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Studies on the Possible Effects of Adsorption on the Product Distribution of Organic Electrode Reactions. I. Stereochemistry of the Anodic Acetoxylation of 2-*t*-Butylindan [1]

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The anodic acetoxylation of 2-*t*-butylindan has been studied at platinum, carbon, and lead dioxide electrodes. The predominant reaction at platinum and lead dioxide is side-chain acetoxylation, minor amounts of 4- and 5-acetoxy-2-*t*-butylindan and 2-*t*-butylindene being obtained among the by-products. At the carbon anode, 2-*t*-butylindene becomes the major product. The *cis-trans* ratio of the two side-chain acetates is significantly higher in the anodic processes than in related homogeneous reactions, indicating that adsorption at least partially controls the stereochemistry of the anodic acetoxylation reaction.

In many cases the product distribution from an organic electrode process displays features which are not easily accounted for by invoking concepts or analogies from homogeneous solution chemistry. The most obvious way out of this difficulty is to involve the heterogeneity of the electrode reaction in the mechanistic picture, most commonly by postulating that the electrode surface exerts some degree of steric control over the molecular events following electron transfer. In many cases adsorption of substrate and intermediates is explicitly postulated, in others phrases such as "steric shielding by the electrode from attack on one side of the substrate/intermediate" are employed. Such explanations have often been put forward to account for the stereochemistry of electrode processes, such as anodic addition of acetoxy groups to *trans*-stilbene [2] (although the adsorption postulate does not appear to be necessary here in the light of more recent work [3,4]), anodic addition of two methoxy groups to stilbene, in which a slight preference for *cis* addition is observed,[5] the addition of alkyl radicals to dienes, in which a very marked stereospecificity is sometimes observed[6], the anodic addition of methoxy and

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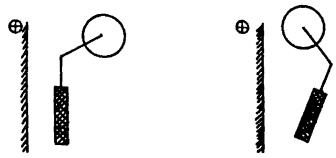
acetoxy groups to anthracenes,[7] the cathodic addition of hydrogen to alkynes and alkenes,[8] and the cathodic reduction of camphor oximes and related compounds.[9] The anodic addition of two acetoxy groups to cyclooctatetraene might also be a case of steric control by the anode surface in view of the strong preference for *cis* addition in the electrochemical process as compared to related homogeneous ones, although the complexities of cyclooctatetraene chemistry makes judgment on this point difficult.[10] The stereochemistry of cathodic halide reduction has also been explained in terms of adsorbed intermediates.[11]

Also, explanations of other observations than stereochemical have been thought to require the adsorption postulate. Anodic substitution processes such as methoxylation,[12] acetoxylation,[13] and cyanation [14] presumably involve adsorbed species, although the experimental consequences of this assumption for at least the two last-mentioned reactions have not been established yet. The increase in the formation of dimer and trimer with increasing water concentration in the anodic oxidation of anthracene in acetonitrile/water/sodium perchlorate seems to indicate that the reaction takes places between adsorbed species.[15] The failure to detect the elimination product, indene, as such in the anodic acetoxylation of indan was explained in terms of adsorption; indene is formed in the adsorbed state by proton loss from the likewise adsorbed 1-indanyl cation and undergoes follow-up reactions to form addition products directly [16] without leaving the electrode surface.

While the cases referred to above point to an involvement of the electrode surface in the product-forming step, it is desirable to study systems which have been specifically designed to give more definitive answers to the problem of assessing the role of adsorption. In this series of papers, we wish to report results from studies on systems in which there is reason to assume that adsorption plays a certain role for the product distribution and where there is hope that these effects might be disentangled from other effects. The starting point has been to utilize current ideas regarding the adsorption of aromatic hydrocarbons onto anode surfaces.[17–19] It was found that molecules such as naphthalene and anthracene are adsorbed on Pt and Au anodes with adsorption enthalpies of $-(6-10)$ kcal/mol, and it was furthermore made probable that adsorption takes place with the molecular plane of the hydrocarbon parallel to the anode surface. The nature of the bond between substrate and electrode was assumed to be of the π-donor-acceptor type, *i.e.*, of the same type as in charge-transfer complexes. Extension of this analogy somewhat further would lead to the postulate that the distance between substrate and electrode should be approximately the same as in charge-transfer complexes or about 3.5 Å.

If these ideas about adsorption of aromatic hydrocarbons are accepted, it should be possible to design hydrocarbon molecules in which one side exerts steric hindrance toward adsorption whereas the other side does not, as schematically shown for the following two hydrocarbon-electrode configurations (viewed as a cross-section of the system perpendicular to the electrode plane):



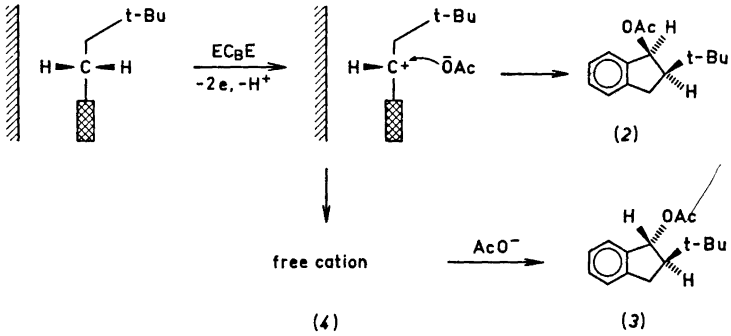
Non-parallel alignment Parallel alignment

If one then carries out a suitable electrode process with such a compound, testable predictions about stereochemistry become possible for the case that the parallel orientation is favored in the adsorption process and this orientation prevails during the sequence of events following electron transfer.

This idea is best demonstrated by looking at the molecule first chosen for this study, 2-*t*-butylindan (*1*). This hydrocarbon has a flat aromatic portion annelated to a cyclopentane ring, which in its turn carries a bulky alkyl group pointing out from one side of the plane defined by the aromatic ring, as the formulas *1* and *1a* indicate:

(*1*) (*1a*)

Apart from these desirable features, the system was chosen on the basis of other results pointing to adsorption being important in the anodic reactions of the indan system.[16] Even if the cyclopentane ring in indan is slightly puckered (*1a*),[20] the molecule would be expected to align itself with the electrode surface with the *t*-butyl group pointing away from the surface:

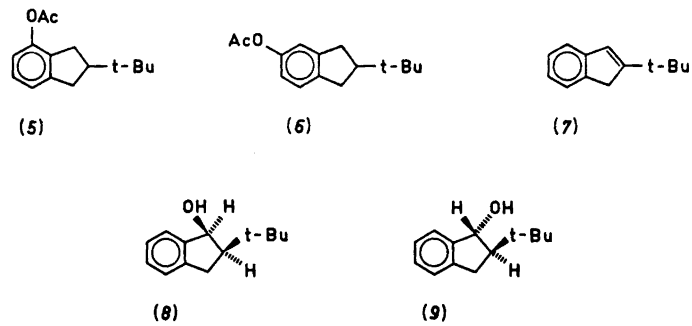


Now it is easy to see that *in this orientation* an anodic substitution reaction, *e.g.*, acetoxylation, which is presumed to be of the EC_BE type,[21,22] carried out at the α carbon of *1* would lead to the thermodynamically less favoured *cis* isomer *2*, whereas the free cation obtained after desorption would be

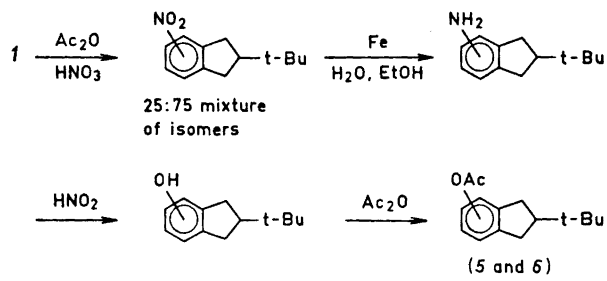
expected to give the *trans* isomer *3*. This latter prediction can in principle be tested by generation of carbonium ion *4* in a homogeneous solution process, and since the non-parallel orientation likewise would lead to *3*, it is obvious that a high *cis-trans* ratio in the anodic process as compared to the homogeneous one would support the view that adsorption plays a role in determining the product distribution.

RESULTS

2-*t*-Butylindan (*1*) was prepared according to the method given by Herz.[23] Anodic oxidation of *1* under different conditions (see below) gave product mixtures containing predominantly side-chain monoacetates *2* and *3* and nuclear acetates *5* and *6*. In addition small amounts of 2-*t*-butylindene (*7*), the two isomers of 1-hydroxy-2-*t*-butylindan (*8* and *9*), and three compounds with mass spectra corresponding to nuclear acetates of *7* were detected.



The identity of *5* and *6* was established *via* the following reaction sequence:

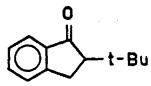


Throughout this reaction sequence no attempt was made to separate the isomers. The two components of the final mixture of acetates were identical with the two compounds formed in the acetoxylation reaction and assigned the nuclear acetate structure on the basis of their mass spectra. By analogy with the known similarity between nuclear anodic acetoxylation and electrophilic aromatic substitution in general we assign the major nuclear

acetate isomer formed in the anodic acetoxylation of *1* the structure *6*. This is also the predominant isomer formed in the chemical reaction sequence above and in line with the results obtained in the anodic acetoxylation of indan itself [16] where the 5-isomer is formed in larger amounts.

The assignment of relative configurations to the two side-chain acetates obtained in the anodic oxidation of *1* proved to be more difficult than expected. It has recently been established that coupling constants are unreliable for stereochemical assignments in the indan system,[24] and this was also evident in the 2-*t*-butylindan derivatives. The side-chain acetates formed from the anodic oxidation of *1* at a platinum anode in glacial HOAc/NaOAc could not be separated by GLCP on any of a large number of columns and column combinations, so the composition had to be analyzed by integration of suitable signals in the NMR spectrum of the mixture. An average value of 16:84 was obtained by integration of the signals corresponding to the *t*-butyl group, the methyl group in the acetoxy group, and the hydrogen α to the acetoxy group. The last-mentioned signal was composed of two doublets, one at δ 6.16 ppm with $J = 5.4$ cps corresponding to the 16 % isomer, and one at δ 6.34 ppm with $J = 6.0$ cps. The difference between the coupling constants is obviously not useful for assignment of stereostructures of the isomers. Of more significance is perhaps the fact that the low-field doublet is broadened as compared to the high-field one. Since the cyclopentane ring of the indan system is puckered [20] and this effect should be even more pronounced in 2-*t*-butylindan due to the steric effect of the *t*-butyl group (see *1a*), the C – H bond α to the acetoxy group in the *trans* isomer will be suitably oriented for long-range coupling with the *ortho* aromatic hydrogen (the most favored orientation for such coupling has been shown to be an arrangement where the benzylic C – H bond is perpendicular to the aromatic ring [25]). On the other hand, in the *cis* isomer this bond will be close to parallel with the aromatic ring and hence coupling to the *ortho* hydrogen should have a smaller coupling constant. Thus the first tentative assignment is that the predominant side-chain acetate is the *trans* isomer.

However, more definitive evidence was needed and obtained through chemical methods. The ketone *10* was reduced by lithium aluminium hydride or aluminium isopropoxide to give a mixture of isomeric alcohols (*8* and *9*). Since attack by these reagents is known to take place from the least hindered side of the molecule, the major isomer is assigned the *cis* configuration (*8*).



10

Reduction →

	8	+	*9*
$LiAlH_4$	78 %		22 %
$Al(i\text{-}PrO)_3$	94 %		6 %

Again, coupling constants for the proton α to the hydroxy group (*cis* form, doublet at δ 4.99 ppm with $J = 5.4$ cps; *trans* form, doublet at δ 4.91 ppm with $J = 7.0$ cps) proved to be of little value for assignment of stereo-structures. However, the NMR spectrum of the isomer assigned the *trans* conformation

has a broadened doublet corresponding to the proton α to the hydroxyl group, similar to the behavior of the *trans* acetate *3*. This further supports the assignment made above.

Having established that the major isomer from reduction of *10* must have the *cis* configuration, the mixture of alcohols was converted to a mixture of acetates *2* and *3* by treatment with acetic anhydride-pyridine. NMR comparison between this acetate mixture and the one obtained by anodic odixation of *1* shows that the major alcohol isomer from reduction of *10* corresponds to the minor acetate from anodic oxidation. Hence the *cis-trans* ratio in the anodic oxidation experiment referred to above is 16:84.

The results from anodic oxidations of *1* in glacial acetic acid/0.5 M sodium acetate or 0.5 M Bu_4NBF_4 at different anode materials are given in Table 1. The anodic half-wave potential of *1* in HOAc-NaOAc at platinum is 1.50 V *vs.* SCE, and the preparative runs were performed at slightly higher potentials (between 1.9 and 2.0 V). The electrolyses were run until 2.1 – 2.2 *F* per mol of *1* had been passed through the electrolyte. In separate experiments it was established that the product distribution, especially the ratio between *2* and *3*, was not significantly different from that obtained at lower conversions, showing that selective further oxidation of the primarily formed products takes place to a negligible extent. The proportion of *8* and *9* was, however, slightly higher at low conversions, presumably due to the fact that the small amount of water inevitably present in the electrolyte is used up in the beginning of the electrolysis.

Table 1. Product composition from the anodic oxidation of 2-*t*-butylindan under different experimental conditions. Temp. 25.0°.

Electrolyte	Anode material	Relative yield of products[a,b]				*cis-trans* ratio, *2/3*
		Side-chain acetates,[c] *2+3*	Nuclear acetates, *5+6*	2-*t*-Butyl-indene *7*[d]	Side-chain alcohols *8+9*	
HOAc/0.5 M NaOAc	Pt	79	16	3	2	16:84
HOAc/0.5 M Bu_4NBF_4	Pt	71	2	21	<1	5:95
HOAc/0.5 M NaOAc	C	32	10	57	<1	5:95
HOAc/0.5 M Bu_4NBF_4	C	21	3	52	<1	<2:98
HOAc/0.5 M NaOAc	PbO_2	87	3	10	<1	5:95

[a] GLPC analysis. [b] Current yields range between 40 and 60 %, the surplus charge being assumed to be used for oxidation of solvent/supporting electrolyte. [c] Analyzed by NMR. [d] Analyzed as 7 + the three components assumed to be nuclear substitution products of *7*.

Inspection of Table 1 reveals that monoacetoxylation is the predominant reaction in the system on platinum and lead dioxide, but that formation of the elimination product, 2-*t*-butylindene (*7*), is favored on the carbon anode. The *cis-trans* ratio for the side-chain acetates changes with anode material in

that Pt gives the highest ratio, 16:84, and the two other anode materials, lead dioxide and graphite, give a considerably lower ratio (Table 1), *ca.* 5:95. At these low ratios the NMR analytical method employed unfortunately is not so accurate, but it is nevertheless evident that there is a change in the *cis-trans* ratio by a factor of at least 3 in going from platinum to lead or graphite anodes.

Experiments were also performed in a medium that would be expected [13,26] to direct the substitution process to exclusively side-chain products. Thus, in glacial acetic acid-tetrabutylammonium tetrafluoroborate at a platinum anode side-chain acetates *2* and *3* are formed as monoacetoxylation products to a large extent, with a ratio of $2:3 = 5:95$. On graphite the ratio is lower, $< 2:98$. Hence the change in the *cis-trans* ratio follows the same trend as in HOAc/NaOAc, although the preference for *trans* substitution has been increased with the change in electrolyte.

In order to have a homogeneous reference reaction to compare with, several direct acetoxylation processes were investigated. Lead tetraacetate oxidation of *1* indeed gives a fairly good yield of side-chain acetates *2* and *3* (ratio 5:95) besides other products, but this reaction is less suitable as a reference for several reasons. Firstly, the reaction had to be run with solid lead tetraacetate present during most of the reaction period in order to get a good yield of *2* and *3* and hence the heterogeneity might have influenced the *cis-trans* ratio. Secondly, the mechanism of lead tetraacetate oxidation of the aromatic side-chain is not very well established; in particular, the possible role of carbonium ion *4* in the reaction sequence is not ascertained. Therefore, we resorted to a non-oxidative process for generation of *4*, namely solvolysis of the *p*-nitrobenzoates (PNB) of *8* and *9*. Pure *8*-PNB on solvolysis in HOAc/0.5 M NaOAc at 75° gave a mixture of elimination product (*7*) and side-chain acetates ($2+3$) in a ratio of 32:68. Since it proved difficult to get enough of a pure sample of *9*-PNB, a 50:60 mixture of *8*- and *9*-PNB was solvolyzed under identical conditions. From this run a 36:64 mixture of $7/(2+3)$ was obtained, showing that the two *p*-nitrobenzoates give identical product distribution in this respect. The stereochemical outcome also was the same in in both cases, in that the *cis-trans* ratio was $< 2:98$.

DISCUSSION

In discussing the data above, it is perhaps first appropriate to point out that the original expectations of *drastic* differences in the *cis-trans* ratio between the electrochemical and homogeneous reactions of carbonium ion *4* have not been borne out in the experiments in this system. The interpretation of the effects observed is therefore rather difficult and should be viewed with reserve until more data have accumulated. However, even if the *trans* isomer is the favored one in all cases studied, the *cis-trans* ratio is significantly higher in the electrochemical processes. Thus in the most favorable case, the anodic acetoxylation of *1* at platinum in HOAc/NaOAc, the *cis-trans* ratio is at least 9 times higher than in the solvolysis of *8*- or *9*-PNB in the same medium. Assuming that these reactions proceed *via* the free carbonium ion *4* (and this

is strongly suggested by the near identity of the product distributions from the solvolyses), there is indeed a stronger tendency for formation of the *cis* isomer in the anodic process. This is exactly what our admittedly naive model based on adsorption control of stereochemistry predicts, and it is therefore reasonable to conclude that part of the reaction proceeds *via* an intermediate which is adsorbed parallel to the anode surface with the least hindered side facing the surface. This cannot, however, be the whole story, since such a high proportion of *trans* isomer is actually observed. Here we can only conclude that either is the non-parallel orientation only little less favored that the parallel one, or does the reaction take place *via* desorbed, free, carbonium ion *4*. It is maybe unfortunate that the system under study has such a strong inherent preference for formation of the *trans* isomer; it is worth pointing out that in a hypothetical system with a 10:90 *cis-trans* ratio for the homogeneous process the factor of >9 would make the *cis-trans* ratio from the anodic process to be 50:50, a seemingly more significant change but in fact the same as above. Experimentally, such a system would be much easier to study.

Turning to the differences between different anode materials, it is noticeable that the weaker adsorbing materials, graphite and lead dioxide, give rise to lower *cis-trans* ratios than the stronger adsorbing platinum, again in line with predictions based on the adsorption model. In these cases it is difficult to make any definitive statements with respect to a comparison between the heterogeneous and homogeneous processes because of the errors involved in determining small *cis-trans* ratios, but it seems as if the ratio is higher also on graphite and lead dioxide, perhaps by a factor of $2-3$, except possibly when Bu_4NBF_4 is used as a supporting electrolyte.

Hence one can safely conclude that the trend in the data is in satisfactory agreement with the model outlined in the introduction. The electrochemical reactions do give a higher *cis-trans* ratio than the homogeneous reference reaction, and the ratio is higher for the more strongly adsorbing electrode material, platinum. It would of course be more satisfactory if the experimental results had been more decisive, but we think that the trends observed are promising enough to encourage us to continue experimentation in this area.

There are several reasons why 2-*t*-butylindan is not an ideal model system for stereochemical studies of the kind described here. Some of these have been touched upon already: the inherent strong preference for *trans* substitution, which makes analyses experimentally difficult, the failure of the gas chromatographic method for analyzing the *cis-trans* mixture, and the puckering of the molecule (see *1a*) which partly counteracts one of the desirable features of the system, namely that the *t*-butyl group should hinder the approach to the electrode on one side of the molecule. The following paper [27] of this series will describe an analogous stereochemical study on a less flexible molecule, 1-*t*-butylacenaphthene.

EXPERIMENTAL

Materials. Analytical grade acetic acid and anhydrous sodium acetate were used as purchased (Merck AG, Germany). Tetrabutylammonium tetrafluoroborate was prepared according to the method described by Nyberg.[28]

Electrolysis experiments. These were performed using equipment described previously,[16]

except for the use of a slightly larger vessel (*ca.* 150 ml volume). The lead dioxide electrode was prepared by electrochemical plating of lead dioxide onto a planar graphite anode from acidic lead nitrate solution. The surface area of this electrode was *ca.* 10 cm.^{2}

Analytical procedures. Gas chromatographic analysis was carried out using a Perkin-Elmer 880 gas chromatograph, equipped with the Perkin-Elmer Model D-26 Integrator on a 2m × 0.3 cm 5 % NPGS on Chromosorb W column (retention times for compounds of interest, see Table 2). Mass spectrometric analysis was performed with an LKB 9000 mass spectrometer (see Table 2) in combination with a GLPC inlet. NMR spectra were recorded with a Varian A-60 NMR spectrometer.

Table 2. GLPC retention times and mass spectral data for 2-*t*-butylindan and derivatives.

Compound	Retention time, min (column temp.)	Mass spectral data, *m/e* (% of largest peak)
1	1.3 (160)	
7	2.0 (160)	173(9), 172(61), 158(15), 157(100), 142(11), 116(17), 57(43)
10	4.3 (160)	
8	5.4 (160)	191(5), 190(27), 172(58), 158(14),
9	6.7 (160)	157(100), 142(13), 133(25), 132(17), 120(55), 119(13), 116(28), 57(48)
2	5.2 (160)	232(1), 190(20), 172(80), 157(100), 116(45), 57(40)
3	5.2 (160)	
5	7.8 (160)	232(11), 191(15), 190(100), 175(15),
6	11.9 (160)	134(75), 133(40), 132(27), 120(29), 57(75), 43(25), 41(16)
4-Nitro-2-*t*-butylindan	23 (192)	219(9), 163(33), 146(14), 57 (100)
5-Nitro-2-*t*-butylindan	34.5 (192)	
4-Amino-2-*t*-butylindan	20.8 (192)	190(17), 189(100), 133(21), 132(92),
5-Amino-2-*t*-butylindan	20.8 (192)	131(16), 130(18), 119(51), 115(11), 57(19)
4-Hydroxy-2-*t*-butylindan	20.5 (180)	191(10), 190(67), 175(15), 134(53),
5-Hydroxy-2-*t*-butylindan	26.1 (180)	133(68), 132(25), 131(11), 120(74), 105(12), 77(11), 57(100)

2-t-Butylindan. This compound was prepared according to the method described by Herz;[23] b.p. 47 – 49°/0.2 mm; NMR δ 0.93 (s, 9, *t*-butyl protons), 1.70 – 3.00 (m, 5, aliphatic protons in side-chain), and 7.13 ppm (s, 4, aromatic protons).

4- and 5-Nitro-2-t-butylindan. 2-*t*-Butylindan, 5.0 g, was dissolved in acetic anhydride, 10 ml, and the solution cooled to 1 – 2° by external cooling. Freshly distilled nitric acid (100 %), 1.3 ml, in acetic anhydride, 10 ml, was then added at such a rate that the temperature was kept between 1 and 2°. The solution was then stirred for an additional period of 20 min. Water was added and the mixture allowed to stand for 2 h. The organic material was extracted by ether and the ether solution was washed with hydrogen carbonate solution and water. After drying the extracts with $MgSO_4$, the ether was distilled off and the residue distilled *in vacuo*. The main fraction (b.p. 118 – 128°/0.6 mm, 2.0 g) contained the two nitro compounds in a ratio of 25:75 (MS, see Table 2). A similar mixture of nitro compounds was obtained by using sulfuric acid/nitric acid as a nitrating

agent. By analogy with other electrophilic reactions in the indan system the major nitro isomer was assigned the 5-nitro-2-*t*-butylindan structure.

*4- and 5-Amino-2-*t*-butylindan.* The main fraction from the preceding experiment was dissolved in a mixture of ethanol (5 ml) and water (5 ml). Ferric chloride (0.1 g) was added, whereafter iron powder (0.4 g) was added slowly with stirring. The reaction mixture was then refluxed for 3 h. After cooling hydrogen carbonate solution was added and the solid material filtered off. The solid was then washed thoroughly with ethanol. The combined filtrates were concentrated in a rotating film evaporator, and the residue extracted with ether. GLPC demonstrated the presence of two compounds (overlapping peaks) both exhibiting $M^+ = 189$ (MS, see Table 2) and assigned the structure of 4- and 5-amino-2-*t*-butylindan (the major isomer is assumed to be the 5-isomer). Evaporation of the ether yielded crude material, 1.1 g, which was used directly for the synthesis of the corresponding phenols.

*4- and 5-Hydroxy-2-*t*-butylindan.* The crude amine fraction, 1.1 g, was dissolved in acetic acid (10 ml), and a mixture of sulfuric acid (1.5 ml) and water (1.8 ml) was added. The solution was stirred and cooled to $+2°$. Sodium nitrite (1.2 g) in water (3 ml) was then added while the temperature was kept below 5°. After the addition the solution was kept at $+2°$ for 30 min and at reflux temperature during 30 min. Addition of water and extraction with ether in the usual manner gave a crude mixture of the two phenols (MS, see Table 2).

*4- and 5-Acetoxy-2-*t*-butylindan* (*5* and *6*). The phenol mixture was treated with acetic anhydride-pyridine in the usual way, yielding a mixture of compounds *5* and *6* (MS, see Table 2).

*Reduction of 2-*t*-butylindanone-1 (10) by aluminium isopropoxide.* The ketone [NMR: $\delta = 1.00$ (s, 9, protons of *t*-butyl group), 2.35 (q, 1, CH in indan part), 2.87 – 3.17 (m, 2, CH_2), and 7.05 – 7.75 ppm (m, 4, aromatic protons)] was prepared according to the method given by Herz.[23] In the reduction experiment the ketone (5.0 g) was dissolved in a solution of aluminium triisopropoxide in isopropyl alcohol (130 ml, 17 g of the isopropoxide per 100 ml of solution). The solution was then distilled very slowly using a distillation column of 7 – 8 theoretical plates for 160 h, dry isopropyl alcohol being added when necessary. The solvent was distilled off toward the end and the residue was decomposed with water and dilute hydrochloric acid. Work-up in the usual manner gave a crude mixture of *8* and *9* in a ratio of 94:6. NMR of *8*: δ 1.10 (s, 9, *t*-butyl protons), 1.6 – 3.2 (m, 3, aliphatic protons except α to OH), 2.16 (s, 1, OH proton), 4.99 (d, $J = 5.4$ cps, 1, H α to OH group), and 7.1 – 7.3 ppm (m, 4, aromatic protons). NMR of *9*: δ 0.95 (s, 9, *t*-butyl protons), 1.6 – 3.2 (m, 3, aliphatic protons except α to OH), 2.11 (s, 1, OH proton), 4.91 (d, $J = 7.0$ cps, 1, H α to OH group), and 7.1 – 7.3 ppm (m, 4, aromatic protons).

*Reduction of 2-*t*-butylindanone (10) by lithium aluminium hydride.* To a slurry of $LiAlH_4$ (0.3 ml) in dry ether (5 ml) was added a solution of *10* (0.5 g) in dry ether (3 ml). The reaction was worked up in the usual manner after 20 min, giving a 78:22 mixture of alcohols *8* and *9*, respectively.

cis-*1-Acetoxy-2-*t*-butylindan (2).* *cis*-1-Hydroxy-2-*t*-butylindan (*8*) (0.10 g, containing 6 % of the *trans* form) was dissolved in acetic anhydride and one drop of pyridine added. The solution was heated on a steam bath for 3 h and then worked up by water treatment and ether extraction. The washed and dried ether extracts were evaporated and the residue analyzed by NMR: 1.08 (s, 9, *t*-butyl protons), 1.97 (s, 3, methyl group), 2.1 – 3.5 (m, 3, CH_2 and CH protons), 6.16 (d, $J = 5.4$ cps, 1, H α to OAc group), and 7.20 – 7.30 ppm (m, 4, aromatic protons).

cis- *and* trans-*1-Acetoxy-2-*t*-butylindan (2 and 3).* A mixture of *cis*- and *trans*-1-hydroxy-2-*t*-butylindan (distilled sample; the *cis-trans* ratio was 41:59, the change in ratio having been accomplished by partial isomerization of the 94:6 mixture in isopropyl alcohol-aluminum isopropoxide in the presence of a trace amount of acetone) was dissolved in acetic anhydride (5 ml) and a drop of pyridine added. After 3 h heating on a steam-bath the reaction mixture was worked up by water treatment and ether extraction. The ratio between *2* and *3* according to NMR analysis was 46:54. The *trans* isomer (*3*) had the following NMR spectrum: $\delta = 0.95$ (s, 9, *t*-butyl protons), 2.06 (s, 3, acetoxy methyl group), 2.1 – 3.4 (m, 3, CH_2 and CH), 6.34 (d, $J = 6.0$ cps, 1, H α to acetoxy group), and 7.1 – 7.3 ppm (m, 4, aromatic protons).

*Anodic oxidation of 2-*t*-butylindan.* The electrolyte consisted of a solution of *1* (7.0 g)

in acetic acid, 0.5 M in anhydrous sodium acetate (100 ml). The solution was electrolyzed at the platinum anode until a charge corresponding to 2 F/mol had been passed. The reaction mixture was then worked up by neutralization with sodium bicarbonate solution followed by ether extraction. The washed and dried extracts were evaporated and distilled, yielding starting material (1.65 g, b.p. range 58 – 94°/1.5 mm), and a mixture of predominantly *2* and *3* (3.5 g, b.p. 94 – 106°/1.5 mm). The detailed composition of this fraction is given in Table 1. The ratio between *2* and *3* was determined by integration of the area under the signals corresponding to the *t*-butyl, acetoxy methyl, and α-H to the acetoxy group.

The runs at the carbon and lead dioxide anodes were performed in the same manner. Each anode material has been used in several runs, and the results given in Table 1 were found to be satisfactorily reproducible.

cis-*1-(*p-*Nitrobenzoyloxy)-2-*t-*butylindan.* *8* (2.0 g, containing 6 % of *9*) was dissolved in pyridine and *p*-nitrobenzoyl chloride (8.0 g, recryst. from heptane) added slowly with stirring. The mixture was left at room temperature for 1 h and then heated to 100° for 10 min. The solution was then poured into ice-water, the resulting mixture stirred for 15 min, and finally made alkaline by addition of sodium hydroxide solution. The precipitate was filtered off, washed with water, and air-dried (3.4 g). Two recrystallizations from ethanol gave the pure *cis* form, m.p. 131 – 132°. NMR: $\delta = 1.13$ (s, 6, *t*-butyl protons), 2.0 – 3.5 (m, 3, CH_2 and CH protons), 6.48 (d, $J = 5.1$ cps, 1, α-H to acyloxy group), 7.1 – 7.6 (m, 4, aromatic protons in the indan system), and 8.06 ppm (s, 4, aromatic protons in *p*-nitrobenzoyloxy group).

cis- *and* trans-*1-(*p-*Nitrobenzoyloxy)-*2-t-*butylindan.* The 41:59 mixture of *8* and *9* was treated with *p*-nitrobenzoyl chloride in the same way as for the *cis*-isomer, yielding a 56:44 *cis-trans* mixture of *p*-nitrobenzoates, m.p. 102 – 107° after recrystallization from ethanol. From this mixture the NMR spectrum of the *trans* form could be disentangled: δ 0.98 (s, 9, *t*-butyl protons), 2.0 – 3.5 (m, 3, CH_2 and CH protons), 6.51 (d, $J = 6.4$ cps, 1, H α to *p*-nitrobenzoyloxy group), 7.1 – 7.6 (m, 4, aromatic protons in the indan system), and 8.14 ppm (s, 4, aromatic protons in *p*-nitrobenzoyloxy group).

*Solvolysis of cis-1-(*p-*nitrobenzoyloxy)-2-*t-*butylindan.* Pure *cis* isomer, m.p. 131 – 132° (0.30 g), was dissolved in acetic acid, 0.5 M in anhydrous sodium acetate (10 ml), and then kept at 75 ± 1° for 24 h. The solution was then treated with sodium bicarbonate solution and the organic material extracted into ether. After washing and drying the extracts the ether was carefully evaporated and the residue analyzed by NMR. It consisted of a mixture of alkene *7* and *trans* acetate *3* in the ratio of 32:68 (integration of *t*-butyl signals). The *t*-butyl signal of the *cis* acetate (*2*) was barely visible at 1.08 ppm, showing that the ratio between *2* and *3* was less than 2:98 (the lower limit for detection of *2* in *3*). The NMR spectrum of *7* was found to be: δ 1.22 (s, 9, *t*-butyl protons), 3.38 (m, 2, CH_2), 6.50 (s, 1, vinylic proton), and 7.21 ppm (m, 4H, aromatic protons).

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