

Studies on Electrolytic Substitution Reactions

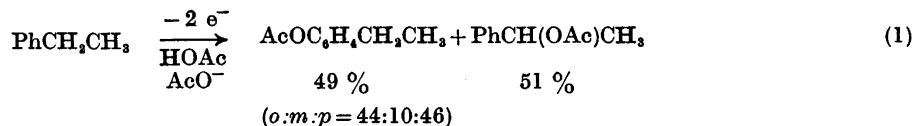
VII.* The Fate of the Elimination Product in the Anodic Acetoxylation of Indan

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The anodic oxidation of indan in HOAc/NaOAc has been studied in order to find out whether indene, the elimination product from the postulated cationic intermediate, 1-indanyl cation, is formed. The results show that the elimination/substitution ratio is 0.11, but that indene is not formed as such, but rather as a product mixture of further two-electron oxidation (addition products). Since none of the indene formed leaks into the solution bulk, it appears probable that indene is formed absorbed to the electrode surface and thus is very effectively further oxidized.

Anodic acetoxylation of alkylaromatic hydrocarbons containing at least one carbon-to-hydrogen bond in the α position to the aromatic ring in glacial acetic acid-sodium acetate gives a mixture of ring and α -acetoxylation products,¹⁻³ as exemplified below for ethylbenzene² (eqn. 1). In the light of recent investigations^{4,5}



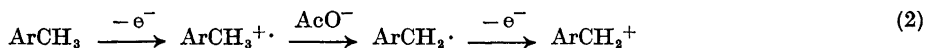
regarding the mechanism of anodic substitution processes, it appears reasonably safe to postulate that this type of reaction takes place *via* an ECE mechanism (eqns. 2 and 3), *i.e.*, the initial step is a one-electron transfer to form a very reactive cation radical, capable of reacting with acetate ion in two ways. Either acetate ion acts as a base to abstract a proton from the α position with

* Part VI, see Ref. 23.

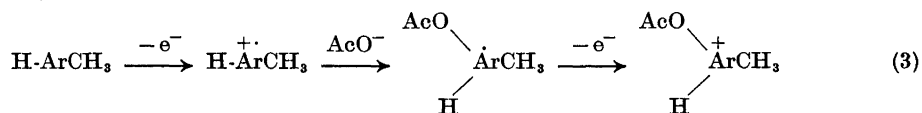
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formation of a benzyl radical, or it attacks a ring position as a nucleophile to form an acetoxycyclohexadienyl radical. Both of these intermediates are more easily oxidized than the starting material, so at the anode potential required to oxidize this, a second electron transfer follows immediately upon the chemical step. These two cases of ECE processes have been denoted $EC_B E$ and $EC_N E$, respectively, where subscripts B and N indicate base or nucleophile action in the chemical step:⁶

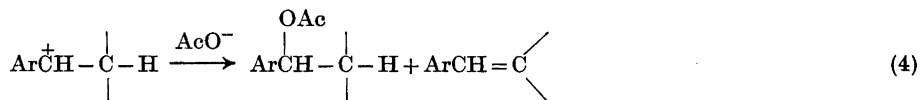
$EC_B E$ mechanism:



$EC_N E$ mechanism:



For α -substitution, the $EC_B E$ mechanism requires that a benzylic carbonium ion is formed as an intermediate. It is therefore to be expected that for substrates containing hydrogen(s) on the β carbon atom, the elimination product should be formed in addition to the substitution product, the benzylic acetate (eqn. 4). However, available

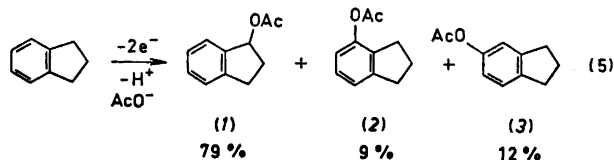


evidence indicates that no elimination product is formed in anodic acetoxylation of suitable substrates. Thus, Ross *et al.*³ did not detect any styrene in the reaction mixture from the anodic oxidation of ethylbenzene in glacial acetic acid – sodium acetate. We have been able to verify this result, although it is difficult to tell whether the absence of styrene is due to the fact that it is not formed or that it has polymerized under the reaction conditions prevailing during the experiment.⁷ Likewise, preliminary runs indicate that isopropylbenzene appears to give no elimination product (α -methylstyrene) upon anodic oxidation in acetic acid – sodium acetate, although this result is less reliable due to analytical difficulties (the α -substitution product, cumyl acetate, very easily eliminates acetic acid on GLC analysis).

Since neither ethylbenzene nor isopropylbenzene are satisfactory for an investigation of the fate of the elimination product, we eventually chose indan as a suitable substrate for further studies of the problem. Here, the substitution product, 1-indanyl acetate, has no tendency to decompose under GLC conditions, provided the temperature of the injection port and column is not too high. Moreover, it is known⁸ that in a homogeneous system, solvolytically formed 1-indanyl cation (from 1-chloroindan) in acetic acid – sodium acetate forms appreciable amounts of indene, the molar ratio between substitution and elimination product being about 1.7.

RESULTS AND DISCUSSION

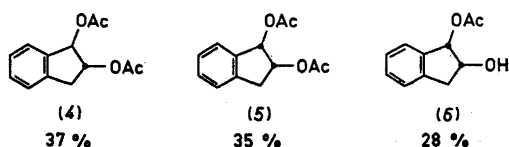
Anodic oxidation of indan, 0.6 M in 1.0 M sodium acetate – glacial acetic acid, at a platinum anode at an anode potential of 2.1 V vs. the saturated calomel electrode (SCE) gave a mixture of the expected nuclear and side-chain acetates in a 35 % current yield according to eqn. 5:



This is the product distribution after passage of 0.2 F/mol of indan (10 % reaction in a two-electron process), *i.e.*, at a stage where further oxidation of products would not be expected to obscure quantitative measurements, at least not when judged by the behavior of the acetoxylation reaction in other aromatic substitution processes.² Here the product distribution remains unchanged during the first 10 % of the reaction, in spite of the fact that nuclear acetates normally are easier to oxidize than the starting material.¹

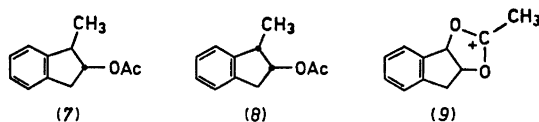
The reaction mixture was analyzed very carefully for indene, but with negative result (the GLC method employed would have detected 0.1 % of indene formed). A second semi-micro electrolysis experiment, in which enough charge to consume 50 % of the substrate was passed through the electrolyte, gave the same result; no indene was formed. Small amounts of a methyl-substituted indan was detectable in the reaction mixture, presumably 1-methylindan formed by a radical mechanism analogously to the formation of 1-ethyl-3,5-dimethylbenzene from mesitylene under similar conditions.³ Also in large-scale runs, in which indan was electrolyzed on a 0.5 molar scale and 1.2 F/mol of substrate was passed through the electrolyte, indene was not detectable in the low-boiling fractions. It must therefore be concluded that indene either is not formed and hence that the mechanism depicted in eqn. 2 is wrong or at least open for doubt, or that indene is consumed in secondary processes as it is formed without having a chance to leak out into the electrolyte bulk. Since indene has a half-wave potential which is 0.36 V lower than that of indan,⁹ this is an entirely reasonable assumption, although it is somewhat surprising that any indene formed should be quantitatively consumed. With the acetoxylation reaction in mind, where products normally have lower half-wave potential than starting material, some leakage would be expected to occur.

A careful search for other possible products revealed the formation of a 7 % current yield (based on a 4-electron process) of a mixture of mono- and diacetates of indan-1,2-diol:



These compounds were identified by comparison with samples of authentic specimen prepared otherwise and/or with data from the literature (see Experimental section). It is known that olefins, especially aryl olefins, on oxidation in the presence of acetate ion give addition products. Thus, Mango and Bonner¹⁰ found that stilbene gives rise to a mixture of *meso*-1,2-diphenylethane-1,2-diol diacetate and *threo*-1,2-diphenylethane-1,2-diol monoacetate, the stereochemistry being explained in terms of an acetoxonium ion intermediate. The same stereochemistry is observed for anodic oxidation of 4,4'-dimethoxystilbene in acetonitrile-acetic acid-sodium acetate. Hence, it is to be expected that a similar mechanism in the case of indene should give *trans*-diacetate **4** and *cis*-hydroxyacetate **6** but not *cis*-diacetate **5**.

Indene itself on anodic oxidation under the same experimental conditions (Pt anode, anode potential 2.0 V *vs.* SCE) gave a 35 % current yield of a mixture of products, the major (85 %) portion of which had almost the same composition as the high-boiling portion from the anodic oxidation of indan: **4**, 35 %; **5**, 37 %; **6**, 28 %. The remaining 15 % consisted of two components with retention times in the monoacetate region. NMR and GLC comparison with an authentic specimen showed that these compounds were *trans*- and *cis*-isomers of products of addition of one methyl and one acetoxy group across the double bond (**7** and **8**; ratio between isomers 2:3). Analogous reac-



tions have been found to occur in the anodic acetoxylation of styrene,⁷ cyclooctatetraene,¹¹ and simple olefins.¹²

Compounds **7** and **8** could be detected by GLC analysis in small amounts in the electrolysis mixture from indan too, although these very small peaks were partly obscured by the peaks originating from the nuclear acetates of indan. Thus, all products formed in the anodic oxidation of indene can be found in the reaction mixture from the electrolysis of indan, the indene reaction products constituting 9 mol % of the total product mixture. From this it can be concluded that elimination from the 1-indanyl cation takes place to an extent of 11 %, but that the indene formed is oxidized further very effectively, since none of it leaks out into the solution bulk.

The above-mentioned reactions were also performed using graphite as an anode material but under otherwise identical conditions. Indan then gave a 55 % current yield of the monoacetate fraction (*1:2:3* = 94:2:4) and a 6 % current yield of the diacetate fraction (*4:5:6* = 32:40:28), corresponding to 5 % elimination from the intermediate 1-indanyl cation. Indene gave a 32 % current yield of the diacetate fraction (*4:5:6* = 32:40:28) and a 5 % current yield of a mixture of **7** and **8** (ratio about 2:3).

A comparison between the results obtained with different anode materials reveals no significant difference between platinum and carbon. It may be that the substitution/elimination ratio is slightly higher on carbon than on

platinum, but the difference is hardly of a magnitude worth discussing. Perhaps more surprising is that 7 and 8 are formed at all at the graphite anode, since the analogous product from cyclooctatetraene is completely eliminated when changing anode material from platinum to carbon.¹¹ This latter behavior would be in agreement with a mechanism in which the initial step is attack of a methyl radical on the double bond; in view of the results in the indene case this mechanism must be regarded as doubtful.

A competition experiment using a mixture of indan and indene was run under conditions, in order to see if there is any strong preferential consumption of indene in the beginning of the reaction. The electrolyte originally contained a 94.3:5.7 mixture of indan and indene, respectively, and analyses were performed after passage of 0.05, 0.1, and 0.2 F/mol of substrate. The following results were obtained after correction for the formation of 9 % of diacetate fraction from indan:

Charge passed/mol of substrate	% indene in substrate	Products from indan, %	Products from indene, %
0	5.7	0	0
0.05	4.7	44	56
0.10	4.0	54	46
0.20	2.9	66	34

Finally, in order to have a homogeneous reaction to compare with, 1-indanyl *p*-nitrobenzoate was solvolyzed at 50° in acetic acid–sodium acetate, and the product mixture analyzed by GLC; in this case the substitution/elimination ratio is 97:3.

The results described above, clearly demonstrate that electrochemically generated 1-indanyl cation behaves qualitatively according to predictions based upon the behavior of this species when generated in homogeneous media, *i.e.*, both substitution and elimination occur. In the electrochemical reaction, however, the elimination product does not appear in the product mixture as such, but rather as compounds formed upon its further oxidation (4–8). It now becomes of immediate interest to find out whether the non-appearance of indene in the electrolyte bulk is explicable in terms of differing reactivities of indan and indene. The electrolyses have been run at fairly high potentials so as to assure that conditions of diffusion control prevail, and therefore the competition experiment should give a reasonably reliable estimate of the ratio between indene and indan “reactivities” due to other factors than differences in diffusion coefficients.¹³ Calculations based on the analyses given above show that this ratio is roughly 20; *i.e.*, indene is oxidized about 20 times faster than indan under the conditions employed. Now, putting the elimination/substitution ratio at 0.1, it is possible to show (using the equation valid for cpe at the plateau) that in the electrolysis of indan alone, the ratio of indene to indan should build up gradually to about 5×10^{-3} during the first 30 % of the reaction, and then remain approximately constant, *provided all of the indene first leaks out in the electrolyte bulk and then is oxidized further in competition with indan*. This proportion of indene would have been easily detected by our

GLC method, and it therefore remains to explain why none can be found. The most reasonable assumption is that indene is formed in an adsorbed state, and hence cannot leak out into the solution bulk before it is oxidized further.

It can be argued that since $E_{1/2}$ of indene is 0.36 V lower than that of indan, it is hardly necessary to invoke adsorbed indene as an intermediate in order to explain its rapid disappearance; the electrode has a potential high enough to oxidize indan. However, in that case, one will have to explain why the anodic nuclear acetoxylation reaction is at all feasible for aromatic hydrocarbons, since here one is generating aryl acetates with considerably lower oxidation potentials than the starting material. Yet, aryl acetates do form, often in at least fair yields. We would therefore like to suggest that both of these cases should be rationalized on the basis of differences in adsorption behavior of the participating species. Further consequences of this postulate are being actively sought in this Laboratory.

Finally, it is worth noticing that the acetoxonium ion mechanism for the anodic formation of diacetate and hydroxy acetate from olefins¹⁰ would appear not to be valid for indene. The products from an acetoxonium ion (9) in this case would be *trans*-diacetate 4 and *cis*-hydroxy acetate 6, but not the *cis*-diacetate 5. However, we do not wish to rule out the acetoxonium ion mechanism on this fact alone, since it is known that what appear to be anodic esterification reactions are known to occur as side-reactions during Kolbe electrolyses.^{14,15} Since the Kolbe reaction runs parallel to indene oxidation under the conditions used, 5 might in principle originate from 6.

EXPERIMENTAL

Materials Analytical grade acetic acid and anhydrous sodium acetate were used as purchased (Merck, Germany). Indan and indene (Fluka, Switzerland) were distilled carefully before use. The indene contents of the indan fraction used in the electrolyses was 0.45 %.

1-, 4-, and 5-indanyl acetate (1, 2, and 3, respectively) were prepared by acetylation of the appropriate hydroxy derivatives.¹⁶⁻²⁰ *trans*-1,2-Diacetoxyindan (4) was prepared according to the method given by Winstein and Roberts.²¹ 1-Indanyl *p*-nitrobenzoate was prepared according to the general method for synthesis of aralkyl *p*-nitrobenzoates given by King,²² m.p. 76–78°, after recrystallization from light petroleum.

Electrolysis experiments. The semi-micro electrolyses were run in the cell described in paper VI²³ and with that cell equipped with a planar graphite anode (area about 12 cm²). The reference electrode was a saturated calomel electrode, and anode potential control was achieved by means of the Model 557 potentiostat from Milan, Italy. The amount of charge passed through the electrolyte was measured by the Model 558 Integrator from the same company.

Large-scale runs were performed in an 800 ml water-jacketed vessel, equipped with either a planar Pt (50 cm²) or graphite (50 cm²) anode, and, in both cases, a nickel cathode. The spacing between the electrodes was about 1 cm.

Anodic oxidation of indan (semi-micro experiment at the Pt anode). A solution (50 ml) of indan (0.030 mol) in 1.0 M sodium acetate/glacial acetic acid was electrolyzed at a potential of 2.10 V, until 0.2 F/mol of indan had passed. The solution was worked up by dropping it slowly into an aqueous slurry of sodium bicarbonate, followed by ether extraction. After washing the extract with sodium bicarbonate solution and water, it was concentrated to a volume of about 15 ml. This solution was then analyzed for products (acetate and diacetate fraction) by GLC (Perkin-Elmer 880 Gas Chromatograph, D-26 Integrator) and GLC/mass spectrometry (LKB A-9000 mass spectrometer with GLC inlet). Hydroquinone diacetate was used as an internal standard.

GLC (2 m × 0.3 cm 5 % neopentyl glycol succinate on Chromosorb P 80–100) at 140° showed three peaks, which according to retention time (r.t.) and mass spectra comparison with authentic specimen was 1-indanyl acetate (1, r.t. 2.43 min), 4-indanyl acetate (2, r.t. 3.84 min), and 5-indanyl acetate (3, r.t. 5.83 min) in the proportions 79:9:12. The combined current yield of 1, 2, and 3 was 35 % (the r.t. of hydroquinone diacetate was 25.0 min under the conditions used).

Raising the column temperature to 160° revealed the presence of a group of three peaks with longer retention times (18.4, 21.6, and 23.8 min, respectively, at 160°). GLC and mass spectral comparison showed these peaks to correspond to those obtained on GLC of the high-boiling fraction from the preparative acetoxylation of indene (4, 5, and 6); (for identification of these compounds, see below). The combined current yield of 4, 5, and 6 (proportions 37:35:28) was 7 % (4-electron process).

Analysis for indene was performed on a 4 m × 0.3 cm column, containing the same stationary phase as used above with the column temperature at 90° and the injection port temperature at 120°. No indene (r.t. 11.4 min) had been formed, but small amounts of a compound with slightly shorter retention time (9.1 min) than indene could be detected (see below).

In a second experiment, using the same conditions but with charge corresponding to 50 % consumption of substrate passed through the electrolyte, there was still no indication that indene had been formed during electrolysis. A gas chromatographic peak with retention time 9.1 min was identified by mass spectrometry as a methylindan, probably 1-methylindan.

Anodic oxidation of indan (semi-micro run at the graphite anode). This experiment was performed similarly to the preceding one, except that the anode potential required to pass roughly the same current was considerably lower, 1.50 V vs. SCE. The results obtained have been given in the Results section.

Anodic oxidation of indan (large-scale run at the Pt anode). The electrolyte was a solution of indan (0.40 mol) in 1 M sodium acetate–glacial acetic acid (300 ml). After passage of 1.2 F/mol of indan, the electrolyte was worked up in the usual way. Distillation afforded a low-boiling fraction of indan (10.8 g) with no trace of indene in it, a second fraction containing 1, 2, and 3 (b.p. 88–92/1.5 mm; 10.6 g), and a third fraction containing 4, 5, and 6 (b.p. 125–126/1.5 mm; 0.8 g). The current yield of isolated product was 27 %.

Anodic oxidation of indene (large-scale run at the graphite anode). Indene (1 mol) was oxidized anodically in a solution of sodium acetate (45 g) and glacial acetic acid (650 ml) until 1.60 F/mol of indene had been passed through the cell. After the usual work-up, distillation gave two main product fractions, one boiling at 92–110°/1.3 mm (3.7 g), and one at 111–125° (60.3 g). The residue weighed 25.6 g and was a black tar.

GLC analysis of the low-boiling fraction showed it to consist of at least two components in a ratio of 3:2 (r.t. 12.0 and 14.4 min at 120° on the same column as above) in addition to minor amounts of the components of the high-boiling fraction. GLC analysis of both the low- and high-boiling fraction showed these two components to account for 15 % of the total product mixture.

The NMR spectrum of the low-boiling fraction had signals centered at 1.25 ppm (two doublets in the ratio of 2:3; each of the coupling constants 7.0 cps), 2.00 ppm (two singlets in the ratio of 2:3), 3.2 ppm (multiplet), 5.1 ppm (multiplet), and 7.18 ppm (singlet) with integrated areas in the proportions 3:3:3:1, assigned to the methyl group protons, the acetate methyl group protons, the methylene group proton adjacent to the methyl group, the proton α to the acetoxy group, and the aryl group protons, respectively. The position of the signal for the proton α to the acetoxy group is in the region for an acetoxy group β to an aryl group; an acetoxy group in the 1-position shifts the position of the signal of the α -proton to considerably lower field, 6.0–6.3 ppm.²⁴ The orientation of addition is the same as for addition of one methyl and one acetoxy group to styrene.⁷ The mass spectra of these compounds do not show peaks corresponding to the parent ion (m/e 190) even at 15 eV, but show very strong peaks formed by loss of acetic acid (m/e 130). In addition, a small peak at m/e 174 is observed, corresponding to loss of methane.

The NMR spectrum of the high-boiling fraction clearly showed it to consist of a mixture of *trans*- and *cis*-1,2-diacetoxyindan (4 and 5) by comparison with the authentic *trans* compound and with literature data,²⁴ in addition to a third component. The third component was identified on the basis of its NMR spectrum, the interesting parts of which was easily distinguished from the spectra of 4 and 5, and on its behavior upon

treatment with acetic anhydride. This converted a small sample of the high-boiling fraction to a clean mixture of 4 and 5; the stoichiometry of the reaction was such as to show that about 30 % of the high-boiling fraction had been converted quantitatively to the *cis*-diacetate 5. The position of the acetoxy group in the *cis*-hydroxyacetate was demonstrated to be as in 6 by the NMR spectrum, which has a doublet at 5.95 ppm, *i.e.* in the region expected for a proton α to an acetoxy group and an aryl group; a proton α to a hydroxyl group and aryl group would be shifted upfields.²⁴

GLC analysis as well as integration of the appropriate signals in the NMR spectrum of the high-boiling fraction gave the proportions of 4:5:6 as 32:40:28. The current yield of total product mixture (4-8) was 37 %.

In view of the fact that indene and ether aryl olefins undergo an additive or eliminative dimerization reaction on anodic oxidation in methanol/sodium methoxide/sodium perchlorate,²⁵ the crude product mixture was checked by GLC for such products (using 2-(1-indanyl)-indene²⁶ as a calibration compound). However, no dimers of any kind were discernible.

Anodic oxidation of indene (large-scale run at the graphite anode). The electrolyte consisted of indene (0.4 mol) in 300 ml of 1 M sodium acetate-glacial acetic acid. The amount of charge passed was 1.5 F/mol of indene. The results have already been given in the Results section.

Acetolysis of 1-indanyl-p-nitrobenzoate. 1-Indanyl-*p*-nitrobenzoate (261 mg) and anhydrous sodium acetate (820 mg) were dissolved in glacial acetic acid to a volume of 10.0 ml. The solution was kept at 50° for 28 h. The usual work-up produced an ether solution which was analyzed by GLC. It contained indene (3 %) and 1-indanyl acetate (97 %).

Acknowledgements. One of the authors (L. E.) gratefully acknowledges generous financial support from the *Swedish Natural Science Research Council*, and from *Carl Tryggers Stiftelse*.

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Received September 4, 1970.