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# *Use of ion exchange membranes in preparative organic electrochemistry. I. Anodic methoxylation of some olefins*

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Electro-oxidation of a solution of an olefin in methanol can be carried out, in the absence of supporting electrolyte, at a platinum grid lying on a cationic exchange membrane. 1,1-diphenylethylene, *trans*-stilbene, cyclohexene, acenaphthylene, 2-methyl-3-phenylindenone, and furan have been investigated. The corresponding dimethyl ethers are generally the main products of electrolysis; the yield depends on the olefin structure. Up to 80% of 2,5-dimethoxy-2,5-dihydrofuran is reached from furan.

The results are compared to those obtained by classical electrochemical processes.

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## 1. Introduction

A preliminary note devoted to the use of ion exchange membranes in preparative organic electrochemistry has previously been published [1]. The main interest of the new process described is to perform electrolytic oxidation or reduction on a solution of an organic substance without any supporting electrolyte.

The membrane divides the electrolysis cell into two compartments:

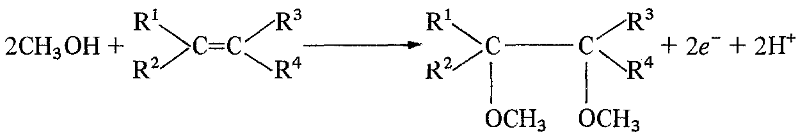
i. the working compartment containing a solution of the organic substrate to be oxidized or reduced, the working electrode being a metallic grid which lies flat on the membrane.

ii. an auxiliary compartment containing a supporting electrolyte dissolved in a polar solvent such as water, and a counter electrode.

Moreover, the nature of the membrane is chosen so that the ions produced at the working electrode are removed by transfer through the membrane towards the auxiliary compartment.

Examples were given [1] of: i. the two-electron reduction of a 1,2-dibromo compound to the corresponding ethylene with elimination of bromide ions through an anionic membrane and ii. the two-electron oxidation of hydrazobenzene to azobenzene with elimination of protons through a cationic membrane. In both cases, chemical and current yields were fairly good, but the current intensity was rather low.

In order to avoid such a disadvantage, we investigated electrochemical reactions involving the solvent. We report in the present paper results obtained in attempts at electrosynthesis of dimethoxylated compounds by oxidizing solutions of olefins in methanol according to the reaction:



$$2CH_3OH + R^1R^2C{=}CR^3R^4 \longrightarrow R^1R^2C(OCH_3){-}C(OCH_3)R^3R^4 + 2e^- + 2H^+$$

The investigated olefins are collected in Table 1.

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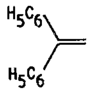
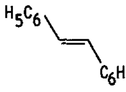
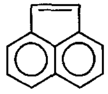
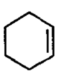
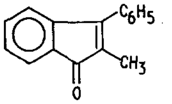
*Table 1. Investigated olefins*

| | | |
|---|---|---|
| 1. 1,1-diphenylethylene | 2. *trans*-stilbene | 3. Acenaphthylene |
|  |  |  |
| 4. Cyclohexene | 5. 2-methyl-3-phenylindenone | 6. Furan |
|  |  |  |

## 2. Experimental details

### 2.1. *Electrolyses*

The electrolytic cell has been dealt with by Moinet *et al.* [2]. The electrolyses were performed with IONAC MC 3470 cationic membrane which had previously been prepared by immersion for a few days in aqueous 0.5 M sulphuric acid at room temperature.

The working electrode was a disc ($\phi$ 4 cm) cut from a platinum grid (thread: $\phi$ 0.06 mm; 1024 meshes per cm$^2$). The auxiliary cathode was a graphite bar and the auxiliary compartment contained sodium sulphate (0.1 M) in water.

The working compartment was filled with 80 cm$^3$ methanol and a constant 15 V voltage was applied between the electrodes. The current intensity was then about 150 mA. The olefin was then introduced to the anodic compartment. Intensity usually fell and, after a few minutes, reached a value which depended on the olefin: 1. 25 mA; 2. 90 mA; 3. 40 mA; 4. 65 mA; 5. 70 mA; 6. almost unchanged intensity.

The electrolytic cell works as shown in Scheme 1 and the experiment was stopped after the desired amount of electricity had passed through the cell.

### 2.2. *Identification of products for the different oxidations*

*2.2.1. 1,1-Diphenylethylene.* Methanol was evaporated under reduced pressure. The residue was poured into ether; the ethereal solution was washed with water and then dried over sodium sulphate. After the ether had been removed, the oily residue was analysed as follows:

GLC (SE 30 column; 1.4 m; 1/8 inch; 150° C, carrier gas $N_2$) showed the presence of unreacted olefin, benzophenone and 1,1-diphenyl-1,2-dimethoxyethane. Benzophenone was also characterized by its IR spectrum. 1,1-Diphenyl-1,2-dimethoxyethane was identified by means of mass spectroscopy

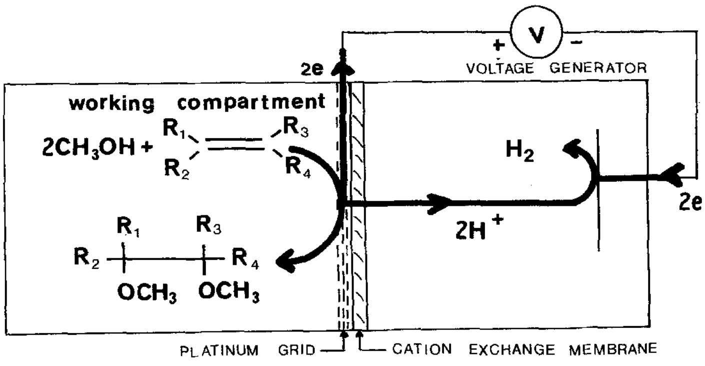


*Fig. 1.* A scheme of a typical electrochemical cell.

(source: temperature 180° C; energy 70 eV; emission intensity 100 $\mu$A) $M^+ = 197, 165, 105, 77$ and NMR ($CDCl_3$): $\delta$ (ppm): 7.3 (m, 10, $C_6H_5$); 4.07 (s, 2, $CH_2$); 3.28 (s, 3, $OCH_3$); 3.21 (s, 3, $OCH_3$); no mass nor NMR spectral data previously given.

Amounts of products were determined both from GLC and NMR data.

*2.2.2. trans-Stilbene.* The amount of remaining stilbene was first determined from GLC (Carbowax 20 M 10%; 200° C; carrier gas $N_2$; $P = 2.3$ atm) measurements. Afterwards, the electrolysis mixture was treated by ether as described above. Products were separated by means of chromatography on a silica column eluted with hexane and ethyl acetate (1/1), and characterized by their IR and NMR spectra. The *meso*-/DL-ratio of 1,2-diphenyl-1,2-dimethoxyethanes was determined from NMR spectra according to literature data [3].

*2.2.3. Acenaphthylene.* The electrolysis solution was first treated with ether and the extract fractionated by means of a silica column as in the preceding case. 1,2-Dimethoxyacenaphthenes were identified by comparison (GLC) with authentic samples synthesized [4] from the corresponding diols kindly provided by Professor Barba.

*2.2.4. Cyclohexene.* The crude electrolysis solution was analysed by means of combined GLC/Mass Spectroscopy (Carbowax 20 M 10%; 100° C, helium flow rate 24 $cm^3 min^{-1}$; mass spectra were obtained at 70 eV with an emission intensity of 100 $\mu$A, the ion source being at 170° C). Retention time = 1.7 min, $m/e = 112$, 1-methoxycyclohexane; $RT = 1.93$ min, $m/e = 98$, cyclohexanone; $RT = 3.06$ min, $m/e = 1.44$, dimethoxycyclohexane.

*2.2.5. 2-Methyl-3-phenylindenone.* After evaporation of the methanol, the products were identified by NMR from literature data [5] and amounts were confirmed from GLC (Carbowax and SE 30 columns) measurements after comparison with authentic samples.

*2.2.6. Furan.* 2,5-Dimethoxy-2,5-dihydrofuran was characterized by means of NMR [6] and amount measurements were performed by GLC (Carbowax 20 M 10%; 120° C; carrier gas $N_2$; $P = 1.5$ atm) by comparison with authentic commercial (Aldrich) sample.

## 3. Results and discussion

The main results are summarized in Table 2. From the data, it is clear that the results dramatically depend on the structure of the initial olefin.

The current efficiency for the dimethyl ethers is very low in the case of the electrolyses performed in the presence of cyclohexene, whereas it reaches a value higher than 75% in the case of furan and is close to 10–15% for the other ethylenic compounds.

In the same way, increasing the duration of the electrolysis does not always increase the amount of dimethyl ether. It seems that, except in the case of furan, the dimethoxy compound is more sensitive to oxidation in methanol than the starting olefin. Products of higher states of oxidation, such as benzophenone with 1,1-diphenylethylene, benzaldehyde with trans-stilbene or cyclohexanone with cyclohexene are actually recovered at the end of the experiment. As a rule, the solution also contains other by-products as indicated in Table 2, and some probably polymeric methoxylated compounds that could not be analysed. However, no by-product was observed in the case of furan (the difference between introduced and recovered amounts of substrate will be explained further).

In order to assess the value of our process, the results have to be compared with previously published electrochemical methoxylations of olefins performed with classical electrolysis processes.

An experiment performed by Inoue and Tsutsumi [7] using 1,1-diphenylethylene and sodium methoxide as supporting electrolyte afforded current and chemical yields of about 22%. Later, Kojima

*Table 2. Anodic dimethoxylation of olefins. Percentages are calculated as the ratio of the amount of product to the amount of olefin introduced (in moles)*

| *Olefin* | *Amount* (mole) | *Coulometry (Faradays per mole)* | *Recovered unreacted olefin* (%) | *Dimethyl ether* (%) | *Other identified products* |
|---|---|---|---|---|---|
| 1,1-diphenylethylene | $10^{-2}$ | 4 | 60 | 24 | 10% benzophenone |
| 1,1-diphenylethylene | $10^{-2}$ | 12 | 26 | 16 | 12% benzophenone<br>3% $(C_6H_5)_2C(OCH_3)CH(OCH_3)_2$ |
| trans-stilbene | $1/3 \times 10^{-2}$ | 3.5 | 50 | 22[a] | 9% benzaldehyde |
| trans-stilbene | $1/3 \times 10^{-2}$ | 5.2 | 32 | 26[a] | 5% benzaldehyde |
| Acenaphthylene | $10^{-2}$ | 2.9 | 51 | 15 | |
| Acenaphthylene | $2 \times 10^{-2}$ | 4.7 | 39 | 10 | |
| Cyclohexene | $2 \times 10^{-2}$ | 3.9 | | $< 4$ | 1-methoxycyclohexene, cyclohexanone |
| 2-methyl-3-phenylindenone | $5 \times 10^{-3}$ | 2.7 | 52 | 22[b] | |
| 2-methyl-3-phenylindenone | $5 \times 10^{-3}$ | 3.6 | 49 | 20[b] | |
| Furan | $3 \times 10^{-2}$ | 1.9 | | 75 | |
| Furan | | 3.0 | 10 | 80 | |

[a] The DL/*meso* dimethyl ether ratio is about 1/4.
[b] The *cis*/*trans* dimethyl ether ratio is about 1/1.

*et al.* [8] showed that when electrolysis was run to almost complete consumption of 1,1-diphenylethylene, the amount of dimethyl ether obtained depended on the nature of the supporting electrolyte and chemical yield varied from 17 to 46%.

The case of trans-stilbene was also studied by Inoue *et al.* [9] who succeeded in obtaining 64% of dimethoxylated compounds when using sodium methoxide as supporting electrolyte. With ammonium perchlorate, the main product was benzaldehyde and the use of sodium bromide lead to a mixture resulting from brominations and methoxylations of the olefin [10].

The influence of the nature of the supporting electrolyte was also shown by Engels *et al.* [11] in the case of styrene derivatives.

Electrochemical dimethoxylations of acenaphthylene by Guirado *et al.* [4] and of the indenone olefin (5) by Orliac-Le Moing *et al.* [5] gave better results than the present experiments.

As for furan, the electrochemical reaction has been the object of numerous studies [12] and is used by BASF [13] on the industrial scale to synthesize 2,5-dimethoxy-2,5-dihydrofuran. In this case, current and chemical yields are good in both processes.

As a conclusion of this comparison, it appears that the results obtained with classical processes and those presented in this paper dealing with our membrane process are not basically different. This is encouraging because of the interest in obtaining the product in the absence of supporting electrolyte. So, the present process merits further study, embracing such factors as cell voltage, substrate concentration, nature of the membrane, etc. Nevertheless, because of the poor selectivity in the reactions with substrates (olefins) 1 to 5, furan 6 is the only substance among the ones tested here that may allow such a study.

However, two further conclusions can already be drawn from a more complete description of the experiments. In order to avoid the presence of inorganic ions in the working compartment, a supporting electrolyte for the auxiliary compartment must be chosen so that the transport number of the anion through the membrane is as low as possible. The transport number of sulphate ions in the experiments was determined as follows: after electrolysis, a sample of the methanolic solution was taken out of the working compartment and the amount of $SO_4^{2-}$ in the sample was measured by amperometric titration with $Pb^{2+}$ ions [14]. From the knowledge of the quantity of sulphate ions in the working compartment, $t^-$ was calculated as the ratio of the amount of electricity transported by these sulphate anions to the total amount of electricity which passed through the cell. Thus $t^-$ is close to $5 \times 10^{-3}$. This value means that the selectivity of the membrane under these conditions is very high (using aqueous solutions of sodium chloride, the transport number of $Cl^-$ is about $5 \times 10^{-2}$) and that sulphate is an excellent anion to work with in our experiments. Another quality of the sulphate ion is its low nucleophilicity. Indeed, performing an electrolysis of 1,1-diphenylethylene with chloride ion as anion in the auxiliary compartment led to a significant amount of $(C_6H_5)_2C(OCH_3)CH_2Cl$.

The second phenomenon to be pointed out is the slow decrease of the current intensity after the addition of the substrate to methanol. This can probably be attributed to the increase of the membrane electrical resistance because of its permeation by organic compounds. We could actually see the presence of 2,5-dimethoxy-2,5-dihydrofuran in the auxiliary compartment after the electrolysis of furan; this also explains the lack of an entry in the corresponding line of Table 2.

## Acknowledgement

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