

# Studies of the Possible Effects of Adsorption on the Product Distribution from Organic Electrode Reactions. V. Stereochemistry of the Anodic Addition of Acetoxy Groups to 1-Alkylindenes

LARS CEDHEIM and LENNART EBERSON\*

Division of Organic Chemistry 1, Chemical Center, University of Lund, P.O. Box 740, S-220 07 Lund 7, Sweden

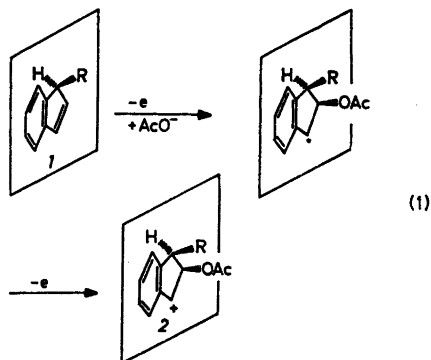
A series of 1-alkylindenes (alkyl = Me, Et, Pr, *i*-Pr, Bu, and *t*-Bu) has been subjected to anodic oxidation in acetic acid/sodium acetate and oxidation by  $\text{Co}(\text{OAc})_2$  in acetic acid/sodium acetate solution. No significant differences in the isomer distribution of the 3-alkyl-1,2-indandiol diacetates formed were found. Thus it is concluded that the product-determining reactions do not take place at the electrode surface.

In previous studies of the anodic oxidation of substituted alkenes in  $\text{HOAc}/\text{NaOAc}$ , our main interest was focused on the stereochemical course of the addition of two acetoxy groups across a double bond.<sup>1-3</sup> Previous studies in this series<sup>4-6</sup> have aimed at elucidating the steric course of anodic substitution reactions of suitable alkylaromatic hydrocarbons. Since the results obtained were not conclusive as to whether the stereochemistry of these reactions is controlled by adsorption or not, we decided to investigate the addition of acetoxy groups to 1-alkylindenes (*I*). These compounds have attractive steric features for such a study (see below).

It has been shown<sup>1</sup> unambiguously that the anodic oxidation of an arylolefin is initiated by a one-electron transfer from the  $\pi$ -electron system to the anode. The radical cation thus formed will react very fast with any nucleophile present in the solution, *e.g.*, acetate ion, to give a radical. This radical can then be further oxidized to a cation which may be

trapped by a nucleophile to give the end product(s). During the first two steps there are several possibilities for the orientation of the intermediates with respect to the anode surface. We shall consider here only the two extreme cases, *i.e.*, (1) the reaction occurs entirely at the anode surface due to adsorption, or (2) the reaction occurs entirely in the solution phase. By using a molecule in which one side is more crowded than the other, *e.g.*, a 1-alkylindene (*I*), adsorption at the least hindered side (eqn. 1) should be favoured. The radical cation formed in this orientation will then, after reaction with a nucleophile, give a sterically more crowded intermediate than if the reaction occurs in the solution.

If, on the other hand, the reaction occurs in the solution, the isomer ratio of the products should follow the same pattern as that from analogous homogeneous electron transfer oxidations.<sup>7</sup> *e.g.*, oxidation with  $\text{Co}(\text{OAc})_2$ . Any



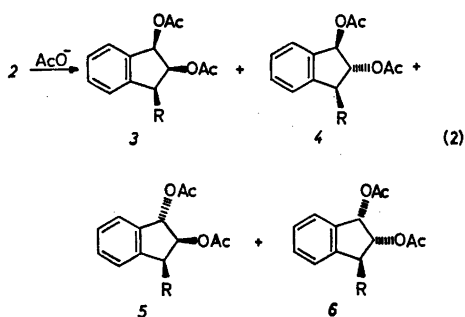
\* To whom correspondence should be addressed.

large difference in product distribution between these reactions, specifically a stronger preference for a *cis* 2-acetoxy-/alkyl relationship in the electrochemical process, will thus be an indication of adsorption controlled stereochemistry.

## RESULTS AND DISCUSSION

The mechanistic study made earlier<sup>3</sup> suggested that the first acetoxy group attacks position 2 in indene radical cation. The next reaction is removal of one electron and the creation of an acetoxy-carbonium ion (2, eqn. 1, R=H).

Intermediate 2 can then react further with acetate ion to give the products. Accordingly, for the 1-alkylindene, formation of 3 and 5 from 2, and 4 and 6 from a species adsorbed with R pointing toward the electrode surface, might be anticipated, 3 and 5 being the predominating products in the case of a sterically demanding R group (eqn. 2).



R = Me, Et, Pr, *i*-Pr, Bu, and *t*-Bu

The oxidation of the 1-alkylindenes was carried out in acetic acid, 1 M in sodium acetate. The anode material was graphite and the oxidation was run at a constant potential of +1.2 V vs. SCE. When the current fell below 10 mA (0.25 mA/cm<sup>2</sup>), coinciding with the passage of 2 F/mol of substrate, the electrolysis was interrupted and the reaction mixture worked up. To determine the product distribution of compounds 3–6 as accurately as possible, the reaction mixture was first treated with acetic anhydride and pyridine to convert any hydroxy acetate formed into diacetate.<sup>3</sup> Product distributions were determined by GLC. The results are summarized in Table 1. The main product, isolated by distillation, was a mixture of the four stereoisomers of 3-alkyl-1,2-indandiol diacetate, (3–6), previously synthesized and identified by unambiguous methods.<sup>8</sup>

These isolated total yields were in all cases reasonably high. There is however, no real synthetic value of preparing the individual diastereoisomers in this way, with two exceptions (see below), due to difficulties of separation.

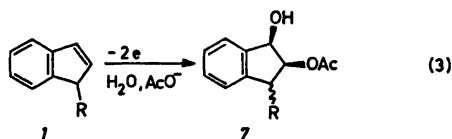
Analysis of the reaction mixture without prior acetylation disclosed an additional product 7\* that could be converted to the diacetoxyalkylindans (3 and 6) on treatment with acetic anhydride and pyridine (eqn. 3).

\* This is the most likely arrangement of –OH and –OAc; cf. Ref. 3.

Table 1. Product distribution from the anodic oxidation of 1-alkylindenes in HOAc/KOAc (1 M) at a carbon anode.

R	<i>n</i> /F	Product distribution, % <sup>a</sup>				Isolated yield, % <sup>b</sup>	<i>γ</i> <sup>c</sup>
		3	4	5	6		
H	—	(63) <sup>d</sup>		(37) <sup>e</sup>		32	20
Me	1.80	20	28	52 <sup>f</sup>		55	6
Et	1.87	12	35	9	44	75	10
Pr	1.95	12	34	8	46	73	20
<i>i</i> -Pr	1.94	2	41	2	55	58	16
Bu	2.03	11	31	7	50	62	14
<i>t</i> -Bu	1.89	0	38	1	62	73	18

<sup>a</sup> After treating the reaction mixture with acetic anhydride and pyridine, *i.e.*, including 7 after acetylation. GLC analysis normalized to 100%. <sup>b</sup> Combined 3–6, isolated by distillation, based on starting material. <sup>c</sup> Estimated from pre-acetylation data not shown here. <sup>d</sup> Combined yield of 3 + 6, as previously reported (Ref. 3). <sup>e</sup> Combined yield of 4 + 5 as previously reported (Ref. 3). <sup>f</sup> Combined yield of 5 + 6 as previously reported.



Accordingly, the amount of compound 7 in the reaction was estimated by determining the amount of 3–6 before and after treatment with acetic anhydride and pyridine. This made it possible to estimate the relative amount (Table 1) of 7 accurately without determining the GLC sensitivity factor of these compounds.

In order to investigate the influence of water on the product distribution, a series of runs with 1-isopropylindene was made involving varying concentrations of added water or acetic anhydride. The relative amount of (7) was essentially independent of the water concentration as has earlier been found for indene.<sup>3</sup> These reactions were performed at both platinum and carbon anodes under constant current conditions (Table 2).

In the cases of 1-*t*-butylindene and 1-isopropylindene, electrolysis is a useful way of preparing the isomers 4 and 6 in reasonable yields. So far no satisfactory conventional synthetic pathway for 4, R=isopropyl or *t*-butyl has been reported. Separation of the two diacetates was performed by first hydrolyzing them to their parent *cis* and *trans* diols. The *cis* diol could be separated from the *trans* diol by reacting the mixture of diols with acetone and then extracting the *cis* acetone ketal into pentane.

The structure of 4, R=*t*-butyl was demonstrated by the above mentioned reaction of its diol with acetone, its mass, NMR, and IR spectra, and assignment of structure to its stereoisomers. The stereochemistry of all the remaining compounds has been previously reported.<sup>8</sup> The stereochemistry of 7 was similarly established to be exclusively *cis* for the hydroxy/acetate groups.

In the mechanism outlined above (eqn. 2) the attack of the nucleophile was assumed to occur at position 2 of the radical cation. If the molecule is adsorbed on the electrode surface in its least hindered configuration during this reaction, an increasing ratio of 3+5 to 4+6 would be expected for an increasing bulk of R. These ratios are given in Table 4. It is obvious that the larger the alkyl group, the less is the proportion of 3+5, contrary to predictions based upon an adsorption-controlled mechanism (eqn. 1). Instead, these results support the hypothesis that the reaction occurs in the solution phase, *i.e.*, not close enough to the surface for it to exert any stereochemical control.

The oxidation of 1-alkylindenes was also carried out with Co(OAc)<sub>2</sub> in acetic acid/sodium acetate (0.5 M). The products consisted of more than 70 % of the four isomers 3–6. The isolated yield of these isomers increased by about 10 % when the crude reaction product was treated with acetic anhydride and pyridine prior to analysis (Table 3). Analytical difficulties prevented more exact evaluation of the crude reaction mixture. A comparison

Table 2. Electrolysis of 1-isopropylindene in HOAc/KOAc (1 M) in the presence of added water or acetic anhydride.

Anode	[H <sub>2</sub> O]/ [KOAc]	Product distribution, % <sup>a</sup>				
		3	4	5	6	7
C	<sup>b</sup>	3	43	2	37	15
C	0.0	4	42	3	34	17
C	1.1	2	38	2	38	20
C	2.7	2	37	2	38	21
Pt	<sup>b</sup>	5	40	5	32	18
Pt	0.0	5	38	5	32	20
Pt	1.1	4	36	3	33	24
Pt	2.7	4	33	4	35	24

<sup>a</sup> GLC analysis normalized to 100 %. Actual yield assumed about 73 % (see Table 1). <sup>b</sup> The reaction solution was a mixture of HOAc (30.0 g) and acetic anhydride (2.0 g).

Table 3. Co(OAc)<sub>3</sub> oxidation of 1-alkylindenes in HOAc/KOAc (0.5 M).

R	Product distribution, % <sup>a</sup>				Total yield, %
	3	4	5	6	
Me	6	37	57 <sup>b</sup>		100
Et	6	41	9	44	99
Pr	6	34	6	54	86
i-Pr	1	37	3	59	79
Bu	6	41	6	47	85
t-Bu	1	44	1	55	85

<sup>a</sup> GLC analysis normalized to 100 %. <sup>b</sup> Combined yield of 5 + 6 as previously reported.

Table 4. A comparison of the product distributions from the anodic and the Co(OAc)<sub>3</sub> oxidation of 1-alkylindenes.

R	Electrolysis, %			Co(OAc) <sub>3</sub> , %		
	A <sup>a</sup>	B <sup>a</sup>	A/B	A	B	A/B
Et	21	79	0.26	15	85	0.18
Pr	20	80	0.25	12	88	0.14
i-Pr	4	96	0.02	4	96	0.04
Bu	18	82	0.22	12	88	0.14
t-Bu	1	99	0.01	1	99	0.01

<sup>a</sup> A = 3 + 5, B = 4 + 6; from Tables 1 and 3.

between the anodic and the Co(OAc)<sub>3</sub> oxidations (Table 4) reveals a very close similarity in the product distribution pattern, confirming the conclusion reached above about the essentially homogeneous nature of the follow-up reactions of the anodic process.

It is pertinent to note that a study of the adsorption of aromatic compounds on a gold anode has been reported.<sup>10</sup> A plot of coverage against anode potential shows a bell-shaped curve with a maximum around +0.5 V vs. NHE. The coverage process was shown to take place slowly. As an example, maximum coverage of naphthalene was reached after about 800 s from a 10<sup>-6</sup> M solution. This can be compared to the electrochemical and chemical steps proposed above, which under these circumstances must be fast. The adsorption of acetate ion<sup>10</sup> or acetic acid<sup>11</sup> is an irreversible process above +0.8 V vs. SCE and once such a layer is formed, it may be difficult to introduce an indene molecule.

## EXPERIMENTAL

*1-Alkylindenes*<sup>12,13</sup> and *3-alkyl-1,2-indandiol diacetates*.<sup>9</sup> These compounds were prepared as described earlier, except *trans*, *trans*-3-*t*-butylindandiol diacetate.

*Preparative anodic oxidation of 1-alkylindenes.* The controlled potential preparative electrolyses were carried out in a water-jacketed cylindrical cell (150 cm<sup>3</sup> volume), equipped with a carbon anode (40 cm<sup>2</sup>) and a carbon cathode (40 cm<sup>2</sup>). The saturated calomel electrode was used as a reference electrode and a Chemical Electronics Model TR 70/2A type potentiostat was employed.

A solution of a 1-alkylindene (0.1 mol), anhydrous sodium acetate (0.1 mol), and HOAc (106 g) was electrolyzed at a constant potential of +1.2 V vs. SCE until the current had dropped to less than 10 mA (0.25 mA/cm<sup>2</sup>). This occurred when (1.9 ± 0.1) F/mol of 1-alkylindene had been passed.

The electrolyte was poured into ether (100 ml) and washed free of acetic acid with 5 × 200 ml of water. The content of 3-alkyl-1,2-indandiol monoacetate was analyzed by GLC.<sup>9</sup> The ether was evaporated and the residue was treated with a mixture of acetic anhydride (30 ml) and pyridine (1 ml) and refluxed for 15 min. After cooling and addition of water

(200 ml) the organic material was extracted into ether. The ether solution was washed free of acetic acid, dried, evaporated, and distilled. The 3-alkyl-1,2-indandiol diacetates were collected around 130 °C/1 mmHg (for more exact boiling points, see Ref. 8). The individual diastereoisomers were identified by comparison with authentic material. The results are found in Table 1.

*Small-scale anodic oxidation of 1-isopropylindene.* Small-scale controlled current electrolyses were carried out in a water-jacketed cylindrical cell (50 ml volume), equipped with a carbon anode (6 cm<sup>2</sup>) or a platinum anode (3.7 cm<sup>2</sup>) and a carbon cathode (6 cm<sup>2</sup>), using a Radiak power supply.

A solution of 1-isopropylindene (3.2 mmol), analytical grade potassium acetate (3.0 g), and HOAc (30.0 g) was electrolyzed together with the additives in Table 2 at a constant current of 0.2 A. Work-up and identification were as described above. The results are summarized in Table 2.

*Cobalt(III) acetate.* This compound was prepared according to a literature procedure.<sup>14</sup>

*Cobalt(III) acetate oxidation of 1-alkylindenes.* A solution of 1-alkylindene (2.5 mmol), Co(OAc)<sub>3</sub> (5.3 mmol; iodometrically titrated value), acetic acid (75 ml), and sodium acetate (3.0 g) was refluxed for 30 min. After cooling and addition of water (200 ml), the organic material was extracted with ether and worked up as for small-scale electrolyses. The data are shown in Table 3.

*Trans, trans-3-t-Butylindandiol diacetate.* This compound was prepared from the diacetate mixture obtained in the electrolysis. The procedure is described in the text.

*Acknowledgements.* This work was supported by grants from the Swedish Natural Science Research Council, the Carl Trygger Foundation, and the Royal Physiographic Society of Lund. Part of the costs for the analytical equipment was defrayed by a grant from the Knut and Alice Wallenberg Foundation.

## REFERENCES

1. Ebersson, L. and Parker, V. *Chem. Commun.* (1969) 340; *Acta Chem. Scand.* 24 (1970) 3553.
2. Bernhardsson, E., Ebersson, L., Nyberg, K. and Rietz, B. *Acta Chem. Scand.* 25 (1971) 1224.
3. Cedheim, L. and Ebersson, L. *Acta Chem. Scand. B* 29 (1975) 969.
4. Ebersson, L. and Sternerup, H. *Acta Chem. Scand.* 26 (1972) 1431.
5. Dirlam, J. P. and Ebersson, L. *Acta Chem. Scand.* 26 (1972) 1454.
6. Dirlam, J. P., Ebersson, L. and Sternerup, H. *Chem.-Ing.-Tech. Z.* 44 (1973) 178.
7. Heiba, E.I., Dessau, R. N. and Koehl, Jr., W. J. *J. Amer. Chem. Soc.* 91 (1969) 6830.
8. Cedheim, L. and Ebersson, L. *Acta Chem. Scand. B* 28 (1974) 344.
9. Dahms, H. and Green, M. J. *Electrochem. Soc.* 110 (1963) 1075.
10. Yalovleva, A. A., Kaidalova, S. N., Skuratnik, Ya. B. and Veselovskii, V.I. *Soviet Electrochem.* 8 (1972) 1742 (Engl. Ed.).
11. Horányi, G., Solt, J. and Nagy, F. *Acta Chim. (Budapest)* 64 (1970) 113.
12. Cedheim, L. and Ebersson, L. *Synthesis* (1973) 159.
13. Meurling, L. *Acta Chem. Scand. B* 28 (1974) 295.
14. Sharp, J. A. and White, A.G. *J. Chem. Soc.* (1952) 110.

Received March 6, 1975.