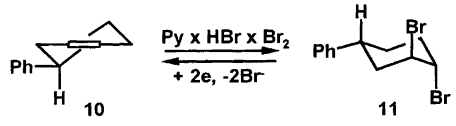
6: R = CH_3, X = 2H
7: R = H, X = 2H
8: R = H, X = Co
9a: R = $(CH_2CH_2O)_2$-CH_2-CH=CH_2
9b: R = CH_2-CH=CH_2

Scheme 2.



I: c = 6 (n = 2); m = 10 (n = 6); h = 44
II: c = 10 (n = 0); m = 10 (n = 6); h = 40

Scheme 3.



Scheme 4.

Table 1. Homogeneous catalysis of the reduction of **11** by various Co^{II} porphyrins.[a]

Porphyrin	TPP	OEP	**8**	OMOP
$E_{1/2}$/V	−0.77	−0.98	−0.97	−1.25
Conc./mmol dm^{-3}	0.5	0.1	0.5	0.2
i_p (porph)/A	4.8	1.5	3.6	5.0
i_{cat}/i_{porph} sat	7.3	26	10.7	7.6

[a] $E_{1/2}$ (**11**) = −2.05 V (DMF, vs. SCE, 0.1 V s^{-1}).

Results

(a) *Catalysis of dibromide reduction using porphyrins in homogeneous solution.* The cobalt(II) complexes of tetraphenylporphyrin (TTP), octaethylporphyrin (OEP), the functionalized porphyrin **8** and octamethoxypophyrin (OMOP)[21] were tested as catalysts in the debromination of **11**. As can be seen from Table 1, the catalytic efficiency of the functionalized porphyrin **8** is in the same range as other porphyrins with an overpotential lowering of 1 V. In Fig. 1a,b the catalytic activity of dissolved OEP (saturated, ca. 1×10^{-4} M) towards DBCH in DMF is shown. The catalytic enhancement is about 35-fold.

In contrast with siloxane films with incorporated nitroxide catalyst[9] only very thin films of porphyrin modified films can be obtained, but these films show a high activity. Thus, a spin-coated film of **II** at a glassy carbon electrode with a current peak of only 0.5 μA, too small to be visible in Fig. 1c, gives rise to a huge catalytic wave at saturation of catalysis corresponding of a 1400-fold enhancement of the catalyst wave. Thus, at comparable substrate concentration and at the same electrode area the catalytic efficiency is further enhanced by a factor of 40 compared with the dissolved catalyst.

(b) *Preparative catalysis on a millimole scale.* Cylindrical cathodes of impregnated carbon felt (4 cm^2 geometrical area, see the Experimental section) in CH_3CN–0.1 M Bu_4N^+ ClO_4^- gave cyclic voltammograms as shown in Fig. 1d, which are characterized by a wide capacitive current gap. However, the reversible peak pair of the catalyst is well developed with a peak-to-peak distance of 140 mV. The integration of the mean peak areas gives a value for the accessible redox centers of roughly 0.1 μmol of catalyst.

Five batches of **11** (0.4 mmol in 8 ml catholyte) were electrolyzed at −1.3 V. After 30–40 min the calculated amount of 77 mC had passed and the microelectrolyses were stopped. The initial current was of the order of 10 mA but it dropped fairly rapidly to about a fifth of this value at the end. The contents were analyzed by GC and ^1H NMR spectroscopy. The current yield of **10** was 65 ± 10% and it was shown by NMR analysis that the shortfall was unreacted **11**. In addition some tributylamine was detected which stems from the supporting electrolyte, possibly also catalytically formed by the basic cobalt(I) species.

With DBCH the results were quite similar, although

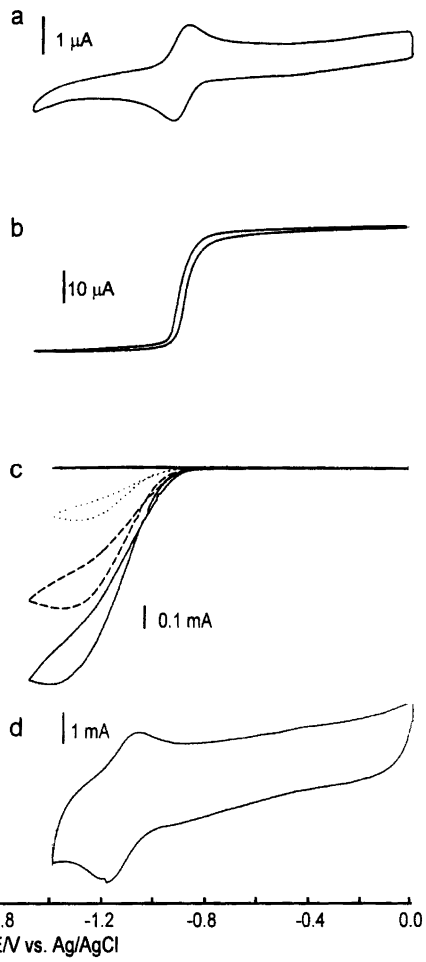


Fig. 1. (a) Cyclic voltammogram (CV) of a 10^{-4} M solution of OEP-Co^{II}-complex; (b) CV of OEP-Co^{II}-complex in the presence of 5.0 mM DBCH; (c) CV of a glassy carbon disk with spin coated film **II** in the presence of increasing concentrations (2.5, 7.5, 12.5×10^{-3} M) of **11** (the porphyrin peak of **II** is only 0.5 μA); (d) CV of a 4 cm^2 carbon felt electrode impregnated with film **I**.

it seems that some of the volatile olefin was lost. Interestingly, with DBCH both types of silicon matrix, **I** and **II**, were active, whereas with sterically more demanding **11** only **I** was active in the catalytic electroreduction. This means that the sterically more demanding **11** cannot properly approach the catalyst sites of **I**. This again shows the importance of the of the spacer groups between the polymer chain and catalytic center.

The spent electrodes were no longer active and cyclic voltammograms after use gave no signals. Amazingly though, the average turnover number of the catalyst species, which can be calculated from the integration of the total active catalyst and the reacted substrate was 4000–6000. These results and our previous work show, as predicted, that electrodes modified with polymer bound catalytic layers can sustain large electrolysis currents when the diffusivity of the polymer film is high. Presently we are working on silicon coatings that are still

more solvent-like and, and on the other hand, are covalently bound to the electrode surface.

Experimental

α,α-Bis(3-methyl-4-ethyl-2-pyrrolyl)toluene-4,5',5''-tricarboxylic acid **3**. A solution of ethyl 3-ethyl-4-methylpyrrole-2-carboxylate **1**[16] (1.81 g, 10 mmol), terephthalaldehyde (0.75 g, 5.00 mol) in EtOH (50 ml) and 12 M HCl (0.8 ml) was refluxed for 1 h. The solvent was stripped off to give a crystalline 1:2 mixture of the di- and tri-ester of **3**, m.p. 84–100; 2.25 g (96%). The mixture was refluxed for 18 h in a solution of NaOH (0.5 g, 13 mmol) in EtOH (15 ml) and water (0.5 ml). After removal of the solvent, the remainder was dissolved in H_2O (10 ml) and the product was precipitated with HOAc. 0.99 g (89%), m.p. 157–160 °C. $C_{24}H_{26}N_2O_6$ (438.2) calcd. C 65.72, H 5.96, N 6.40; found C 64.91, H 6.25, N 6.48. IR: $\tilde{\nu}$=3420, 3000–3400, 1660 cm^{-1}. ^1H NMR (250 MHz, DMSO-d_6–TMS): δ 1.05 (t, 6 H, CH_2CH_3, 7.0 Hz), 2.01 (s, 6 H, CH_3), 2.59–2.74 (m, 4 H, CH_2), 5.75 (s, 1 H, CH), 7.03–7.87 (AA'BB', 4 H, J=8.2 Hz, C_6H_4), 11.1 (s, 2 H, NH), 12.4 (br s, 3 H, COOH).

α,α-Bis(3-methyl-4-ethyl-2-pyrrolyl)toluene-4-carboxylic acid **4**. Compound **3** (1.75 g, 4.00 mmol) was added to boiling ethanolamine (20 ml) under an Ar atmosphere and heating was continued for 5 min. The hot mixture was immediately poured into ice–water (100 ml) and 2 M HCl was added to reach pH 8. The product precipitated as a tan solid. 1.26 g (90%), m.p. 75–78 °C. IR (KBr): $\tilde{\nu}$=3400(s), 3000–3330, 1690. ^1H NMR (250 MHz, DMSO-d_6–TMS): δ 1.09 (t, 6 H, J=7.1 Hz, CH_2CH_3), 1.84 (s, 6 H, CH_3), 2.38 (q, 4 H, CH_2CH_3), 5.5 (s, 1 H, CH), 6.37 (d, 2 H, 5',5''-H), 7.08–7.85 (4 H, AA'BB', J=8 Hz), 9.7 (2 H, br s, NH).

Methyl(2,8-diethyl-3,7,13,17-tetramethyl-12,18-dipropyl-5-phenylporphyrin)-4'-carboxylate **6**. To a solution of bis(3-methyl-4-propyl-5-formyl-2-pyrrolyl)methane **5**[17] (1.10 g, 3.50 mmol) and **4** (1.30 g, 3.70 mmol) in CH_3OH–THF (150/75 ml) was added 70% aqueous $HClO_4$ and the mixture was stirred in the dark for 18 h. The dark red solution was neutralized with aqueous $NaHCO_3$. Tetrachloro-1,2-benzoquinone (0.66 g, 5.3 mmol) in $CHCl_3$ was added to the organic phase with stirring and after 1 h the solvent was evaporated off. To the brown residue CH_3OH (350 ml) and H_2SO_4 were added and the mixture was stirred for 3 days at r.t. The solution was extracted with $CHCl_3$ (3 × 150 ml). Traces of acid were removed by careful extraction with aqueous $NaHCO_3$. **6** was isolated by chromatography (SiO_2–$CHCl_3$) and recrystallisation ($CHCl_3$–hexanes), 675 mg (30%), m.p. 283–284 °C. $C_{42}H_{48}N_4O_2$ (640.5) calcd. C 78.70, H 7.50, N 8.70; found 77.62, H 7.31, N 8.53. IR (KBr): $\tilde{\nu}$=3320, 3000–2900, 1730 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$–TMS): δ −3.30, −3.21 (2 s, NH), 1.29 (t, 6 H, $CH_2CH_2CH_3$), 1.74 (t, 6 H, CH_2CH_3), 2.34 (q, 4 H, CH_2CH_3), 2.42 (s, 6 H, 13,17-CH_3), 3.62 (s, 6 H, 3,7-CH_3), 3.95–4.04 (m, 8 H, $CH_2CH_2CH_3$, $CH_2CH_2CH_3$), 4.12 (s, 3 H, $COOCH_3$), 8.40–8.44 (AA'BB', J=8.1 Hz), 9.93 (s, 1 H, 15-H), 10.15 (s, 2 H, 10,20-H).

(2,8-Diethyl-3,7,13,17-tetramethyl-12,18-dipropyl-5-phenylporphyrin)-4'-carboxylic acid **7** *and* Co^{II} *complex* **8**. Compound **6** (130 mg) was dissolved in EtOH (30 ml) and aqueous KOH (38.0 mg, 2 mmol, 1.3 ml) and the mixture was heated at reflux for 5 h. The solvent was then removed and the residue was taken up in H_2O neutralized with HOAc and extracted into ether, 125 mg (99%) red solid, **7**, m.p. >320 °C. IR (KBr): $\tilde{\nu}$=3300, 3280, 1690. UV–VIS (MeOH): λ_{max}/nm (log ε)=408 (5.20), 502 (4.11), 536 (3.81), 570 (3.80), 623 (3.29). ^1H NMR (250 MHz, DMSO-d_6–TMS): δ −3.52, −3.39 (2 s, NH), 1.25 (t, 6 H, $CH_2CH_2CH_3$), 1.71 (t, 6 H, CH_2CH_3), 2.27 (q, 4 H, CH_2CH_3), 2.39 (s, 6 H, 13,17-CH_3), 3.62 (s, 6 H, 3,7-CH_3), 3.96–4.06 (m, 8 H, $CH_2CH_2CH_3$, $CH_2CH_2CH_3$), 8.15–8.37 (AA'BB', J= 8.2 Hz), 10.04 (s, 1 H, 15-H), 10.22 (s, 2 H, 10,20-H). Compound **7** (0.1 mmol) and $Co(acac)_2$ (76.8 mg, 3.00 mmol) were dissolved in $CHCl_3$ (30 ml) and refluxed for 2 h. **8** was isolated and purified by chromatography (SiO_2–CH_2Cl_2), 55 mg (86%), bright red microcrystalline powder, m.p. >320 °C. $C_{41}H_{44}CoN_4O_2$ (682.9) calcd. C 72.00, H 6.46, N 8.20; found 70.78, H 6.69, N 8.07. UV–VIS ($CHCl_3$): λ_{max}/nm (log ε)=395 (5.30), 519 (4.01), 554 (4.19). MS (FAB): M=683.

Co^{II} complexes of (2,8-diethyl-3,7,13,17-tetramethyl-12,18-dipropyl-5-phenylporphyrin)-4'-carboxylic acid 2-allylethoxyethoxy ester **9a** *and (2,8-diethyl-3,7,13,17-tetramethyl-12,18-dipropyl-5-phenylporphyrin)-4'-carboxylic acid allyl ester* **9b**. The cobalt complex **8** (70.0 mg, 0.10 mol) dissolved in CH_2Cl_2 (4 ml) containing dry tributylamine (57 µl, 0.24 mmol) and diethyleneglycol monoallyl ester was added to a suspension of 2-chloro-*N*-methylpyridinium iodide in CH_2Cl_2 (1 ml) and the mixture was refluxed for 20 h. The cold solution was washed with H_2O (2 × 2 ml), dried and concentrated. Chromatography (SiO_2–Et_2O) yielded 15.4 mg (19%) of **9a**, red microcrystalline solid, m.p. 104–106 °C. FAB-MS: $C_{48}H_{56}CoN_4O_4$ (811.9), MH^+=813. In a similar way allyl ester **9b** was obtained in 20% yield, m.p. 269–273 °C.

4-Phenylcyclohexene **10**. 4-Phenylcyclohexanol (7.0 g, 40 mmol), obtained in 97% yield as a 1:8 *cis–trans* mixture (according to NMR spectroscopy), by reduction of 4-phenylcyclohexanone (Aldrich) with $LiAlH_4$ in ether, was heated at 200 °C with $K_2S_2O_3$ (6.4 g) with distillation of the product. Redistillation at 0.1 mmHg gave **10** as a colorless oil, 4.54 g (75%), b.p. 130 °C at 0.1 mmHg (Lit.[22] 112–115 °C/0.1 mmHg). ^1H NMR: δ 1.50–2.32 (m, 6 H), 1.35–2.32 (1 H), 5.76 (s, 2 H), 7.15–7.15 (m, 5 H).

1,2-t-Dibromo-4c-phenylcyclohexane **11**. To a solution of **10** (4.50 g, 29 mmol) in $CHCl_3$ (30 ml), pyridinium bromide perbromide (9.60 g, 30 mmol) was added in small portions followed by 2 h of reflux. The solution was then washed with H_2O, dried with Na_2SO_4. The solvent was removed and **11** was obtained by distillation of the residue as a slightly yellow oil: 6.9 g (76%), b.p. 145 °C (0.1 mmHg). IR (KBr): $\bar{\nu}$ = 3060–3020, 2900–2830, 650 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.77–1.83 (m, 1 H, $H5_{eq}$), 2.18–2.01 (m, 3 H, H6, $H5_{ax}$), 2.57–2.71 (symm. m, 2 H, 3.12–3.23, H3), 3.11–3.24 (symm. m, 1 H, H4), 4.68, 4.90 (2 narrow m, 2 H, H1,H2), 7.15–7.40 (m, 5 H, C_6H_5) + ≤5% of the 1,2*t*,4*t*-isomer. EI-MS: 320/318/316 (M^+, 52%), 237, 239 ($M^+ - Br$, 43%), 157 ($M^+ - Br$, $-HBr$, 67%), 104 ($PhCH{=}CH_2^+$, 74%), 91 ($C_6H_7^+$, 100%).

Preparation of the porphyrin modified siloxane oligomers **I** *or* **II**. Under rigorously dry conditions, a solution of H-Siloxane-60 (4.7 ml, 1.3 mmol), the desired stoichiometric amount of catalyst and modifyer chain and VP 1509 toluene solution (2 ml), both supplied by WACKER, in toluene (0.5 ml) was heated at 95 °C for 18 h. This solution was used directly for spin-coating or soaking.

Electrochemical methods. A PAR model 273 was used for cyclic voltammetry and preparative electrolyses. The reference electrode for DMF–TEAP solutions was a miniature home-made SCE which was separated from the analyte by a Vycor plug. ($E_{ferrocene} = 298 \pm 5$ mV); for CH_3CN solutions an Ag/AgCl electrode was used, $E_{Fc} = 285 \pm 5$ mV). The analytical working electrode was a 0.28 cm^2 glassy carbon disk on which the polymer films were spin-coated. The micropreparative cell was a 10 ml water jacketed cylindrical Teflon-topped cell with the suitable bores. Carbon felt pieces (20 × 20 × 5 mm) were soaked with 150 ml of the polymer solution and dried under N_2. The modified felt cathode was glued to the inner area of a glass cylinder with silver epoxy together with the Pt wire lead. The anode was a Pt wire in a glass frit placed in the center of cylinder. **11** (0.4 mmol, 126 mg) was electrolyzed in CH_3CN–0.1 M TBAP at 1.3 V vs. SCE until the calculated amount of 77.8 C had been consumed. The amount of **10** was determined by GC (SE-30) using *n*-decane as tracer; the ratio of **10** and unconsumed **11** was determined independently by NMR spectroscopy after extractive work-up.

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