

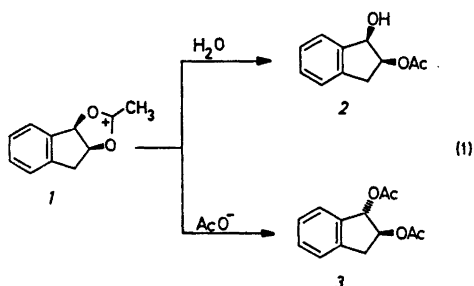
# On the Mechanism of the Additive Anodic Acetoxylation of Indene

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The anodic acetoxylation of indene has been performed in acetic acid/potassium acetate (1 M) with water or acetic anhydride as additives. The influence of these additives on the product distribution is negligible. INDO calculations have been carried out on the neutral molecule and its radical cation. On basis of these results a simple acetoxy-carbonium ion mechanism is suggested to operate simultaneously with the previously suggested acetoxonium ion mechanism.

The mechanism of the anodic addition of acetoxy groups to an arylolefin has been studied earlier.<sup>1,2</sup> According to these investigations, the key intermediate formed in the anodic process is an acetoxonium ion which reacts as exemplified by eqn. (1)<sup>3</sup> by the acetoxonium ion derived from indene, *i.e.* with formation of *trans* diacetate (3) in the reaction with acetate ion and a *cis* hydroxy acetate (2)\*\* in the reaction with water (eqn.1).

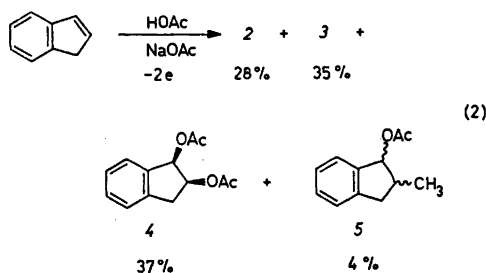


The additive acetoxylation of indene in HOAc/NaOAc (1 M) gave,<sup>4</sup> however, a 32 %

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\*\* NMR comparison between the compounds in Ref. 18 and compound 2 suggests the proposed structure.

yield of a mixture of addition products that contained an appreciable amount of the *cis* diacetate (4) in addition to the products expected on the basis of eqn. 1 (2 and 3). A small yield of the CH<sub>3</sub>/OAc addition product (5) was also isolated.

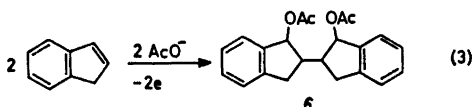


Since the formation of 4 is not satisfactorily accounted for by the acetoxonium ion mechanism, we have performed further experiments designed to elucidate its possible mode of formation. The results indicate that a mechanism involving a benzylic cation may be invoked to account satisfactorily for its appearance. In addition it appears rather improbable that water plays any role in the route to the *cis* hydroxy acetate (2). Finally, as will be discussed below, the formation of the corresponding *trans* hydroxy acetate (7) in water-containing electrolyte solutions cannot be reconciled with the cyclic acetoxonium ion mechanism.

## RESULTS

**Experiments.** A large-scale run (2 mol of indene) using a capillary gap cell<sup>5-7</sup> with a graphite anode gave a mixture of 2, 3, and 4

in a combined yield of 34 %. The yield of methyl derivative (5) was the same as that obtained before.<sup>4</sup> Using a slightly different work-up procedure than that employed earlier,<sup>4</sup> an 8 % yield of an additive dimer of indene and acetate ion was isolated (eqn. 3). This product was assigned the structure of 2,2'-additive dimer (6) on the basis of its mass, NMR and IR spectral properties. It consisted of two diastereoisomers. The yield of the dimer



did not increase significantly upon increasing the indene concentration from 1.6 to 10.5 M. A run with sodium perchlorate as the supporting electrolyte was unsuccessful due to the formation of a polymeric coating on the anode. With platinum as the anode material the combined current yield of 2, 3, and 4 increased to 47 %.

In order to trace the origin of the *cis* hydroxy acetate (2), a series of semi-micro scale runs with either acetic anhydride or water added at graphite or platinum anodes was carried out. As indicated in Table 1, no significant change in product distribution was observed when the solvent was changed from 50 % acetic anhydride/acetic acid to 9 % water/acetic acid, independently of whether graphite or platinum was used as anode material. This

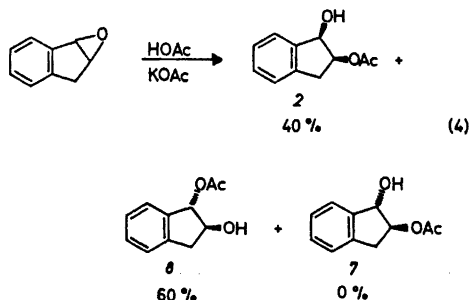
Table 1. Product distribution from electrolysis of indene in HOAc/KOAc (1 M) in the presence of added water or acetic anhydride.

Anode	Additive [H <sub>2</sub> O]/[KOAc]	Product distribution			% <sup>a</sup>
		(3)	(4)	(2)	
C	<sup>b</sup>	46	40	14	0
C	0.0	45	40	15	0
C	1.1	44	38	15	3
C	2.7	43	38	16	4
C	5.5	38	36	20	6
Pt	<sup>b</sup>	39	44	18	0
Pt	0.0	40	42	18	0
Pt	1.1	41	40	18	1
Pt	2.7	40	37	19	4
Pt	5.5	38	34	20	8

<sup>a</sup> GLC analysis normalized to 100 %. <sup>b</sup> The reaction solution was a mixture of acetic anhydride (15.0 g) and of acetic acid (15.0 g).

observation would seem to rule out the reaction between 1 and water as a possible source of 2 (eqn. 1). No effect upon product distribution was noted when the current density on a platinum anode was changed from 13 to 850 mA/cm<sup>2</sup>.

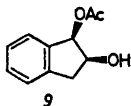
With varying amounts of water added to the electrolyte solution, a new product (7 in Table 1) was observed. The identity of this compound was established from the following experiments. A mixture of 2 and 7 in the proportions 85:15, isolated from the product mixture from the anodic oxidation of indene by repeated recrystallization from hexane, reacted with acetic anhydride/pyridine to give 3 and 4 in the proportions 15:85. The NMR spectrum of 7 was similar to that of 2 (see experimental part). Ring-opening of 1,2-epoxyindane in HOAc/KOAc gave two products, one of which was identical with 2 and the second one was the *trans* hydroxy acetate 8, compound 7 not being observed. Exactly how this reaction occurs has not been established.<sup>8</sup> The mixture



of hydroxy acetates from this experiment upon treatment with acetic anhydride/pyridine was converted to a mixture of (3) and (4) in the proportions of 60:40.

A further complication was noted when the electrolysis was performed in a neutral medium. In this experiment dichloromethane was used as the solvent with solid potassium acetate and dicyclohexyl-18-crown-6 present to generate crown-ether solubilized KOAc as the supporting electrolyte. Under these conditions a new *cis* hydroxy acetate, 9, was formed in addition to 2, 3, and 4. The composition of the mixture was 2:3:4:9 equal to 36:22:23:19. The structure of 9 was inferred from its non-identity with 2 and conversion to 4 by treatment with

acetic anhydride/pyridine. It is well documented that **9** rearranges to **2** in acidic solution<sup>9</sup> (probable route for the formation of **2** from the epoxide in eqn. 4), so that **9** cannot be ruled out as an intermediate in the electrolyses performed in acetic acid.



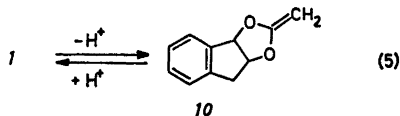
It is known that indene reacts with oxygen to give diindanylperoxide.<sup>10</sup> In order to eliminate this possible source of ambiguity, indene was carefully distilled in an argon atmosphere and a middle fraction collected. Two reactions with this sample were performed, one under argon and one under carbon dioxide atmosphere and both with platinum as the anode material. No influence on the product composition was noted, however.

With reference to the somewhat curious fact that the relative amount of **2** formed from indene under conditions ranging from a completely anhydrous medium (with 50% acetic anhydride present) to one containing nearly 10% of water does not change at all (Table 1), we performed a few experiments in order to find the relative rate of cation trapping by acetate ion and water, respectively. As a model reaction benzylamine was reacted with sodium nitrite in HOAc/KOAc with water present in varying concentrations and the ratio benzyl acetate/benzyl alcohol determined. A ratio of about 300 was calculated for  $k_{\text{OAc}^-}/k_{\text{H}_2\text{O}}$ . That acetate is a stronger nucleophile than water by a factor of 525 was established by Swain and Scott<sup>21</sup> for  $\text{S}_{\text{N}}2$  reactivity. One would therefore expect cation capture by acetate ion to predominate to a large extent even in the electrolysis experiments with added water.

Check experiments in which diacetates **3** and **4** were anodically oxidized under the same conditions as those employed for indene, showed that no *cis* hydroxy acetate (**2**) was formed in a secondary process.

Finally, in order to see if the work-up procedure might influence the product composition (due to survival<sup>3</sup> of the acetoxonium ion or its corresponding base, the ketene acetal (**10**),

or both during electrolysis; see eqn. 5) two different work-up techniques were tried.



After a charge of 2 F/mol of indene had passed, the electrolyte solution was divided into two equal parts. The first one was poured into a large excess of water, and the second one into absolute ethanol. Capture of **1** or **10** by water would be expected to take place to a larger extent in the former case. However, no difference in product composition was observed between the two procedures.

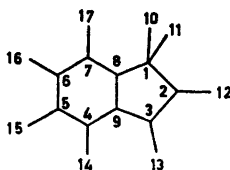
*INDO calculations.* The first step in the anodic oxidation of an aryleolefin is to remove an electron from the highest occupied molecular orbital and thus form a radical cation.<sup>11</sup> In order to get an idea of the most probable reactions of the indene radical cation ( $\text{I}^{\cdot+}$ ), INDO calculations were carried out for this ion and its parent hydrocarbon. It has been shown that this type of calculations describes charge densities almost as well as STO-3G *ab initio* calculations.<sup>12</sup> The results are shown in Table 2, from which the following picture emerges. In the radical cation both charge and spin densities are predominantly located at positions 2 and 6, whereas positions 4 and 8 have relatively low charge densities. Using bond orders, as defined by Ehrenson and Seltzer,<sup>13</sup> as a measure of bond strength, it is seen that the strength of the bond between atoms 3 and 2 decreases and that of the bond between atoms 3 and 9 increases when one electron is removed from indene.

Thus, these calculations predict that the coupling of two  $\text{I}^{\cdot+}$  should give the 2,2'-, 2,6'-, and/or 6,6'-dimers rather than the 2,3'- or 3,3'-dimer. The electrophilic attack of  $\text{I}^{\cdot+}$  on a neutral indene molecule should likewise occur at position 2 and thus give a 2,2'- and/or 2,6'-dimer.

As shown above for the dimerization of indene and demonstrated by others,<sup>14</sup> coupling *via* the 2,2'-mode is predominant. No coupling *via* the 6-position was observed in either case.

If the radical cation is trapped by acetate ion, the calculations predict that this should

Table 2. INDO calculation on indene (I) and indene radical cation ( $I^+$ ). The numbers 1–9 refer to carbon and 10–17 to hydrogen atoms.



Atom No.	Charge density (I)	Charge density ( $I^+$ )	Radical density	Bond	Bond order (I)	Bond order ( $I^+$ )
1	0.0607	0.0243	-0.0305	1-2	0.7329	0.7375
2	-0.0070	0.1580	0.4035	1-8	0.7226	0.7210
3	0.0055	0.0718	0.0588	2-3	1.0674	1.0025
4	0.0130	0.0814	0.1489	3-9	0.7858	0.8295
5	0.0254	0.0275	-0.0772	4-9	0.9238	0.9088
6	0.0228	0.1506	0.2889	4-5	0.9666	0.9787
7	0.0223	0.0228	-0.0803	5-6	0.9589	0.9392
8	0.0046	0.0794	0.1510	6-7	0.9641	0.9432
9	0.0314	0.0941	0.1424	7-8	0.9536	0.9675
10	-0.0116	0.0503	0.0134	8-9	0.9224	0.8855
11	-0.0116	0.0503	0.0134			
12	-0.0099	0.0532	-0.0164			
13	-0.0240	0.0401	-0.0033			
14	-0.0317	0.0194	-0.0065			
15	-0.0290	0.0289	0.0025			
16	-0.0276	0.0259	-0.0115			
17	-0.0331	0.0223	0.0023			

also occur to a large extent at positions 2 and/or 6. Experimentally, acetoxylation takes place at the olefinic bond of indene and no nuclear acetoxylation is observed. It appears reasonable that the attack should occur at the 2-position.

The reasoning above is based upon the simple view that the reaction between two radicals should take place at the position(s) of highest spin density, and that the attack of acetate ion should occur at the position(s) of the highest positive charge density. In both cases an early transition state is implied. Should one, however, adopt the view that the transition state is late—resembling the first intermediate—resonance theory predicts that attack on position 6 should lead to rather unfavourable intermediates (in which the aromatic  $\pi$ -electron system is lacking) as compared to those originating at the 2-position.

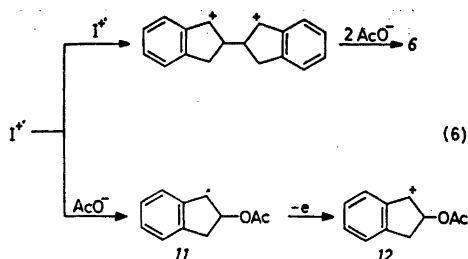
## DISCUSSION

Considering the results described above, the simple acetoxonium ion mechanism previously proposed<sup>1</sup> cannot be extended to indene

system. We would therefore like to suggest a somewhat modified mechanism, still involving the acetoxonium ion as a critical intermediate, but with elements of a second mechanism involving a benzylic cation added.

The first step is formation of  $I^+$ , which either reacts with another "indene species" or with acetate ion (eqn. 6), in both cases at position 2. In the former case, the "indene species" can either be the indene molecule or  $I^+$ ; we prefer the latter alternative in view of the findings from earlier investigations<sup>2</sup> and the fact that the relative yield of additive dimer (6) is independent of the concentration of indene in the range of 1.6 to 10.5 M. Other types of anodic couplings, such as biaryl and diphenylmethane coupling, show a strong dependency of relative product distribution with substrate concentration<sup>16-17</sup> and this has been taken as evidence for a substrate-radical cation reaction as the product-determining step.

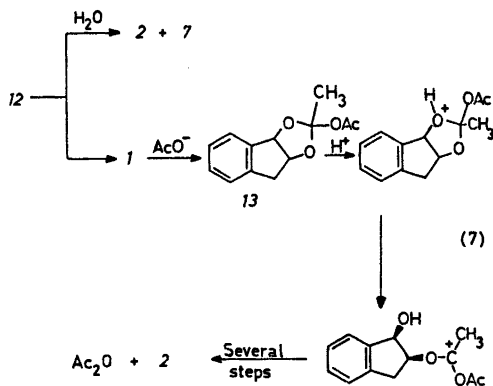
The acetoxy species (11), a benzylic radical and hence easily oxidizable, will lose an electron to the anode to give cation 12 in a very fast reaction. From this species one can in principle



derive all the addition products that have been obtained by invoking its capture by acetate ion or water to give 2, 3, 4, 7, and 8. However, the results in the anhydrous media clearly do not support such a simple mechanism; especially the formation of 2 cannot be accounted for in this way. We therefore propose that 12 is indeed partially converted to acetoxonium ion 1 which reacts further with acetate ion to give 13 (eqn. 7).<sup>3</sup> Protonation of 13 at the benzylic oxygen produces a species that might undergo heterolytic cleavage at the bond between the protonated oxygen atom and the former carboxyl carbon atom. This would ultimately produce 2 and one molecule of acetic anhydride.

Acetic anhydride was specifically sought for (GLC analysis with a detection limit of 1%) in a run with no additive present but not detected. This negative result does not add much to our knowledge of the reaction mechanism, since acetic anhydride is oxidizable at the platinum anode and hence may disappear as soon as it is formed.<sup>15</sup>

The formation of 3 might likewise partially occur *via* 1, whereas both 4 and 7 most likely are derived directly from 12.



## EXPERIMENTAL

**Large-scale anodic oxidation of indene.** A large-scale electrolysis was carried out in a capillary gap cell equipped with a graphite rod anode (800 cm<sup>2</sup>) and a steel cathode. The cell construction has been described earlier.<sup>5-7</sup>

A solution of indene (2.0 mol), KOAc (1.0 mol), acetic anhydride (20 ml), and glacial acetic acid (1200 ml) was electrolysed at a current of 10 A and a temperature between 20 and 27 °C until 2 F/mol of indene has passed.

The solution was poured into ether (3000 ml) and successively washed with 5 × 1 l of water. At the end of this procedure a black-grey solid appeared at the interface and was filtered off. The solid (6.6 g) consisted of a 2,2'-dimer and fragments from the carbon rod. The dimer was separated and purified by recrystallization from ethanol, m.p. 188 °C. NMR (CDCl<sub>3</sub>): δ 2.1 (s, 6 H, CH<sub>3</sub>CO-), 2.5–3.3 (m, 6 H, -CH<sub>2</sub>-CH-), 6.2 (d, 2 H, -CH-O), and 7.3 (br s, 8 H, Ar); (CDCl<sub>3</sub> and Eu(fod)<sub>3</sub>/substrate = 0.36): δ 3.6 (s, 6 H, CH<sub>3</sub>CO-), 3.6–3.8 (m, 6 H, -CH<sub>2</sub>-CH-), 7.2–7.5 (m, 6 H, Ar), 7.9–8.3 (m, 2 H, Ar), and 10.3 (d, 2 H, -CH-O-). The mass spectrum had the highest *m/e* at 230 (elimination of 2 molecules of HOAc from the parent ion). The IR spectrum showed a carbonyl band at 1745 cm<sup>-1</sup>.

The ether was evaporated and the residue was treated with a mixture of acetic anhydride (200 ml) and pyridine (5 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, and evaporated. The residue (310 g) was continuously extracted with pentane to separate the "monomeric" products from oligomers and polymers. From the crude product 260 g of material was extracted into the pentane solution. A second crop of 2,2'-dimer (2.6 g) was collected from the filtrate after concentration. This second crop consisted of two of the ten possible isomers and had NMR, IR, and MS characteristics similar to the first one. By distillation a mixture of 3 and 4 (145 g, 31%) was collected at 101–104 °C/0.15 mmHg. The residue was treated with a mixture of KOH (50 g), ethanol (400 ml), and water (20 ml) and refluxed for 30 min. After cooling and addition of water (2000 ml) the crystals were filtered off and washed with acetone. Treatment with acetic anhydride (20 ml) and pyridine (1 ml) gave a third crop of 2,2'-dimer (18.5 g), similar to the second one.

**Small-scale anodic oxidation of indene.** The small-scale electrolyses were carried out in a water-jacketed cell (volume 50 ml) equipped with a carbon or platinum anode, a carbon cathode, and a magnetic stirrer. The electrolyses were performed at constant current supplied from a 60 V/2 A power supply from Radiak, Sweden.

A solution of indene (0.5 g), and KOAc (3.0 g) in the solvent mixtures (30 g) given in Table 1 was electrolysed until 1.6 F/mol of indene had passed. The solution was poured into water (100 ml) and extracted with ether (100 ml) containing bimesityl (100 mg) as an internal standard. The ether solution was concentrated and analyzed by GLC.

The electrolysis with dicyclohexyl-18-crown-6 present was performed in the following way: A solution of indene (0.5 g), dicyclohexyl-18-crown (0.4 g), and dichloromethane (30 ml) was mixed with solid potassium acetate (3.0 g) and electrolysed until 1.6 F/mol of indene had passed. The dark black-brown solution was worked up as described above.

In order to determine the product 7, the crude electrolyte from a run of indene (10 g), acetic acid (95 g), water (10 g) and potassium acetate was worked up as described above except that no bimesityl was added. By repeated recrystallization from hexane, and careful washing with pentane, a mixture of 2 and 7 was isolated in better than 80 % purity, as analyzed by GLC. The remainder consisted of the two diacetates 3 and 4. The NMR spectrum was strongly dominated by 2 but  $\delta$  values of protons CH-OH and CH-OAc of 7 would be expected to come close to the corresponding ones of 2, which was the case (compare with  $\delta$  values of the 2-formate of *cis*- and *trans*-indan-1,2-diol).<sup>18</sup>

*Reaction of 1,2-epoxyindan with acetic acid/potassium acetate.* A solution of 1,2-epoxyindan<sup>8</sup> (0.5 g), HOAc (10 ml), and KOAc (1.0 g) was allowed to stand for 24 h at room temperature. The reaction mixture was worked up as described above. NMR,  $\delta$  (CDCl<sub>3</sub>) of 2: 5.1 (d, 1 H, CH-OH) and 5.4 (q, 1 H, CH-OAc); and of 3: 4.5 (q, 1 H, CH-OH) and 5.9 (d, 1 H, CH-OAc). After reflux for 30 min with acetic anhydride (10 ml) and pyridine (1 ml) the products were identified as 3 and 4.

*The INDO calculations.* The INDO calculations were performed on the UNIVAC 1108 computer of Lund University Computing Center using the CNINDO program by Pople, Beveridge, and Dobosh.<sup>19</sup> Bond distances for indene, determined by electron diffraction<sup>20</sup> were applied to the radical cation without any effort to minimize the energy. The results appear in Table 2.

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## REFERENCES

- Mango, F. D. and Bonner, W. A. *J. Org. Chem.* 29 (1964) 1367.
- Ebersson, L. and Parker, V. *Chem. Commun.* (1969) 340; *Acta Chem. Scand.* 24 (1970) 3553.
- Anderson, C. B., Friedrich, E. C. and Winstein, S. *Tetrahedron Lett.* (1963) 2037.
- Bernhardsson, E., Ebersson, L., Nyberg, K. and Rietz, B. *Acta Chem. Scand.* 25 (1971) 1224.
- Ebersson, L., Nyberg, K. and Sternerup, H. *Chem. Scr.* 3 (1973) 12.
- Ebersson, L. *Proceedings of the XXIVth International Congress of Pure and Applied Chemistry*, Vol. 5, Hamburg, 2-8 September 1973, Butterworths, London.
- Cedheim, L., Ebersson, L., Helg e, B., Nyberg, K., Servin, R. and Sternerup, H. *Acta Chem. Scand. B* 29 (1975) 617.
- Balsamo, A., Berti, G., Grotti, P., Ferretti, M., Macchia, B. and Macchia, F. *J. Org. Chem.* (1974) 2596.
- Berti, G., Bottari, F. and Macchia, B. *Tetrahedron* 20 (1964) 545.
- Russell, G. A. *J. Amer. Chem. Soc.* 78 (1956) 1035.
- Ebersson, L. In Baizer, M. M., Ed., *Organic Electrochemistry*, Dekker, New York 1973, p. 447.
- McIver, J. W., Coppens, P. and Novak, D. *Chem. Phys. Lett.* 11 (1971) 8.
- Ehrenson, S. and Selzer, S. *Theor. Chim. Acta* 20 (1971) 17.
- Sch fer, H. and Steckhan, E. *Angew. Chem.* 81 (1969) 532.
- Nyberg, K. *Thesis*, Lund 1971.
- Nyberg, K. *Acta Chem. Scand.* 25 (1971) 534.
- Nyberg, K. *Acta Chem. Scand.* 27 (1973) 503.
- Austin, R. A. and Lillya, C. P. *J. Org. Chem.* 34 (1969) 1327.
- Pople, J. A., Beveridge, D. L. and Dobosh, P. A. *J. Chem. Phys.* 47 (1967) 2026; Pople, J. A. and Beveridge, D. L. *Approximate Molecular Orbital Theory*, McGraw-Hill, New York 1970.
- Southern, J. F. and Sch fer, L. *J. Chem. Phys.* 55 (1971) 2418.
- Swain, C. G. and Scott, C. B. *J. Amer. Chem. Soc.* 75 (1953) 141.

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