

Studies on the Possible Effects of Adsorption on the Product Distribution of Organic Electrode Reactions. II. Stereochemistry of the Anodic Acetoxylation of 1-*t*-Butylacenaphthene

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The anodic acetoxylation of acenaphthene and 1-*t*-butylacenaphthene has been found to give predominantly side-chain acetates. In 1-*t*-butylacenaphthene substitution occurred almost exclusively in the 2-position, and it was observed that the *cis-trans* ratio was slightly greater at a platinum than at a carbon anode. Both these observations are in agreement with a mechanism involving adsorbed species, even if it is not possible to draw any firmer conclusions in the absence of suitable homogeneous reference experiments.

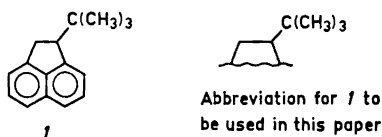
In the preceding paper of this series¹ the anodic acetoxylation of 2-*t*-butylindan was investigated in order to establish if adsorption is a controlling factor for the stereochemistry of anodic side-chain acetoxylation. The guiding idea was to study a molecule which had one side hindered for approach to the electrode surface by a bulky group, thereby increasing the tendency for formation of a thermodynamically less favored *cis* isomer (in this particular case, *cis*-1-acetoxy-2-*t*-butylindan) as compared to suitable homogeneous reference reactions. Indeed, 2-*t*-butylindan behaves as predicted with regard to stereochemistry, in that the *cis-trans* ratio of 1-acetoxy-2-*t*-butylindans is approximately one order of magnitude greater in the anodic reaction (at the platinum anode) than in a homogeneous reference process (generation of the 2-*t*-butyl-1-indanyl cation by solvolysis of either of the two isomeric 2-*t*-butyl-1-(*p*-nitrobenzoyloxy)indans). The trend upon change of anode material to less strongly adsorbing materials was also the expected one.

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However, 2-*t*-butylindan is not the ideal molecule for the purpose at hand, since the slight puckering of the five-membered ring already present in indan itself² seems to be even more pronounced when the 2-position is substituted by the bulky *t*-butyl group. Hence, the difference between the two sides of the molecules with respect to steric hindrance toward the anode surface is not as large as a casual inspection of molecular models might indicate. Accordingly, the effect of adsorption on stereochemistry might not be the maximally obtainable one (the highest anodic *cis-trans* ratio observed in the 2-*t*-butylindan case was 16 : 84, so there should be ample room for increases).

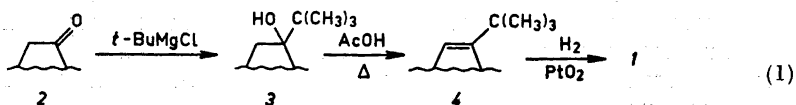
With this in mind, we decided to undertake a study of the anodic acetoxylation of 1-*t*-butylacenaphthene (*1*). The parent hydrocarbon is a very rigid



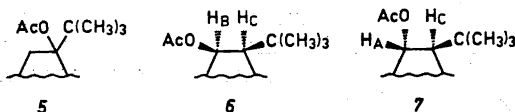
system, and there is no evidence that 1-alkyl substituents change the planar geometry to any extent.³ Therefore, this compound should exhibit stronger interference with the anode surface on the side of the *t*-butyl group than is the case for 2-*t*-butylindan. In addition, the presence of a naphthalene nucleus in *1* should increase the adsorption enthalpy as compared to 2-*t*-butylindan with only one benzene ring. Both of these factors ought to influence the *cis-trans* ratio in anodic acetoxylation to an even larger extent than observed for 2-*t*-butylindan.

RESULTS

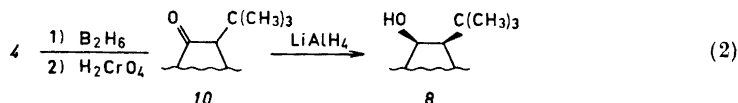
Synthesis of compounds. 1-*t*-Butylacenaphthene was prepared from acenaphthenone **2** according to the method outlined in eqn. 1. The yield of *1*, based on **2**, was 16 %. Reference compounds, acetates **5**–**7**, were prepared



by acetylation (acetic anhydride-pyridine treatment) of the appropriate alcohols **3**, **8**, and **9**.

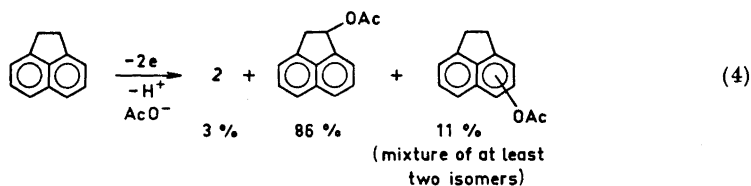


Compounds 8 and 9 were prepared as outlined in eqns. 2 and 3.



Apart from their mode of formation, the relative configuration of 6 and 7 was substantiated by comparison of their NMR spectra. Compound 6 gave $J_{\text{BC}} = 6$ cps, whereas 7 showed $J_{\text{AC}} = 2$ cps in good agreement with published values for other derivatives of acenaphthene³ and with the Karplus rule⁵ which predicts $J_{\text{cis}} \gg J_{\text{trans}}$. Similarly, the NMR spectra of 8 and 9 showed the corresponding coupling constants to be 6 and 2 cps, respectively.

Anodic oxidation of acenaphthene. At first the anodic acetoxylation of the parent hydrocarbon, acenaphthene, in acetic acid - 1.0 M sodium acetate at a platinum anode was studied as a model reaction. This was done mainly for establishing if enough side-chain acetoxylation takes place to allow for accurate analyses of the *cis-trans* ratio in the *t*-butyl derivative (a comparison between acetoxylation of indan⁶ and 2-*t*-butylindan¹ suggests that this model reaction is suitable for this purpose). The result is shown in eqn. 4:

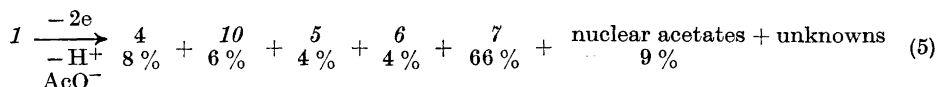


This is the product distribution after passage of 1.0 F/mol of substrate. Compound 2 and 1-acetoxyacenaphthene were assigned on the basis of identical GLPC retention times and mass spectra with authentic samples. The structures of the nuclear acetates were assigned on the basis of mass spectral data only, taking advantage on the characteristic fragmentation of aryl acetates⁷ (prominent peaks at m/e [$M^+ - 42$] and 43).

The results depicted in eqn. 4 shows preponderant formation of side-chain acetates in the acenaphthene system, similarly to the behaviour of indan and 2-*t*-butylindan. Hence, side-chain acetoxylation would be expected to be the major reaction in the 1-*t*-butylacenaphthene case also.

*Anodic oxidation of 1-*t*-butylacenaphthene (1).* This compound was first briefly examined by cyclic voltammetry in acetic acid, 0.1 M in lithium perchlorate. It shows irreversible 2e behavior at the Pt anode, the peak potential being 1.32 V vs. SCE. Olefin 4 under the same conditions displayed an irreversible 2e peak at 1.39 V vs. SCE.

Anodic oxidation of *I* at platinum in acetic acid – 1.0 M sodium acetate (at 1.3 V *vs.* SCE) gave the product mixture shown in eqn. 5 in addition to diacetate derivatives and other unidentified products. This is the product



distribution after passage of 2.8 *F*/mol of *I* (140 % reaction for a 2e process). The structures of compounds 4, 5, 6, 7, and 10 were established on the basis of identical GLPC retention times and mass spectra with authentic samples. The structures of the nuclear acetates were assigned on the basis of mass spectral data only. The major component, 7, was also identified by NMR analysis of the monoacetate fraction, separated by column chromatography on silica gel.

After identification of the main products from the anodic acetoxylation of *I*, a number of small-scale runs under different conditions were performed. At first, product analysis was carried out at several low conversions on platinum (Table 1) since the product distribution shown in eqn. 5 no doubt is con-

Table 1. Anodic acetoxylation of 1-*t*-butylacenaphthene (*I*) using a platinum anode.^a

Charge passed/mol of substrate	Product distribution, %				
	4	10	7	6	5
0.05	21	47	32	—	—
0.10	23	36	39	≤ 1	≤ 1
0.60	24	12	60	2	2
1.20 ^b	25	10	61	2	2

^a Cce, 60 mA; [AcO⁻]=1.00 M, [*I*]=0.075 M. ^b Current yield 52 %, based on consumption of *I*. Unknown products constitute *ca.* 27 % of the total reaction mixture.

siderably influenced by further oxidation of primarily formed products. Indeed, one can note from Table 1 that, *e.g.*, the percentage of alkene 4 is higher at low conversions, as would be expected. Also 10 is present in larger amounts at low conversions, due to the fact that adventitious water in the electrolyte plays a more important role in the beginning of the electrolysis.

Table 2. Anodic acetoxylation of 1-*t*-butylacenaphthene (*I*) in wet^a acetic acid.^b

Charge passed/mol of substrate	Product distribution, %				
	4	10	7	6	5
0.10	26	55	19	—	—
1.20 ^c	23	18	57	≤ 1	≤ 1

^a 5.0 % water added. ^b Cce, 60 mA; [AcO⁻]=1.00 M, [*I*]=0.037 M; platinum anode. ^c Current yield 40 %, based on consumption of *I*. Unknown products constituted *ca.* 26 % of the total reaction mixture.

Table 2 summarizes results from acetoxylation in wet (5 % water added) acetic acid. This experiment was done in the hope that a water-containing medium would increase the adsorption tendency of the non-polar hydrocarbon. However, no such effect is discernible, at least not on the stereochemistry of side-chain acetoxylation. Table 3 shows results from electrolysis at a carbon anode, whereas Table 4 summarizes how the ratio of 6 to 7 changes with

Table 3. Anodic acetoxylation of 1-*t*-butylacenaphthene (1) using a carbon anode.^a

Charge passed/mol of substrate	Product distribution, %				
	4	10	7	6	5
0.05	19	49	32	—	—
0.10	24	36	40	—	—
0.60	24	9	67	—	—
1.20 ^b	20	4	74	≤1	≤1

^a Cce, 60 mA; [AcO⁻]=1.00 M, [1]=0.075 M. ^b Current yield 80 %, based on consumption of 1. Unknown products constituted ca. 21 % of the total reaction mixture.

Table 4. Ratio of 6 to 7 as function of experimental conditions.

Experimental conditions	Ratio 6/7 ^a
HOAc/1.0 M NaOAc, Pt anode	0.033
HOAc/5 % H ₂ O/1.0 M NaOAc, Pt anode	0.018
HOAc/1.0 M NaOAc, C anode	0.014

^a Determined at 60 % conversion (see Tables 1–3).

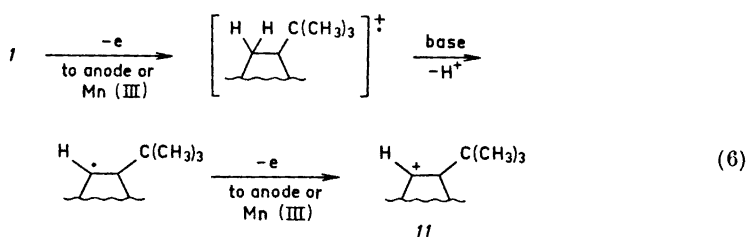
Table 5. Control experiment. Electrolysis of a mixture of 6 and 7 in acetic acid – sodium acetate.^a

Charge passed/mol of substrate	Ratio of acetates	
	6	7
0.00	1	1.66
0.18	1	1.79
2.24	1	1.73
4.00 ^b	1	1.60

^a Cce, 60 mA, platinum anode; [AcO⁻]=1.00 M, [6]=0.0075 M, [7]=0.0125 M. ^b The acetates were consumed with a current efficiency of 30 %. No additional products were detected.

experimental conditions. In order to establish that the 6/7 ratio is not influenced by preferential oxidation of either isomer, a mixture of 6 and 7 was subjected to the electrolysis conditions and the composition analyzed at various conversions. The results from this control experiment (Table 5) show that the ratio is largely constant over the range between 9 and 200 % conversion (calc. for a 2e-process).

Homogeneous reference reactions. Manganic acetate oxidation is a suitable homogeneous reference reaction for comparison with anodic acetoxylation, since this type of oxidation has been shown to take place *via* an electron transfer mechanism,⁸ entirely analogous to the electrochemical ECE mechanism (shown in eqn. 6 using hydrocarbon *1* as an example). However, several attempts at oxidation of *1* with Mn(OAc)₃ at 100° in acetic acid (the solution was preconditioned with 5 % acetic anhydride in order to remove traces of water⁹) produced none of the expected acetates but only olefin *4* (3 %) and ketone *10* (2 %), 95 % of the starting material being recovered. The low yield and nature of the products indicates that manganic acetate may be too weak an oxidizing agent to oxidize *1* to a significant extent, and that



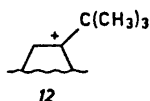
elimination from the intermediate cation *11* is the predominant process anyway. Moreover, the last traces of water in the solution evidently are able to compete successfully with acetate ion in reaction with *11*, ketone *10* presumably being produced by secondary oxidation of the 2-alcohols (*8* and/or *9*).

We also made several unsuccessful attempts to prepare the tosylate or *p*-nitrobenzoate of *9* (for generation of *11* in HOAc–NaOAc) by treatment of *9* with *p*-toluenesulfonyl or *p*-nitrobenzoyl chloride in anhydrous pyridine. In both cases olefin *4* and unreacted starting material were the only products obtained, indicating that both derivatives were too reactive for isolation.

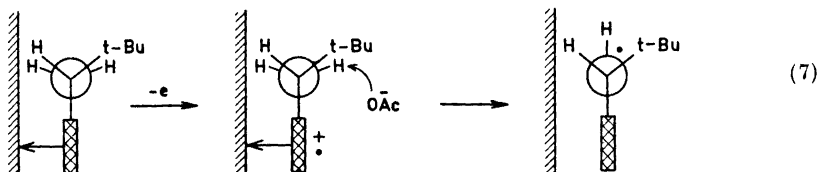
DISCUSSION

The results from the anodic acetoxylation of the 1-*t*-butylacenaphthene system unfortunately do not allow any firmer conclusions to be drawn with regard to the role of adsorption for stereochemistry than was previously possible in the study of 2-*t*-butylindan.¹ This is mainly due to the lack of a suitable homogeneous reference reaction, so that it is not possible to establish if the anodic oxidation of *1* really does produce an anomalously high 6/7 ratio (*i.e.*, with respect to a related homogeneous process). One can, however, note that the *cis-trans* ratio is somewhat higher on platinum than on carbon, as required if adsorption plays a role for the product distribution.¹

The most interesting feature of the reaction is the low yield of the 1-acetate *5* (Tables 1–3), in spite of the fact that this compound originates from the tertiary carbonium ion *12*. According to the usual reasoning, formation of *12* from the cation radical in eqn. 6 should be favored over formation of the secondary cation *11*, so that the preference for formation of 2-acetates *6* and *7*



is rather unexpected.* An attractive rationalization of this anomaly is to invoke preferential adsorption of the substrate with the least hindered side oriented towards the electrode (eqn. 7). Assuming that the cation radical remains adsorbed in this position, only one hydrogen *in the 2-position* is exposed



toward action of a base from the side of the solution. The hydrogen in the 1-position is shielded from base attack both by the electrode surface and the *t*-butyl group. After formation of the benzylic radical the second electron transfer takes place with formation of 11. It then appears necessary to assume that the 2-acetates (6 and 7) are formed to a very high extent from the desorbed carbonium ion, since the alternative, that adsorption with the most hindered side toward the electrode should be the controlling factor for the stereochemistry, appears to be ruled out by the fact that 1-substitution occurs to such a low extent. In this substrate-electrode configuration there is no reason why the base should attack the 2-position preferentially; on the contrary, formation of the tertiary cation 12 should be the predominant mode of reaction.

We therefore propose that at least the two first steps (E and C_B) of the EC_BEC_N oxidation¹⁰ of 1 involve adsorbed species, oriented with the least hindered side toward the electrode. The last (C_N) step most probably takes place *via* a desorbed carbonium ion to a high extent, but this is difficult to establish with certainty. None of the features of this mechanism is contradicted by the results from the 2-*t*-butylindan study. What one can conclude in retrospect is that the two systems chosen may be too highly hindered for the purpose at hand. One of the desired features was that the formation of a thermodynamically less stable isomer should be an indication of adsorption control. In both systems, the bulky *t*-butyl group may actually block reaction at the cationic center to form this isomer in the favored substrate-electrode configuration, and hence reaction with desorbed carbonium ion will be promoted. One might therefore hope for a higher degree of adsorption control of stereochemistry in systems with less bulky groups, *e.g.*, with a methyl or ethyl group instead of the *t*-butyl group in the two compounds hitherto studied.

* It should be pointed out that one cannot get a precise ratio between 11 and 12 from the product distribution observed since olefin 4 might originate from both cations. However, even if *all* of 4 would be formed from cation 12, there is still a preference for formation of secondary cation over the tertiary one by a factor of about 75 : 25 (6 + 7 + 10/4 + 5).

It should moreover be possible to elucidate the stereochemistry of the two first steps (E and C_B) in the anodic oxidation of 1 (or any other suitable system, for that matter) by introduction of one deuterium at the 2-position in either *cis* or *trans* position to the *t*-butyl group. Using this method it should be possible to map the stereochemistry of the process throughout the whole four-step EC_BEC_N sequence. This problem is under study in this Laboratory.

EXPERIMENTAL

General. Melting points and boiling points are uncorrected. IR spectra were determined with a Perkin-Elmer Model 257 grating spectrometer using carbon tetrachloride solutions. The NMR spectra were recorded on a Varian A-60 spectrometer using chloroform-*d* solutions with TMS as internal standard. Mass spectra were obtained with an LKB 9000 mass spectrometer coupled to a gas chromatograph. Analytical GLPC was performed using a Perkin-Elmer Model 880 instrument equipped with a disk integrator and a 1.5 meter \times 0.3 cm column of 5 % neopentyl glycol succinate on acid washed Chromosorb W 60-80.

NMR. Protons H_A, H_B, and H_C are designated in the experimental section as shown below. Structure 13 represents monofunctional acenaphthenes (*i.e.*, 1 and 4), whereas 14 represents *t*-butylacenaphthenyl derivatives where H_A, H_B, or H_C is replaced by OH or OAc (*i.e.*, 3, 5, 6, 7, 8, and 9).



1-t-Butylacenaphthylene (4). After trying numerous variations, the following procedure was adopted as the most satisfactory. To the Grignard reagent,¹¹ prepared over a 10 h period from magnesium (61 g, 2.5 mol) and *t*-butyl chloride (232 g, 2.5 mol) in ether (1300 ml), was added ketone **2** (114 g, 0.68 mol). The ketone **2** was added in small portions within 1 h and the reaction mixture was stirred overnight. The complex was decomposed by slowly pouring the reaction mixture onto 2000 g of ice in a 5 l flask. A 2.5 M sulfuric acid solution (700 ml) was added slowly to react the remaining magnesium. The ether layer was separated in a 5 l funnel yielding 400 ml of a dark brown solution. The aqueous phase was extracted with ether (2 \times 400 ml) and the combined ether extract was washed with water (700 ml), 5 % sodium bicarbonate solution (700 ml), water (700 ml), and dried over anhydrous sodium sulfate. The solvent was evaporated leaving a dark brown oil. The GLPC-mass spectrum indicated that the material contained *ca.* 30 % 1-*t*-butyl-1-acenaphthenol (**3**) ($M^+ = 226$) and mainly unreacted ketone **2**. The crude material was refluxed with 500 ml of acetic acid for 1 h and the dark solution was poured into 1200 ml of water and extracted with benzene (4 \times 300 ml). The combined benzene extract was washed with 5 % sodium carbonate solution (2 \times 600 ml) and dried over anhydrous sodium sulfate. The solvent was evaporated and the residue was passed through a 7 \times 70 cm tower of neutral alumina (Merck, 1600 g) packed with hexane. The column was washed with hexane until the yellow-orange zone due to the unsaturated compound, which migrates rapidly, had passed into the filtrate. The yield of the olefin **4**, as a mobile yellow-orange oil, was 23.5 g (15 %); NMR: δ 7.2-7.8 (m, 6, aromatic protons), 6.63 (s, 1, H_A), and 1.45 ppm (s, 9, (CH₃)₃C). GLPC indicated that the compound was 98 % pure. Crystallization from methanol gave material that melted slightly below room temperature. A 5 g sample of the olefin was passed through another column (3 \times 25 cm) of neutral alumina (Merck) with hexane and the 2 % impurities were removed in the first 200 ml fraction along with *ca.* 0.5 g of **4**. The remaining olefin **4**, eluted with hexane, was judged pure from GLPC analysis.

1-t-Butylacenaphthene (1). A solution of olefin **4** (2.08 g) in 100 ml of ethanol was

reduced at room temperature with Adams catalyst (0.20 g) and hydrogen at 25 p.s.i. When hydrogen uptake was completed, the solution was filtered and the solvent removed, giving a yellow oil (95 % yield); NMR: δ 6.9–7.8 (m, 6, aromatic protons), 3.1–3.6 (m, 3, H_A, H_B, and H_C), and 0.97 ppm (s, 9, (CH₃)₃C). GLPC indicated **1** to be of 95 % purity. Further purification by crystallization from methanol and sublimation at 5 mm was unsuccessful. The major impurity (ca. 5 %) had a GLPC retention time that was shorter than that of **1**. It was inert during anodic acetoxylation of **1**, and it did not interfere with GLPC analysis of products.

trans-2-*t*-Butyl-1-acenaphthenyl acetate (**7**). *trans*-2-*t*-Butyl-1-acenaphthenol (**9**) was prepared by Brown's hydroboration-oxidation reaction¹² of 1-*t*-butylacenaphthylene (**4**). A 100 ml round bottomed three-necked flask equipped with an addition funnel, magnetic stir bar, and calcium chloride drying tubes was utilized. To a well-stirred suspension of sodium borohydride (0.716 g) in 25 ml of tetrahydrofuran (THF) containing 5.20 g (25 mmol) of **4** was added 3.15 ml of boron trifluoride diethyl etherate in 13 ml of THF over 1 h while the temperature was maintained at ca. 25°. The reaction mixture was stirred an additional hour at 25° before the excess hydride was decomposed with water (4 ml). The organoborane was oxidized at 30–45° by the addition of 3 ml of 3 M sodium hydroxide solution, followed by the dropwise addition of 3 ml of 30 % hydrogen peroxide over 30 min. The mixture was stirred at ca. 45° for 2 h and then washed with a saturated sodium chloride solution (25 ml). The aqueous phase was extracted with THF (15 ml) and the combined THF extracts were dried over anhydrous potassium carbonate. The solvent was removed leaving 5.95 g of crude *trans*-alcohol **9** (90 % pure by GLPC). A small portion of *trans*-alcohol **9** was eluted as a yellow oil by column chromatography on neutral alumina (Merck) with benzene as solvent; δ 7.3–7.7 (m, 6, aromatic protons), 5.39 (d, 1, H_A, J_{AC} = 2 Hz), 3.15 (d, 1, H_C, J_{AC} = 2 Hz), 2.40 (bs, 1, OH), and 1.00 ppm (s, 9, (CH₃)₃C). The *trans*-alcohol **9** (0.60 g) was mixed with 1.5 ml each of pyridine and acetic anhydride and was allowed to stand overnight at room temperature. The reaction mixture was poured onto 30 ml of cold water in a separatory funnel and then was shaken vigorously to hydrolyze the excess acetic anhydride. The solution was extracted with ether (2 × 30 ml) and the combined ethereal extract was washed with saturated potassium carbonate solution (2 × 30 ml) and dried over anhydrous potassium carbonate. The solvent was evaporated and the *trans*-acetate **7** was eluted as a yellow oil by column chromatography using silica gel (Kebo 100–200 mesh, 80 g) with benzene as solvent, NMR: δ 7.3–7.8 (m, 6, aromatic protons), 6.63 (d, 1, H_A, J_{AC} = 2 Hz), 3.43 (d, 1, H_C; J_{AC} = 2 Hz), 2.03 (s, 3, CH₃CO₂), and 1.00 ppm (s, 9, (CH₃)₃C).

2-*t*-Butyl-acenaphthenone (**10**). Ketone **10** was prepared by hydroboration of the olefin **4** (5.20 g, 25 mmol) in the same manner as described above in the preparation of the *trans*-alcohol **9**. The excess hydride was decomposed with water (5 ml) and then the organoborane was oxidized with 23 ml of a chromic acid solution (5.5 g of sodium dichromate dihydrate and 4.1 ml of 96 % sulfuric acid was diluted to 23 ml).¹³ The chromic acid solution was added dropwise over 20 min and the reaction mixture was maintained at 25–30° with an ice bath. The solution was heated for 2 h at 45° and then worked up as before. The THF was evaporated leaving 6.00 g of crude ketone **10** (< 90 % pure by GLPC). A 2 g sample was column chromatographed on silica gel (Kebo, 100–200 mesh, 80 g). A few per cent of starting material **4** was eluted with benzene and ketone **10** was eluted as a yellow oil with benzene-ether (50 : 50); NMR: δ 7.3–8.1 (m, 6, aromatic protons), 3.43 (s, 1, H_C), and 1.13 ppm (s, 9, (CH₃)₃C).

cis-2-*t*-Butyl-1-acenaphthenyl acetate (**6**). Ketone **10** (1.58 g, 7.05 mmol) in ether was reduced with lithium aluminum hydride (1 g) in ether in the normal manner. A quantitative yield of *cis*-alcohol **8** was obtained as a yellow oil; NMR: δ 7.3–7.7 (m, 6, aromatic protons), 5.50 (d, 1, H_B, J_{BC} = 6 Hz), 3.30 (d, 1, H_C, J_{BC} = 6 Hz), 1.30 (s, 9, (CH₃)₃C), and 1.05 ppm (bs, 1, OH). The *cis*-alcohol **8** (1.00 g, 4.43 mmol) was converted to the *cis*-acetate **6** with 5 ml each of pyridine and acetic anhydride in the same manner described for the preparation of *trans*-acetate **7**. NMR: δ 7.3–7.7 (m, 6, aromatic protons), 6.65 (d, 1, H_B, J_{BC} = 6 Hz), 3.53 (d, 1, H_C, J_{BC} = 6 Hz), 2.00 (s, 3, CH₃CO₂), and 1.28 ppm (s, 9, (CH₃)₃C). Some additional coupling was observed that is assumed to be due to the *ortho*-benzylic protons coupling with H_B and H_C ($J_{B-o-benzylic}$ = 0.4 Hz and $J_{C-o-benzylic}$ = 1.2 Hz).¹⁴

1-*t*-Butyl-1-acenaphthenyl acetate (**5**). The α -alcohol **3** (3.0 g, ca. 30 % purity; main impurity ketone **2**) was allowed to react with 5 ml each of pyridine and acetic acid in the

same manner described for the preparation of *trans*-acetate 7. The NMR spectrum of the crude product (ca. 70 % purity; ketone 2 was lost in the workup due to its relative insolubility in ether) could be rationalized in terms of the desired α -acetate 5; δ 6.9–7.7 (aromatic protons), 3.9 and 3.1 (two doublets, H_A and H_B , $J_{AB} = 18$ Hz), 2.0 (s, CH_3CO_2), and 1.0 ppm (s, $(CH_3)_3$). When the sample was chromatographed on silica gel (Kebo 100–200 mesh, 80 g) with benzene solvent, only olefin 4 was obtained (due to elimination of acetic acid from 5 on the column).

Attempted preparation of trans-2-t-butyl-1-acenaphthenyl p-toluenesulfonate. An attempt was made to prepare this tosylate from *trans*-alcohol 9 with *p*-toluenesulfonyl chloride (m.p. 67–68°, lit. 67.5–68.5) in anhydrous pyridine in the usual manner.¹⁵ Olefin 4 was the main product obtained from this reaction. The tosylate was most likely too reactive for conventional preparation and isolation.

Attempted preparation of trans-2-t-butyl-1-acenaphthenyl p-nitrobenzoate. Two attempts were made to prepare this derivative from *trans*-alcohol 9 (1.00 g, 4.43 mmol) with *p*-nitrobenzoyl chloride (0.99 g, 5.32 mmol) in anhydrous pyridine (20 ml) in the usual manner (+5°, 2 days). The reaction mixture was poured into a separatory funnel containing 75 ml of ether and 75 ml of ice and water. The mixture was shaken for 5 min and the layers were separated. The aqueous layer was extracted with ether (2 \times 50 ml) and the combined ether extracts were washed with ice-cold 5 % hydrochloric acid until the wash showed acid reaction. The ethereal solution was washed two times with ice-cold 5 % sodium bicarbonate and dried over anhydrous potassium carbonate. The ether was evaporated leaving a yellow-orange liquid. Crystals did not form upon addition of petroleum ether (40–60°), even when the solution was cooled to –78°. GLPC and NMR analysis of the liquid product indicated the presence of *trans*-alcohol 9 (ca. 50 %) and olefin 4 (ca. 50 %).

Electrochemical experiments. The constant potential electrolysis (cpe) experiments were carried out using the same electrolysis cell as that described by Ebersson,⁹ using a 60 ml vessel with platinum electrodes. The appropriate electrolyte (50.0 ml acetic acid, 0.2 M in substrate, and 1.00 M in sodium acetate) was poured into the cell and allowed to reach thermal equilibrium (30°). The anode potential was controlled by means of a Model 557 potentiostat from Amel, Milan, Italy, and the charge passed through the electrolyte was measured by means of the Model 558 integrator from the same company. After terminating the reaction, the acetic acid solution was added dropwise to a slurry of $NaHCO_3$ (76 g) and 100 ml of water. After neutralization the solution was extracted with ether (3 \times 50 ml). The combined ethereal extract was washed with saturated sodium hydrogen carbonate solution (2 \times), water (2 \times), and dried over anhydrous sodium sulfate. The ether solution was concentrated, and the products were analyzed by GLPC.

The constant current electrolysis (cce) experiments were performed using a 30 ml beaker equipped with platinum (sheet: 2 cm² area) and carbon (rod: 6 mm diameter) electrodes. The appropriate electrolyte (20.0 ml acetic acid, 0.075 M in substrate, and 1.00 M in sodium acetate) was poured into the cell and electrolyzed at 60 mA by means of a variable-voltage power supply (Radiak, Stocksund, Sweden). After starting the electrolysis, 2.00 ml samples were withdrawn after passage of 2.5, 5, 30, and 60 % of the theoretically calculated amount of charge. Each sample was worked up by pouring it into saturated sodium hydrogen carbonate solution (20 ml), extracting the organic components with ether (2 \times 25 ml), and washing the ether extracts with saturated sodium hydrogen carbonate solution (20 ml). The ether solution was filtered through 3 g of anhydrous magnesium sulfate and the sulfate was washed with ether (10 ml). Finally, the ether solution was concentrated to a volume of about 0.3 ml, and the products were analyzed by GLPC. In some cases, biphenyl was used as an internal standard to measure the consumption of starting material, and therefore the current yield. A column temperature of 100° was used with a programmed temperature increase of 6°/min (up to 200°). The following retention times are representative: biphenyl, 3.7 min; 1, 7.9 min; 4, 10.1 min; 7, 13.1 min; 5, 13.7 min; 6, 14.6 min; and nuclear and diacetates 16–21 min.

Manganic acetate oxidations. The $Mn(OAc)_3 \cdot 2H_2O$ was prepared as described previously.⁹ A 0.125 M solution in acetic acid containing 5 % acetic anhydride was kept at 72° for 21 h before addition of 1. Samples were withdrawn at suitable intervals, worked up, and analyzed as described above.

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