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ELECTROCHEMICAL OXIDATION OF AROMATIC OLEFINS. DEPENDENCE OF THE REACTION COURSE ON THE STRUCTURE OF THE OLEFINS AND ON THE NATURE OF THE ANODES

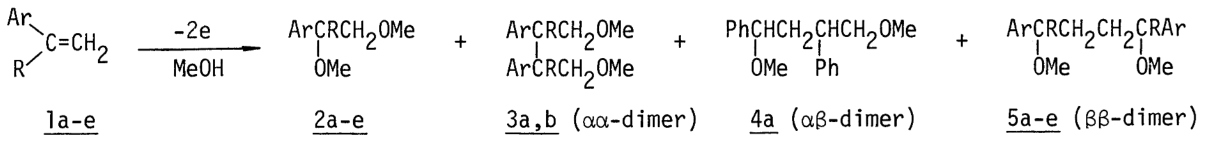
Masanobu KOJIMA, Hirochika SAKURAGI, and Katsumi TOKUMARU*
Department of Chemistry, The University of Tsukuba, Sakura-mura, Ibaraki 305

Anodic oxidation of a series of substituted styrenes was investigated in methanol with a platinum and a graphite electrode. Use of the platinum anode gave mainly dimethoxylated monomers accompanied with one or more of three types of dimethoxylated dimers (αα-, αβ-, and ββ-dimers) depending on the substituents. Use of the graphite anode, however, afforded the ββ-dimers as the main product together with dimethoxylated monomers.

Recently active investigations have been reported in electroorganic chemistry.[1)] Anodic oxidations of aromatic olefins like styrene have been carried out in several laboratories employing different experimental conditions.[2,3)] However, the results are not necessarily consistent, and what factors actually govern the reaction course has not been clear.[2,3)] Inoue and Tsutsumi carried out a pioneering work to describe that, on electrolysis at a platinum anode in methanol in the presence of sodium methoxide, styrene (1a) afforded a dimethoxylated monomer (2a) and a dimethoxylated dimer (αα-dimer 3a, see below), and that α-methylstyrene and 1,1-diphenylethylene (1c) likewise gave the corresponding dimethoxylated monomers.[2,4)] On the other hand, Schäfer and coworkers reported that oxidation of 1a on a graphite anode in methanol in the presence of sodium perchlorate or sodium iodide gave rise to another dimethoxylated dimer (ββ-dimer, 5a), a structual isomer of 3a.[3)]

An attempt has been undertaken to conduct anodic oxidation of a series of styrenes (1) in methanol on a platinum and a graphite anode by the same workers in our laboratory. We have found that styrenes (1), in general, afford dimethoxylated monomers (2) and one or more of three types of dimethoxylated dimers [αα- (3), αβ- (4), and ββ-dimers (5)] as indicated in Scheme 1. This paper presents the effect of substituents on the olefins and of the electrodes upon the course of the reaction; particularly the characterization of the resulting dimethoxylated dimers in low yields enables us to get deeper insight into the reaction course than that based mainly on the major products.[2)]

Scheme 1



a: Ar=Ph, R=H; b: Ar=p-ClC_6H_4, R=H; c: Ar=R=Ph; d: Ar=p-MeC_6H_4, R=H; e: Ar=p-$MeOC_6H_4$, R=H.

The present investigation employed three kinds of procedures, A, B, and C, for anodic oxidation of styrene derivatives 1. In procedure A, 1 (10-50 mmol) was electrolyzed in methanol (120 cm^3) containing sodium methoxide (52 mmol) under a constant current (1 A) with a platinum plate with many holes as an anode (approximate area, 60 cm^2), a platinum wire as a cathode, and SCE as a

Table 1. Electrochemical Oxidation of Styrene Derivatives (1) in Methanol[a]

$\mathrm{ArCR{=}CH_2}$ (1)	E_{ox}/V[b]	Procedure	$\mathrm{Ar\underset{\underset{OMe}{\mid}}{C}RCH_2OMe}$ (2, %)[c]	Dimethoxylated Dimers (%)[d] αα (3)	αβ (4)	ββ (5)
$\mathrm{PhCH{=}CH_2}$ (1a)	1.95	A	19	0.5	1	1
		B	36	1	2	2
		C[e]	trace	—	—	15
$\mathrm{p\text{-}ClC_6H_4CH{=}CH_2}$ (1b)	1.76	A	31	0.3	—	3
		B	31	0.7	—	2
		C[f]	—	—	—	26
$\mathrm{Ph_2C{=}CH_2}$ (1c)	1.48	A	40	—	—	1
		B	69	—	—	5
		C[g]	17	—	—	2
$\mathrm{p\text{-}MeC_6H_4CH{=}CH_2}$ (1d)	1.38	A	36	—	—	4
		B	30	—	—	3
		C[h]	6	—	—	20
$\mathrm{p\text{-}MeOC_6H_4CH{=}CH_2}$ (1e)	1.15	A	17	—	—	(3.5)[i]
		B	—	—	—	13
		C	10	—	—	25

[a] Electrolysis was carried out until the starting olefins were completely consumed except for the following runs where conversion (%) of the olefins was indicated in parentheses: 1a by procedure A (32 %), 1b by procedure A (79 %), and 1c by procedure B (67 %).
[b] Oxidation potential vs. Ag/0.1 mol/dm^3 $\mathrm{AgNO_3}$ in MeCN. [c] Yield for 2: [(moles of 2)/(moles of 1 consumed)] x 100. [d] Yield for 3, 4, or 5: [(moles of 3, 4, or 5)/(moles of 1 consumed)] x 200. [e] Other products: PhCHO and $\mathrm{PhCO_2Me}$. [f] Other products: $\mathrm{p\text{-}ClC_6H_4CHO}$ and $\mathrm{p\text{-}ClC_6H_4CH(OMe)_2}$ (11 %). [g] Another product: $\mathrm{Ph_2CO}$ (30 %). [h] NaI was used as a supporting electrolyte.
[i] $\mathrm{(p\text{-}MeOC_6H_4COCH_2\text{-})_2}$ (1.5 %) and $\mathrm{[p\text{-}MeOC_6H_4C(OMe)_2CH_2\text{-}]_2}$ (2 %) were isolated, which are considered to be derived from 5e. Their structure was determined based on spectral data and elemental analyses.

reference electrode under argon atmosphere at room temperature. This procedure is essentially similar to that described by Inoue and Tsutsumi for 1a, 1c, and α-methylstyrene.2) Procedure B is similar to procedure A except that tetraethylammonium perchlorate (TEAP) was used as a supporting electrolyte instead of sodium methoxide under constant-current electrolysis (0.1 or 1 A). In procedure C, 1 (10-25 mmol) was electrolyzed under a constant current (1 A) in methanol (120 cm^3) in the presence of sodium perchlorate (10 mmol) at a graphite cylindrical anode (effective area 80 cm^2; thickness, 0.3 cm) with a graphite rod (diameter, 1 cm; length, 8 cm) as a cathode and a Ag/AgCl reference electrode. The results are summarized in Table 1.

As Table 1 indicates, use of the platinum electrode (Procedures A and B) leads to nearly the same results for each olefin except 1e, irrespective of the supporting electrolyte employed. Thus 1a and 1b afford 2a and 2b, respectively, together with both of the corresponding αα-dimers 3 and ββ-dimers 5; furthermore, αβ-dimer 4a was obtained from 1a. On the other hand, 1c, 1d, and 1e gave 2c, 2d, and 2e, respectively, along with the corresponding ββ-dimers exclusively; however, no αα-dimers 3 were obtained. Olefins 1a and 1b exhibit higher oxidation potentials among 1's and are now

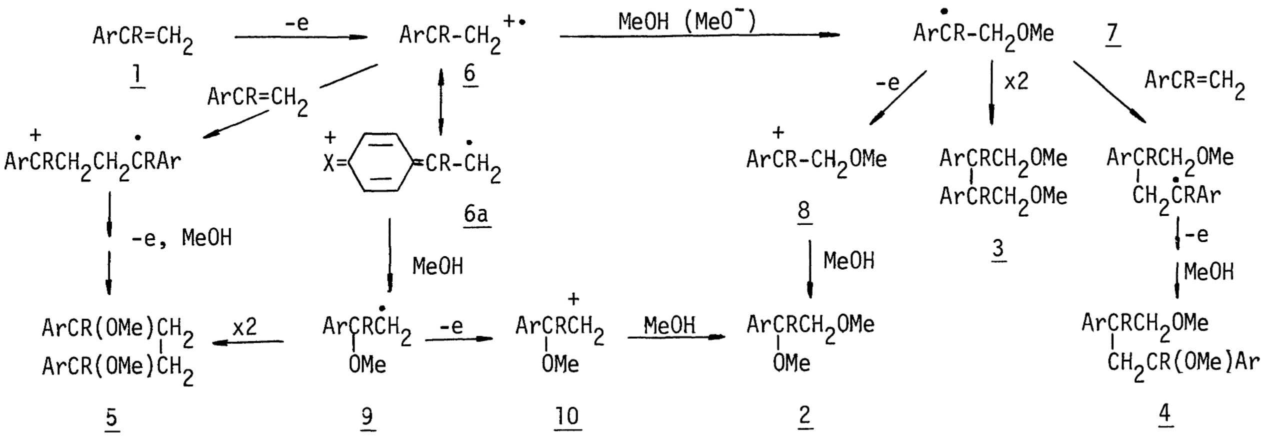
Table 2. Mode of Dimer Production in Anodic Oxidation of Olefins (1)

Olefin		Procedure		
Classified Group	Compound	Pt/MeONa (A)	Pt/TEAP (B)	Graphite/NaClO$_4$ (C)
I	1a	αα, αβ, ββ	αα, αβ, ββ	ββ
	1b	αα, ββ	αα, ββ	ββ
II	1c	ββ	ββ	ββ
	1d	ββ	ββ	ββ
	1e	ββ	ββ	ββ

classified as group I olefins; the other olefins 1c, 1d, and 1e with lower oxidation potentials are classified as group II olefins. Use of the graphite anode produced solely ββ-dimers 5 as the main products regardless of the structure of the olefins employed (except 1c); however, 2's were obtained only from 1c, 1d, and 1e and 2's resulted from 1a and 1b seem to be further oxidized into the corresponding benzaldehydes, acetals, and methyl benzoates under the reaction conditions.5) The mode of dimer production is simply summarized in Table 2.

A mechanistic scheme essential to understand the reaction could be depicted as shown below (Scheme 2). With the use of the platinum anode the olefins are oxidized into their radical cations 6 irrespective of the supporting electrolytes employed. Production of 2, 3, and 4 can be understood by intervention of radicals 7 followed by their further anodic oxidation, dimerization, and addition to the olefins.6) Thus, the radical cations 6 from group I olefins will react with alcohols or alkoxide ions to give radicals 7 which may collapse into 2, 3, or 4 as depicted in Scheme 2. On the contrary, in the oxidation of group II olefins, production of neither αα-dimers 3 nor αβ-dimers 4 suggest that radicals 7 will not participate as reaction intermediate. In the radical cations 6 arising from group II olefins, the positive charge seems to be more delocalized on the aromatic ring, and concurrently the unpaired electron density on the terminal carbon may be higher than in the case of group I olefins as schematically expressed by a resonance canonical form (6a), which was actually observed for the radical cations of N,N-dimethylaminoalkenes.7)

Scheme 2



Therefore, it is reasonable to suppose that 6 arising from group II olefins will more facilely add to the olefins than those from group I olefins finally leading to ββ-dimers 5, and consequently will react with methanol or methoxide ions on their α-carbon atoms to give radicals 9, which are further oxidized on the anode to carbocations 10 finally affording 2.8) However, the fact that 1e gives 2e only in procedure A but not in procedure B suggests that its radical cations 6e can react with methoxide ions but not effectively with methanol probably due to their reduced positive charge density on the ethylenic carbons through delocalization with the methoxy group.

The graphite electrode generally seems to adsorb substrates more strongly than the platinum electrode. Therefore, the results with a graphite anode can be accounted for by strong adsorption of the olefins and their radical cations 6 on the electrode at their β-carbon atoms. The presence of the adsorbed species in high concentration around the electrode will effect their facile combination subsequently giving 5.

Finally, it should be noted that the precise determination of the minor products which have hitherto not been isolated contributes to elucidation of the mechanism of electrochemical reactions, and the remarkable effects of the substituents to control the reaction course would result from sensitive electronic effects of the substituents exerted in the radical cation species.

References

(1) For example, M. R. Rifi and F. H. Covits, "Introduction to Organic Electrochemistry," Marcel Dekker, New York (1974); T. Osa, T. Shono, and K. Honda ed., "Electroorganic Chemistry," Kagaku Dozin, Kyoto (1980); S. Torii, "Yuki Denkai Gosei," Kodansha (1981).

(2) T. Inoue and S. Tsutsumi, Bull. Chem. Soc. Jpn., 38, 661 (1965).

(3) E. Engels, H. J. Schäfer, and E. Steckhan, Justus Liebigs Ann. Chem., 204 (1977).

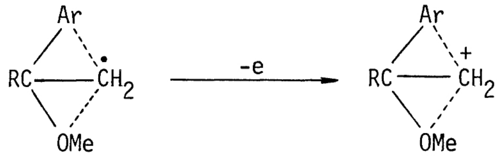
(4) Production of dimethoxylated dimers was suggested without actual determination of their structures.

(5) A control experiment showed that the anodic oxidation of 2a in the condition for procedure C afforded benzaldehyde and methyl benzoate.

(6) For the formation of radicals 7, a possibility for anodic oxidation of methanol or methoxide ions into methoxy radicals followed by their addition on the terminal carbon atoms of the olefins2) is ruled out because the production of 5 from all of the olefins examined needs the participation of radicals 6.

(7) J. M. Fritsch, H, Weingarten, and J. D. Wilson, J. Am. Chem. Soc., 92, 4038 (1970).

(8) Radicals 9 are thermodynamically less stable than the alternative radicals 7, but might be, to more or less extent, stabilized through the possible anchimeric effect of the aryl group on the carbon atom adjacent to the radical center. Also, on further oxidation of radical 9 on the anode, the adjacent methoxy group as well as the aryl group might participate in assisting the oxidation of the radicals to the carbocations 10 which subsequently collapse into 2.



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