

Studies on the Possible Effects of Adsorption on the Product Distribution of Organic Electrode Reactions. IV. Anodic Acetox- ylation of 2-Methylindan, 2,2-Dimethylindan, 5,6-Dimethoxy-2- methylindan and Neopentylbenzene

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2-Methylindan, 2,2-dimethylindan, 5,6-dimethoxy-2-methylindan and neopentylbenzene have been anodically oxidized in an acetic acid/sodium acetate medium with different anode materials. The stereochemistry of the products was analyzed with special attention to the possible steric influence of the electrode surface on product distribution. Further, the influence of pulsing the anode potential has been investigated.

Previous papers in this series have dealt with the possible stereochemical consequences of adsorption in the anodic oxidation of 2-*t*-butylindan (1) and 1-*t*-butylacenaphthene (2) in HOAc/NaOAc.¹ By introducing a sterically demanding substituent on one side of the plane defined by the ring plane it was hoped that adsorption with the less hindered side toward the electrode surface would result in an increased *cis-trans* ratio in the side-chain substitution product. To some extent this hypothesis was substantiated: the *cis-trans* ratio of the α -acetates from 1 was 16:84, as compared to < 2:98 in a related homogeneous reaction. On the other hand, the behaviour of 2 did not show any unambiguous preference for the formation of the *cis* isomer (*cis-trans* ratio 3:97; no related homogeneous reaction could be studied due to experimental difficulties.)

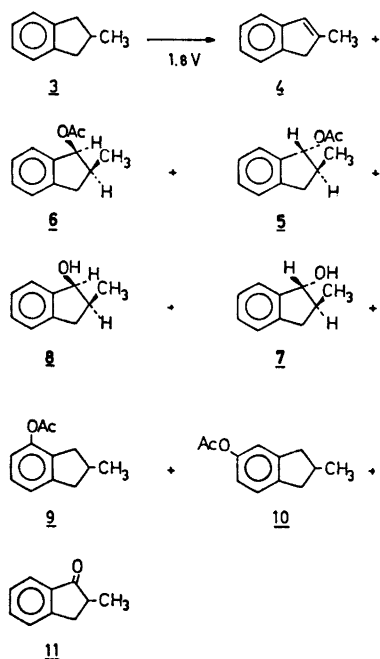
The substrates 1 and 2 might, however, not be quite ideal for studying the problem at hand. NMR data for several 1,2-disubstituted *t*-

butylindan derivatives indicated that the *t*-butyl group does not exert the kind of clearcut steric hindrance of one side of the molecule that might be expected from studies of molecular models. On the contrary, there is evidence that the *t*-butyl group points out in an "equatorial" manner from the saturated ring, due to hydrogen- π -orbital repulsion.² This means that the tertiary carbon atom of the *t*-butyl group is situated almost in the plane of the aromatic ring and thus presents steric hindrance on both sides of the molecule, even if not to the same extent. By instead using 2-methylindan as a substrate, this possibly exaggerated effect should be eliminated. The ratio of the diameters of the rotation bodies swept out by the van der Waals radii of the two substituents is approximately 2:1 as measured perpendicular to the C₂—R bond. Other investigators have reported chemically non-equivalent aromatic faces in homogeneous solution, due to alkyl-aromatic π -electron interaction.³

This paper reports the stereochemical outcome of the anodic oxidation of 2-methylindan in glacial acetic acid/anhydrous sodium acetate. In addition 2,2-dimethylindan, 5,6-dimethoxy-2-methylindan, and neopentylbenzene were examined under the same conditions.

RESULTS

Products formed in the anodic oxidation of 2-methylindan (**3**) in HOAc/1 M NaOAc are 4–11 (Scheme 1).



Scheme 1.

The major products were the side-chain acetates **5** and **6** which made up 80 % of the total product mixture. The *cis-trans* ratio was

51:49 as measured from the NMR integrals of the proton α to the acetoxy group; for **5** δ 5.84 ppm, J 4.3 Hz; and for **6** δ 6.06, J 5.6 Hz. For details of the product distribution see Table 1.

The products were identified in the following manner. The side-chain alcohols **7** and **8** were known from previous work (*trans* isomer, m.p. 88–89 °C; *cis* isomer, m.p. 50–51 °C).⁴ In the present study, the *trans* isomer **7** was prepared by hydration of **4** according to a literature method using lithium aluminium hydride and boron trifluoride etherate in diethyl ether,⁵ m.p. 88 °C (NMR for α -H of **7**: δ 4.51, J 6.8 Hz) after recrystallization from petroleum ether. The crude product contained about 5 % of the *cis* isomer. Lithium aluminium hydride, sodium borohydride, and aluminium isopropoxide reduction of **11** according to standard procedures gave mixtures of **8**:**7** in the ratios of 33:67, 20:80, and 15:85, respectively. From these mixtures, the necessary spectral characteristics (NMR, mass spectrum) of **8** could be obtained (NMR for α -H: δ 4.78, J 6.0 Hz). The mixture of side-chain alcohols **7** and **8** was treated with acetic anhydride and pyridine, which gave acetates **5** and **6** in the same ratio (NMR: **5** δ 5.85, J 4.3 Hz, **6** δ 6.06, J 5.6 Hz).

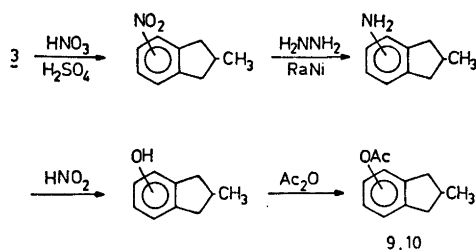
The nuclear acetates were prepared according to the reaction sequence in Scheme 2. The isomers **9** and **10** were formed in the ratio of 45:55, and **10** was considered to be the major product on the basis of earlier studies of the indan system.⁶ 2-Methylindene was prepared

Table 1. Product distribution in the anodic oxidation of 2-methylindan in acetic acid/1 M sodium acetate. Anode potential 1.8 V vs. SCE.

Anode material and additive	Yield of products (in mol % of total products)					Current yield, %	6:5
	4	5+6	7+8	9+10	11		
Pt	1.3	79.6	4.2	7.3	7.6	70	51:49
C	1.1	54.0	18.9	4.5	21.5	33	44:56
PbO ₂	1.0	73.1	10.5	5.7	9.7	62	42:58
Pt, 5 % H ₂ O	1.9	54.8	28.5	7.1	7.7		51:49
Pt, 10 % H ₂ O	2.7	45.2	42.3	3.4	6.4	49	52:48
Pt, Bu ₄ NBF ₄ ^a	1.1	74.4	8.8	—	15.7		48:52
Co(OAc) ₃ oxidation	traces	51.4	17.2	—	31.4		37:63
Solvolysis							43:57

^a In this case no sodium acetate was present.

from the mixture of 7 and 8 by acid-catalyzed elimination.



Scheme 2.

As seen by inspection of Table 1, the products from the anodic oxidation of 3 using Bu_4NBF_4 as supporting electrolyte instead of sodium acetate are the same as above, except for the nuclear acetates 9 and 10 which are not expected to be formed in this case.⁷ Two runs were made with water added, 5 and 10 %, respectively. This increased the amount of 7 and 8 formed (*cis-trans* ratio 34:66) so that with 10 % water added it almost equalled the amount of side-chain acetates. This is in accordance with the accepted reaction mechanism.⁸ The *cis-trans* ratio for the acetates 5 and 6 was in this case 52:48.

No significant influence of the electrode material on the ratio between 5 and 6 could be detected. Table 1 shows the *cis-trans* ratio for the electrode materials used. Cobalt(III) acetate oxidation of 2-methylindane and solvolysis of *trans*-1-(*p*-nitrobenzoyloxy)-2-methylindane were used as homogeneous reference reactions. The mechanism of cobalt(III) acetate oxidation is known to be of the electron transfer type and in the last few years studies have been reported of the oxidation of a number of hydrocarbons,⁹ where one of the main reaction

modes has been acetoxylation in benzylic positions. The cobalt(III) oxidation of 3 gave 5 and 6 as the main products with a *cis-trans* ratio of 37:63.

For the solvolysis experiment the pure *trans* isomer of 1-(*p*-nitrobenzoyloxy)-2-methylindane was prepared by treating the 85:15 mixture of 7 and 8 with *p*-nitrobenzoyl chloride and recrystallization of the product from ethanol. No trace of the α proton from *cis*-1-(*p*-nitrobenzoyloxy)-2-methylindane was evident in the NMR spectrum of the *trans* form, not even when the signal from the α proton of the *trans* isomer (δ 6.04, J 4.0 Hz) was several times off scale. Solvolysis for 24 h in HOAc/1 M NaOAc at 75 °C produced the side-chain acetates 5 and 6 in a *cis-trans* ratio of 43:57.

If two oxidizable substrates with different adsorption properties are present in the electrolyte, the competition factor between them can be changed by pulsing the electrode potential.¹⁰ For 2-substituted indans the two possible modes of adsorption (with the substituent pointing towards and away from the electrode surface, respectively) could be regarded in the same way as two different substrates. As before, the orientation with the substituent pointing away from the electrode surface is expected to be energetically favoured. Pulsing the anode potential should then change the ratio between 5 and 6. As is seen from the results in Table 2, no difference in the *cis-trans* ratio for the side-chain acetates between pulse and constant potential electrolysis can be detected.

Another possibility to change the *cis-trans* ratio of the side-chain acetates, was tried with 2-*t*-butylindane as a substrate, and the results are shown at the last entry of Table 2. It is known that adsorption on electrodes reaches a maximum value at the potential of

Table 2. Results from pulse experiments with 2-methylindane and 2-*t*-butylindane in acetic acid/1 M sodium acetate.

Substrate	Duration of A pulse	B pulse	<i>cis-trans</i> Ratio for side-chain acetates
2-Methylindane	2.5 ms/0.2 V	7.5 ms/1.8 V	46:54
»	0.25 ms/0.2 V	0.75 ms/1.8 V	48:52
»	0.75 s/0.2 V	0.25 s/1.8 V	48:52
2- <i>t</i> -Butylindane	3 s/0.5 V	0.3 s/1.8 V	16:84

Table 3. Product distribution in the anodic oxidation of 2,2-dimethylindan **13** in acetic acid/1 M sodium acetate and neopentylbenzene **12** in acetic acid/0.1 M tetrabutylammonium tetrafluoroborate, anode potential 1.8 V *vs.* SCE, in both cases.

Compound	Anode material, etc.	Yield of products (in mol % of total products)					Current yield, %
		Side-chain acetate	Side-chain alcohol	Nuclear acetate	Ketone	Unknown	
13	Pt	95.4	1.5	1.3	0.4	1.3 ^a	69
13	C	75.5	4.4	13.2	5.1	1.8 ^a	15
13	PbO ₂	78.7	1.1	12.3	2.3	5.6 ^a	57
13	Co(OAc) ₃ ox. ^c	39.4	—	—	44.5	16.1 ^b	—
12	Pt	73.4	—	—	26.6	—	—
12	Co(OAc) ₃ ox.	24.6	—	—	75.4	—	—

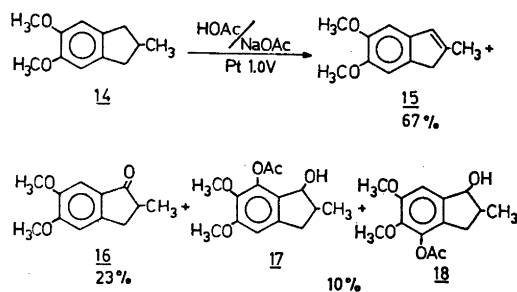
^a See Table 6. ^b This compound has a mass spectrum *m/e* (%) 218(0.6) 176(8) 161(8) 133(10) 118 (100) 90(30) 43(8). ^c Carried out as for 2-methylindan but at 90°C.

zero charge and diminishes as the electrode potential is changed toward both negative and positive potentials.¹¹ In this experiment the anode was kept at a potential where no current passed through the cell, 0.50 V *vs.* SCE, for three seconds to allow an adsorption equilibrium to be established, and then the adsorbed material was oxidized by a short (0.3 s at 1.8 V) pulse. The *cis-trans* ratio, 15:85, for 1-acetoxy-2-*t*-butylindan, does not differ from the value obtained in constant potential electrolysis.

The oxidation of neopentylbenzene (**12**) in HOAc/1 M NaOAc gave a somewhat unexpected result. No products were formed (product integral in GLC less than 0.5 % of recovered starting material). Changing the anode material did not alter this behaviour. On the other hand, with Bu₄NBF₄ as a supporting electrolyte side-chain acetoxylation took place as expected (Table 3). In order to see if the anomalous oxidation behaviour of neopentylbenzene was shown also by its "back-bonded" analogue 2,2-dimethylindan (**13**), this compound was prepared and oxidized. Here the side-chain acetate was formed predominantly. For details of the product distribution, see Table 3. Product identification from neopentylbenzene oxidation was carried out by comparison of mass spectra and GLC retention times with authentic samples. For 2,2-dimethylindan the products were identified by mass spectral analysis.

In order to find out whether the presence of polarizable groups in the molecule would

enhance adsorption and thus influence product distribution, 5,6-dimethoxy-2-methylindan (**14**) was oxidized in HOAc/1 M NaOAc. The preparative run (to 25 % of a 2e transfer) was made at 1.0 V *vs.* SCE. GLC analysis showed four major product peaks corresponding to the elimination product **15**, ketone **16** and side-chain alcohol acetoxylation in the nucleus, **17** and **18**. The product distribution (mol % of total products) was as given in Scheme 3.



Scheme 3.

The products were identified on the basis of their mass spectra and, in addition, for compound **16**, the GLC retention time.

DISCUSSION

The stereochemistry of the anodic oxidation of 2-methylindan in glacial acetic acid/sodium acetate does not give any evidence for a preferential adsorption mode of the substrate. Thus the expectation that there would be a

more distinct difference between the two faces of this molecule than in the case of 2-*t*-butylindan has not been fulfilled.

2-*t*-Butylindan shows a significant difference between anodic and comparable homogeneous reactions¹ which is not the case for 2-methylindan, as can be seen from Table 1. This study is based on the idea of different reactivities of the two sides of the molecule defined by the plane of the aromatic ring. This in turn invokes a kind of selection process where molecules with the "right" side toward the electrode are preferred for reaction. For 2-*t*-butylindan this selection process appears to be operating to some extent. For 2-methylindan the result might be explained by the assumption that the energy difference between the two modes of adsorption, with the methyl group pointing toward and away from the electrode surface, respectively, is so small that it is not sufficient to cause any preferred orientation at the electrode surface once the molecule has arrived there. (This would require an extra desorption-absorption sequence.)

Here it is interesting to note the special stereochemical features of neopentylbenzene. The side-chain of this molecule has rotational freedom around the two bonds connecting the *t*-butyl group with the aromatic nucleus. This makes it possible for the side-chain to orient itself out from the electrode surface at the same time as the molecule is adsorbed at the aromatic ring. This would explain why no α substitution product is formed from neopentylbenzene. In 2,2-dimethylindan, which can be considered as a neopentylbenzene without free rotation, normal product formation takes place. One objection against this kind of reasoning is clearly that 2,2-dimethylindan formally is a dialkylsubstituted aromatic hydrocarbon and consequently should be easier to oxidize than a monosubstituted one.¹²

The differing ease of oxidation of 2-methyl- and 2,2-dimethylindan on the one hand and neopentylbenzene on the other is evident from the voltammograms of the compounds (Figs. 1–4). These have been recorded at the beginning of the experiments. The current-potential curve for the solvent-supporting electrolyte was recorded first, measuring the current at each tenth of volt of anode potential in the range 0 to +3 V *vs.* SCE. The substrate was

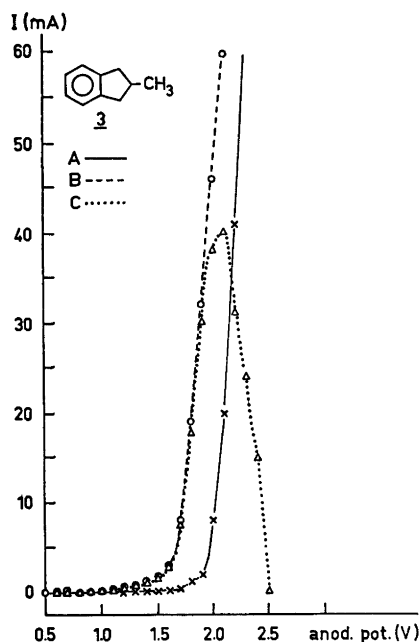


Fig. 1. Voltammogram for compound 3 in HOAc/1 M NaOAc. Curve A: Background current. Curve B: Current with 5 mmol of substrate added. Curve C: Shows the difference between B and A.

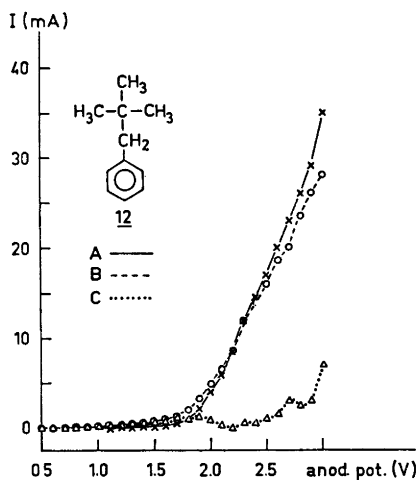


Fig. 2. Voltammogram for compound 12 in HOAc/1 M NaOAc. Curve A: Background current. Curve B: Current with 5 mmol of substrate added. Curve C: Shows the difference between B and A.

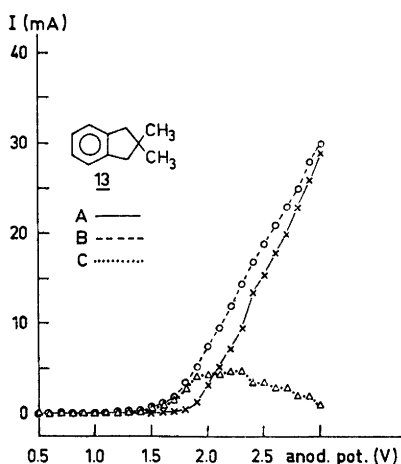


Fig. 3. Voltammogram for compound 13 in HOAc/1 M NaOAc. Curve A: Background current. Curve B: Current with 5 mmol of substrate added. Curve C: Shows the difference between B and A.

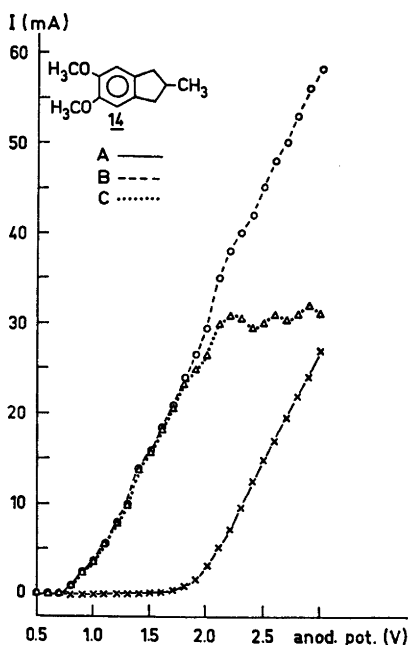


Fig. 4. Voltammogram for compound 14 in HOAc/1 M NaOAc. Curve A: Background current. Curve B: Current with 5 mmol of substrate added. Curve C: Shows the difference between B and A.

then added and the procedure repeated. Thus voltammetric curves and product analyses relate to the same single experiment.

In the pulse experiments, the goal has been to maximize adsorption. At mercury electrodes, it has been shown that substrate adsorption reaches a maximum value at the potential of zero charge. The same behaviour is exhibited by solid electrodes, even if data are relatively scarce in such systems.^{11,13} It is considered that the potential of zero charge (p.z.c.) at platinum lies in the range of 0.20–0.5 V *vs.* SCE. Accordingly, the possibility of revealing any preferential orientation in adsorption should be most favourable at p.z.c. However, neither varying the pulse frequency nor keeping the anode at p.z.c. and using short oxidation pulses, give any results in support of such a behaviour of the substrates used here (2-methylindane and 2-*t*-butylindane). These facts cannot be explained at the present time. In one pulse experiment an attempt was made to increase the yield of the elimination product, 2-methylindene, by expelling the intermediate carbonium ion from the electrode surface. Experimentally this was done by applying a positive pulse at +1.8 V *vs.* SCE for two seconds and a negative pulse at –1.8 V for one second. However, the amount of 4 did not increase. It is interesting to note that the side-chain acetates 5 and 6 made up 88 % of the products in this experiment, the highest value obtained in any experiment with 3. This may have synthetic implications, since the pulse sequence used corresponds to changing polarity over the cell.

In a recent investigation on oxidative coupling of an isoquinoline derivative, the authors found stereospecific behaviour of an electrode process but not of an analogous homogeneous reaction.¹⁴ They explained this behaviour with adsorption of the substrate at the electrode surface. Since the isoquinoline substrate used contained polarizable groups, 5,6-dimethoxy-2-methylindane was oxidized to trace if the presence of such groups in the systems pertinent to this work would enhance adsorption. Unfortunately no side-chain acetates were formed and thus no information regarding this aspect was obtained.

In some experiments using 2-methylindane as a substrate water was added to the electrolysis solution (see Table 1). This increased the

amount of side-chain alcohols formed. The addition of water might have given stereochemical information, since if acetate ions are preferentially adsorbed at the electrode surface, as is known from studies on the Kolbe reaction,¹⁵ a substrate molecule which reacts not on, but in close vicinity of the electrode surface, should have different concentrations of the two nucleophiles on each side of the symmetry plane. If the substrate shows any preferred orientation this should be revealed in the 8:7 ratio. The result (8:7 = 34:66) is, however, almost equal to the *cis-trans* ratio obtained in the homogeneous Co(III) oxidation.

EXPERIMENTAL

Materials. Analytical grade acetic acid (Merck AG, Germany) was frozen out twice. Anhydrous sodium acetate (analytical grade) was used as purchased (Merck AG, Germany). Tetrabutylammonium tetrafluoroborate was prepared as described previously.¹⁶

Electrolysis experiments. The electrolyses were carried out in a water-jacketed vessel, volume 55 ml. The upper part was ground planar to fit a "Quickfit" cover; catalogue number MAFo/50, with five B 10 necks. A saturated calomel electrode (Radiometer K 401 or K 4016) was used as reference electrode.

Electrode arrangement. In the case of platinum two parallel foils, 20 by 30 mm and 0.1 mm thick, at a distance of 15 mm from each other were freely immersed in the solution. When using carbon or lead dioxide anodes, one platinum foil was exchanged for a graphite plate, 20 by 30 mm and 5 mm thick, or a lead dioxide plated (see below) graphite plate of the same dimensions. The electrode distance was the same as above. The porous tip of the reference electrode was placed between the electrodes as close to the anode as possible.

Efficient stirring was achieved with a magnetic stirrer. In all electrolysis experiments the temperature was kept at $25 \pm 0.5^\circ\text{C}$. The potentiostat was the TR.70/2 A type, equipped with an RB 1 type waveform generator, both from Chemical Electronics Co., Newcastle upon Tyne, England. The time calibration of the pulse length was performed with a Philips PM 3220 0–10 MHz oscilloscope. The amount of charge passed through the cell was measured by a 60 mV electronic integrator built by the electronic workshop, Chemical Center, Lund. The integrator was fed over a variable resistor.

Procedure for plating lead dioxide upon graphite. An acidic lead nitrate (200 g $\text{Pb}(\text{NO}_3)_2/\text{l}$, 10 g $\text{Cu}(\text{NO}_3)_2/\text{l}$, 4 g HNO_3/l , 1 g NaF/l) solution was placed in a two-compartment cell with a liquid junction. A copper wire

was placed in the cathode compartment. The piece of graphite to be plated was then rotated in the anode compartment with a speed of half a revolution per second. Sand was added to the anode compartment and stirred by a magnetic stirrer to puncture gas bubbles formed during plating in order to prevent the formation of holes in the lead dioxide layer. The current density was kept at $40 \text{ mA}/\text{cm}^2$.

Analytical procedures. GLC analysis was carried out using a Perkin-Elmer 880 gas chromatograph, equipped with a Perkin-Elmer Model D-26 Integrator. A 4 m 3 % OV-25 on Chromosorb W column was used for all analyses. Mass spectra were recorded by an LKB 9 000 mass spectrometer and NMR spectra by a Varian A-60 NMR spectrometer. Deuteriochloroform was used as solvent.

2-Methylindan was prepared by catalytic hydrogenation of 2-methylindanone-1.¹⁷ 2-Methylindanone-1 (31 g) in acetic acid (93 ml) was shaken with 10 % palladium on carbon (1.5 g) in a Parr low pressure hydrogenation apparatus. The pressure had dropped to a constant value after 2 h. The solution was poured into water (400 ml). Potassium hydroxide (98 g) was used to neutralize the acid. After extraction three times with ether, the extracts were washed twice with water. After drying with anhydrous MgSO_4 , the ether was evaporated and the residue distilled through a 20 cm Vigreux column, giving 19.9 g (72 %) of 2-methylindan, b.p. $66-68^\circ\text{C}/11 \text{ mmHg}$. NMR: δ 1.07 (d, J 5.5 Hz, 3, methyl protons), 2.16–3.16 (m, 5, aliphatic side-chain protons), 7.03 (s, 4, aromatic protons).

4- and 5-Nitro-2-methylindan. 2-Methylindan (6.6 g) was cooled in an ice-bath. A cold ($< 10^\circ\text{C}$) solution of 5 ml concentrated nitric acid (68 %) in 6 ml of concentrated sulphuric acid was added dropwise with stirring. The temperature was kept at $5-10^\circ\text{C}$. After the addition of acid the reaction mixture was stirred for another 20 min with cooling and then the temperature was allowed to rise to ambient for 3 h. The reaction mixture was poured into ice water (200 ml) and stirred for 15 min. After extraction three times with ether the ether solution was washed with water, NaHCO_3 solution and water again. Anhydrous MgSO_4 was used for drying the ethereal solution. The solvent was evaporated and the residue, 7.2 g, was distilled *in vacuo* through a 5 cm Vigreux column giving 5.45 g (62 %) of 4- and 5-nitro-2-methylindan, b.p. $94-98^\circ\text{C}/0.3 \text{ mmHg}$. The isomers were formed in a 37:63 ratio, as determined by GLC, the major product being assigned the 5-structure⁶ MS, see Table 4). NMR: δ 1.13 (d, J 6 Hz, 3, methyl protons) 2.30–3.70 (m, 5, aliphatic protons), 7.05–7.55 and 7.66–8.02 (m, 3, aromatic protons).

4- and 5-Amino-2-methylindan. The above mixture of 4- and 5-nitro-2-methylindan (5.2 g) was dissolved in ethanol (50 ml). Hydrazine hydrate, (100 %, 3.7 g) was added and the

Table 4. Retention times and mass spectral data for 2-methylindan and derivatives. Analysis carried out on a 3 % OV-25, on Chromosorb W column (4 m \times 0.3 mm), temperature 80–250 °C, 6 °C/min, initial period 6 min.

Compound	Retention time, min	Mass spectrum, <i>m/e</i> (% of base peak)
3	7.2	133(7) 132(66) 131(19) 117(100) 115(23) 91(19)
4	12.3	131(9) 130(100) 129(69) 128(37) 127(13) 115(74) 64(13) 51(12)
7 + 8	17.1	149(8) 148(89) 147(100) 133(33) 130(69) 129(65) 128(20) 127(9) 115(57) 105(35) 91(50)
11	18.7	147(13) 146(90) 145(22) 132(20) 131(100) 117(34) 115(28) 103(33) 51(22)
5 + 6	19.7	148(13) 147(12) 131(22) 130(100) 129(25) 115(21) 91(13) 43(26)
9	20.9	190(9) 149(9) 148(100) 147(21) 133(51) 43(11)
10	22.0	see above
4-Nitro-2-methylindan	22.6	178(3) 177(35) 160(100) 130(30) 129(24) 116(17) 115(53) 91(18)
5-Nitro-2-methylindan	23.6	178(10) 177(100) 160(27) 131(34) 130(32) 116(41) 115(48) 91(45)
4- and 5-Amino-2-methylindan	20.6	148(10) 147(100) 146(43) 133(12) 132(86) 131(17) 130(17)
4- and 5-Hydroxy-2-methylindan	20.4	149(6) 148(67) 147(16) 133(100) 131(16) 105(17)

solution warmed to 40 °C. Freshly prepared Raney nickel (0.25 g), suspended in a few ml of ethanol, was added in portions. When no further gas was evolved on adding the catalyst, the reaction was refluxed for one hour. The catalyst was filtered off. After evaporating the solvent *in vacuo*, the residue was distilled through a 5 cm Vigreux column giving 2.68 g (62 %) of 4- and 5-amino-2-methylindan, b.p. 72–74 °C/0.3 mmHg. The two isomers could not be separated by GLC, (MS, see Table 4). NMR: δ 1.10 (d, *J* 5 Hz, 3, methyl protons) 2.0–3.2 (m, 5, broadened aliphatic side-chain and amine protons) and 6.22–7.10 (m, 3, aromatic protons).

4- and 5-Hydroxy-2-methylindan.¹⁸ To the above mixture of 4- and 5-amino-2-methylindan (2.36 g) was added concentrated sulfuric acid (4.7 g), water (2.7 g) and acetic acid (5 ml). Sodium nitrite (1.11 g) in water (6.5 ml) was then added dropwise, the temperature of the reaction mixture being kept below 5 °C. The reaction solution was then stirred at 0 °C for 30 min and at 100 °C for another 30 min. The ether solution was dried with MgSO₄ and the solvent removed in a rotating film evaporator. The residue was distilled yielding 1.04 g (44 %) of 4- and 5-hydroxy-2-methylindan, b.p. 72–74 °C/0.2 mmHg (MS, see Table 4). NMR: δ 1.13 (d, *J* 5.5 Hz, 3, methyl protons), 2.13–3.25 (m, 5, aliphatic side-chain protons), 5.18 (s, broadened, 1, hydroxylic proton), 6.43–7.23 (six discrete bands, with a strong singlet at δ 6.63, 3, aromatic protons).

4- and 5-Acetoxy-2-methylindan. The above mixture of 4- and 5-hydroxy-2-methylindan (0.9 g) was dissolved in acetic anhydride (30 ml). Two drops of pyridine were added and the solution refluxed overnight. After cooling, water (60 ml) was added. The mixture was allowed to stand with occasional shaking for 4 h. The water phase was extracted with ether. After drying with MgSO₄, the ether was removed in a rotating film evaporator. GLC of the residue showed two components in the ratio 44:56, (MS, see Table 4). NMR: δ 1.12 (d, *J* 6 Hz, 3, methyl protons in 2-position), 2.07–3.35 (m, 5, aliphatic side-chain), 2.22 (s, 3, methyl protons in acetoxy group), 6.63–7.20 (m, 3, aromatic protons, strong bands at 6.83 and 7.02).

Hydration of 2-methylindane.⁵ Lithium aluminium hydride (0.2 g) in dry ether (15 ml), boron trifluoride etherate (0.9 g) and 2-methylindene (1.5 g) in dry ether (25 ml) were reacted according to Ref. 5. *trans*-2-Methylindanol-1 (1.49 g, 87 %) was isolated as crude product. NMR analysis showed traces of the *cis* form (appr. 5 %). Recrystallization from petroleum ether gave a sample melting at 88 °C. For NMR and MS, see below.

Reduction of 2-methylindanone-1 by aluminium isopropoxide. Aluminium isopropoxide (0.13 mol) in dry isopropyl alcohol (67 ml) was heated to reflux in a distilling flask connected to a column of 7–8 theoretical plates 2-Methylindanone-1 (19.3 g) dissolved in dry isopropyl alcohol (40 ml) was added dropwise. Simul-

taneously with the addition of ketone, distillate was taken out from the still head at a rate of four drops a minute. When the addition of ketone was completed the distillation was continued until the temperature in the still head was 82.5 °C. The solution was allowed to cool and then poured onto ice (400 g). Hydrochloric acid (6 M) was added until acidic reaction was shown on indicator paper. The organic product was extracted with ether and the solution then washed with water and NaHCO₃ solution. After drying with MgSO₄ the ether was evaporated. Distillation of the white solid residue gave 15.7 g (80 %) of 1-hydroxy-2-methylindan, b.p. 116–117 °C/11 mmHg (MS, see Table 4). NMR: δ 1.16 (d, J 6 Hz, 3, –CH₃), 2.0–3.30 (m, 4, –OH proton at 2.55), 4.51 (d, J 6.8 Hz, α -H in *trans* form), 4.78 (d, J 6.0 Hz, α -H in *cis* form, *cis-trans* = 15:85) and 6.97 (m, 4 aromatic protons).

Reduction of 2-methylindanone-1 by lithium aluminium hydride. 2-Methylindanone-1 (2.92 g) dissolved in dry ether (10 ml) was added dropwise to lithium aluminium hydride (0.84 g) in dry ether (25 ml). After the addition of ketone, the solution was refluxed for 20 min. The excess of hydride was destroyed by water. After acidification, the water phase was extracted with ether. The ether solution was dried with MgSO₄. Evaporation of the ether gave a white solid residue of 1-hydroxy-2-methylindan (2.30 g, 78 %). NMR: as for reduction by aluminium isopropoxide, *cis-trans* = 33:66.

Reduction of 2-methylindanone-1 by sodium borohydride. 2-Methylindanone-1 (25 g) was dissolved in ethanol (99.5 %, 250 ml). Sodium borohydride (25 g) was added. The solution was stirred for 2 h. Additional sodium borohydride was added (12.5 g) and the solution stirred overnight. After addition of water (1 l) the reaction was extracted with ether. The ether solution was washed with water and dried with MgSO₄. Evaporation of the ether gave 11.2 g of 2-methylindanol-1 (44 %). GLC analysis showed no trace of the starting material. NMR analysis gave a *cis-trans* ratio of 20:80. For details of NMR spectrum, see above.

***cis*- and *trans*-1-Acetoxy-2-methylindan.** A sample of 1-hydroxy-2-methylindan (0.4 g) (*cis-trans* ratio 15:85) was dissolved in acetic anhydride (5 ml) with a drop of pyridine added. The solution was refluxed overnight. The work-up procedure was the same as for the nuclear acetates. NMR: δ 1.15 (d, J 6.5 Hz, 3, methyl protons), 2.05 (s, 3, methyl protons of the acetoxy group), *cis* and *trans* isomers not resolved due to the low intensity of the signal due to the *cis* isomer), 2.15–3.50 (m, 3, aliphatic protons in the side-chain), 5.84 (d, J 4.3 Hz, α -H to acetoxy group in the *trans* isomer), 6.06 (d, J 5.6 Hz, α -H to the acetoxy group in the *cis* isomer. The integral over the doublets corresponded to 1 H; *cis-trans* ratio = 15:85), 7.06–7.44 (m, 4 H, aromatic protons).

2-Methylindene.¹⁹ 2-Methylindanol-1 (3.0 g, 85 % *trans* isomer) and phosphoric acid (1.5 g) were warmed slowly under reduced pressure to 130–140 °C. A lime coloured fluid (0.86 g) distilled over at a temperature of 80 °C in the still head. The distillate was taken up in ether, treated with NaHCO₃ solution and dried. The ether evaporated. NMR: δ 2.02 (s, 3, methyl protons), 3.10 (s, 2, –CH₂– in aliphatic ring), 6.33 (unresolved quartet, 1, vinylic proton), 6.86–7.39 (m, 4, aromatic protons).

***trans*-1-(*p*-Nitrobenzoyloxy)-2-methylindan.** 1-Hydroxy-2-methylindan (3 g, 85 % *trans* isomer) was dissolved in pyridine (35 ml). *p*-Nitrobenzoyl chloride (12 g) was added with cooling in an ice-bath. Thereafter, the reaction mixture was heated on a water-bath at 100 °C for 30 min. The reaction mixture was cooled to room temperature, poured on ice and acidified with concentrated hydrochloric acid. After suction and washing of the precipitate it was stirred in 0.05 M sodium hydroxide solution with addition of solid sodium hydroxide until the water remained alkaline to remove excess *p*-nitrobenzoic acid. After filtering, the product was air dried, giving 6.8 g of crude material. Recrystallization from ethanol, gave 2.4 g of *trans*-1-(*p*-nitrobenzoyloxy)-2-methylindan, m.p. 81–82 °C. NMR: δ 1.23 (d, J = 6.8 Hz, 3, methyl protons), 2.26–3.65 (m, 3, aliphatic protons in side-chain), 6.04 (d, J = 4.0 Hz, 1, α -H to acyloxy group). No trace of the signal from the α proton of the *cis* isomer could be seen even when increasing the amplitude ten times, 7.25 (s, 4, aromatic protons in indan ring), 8.11 (s, 4, aromatic protons in *p*-nitrophenyl ring).

Solvolysis of *trans*-1-(*p*-nitrobenzoyloxy)-2-methylindan. The ester (1.0 g) was dissolved in glacial acetic acid (20 ml), 1 M in anhydrous sodium acetate and the solution kept at 75 ± 1 °C for 24 h. The acetic acid was neutralized in a NaHCO₃ slurry and the organic material extracted with ether. After washing and drying, the ether was evaporated. The NMR spectrum for the residue showed that the solvolysis had only run to approximately 60 %. The *cis-trans* ratio for side-chain acetates was 43:57 as measured from the integral of the α protons corrected for remaining *p*-nitrobenzoate. No significant amount of the elimination product, 2-methylindene, was detected. In an attempt to complete the solvolysis, the reaction time was extended to 3 d. The solvolysis still did not go to completion. Besides 12 % starting material, elimination now accounted for 22 % of the product.

Oxidation of 2-methylindan by cobalt(III) acetate. 2-Methylindan (645 mg) was dissolved in glacial acetic acid (50 ml) and cobaltic acetate [290 mg, 20 % in Co(III)]²⁰ was added. The dark green homogeneous solution was kept at 70 ± 1 °C for 20 h. The work-up procedure was the same as for the electrolysis

Table 5. Retention times and mass spectral data for neopentylbenzene and derivatives. Analysis carried out on a 3 % OV-25 on Chromosorb W column (4 m × 0.3 mm), temperature 80–250 °C, 6 °C/min, initial period 6 min.

Compound	Retention time, min	Mass spectrum, <i>m/e</i> (% of base peak)
1-Phenyl-2,2-dimethylpropane	5.0	148(9) 133(8) 92(85) 91(45) 57(100) 41(25)
1-Phenyl-2,2-dimethylpropanone-1	14.6	162(4) 105(100) 77(18) 57(8)
1-Phenyl-2,2-dimethylpropanol-1	14.6	164(2) 149(2) 108(7) 107(100) 105(6) 79(38) 77(12) 57(10)
1-Phenyl-1-acetoxy-2,2-dimethylpropane	17.2	206(5) 149(45) 131(5) 108(22) 107(100) 105(7) 57(20) 43(89)

Table 6. Retention times and mass spectral data for 2,2-dimethylindan and derivatives. Analysis carried out on a 3 % OV-25 on Chromosorb W column (4 m × 0.3 mm), temperature 80–250 °C, 6 °C/min, initial period 6 min.

Compound	Retention time, min	Mass spectrum, <i>m/e</i> (% of base peak)
2,2-Dimethylindan	7.5	146(49) 132(9) 131(100) 115(11) 91(25)
2,2-Dimethylindanol-1	17.0	162(70) 161(25) 131(20) 129(100) 120(27) 119(70) 91(40) 59(27)
2,2-Dimethylindanone-1	17.8	160(50) 145(100) 131(40) 74(44) 59(62) 45(46)
1-Acetoxy-2,2-dimethylindan	19.2	204(trace) 162(18) 161(10) 145(20) 144(100) 143(17) 129(64) 128(15) 91(13) 43(28)
4-Acetoxy-2,2-dimethylindan	20.4	204(11) 163(11) 162(100) 147(83) 131(9) 59(11) 43(20)
5-Acetoxy-2,2-dimethylindan	21.5	204(8) 163(10) 162(100) 161(7) 148(6) 147(62) 131(6) 147(62) 131(6) 91(7) 43(14)
Unknown ^a	28.2	262(1) 202(12) 178(10) 177(11) 161(41) 160(100) 145(26) 43(61)

^a Compound whose mass spectrum corresponds to 1-acetoxy-2,2-dimethylindan, acetoxyated in the nucleus.

Table 7. Retention times and mass spectral data for 5,6-dimethoxy-2-methylindan and derivatives. Analysis carried out on a 3 % OV-25 on Chromosorb W column (4 m × 0.3 mm), temperature 120 °C, 4 °C min.

Compound	Retention time, min	Mass spectrum, <i>m/e</i> (% of base peak)
5,6-Dimethoxy-2-methylindan	12.8	193(12) 192(100) 177(48) 161(9) 117(8) 107(37) 91(13)
5,6-Dimethoxy-2-methylindene	15.8	191(11) 190(100) 175(64) 147(19) 132(15) 115(12) 103(9)
5,6-Dimethoxy-2-methylindanone-1	23.8	207(10) 206(88) 192(11) 191(100) 163(15) 91(13) 89(12)
5,6-Dimethoxy-2-methylindanol-1 acetoxyated in the nucleus	25.2	266(13) 224(38) 206(12) 167(100) 154(16) 131(14) 69(13) 43(21)
»	26.2	266(20) 224(42) 206(20) 205(15) 191(16) 167(100) 154(14) 43(29)

experiments. NMR analysis showed a *cis-trans* ratio of 37:63. GLC, see Table 1.

Neopentylbenzene was prepared according to a literature method,²¹ yield 43 % (lit. 30 %), b.p. 63–67 °C/14 mmHg (MS, see Table 5). NMR: δ 0.89 (s, 9, *t*-butyl protons), 2.47 (s, 2, $-\text{CH}_2-$) and 7.13 (s, 5, aromatic protons).

1-Phenyl-2,2-dimethylpropanol-1. Pivalophenone (2.5 g), dissolved in dry ether (10 ml), was dropped onto lithium aluminium hydride (340 mg) in dry ether (25 ml) and the mixture stirred under reflux for 4 h. Water was then added dropwise. When no more hydrogen evolved, sulphuric acid (10 %, 40 ml) was added to dissolve the aluminium hydroxide. The organic material was collected by extraction with ether. The combined ether extracts were washed with NaHCO_3 solution and water, and then dried with MgSO_4 . After evaporation of the solvent, distillation gave 0.67 g of product, b.p. 92–94 °C/12 mmHg (MS, see Table 5). NMR: δ 0.88 (s, 9, *t*-butyl), 2.16 (s, 1, $-\text{OH}$), 4.30 (s, 1, $-\text{CH}-$) and 7.22 (s, 5, aromatic protons).

1-Phenyl-2,2-dimethyl-1-propyl acetate. *1-Phenyl-2,2-dimethylpropanol-1* (0.48 g) was dissolved in acetic anhydride (5 ml), one drop of pyridine was added and the solution refluxed overnight. Working-up as for 4- and 5-acetoxy-2-methylindanone gave a sample for NMR and mass spectral analysis (MS, see Table 5). NMR: δ 0.91 (s, 9, *t*-butyl), 2.00 (s, 3, $-\text{OC}-\text{CH}_3$), 5.47 (s, 1, $-\text{CH}-$ proton α to acetoxy group) and 7.20 (s, 5, aromatic protons).

Oxidation of neopentylbenzene with cobalt(III) acetate. Neopentylbenzene (776 mg) was dissolved in glacial acetic acid (50 ml). Cobaltic acetate [20 % $\text{Co}(\text{OAc})_3$, 307 mg], was added and the solution kept at 110 °C for 20 h, after which the colour of the solution had turned pink. For product distribution, see Table 3.

2,2-Dimethylindanone-1.²² 2-Methylindanone-1 (7.3 g) and methyl iodide (17.8 g) was dissolved in dry ether (125 ml). Potassium *t*-butoxide (14 g) was added in portions with stirring. After half a minute a vivid reaction started. The remaining base was added at such a rate that the solvent kept boiling. Addition completed, the reaction mixture was stirred under reflux for 2 h. Water (150 ml) was added and the phases separated. The water phase was extracted with ether. The combined ether solutions were washed with NaHCO_3 solution and very diluted sulphuric acid was added dropwise until gas evolution started. After drying and evaporation as earlier 8.3 g of 2,2-dimethylindanone remained. GLC showed only one peak and the product was used without further purification (MS, see Table 5). NMR: δ 1.22 (s, 6, methyl protons), 2.98 (s, 2, methylene protons) and 7.23–7.85 (m, 4, aromatic protons).

2,2-Dimethylindan.²² 2,2-Dimethylindanone-1 (8.3 g) was dissolved in glacial acetic acid (20 ml). Palladium on carbon (10 %, 0.8 g)

was added as a catalyst. Hydrogenation and work-up procedure as for 2-methylindanone. Distillation gave 2,2-dimethylindan (2.53 g), b.p. 65–66 °C/11 mmHg. NMR: δ 1.13 (s, 6, methyl protons), 2.68 (s, 4, methylene protons) and 7.07 (s, 4, aromatic protons).

Electrolysis experiments. The solvent-supporting electrolyte (50 ml) was poured into the electrolysis vessel. A background voltammogram was taken up measuring a stable current at each 0.1 V anode potential from 0 to +3 V vs. SCE. Then approximately 5 mmol of substrate was added. A new voltammogram was taken up and thereafter a preparative run was made until 25 % of the calculated charge for a 2e transfer process had passed. With platinum electrodes the anode potential was pulsed when necessary in order to diminish passivation of the electrodes which otherwise drastically lowered the current (2.9 s at working potential, 0.1 s at 0 V).

Work-up procedure. A sample of 5 ml was withdrawn from the electrolysis solution for determining current yield. Naphthalene (30–50 mg) was added as an internal standard and this solution was taken up in methylene chloride (25 ml). This solution was shaken with water (25 ml) and then with NaHCO_3 solution. After drying with anhydrous MgSO_4 , the analysis was made by GLC. The remaining 45 ml of the electrolysis solution was diluted with methylene chloride (100 ml) and shaken with water (150 ml). The water phase was shaken with further methylene chloride (25 ml) and the combined organic extracts were then shaken with NaHCO_3 solution until no more gas evolved. After separation of the phases, the organic layer was dried and the solvent evaporated. The residue was used for product analysis, NMR and MS.

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