## LITERATURVERZEICHNIS

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# 104. Synthesis of 1,4,9,12-Tetraoxa-dispiro[4.2.4.2] tetradeca-6,13-diene *via* an Electrochemical Path

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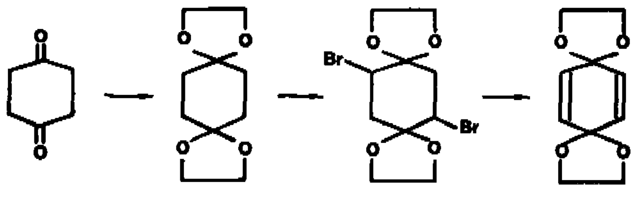
(11. III. 75)

*Summary.* The electrolysis of hydroquinone bis(2′-hydroxyethyl)ether (**3**) in alkaline methanol gives 8-[(2′-hydroxy)ethoxy]-8-methoxy-1,4-dioxa-spiro[4.5]deca-6,9-diene (**4**) which is converted to the title compound by treatment with traces of *p*-toluenesulfonic acid in ether at 0° in 50% overall yield.

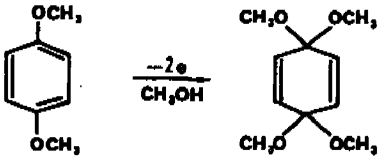
Recently *Dreiding* & *Raphael* [1] published an elegant synthesis of the title compound **1** from 1,4-cyclohexanedione *via* a bromination and a dehydrobromination step (*Scheme 1*).

*Scheme 1*



**1**

*Scheme 2*



**2**

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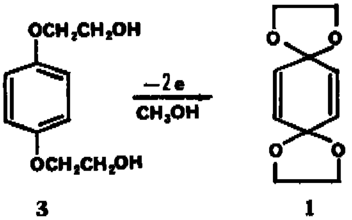
Until then *p*-benzoquinone diacetals had only been accessible by electrochemical alkoxylation, *e.g.* the formation of 3,3,6,6-tetramethoxy-1,4-cyclohexadiene (**2**) from *p*-dimethoxybenzene [2] [3] (*Scheme 2*).

*Weinberg* [4] cites as an intramolecular alkoxylation the formation of **1** from hydroquinone bis(2'-hydroxyethyl) ether (**3**) in 70% yield (*Scheme 3*) under identical conditions as in *Scheme 2*. Similar intramolecular alkoxylations had also been described on furan derivatives [5].

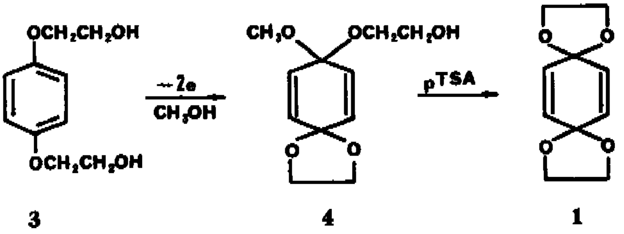
*Scheme 3*



In this paper we report our results on the electrochemical intramolecular alkoxylation reaction **3** → **1**, in particular the synthetic application of the electrolysis of **3** in methanol to yield **1**. We find that the reaction does not proceed as described in *Scheme 3*, and we discuss its mechanistic aspect.

Electrolysis of **3** in a 1% KOH solution in methanol gives 8-[(2'-hydroxy)ethoxy]-8-methoxy-1,4-dioxa-spiro[4.5]deca-6,9-diene (**4**) in almost quantitative yield (*Scheme 4*). The structure of **4** was deduced from its NMR.-, IR.- and mass spectrum. **4** could be converted to **1** by treatment with *p*-toluenesulfonic acid in ether in 50% yield.

*Scheme 4*

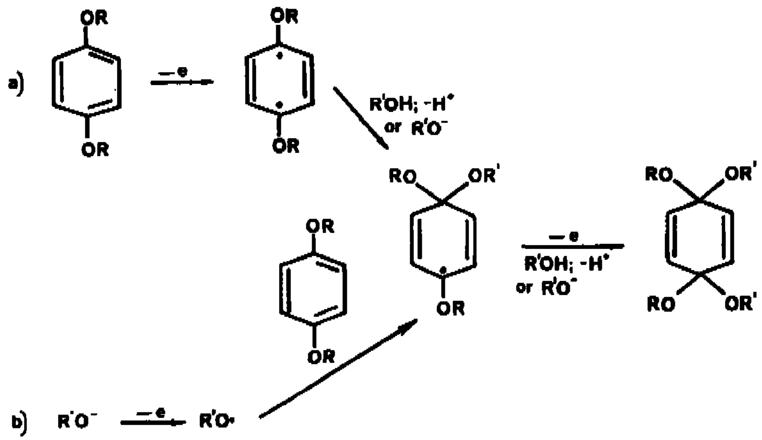


Direct electrochemical conversion of **3** → **1** was observed in other solvents as acetonitrile or tetrahydrofuran using tetrabutylammonium hydroxide as base. The yields were usually low (≈10–15%), and high voltages had to be applied.

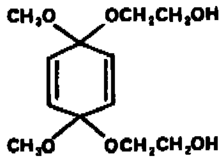
Two mechanisms for these electrochemical alkoxylations have been proposed [6] (*Scheme 5*). Path a) consists in direct oxidation of the hydroquinone ether to give the radical cation which reacts with the alcohol, followed by reoxidation and alcoholysis to the final product. In path b) the primary step is the oxidation of the alcoholate to give an alkoxyl radical which then reacts with the hydroquinone, the consequent steps then being the same as mentioned in path a).

The fact that in the electrolysis of **3** in methanol **4** is formed almost exclusively (less than 5% of **1** are present after electrolysis), and specially that no formation of

*Scheme 5*



the bis-mixed acetal **5** is observed indicate that two essentially different oxidation steps do take place, thus strongly favoring reaction path b) in *Scheme 5*. Oxidation of the alcoholate anions would give mainly methoxyl radicals, while in the anodical oxidation of the radical intermediate intramolecular alkoxylation, *i.e.* formation of **4** should occur preferentially.



**5**

In addition preliminary investigations by cyclic voltammetry support this assumption. Full results will be published in a forthcoming article.

## Experimental Part

The electrolysis apparatus consisted of a 500 ml cell. The electrodes consist of a cylindrical nickel cathode with a surface area of 195 cm$^2$ surrounded symmetrically by 3 platinum anodes with a total surface area of 130 cm$^2$, with a distance of 0.5–1.0 cm between cathode and anode. The power supply is a d.c. adjustable source. The current intensity was maintained constant at 3.25 A (current density: 0.25 A/cm$^2$).

*Preparation* of **4**. 10 g (0.05 mol) **3** were electrolyzed in a solution of 3,2 g KOH in 320 ml Methanol at 10°. After about 3h 10.7 Ah corresponding to 400% of the theoretical current amount were consumed (tension: 12–15 V). The solution is then diluted with 1 l $H_2O$ and extracted 5 times with 100 ml $CHCl_3$. The organic phase is dried over $MgSO_4$ and the solvent evaporated at room temperature. The residual light yellow liquid is practically pure **4**, 10.7 g (93%). – NMR. ($CDCl_3$) ($\delta$): 6.02 *s* (4H), 4.05 *s* (4H), 3.65 *s* (4H), 3.28 *s* (3H), 2.65 (O*H*) (1H). – IR. ($CCl_4$): 3600, 3500, 3050 cm$^{-1}$. – MS. 228 ($M^+$ weak), 167 ($M^+$ -$OCH_2CH_2OH$).

*Preparation* of **1**. 10.7 g **4** are dissolved in 25 ml $Et_2O$ and cooled to 0°. A solution of 10 mg *p*-toluenesulfonic acid in 5 ml $Et_2O$ is added and the mixture kept at 0° for 30 min. The white precipitate is filtered and washed with 10 ml cold $Et_2O$. One obtains 4.9 g (50% overall) pure **1**, m.p. 232–235°, identical with the product obtained in [1].

*Direct conversion* **3** → **1**. 1 g (0.005 mol) **3** was electrolyzed in 320 ml acetonitrile or 50% aqueous tetrahydrofuran in the presence of 30 ml 40% tetrabutylammonium hydroxide as base and supporting electrolyte. In tetrahydrofuran under the same experimental conditions as in methanol 130 mg (13%) **1** are obtained after workup and recrystallization. In acetonitrile the current intensity decreased during the electrolysis so that the voltage had to be risen to 80 V. The yield was similar as in THF (≈10%).

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# 105. A Quantitative Assessment of "Through-space" and "Through-bond" Interactions. Application to Semi-empirical SCF Models

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*Summary*. The scheme of 'through-space' and 'through-bond' interaction of (semi)localized orbitals, originally proposed by *Hoffmann*, is reexamined in terms of SCF many-electron treatments. It is shown that the two types of interaction can be characterized by examining the corresponding off-diagonal matrix elements of the *Hartree-Fock* matrices of the localized or the symmetry adapted localized orbitals and of the partially diagonalized *Hartree-Fock* matrices referring to 'precanonical orbitals'.

The procedure outlined is applied to three practical examples using the semiempirical many-electron treatments SPINDO, MINDO/2 and CNDO/2:

a) A reassessment of 'through-space' and 'through-bond' interaction in norbornadiene indicates, that the latter type of interaction is also of importance for the orbital based mainly on the antisymmetric combination of the localized $\pi$-orbitals. The differences in the predictions derived from the three models are critically examined.

b) The competition between 'through-space' and 'through-bond' interaction in the series of bicyclic dienes from norbornadiene to bicyclo[4.2.2]-deca-7,9-diene and in cyclohexa-1,4-diene, *i.e.* their dependence on the dihedral angle $\omega$ is reexamined. It is found that the rationalization for the orbital crossing near $\omega = 130°$ deduced from PE. spectroscopic data can not be as simple as originally suggested and that the 'relay' orbitals responsible for 'through-bond' interaction affecting both the symmetric and the antisymmetric combination of the $\pi$-orbitals extend over the whole CC-$\sigma$-system of the six membered ring.

c) 'Through-bond' interaction of the two lone pair orbitals in 1,4-diazabicyclo[2.2.2]octane is found to be large for their symmetric and the antisymmetric linear combination.

The analysis quoted, draws attention to some of the dangers involved in using semiempirical treatments for the interpretation of PE. data in terms of *Koopmans*' theorem, without due caution.