Studies on Anodic Substitution Reactions. XI.* The Anodic Acetoxylation of Triptycene and Fluorene and its Implications for the Side-chain Substitution Mechanism

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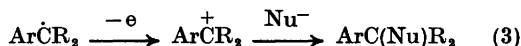P.O. Box 740, S-220 07 Lund 7, Sweden

The anodic acetoxylation of triptycene (*1*) and fluorene (*2*) exhibits a high nuclear to α substitution ratio (250 and 35, respectively) relative to structurally similar substrates. This behaviour is in accordance with the ECEC mechanism generally postulated for anodic α substitution.

Triptycene (*1*, 9,10-*o*-benzeno-9,10-dihydroanthracene, abbreviated Tr-H where appropriate) and fluorene (*2*, abbreviated Fl-H where appropriate) possess structural features which make them critically interesting substrates for anodic substitution. Due to the rigid structure of the triptycene system, its

1   *2*

bridge-head radical (9-Tr·) and carbocation (9-Tr+) are highly strained species,[1] and since radicals and carbocations are postulated as intermediates in anodic side-chain (α) substitution reactions [2] (eqns. 1 – 3) one would qualitatively predict that Tr-H would either not at all undergo α substitution or at least give a

high ratio of nuclear to α substitution product compared to other, structurally related compounds.

$$ArCHR_2 \xrightarrow{-e} (ArCHR_2)^{+\cdot} \qquad (1)$$

$$(ArCHR_2)^{+\cdot} + B: \longrightarrow Ar\dot{C}R_2 + BH^+ \qquad (2)$$

$$Ar\dot{C}R_2 \xrightarrow{-e} Ar\overset{+}{C}R_2 \xrightarrow{Nu^-} ArC(Nu)R_2 \qquad (3)$$

A second critical feature of Tr-H is its inability to orient any of its three aromatic faces parallel to the electrode surface close enough to form a π-donor-acceptor type adsorption complex. The existence of such complexes has been postulated on the basis of adsorption studies on aromatic hydrocarbons.[3] Stereochemical studies [4] of anodic α substitution have, however, largely failed to detect any unambiguous consequences of the substrate-electrode interaction in the later stages of the reaction sequence (eqn. 3).

Also fluorene (*2*) would be expected to undergo α substitution to a low or negligible extent, since one of the corresponding intermediates of the ECE mechanism, 9-Fl+, formally is an antiaromatic species, making its formation energetically less favored. Thus it is predicted that fluorene, like *1*, should exhibit a relatively high nuclear to α acetoxylation ratio.

This paper reports a study of the anodic acetoxylation of Tr-H and Fl-H, showing that α acetoxylation is indeed less favored than for relevant reference compounds (triphenylmethane for *1* and diphenylmethane for *2*).

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* Part X, see Blum, Z., Cedheim, L. and Nyberg, K. *Acta Chem. Scand. B 29* (1975) 715.
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Table 1. Oxidation half-wave potentials of 1—4 and related compounds.

Compound	$E_{1/2}/V$ [a]	Ref.
Triptycene (1)	1.48 [b]	This work
Triphenylmethane (3)	1.62 [b]	This work
9,10-Dihydroanthracene	1.53 [c]	6
Anthracene	0.84 [c]	6
9,10-Diphenylanthracene	0.86 [d]	6
Fluorene (2)	1.32 [b]; 1.25 [c]	This work; 6
Diphenylmethane (4)	1.84 [b]	This work

[a] Vs. the Ag/Ag+ (0.1 M) reference electrode. [b] In acetonitrile/tetrabutylammonium tetrafluoroborate (0.1 M) with 3 % trifluoroacetic anhydride added. [c] In acetonitrile/sodium perchlorate. [d] In acetonitrile/tetraethylammonium perchlorate.

RESULTS

Voltammetry. Tr-H, Fl-H, triphenylmethane (3) and diphenylmethane (4) displayed irreversible two-electron behaviour when studied by cyclic voltammetry in acetonitrile/0.1 M tetrabutylammonium tetrafluoroborate with 3 % trifluoroacetic anhydride added to keep nucleophilic impurities under control.[5] Half-wave potentials for 1 − 4 are given in Table 1, together with those of some structurally related hydrocarbons.

Preparative studies. Anodic oxidation of Tr-H at a carbon anode in the system acetonitrile-acetic acid (2.7:1)/tetrabutylammonium acetate (0.15 M) primarily gave monoacetoxylation products which were further oxidized to di-, tri-, and higher acetoxylation products during the run. Only the monoacetoxylation products were rigorously identified in view of the rather complex mixture of diacetates obtained (in principle, fifteen diacetate isomers are possible) and the low priority of this particular problem. After passage of 3.5 F/mol of Tr-H at constant current (constant potential conditions gave the same result) a 47 % current yield of a mixture of monoacetates (54 %), diacetates (35 %) and higher acetates (11 %) was obtained. Analysis of the monoacetate fraction showed it to consist of predominantly 1- and 2-TrOAc, 31 and 68.5 %, respectively, but also with a small and well reproducible percentage, 0.5 %, of the α substitution product, 9-TrOAc, present. A similar product distribu-

tion (1-/2-/9-isomer: 38/62/0.5) was obtained with platinum as the anode material in a constant potential run.

A few runs were performed using tetrabutylammonium tetrafluoroborate as the supporting electrolyte in order to see if the known tendency of α acetoxylation being favored in the absence of acetate ion [7] would hold for Tr-H too. None of the products discussed above were, however, detectable in these experiments, conducted with both carbon and platinum as the anode material.

When 3 was oxidized at a carbon anode at 1.6 V vs. SCE in acetonitrile-acetic acid (1:1)/potassium acetate (0.6 M) a 50 % current yield of a mixture of monoacetates (98 %) and higher acetates (2 %) was obtained after passage of 0.9 F/mol of 3. The α/nuclear substitution ratio in the monoacetate fraction was 66:34 and the o:m:p proportion 44:24:32.

Fluorene (2) was similarly oxidized at platinum (c.p.e. at 1.6 V vs. SCE) in acetic acid/sodium acetate (1.0 M). After passage of 0.2 F/mol of 2 a 15 % current yield of monoacetates was detectable. The isomer ratio, 2-FlOAc/1-, 3-, 4-FlOAc/9-FlOAc, was 93:3.5:3.5. With tetrabutylammonium tetrafluoroborate as a supporting electrolyte, a 0.5 % current yield of 9-FlOAc was detectable; no nuclear substitution products were formed.

DISCUSSION

To put these results into a wider perspective, a number of relevant isomer distribution ratios for anodic acetoxylation reaction have been collected in Table 2.

The results are reported as the nuclear to α substitution ratios, both the experimental values and those corrected for the differing ratios between the number of nuclear and α hydrogen atoms in different compounds. It should be noted that the experimental value for 1 probably is too small, since it has been obtained in a high-conversion (3.5 F/mol of 1) run in which a large amount of di- and higher acetates were formed. Since the presence of one nuclear acetoxy group facilitates further nuclear acetoxylation in the same ring, it is reasonable to assume that selective removal of the initially formed monoacetates with respect to 9-TrOAc occurs (9-TrOAc would, if anything, be oxidized

Table 2. Isomer distributions in the anodic acetoxylation of certain aromatic compounds.

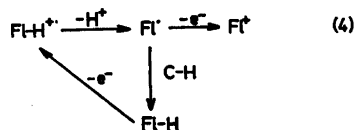| Compound	Ratio of nuclear to α substitution		Ref.
	Exp.	Per α-H [a]	
Triptycene (1)	200	250	This work
Triphenylmethane (3)	0.52	0.17	This work
Fluorene (2)	28	35	This work
Diphenylmethane (4)	4.3	4.3	7
Toluene	2.4	7.2	7
Ethylbenzene	1.0	2.0	7
Isopropylbenzene	1.1	1.1	7
Indan	0.27	1.4	8
2-Methylindan	0.19	1.0	9
2,2-Dimethylindan	0.020	0.1	9

[a] Corrected for differing ratios of the number of nuclear and α hydrogen atoms; scale arbitrary.

at a higher potential than *1*). The *maximal* effect of this phenomenon would bring up the experimental nuclear to α substitution ratio for *1* to $200/0.54 \approx 370$ (assuming that all higher acetates are nuclear and have the acetoxy groups in one ring only). Unfortunately, low-conversion runs could not be performed with *1*, since the analytical method, based on NMR analysis of the monoacetates, was too insensitive under such conditions.

The *first* crucial step in determining the nuclear to α substitution ratio is the attack of the base/nucleophile upon the radical cation, either at an α hydrogen atom (eqn. 2) or at a nuclear carbon atom. Any factor that destabilizes the transition state for proton abstraction relative to that of nuclear attack will increase the nuclear/α substitution ratio. Triptycene, the corresponding bridgehead radical of which is destabilized due to deviation from planarity of the radical center[1] and due to lack of overlap between the aromatic rings and the odd-electron orbital (also manifested[11] in the lack of hyperfine splitting by the bridgehead hydrogens in the ESR spectrum of Tr-H+·), does indeed exhibit an anomalously high nuclear/α substitution ratio relative to that of a structurally similar compound, triphenylmethane.
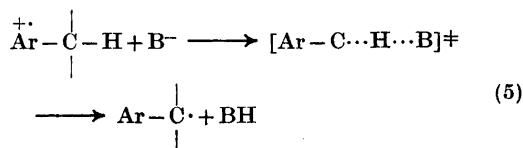
The *second* crucial step in determining the nuclear to α substitution ratio is the further oxidation of the radical to the carbocation (eqn. 3). Any factor which destabilizes the
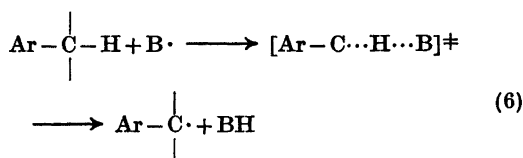
carbocation should lead to an increase of the nuclear/α substitution ratio, provided one can assume that competing processes, such as coupling or hydrogen atom abstraction from other electrolyte components, are unaffected by the very same factor. Fluorene, which can be converted to an antiaromatic species, Fl+, in the course of the reaction sequence of eqns. 1 − 3, gives a relatively high nuclear/α substitution ratio relative to that shown by diphenylmethane. For fluorene, it is also pertinent to note that the current yield of product(s) is low or very low compared to other substrates of similar structure but with higher oxidation potential (*e.g.*, triptycene, triphenylmethane, several alkylbenzenes[12]). If concurrent Kolbe oxidation of acetate ion is the only process competing with Fl-H oxidation, we feel that the yield of substitution product(s) of Fl-H should be considerably higher. One possibility to explain this anomaly is that fluorene is effectively regenerated from Fl· (eqn. 4).

$$Fl-H^{+\cdot} \xrightarrow{-H^+} Fl^\cdot \xrightarrow{-e^-} Fl^+ \quad (4)$$

with branches labelled $-e^-$, C-H leading to Fl-H

We have previously suggested[2b] that the nuclear to α substitution ratio in anodic substitution reactions appears to be governed by the ratio between the positive charge density at a free nuclear position and that of a carbon atom adjacent to the carbon atom carrying the removable hydrogen atom. In view of the results shown in Table 2 this hypothesis is clearly an oversimplification which only covers the gross features of the reaction. Substrates like Tr-H and Fl-H which possess unusual structural elements cannot be treated in this simple manner.

An interesting analogy can be drawn between the radical cation/anion reaction and the corresponding neutral molecule/neutral radical reaction (eqns. 5 and 6) leading to proton abstraction. Here one can note that (a) the

$$Ar-\overset{|}{\underset{|}{C}}-H + B^- \longrightarrow [Ar-C\cdots H\cdots B]^\ddagger$$
$$\longrightarrow Ar-\overset{|}{\underset{|}{C}}\cdot + BH \quad (5)$$

$$Ar - \underset{|}{\overset{|}{C}} - H + B\cdot \longrightarrow [Ar - C\cdots H\cdots B]^{\ddagger}$$

$$\longrightarrow Ar - \underset{|}{\overset{|}{C}}\cdot + BH \qquad (6)$$

initial states are different, (b) the final states are identical, and (c) the transition states in all likelihood must be identical assuming identical reaction conditions in the two cases. It then follows that the energy difference between the two initial states should give an idea of the difference in selectivity between the two types of reactions. Data for the attack by free radicals at the α position of alkylbenzenes are scarce [13] and not entirely compatible with those available for anodic substitution processes, but it is at least known for attack by phenyl radicals that the experimental nuclear to α substitution ratio is 6.7, 0.82, and 0.67 for toluene, ethylbenzene, and isopropylbenzene, respectively.[13a] This should be compared to the corresponding values for the radical cation/acetate reaction, 2.4, 1.0, and 1.1. While these systems of course are not strictly comparable due to the different composition of the reagents (Ph and CH_3COO) we think it would be worthwhile to explore this analogy with a more suitable reagent. One possible candidate would be the benzoate system where both reactions of eqns. 5 and 6 should be feasible.[2a,14]

Finally, the half-wave potentials of Table 1 are worth commenting on. We [4] and others [3] have earlier assumed that, for effective electron transfer to occur, the substrate must be adsorbed to the anode surface with its aromatic face parallel to the surface. Although stereochemical consequences of this hypothesis are so far largely lacking,[4] we have ascribed this to the less than ideal nature of the substrates and reactions studied until now and never questioned this basic assumption. It is then disturbing to find that triptycene, which cannot possibly align any of its aromatic rings parallel to the anode surface and still be close enough to it, is easier to oxidize than, e.g., triphenylmethane and 9,10-dihydroanthracene, both substrates with no problem in this respect. This might indicate that the requirement for overlap between electrode and substrate orbitals is not as stringent as previously assumed.

EXPERIMENTAL

Materials. 9-Acetoxytriptycene was prepared according to known methods.[15–17] The 2-acetoxy isomer was prepared from 2-aminotriptycene [18] analogously to that used for the 9-acetoxy compound.[17] The nuclear acetoxy derivatives of 2 were synthesized according to known methods,[19] as were also 2- and 9-acetoxyfluorene.[20]

Anodic oxidation of triptycene (1). A solution of triptycene (1.0 g) and Bu_4NOAc, HOAc (2.0 g) in acetonitrile (27 ml) – HOAc (10 ml) was oxidized at a carbon anode (9 cm²) at a constant current density of 28 mA cm⁻² until 3.54 F mol⁻¹ of substrate has passed through the solution. The electrolyte solution was poured into water (200 ml) and the mixture extracted with ether (3 × 100 ml). The combined ether extracts were washed with water (3 × 100 ml), saturated sodium hydrogen carbonate solution (100 ml) and water (100 ml). After addition of acetone (50 ml) the solvent was evaporated until a solution, suitable for GLC analysis, was obtained. GLC analysis (2 m × 0.3 mm 3 % OV-101 on Chromosorb W column, 130 – 300 °C/10 °C min⁻¹) with 2,2′,4,4′,6,6′-hexamethylbiphenyl as an internal standard showed that the amount of recovered triptycene was 37 %, the combined yield of 9-TrOAc + 1-TrOAc + 2-TrOAc 34 %, and the residual components 29 %. The amount of diacetates was estimated by GLC/MS to be 22 %.

The isomer distribution of the monoacetate fraction was determined in the following way: The above-mentioned extract was evaporated to dryness and the solid material subjected to column chromatography on acidic alumina. Elution with carbon tetrachloride separated unreacted TrH, whereafter the monoacetate fraction was eluted by dichloromethane. The procedure was repeated once more with the monoacetate fraction (as checked by GLC/MS) in order to obtain material pure enough for further analysis. The material then obtained consisted of the monoacetates to more than 95 % and was subjected to GLC and NMR spectroscopic analysis. ¹H NMR spectrum of mixture in $CDCl_3$: δ 2.09 (3 H, s, CH_3CO), 4.28 (2 H, d, bridge-head H) and 6.60 – 7.46 (11 H, m, aromatic H).

By addition of Eu(fod)₃ the acetoxy signal was split into a doublet (integrated areas 69:31) and the δ 4.28 signal into a quartet. By addition of authentic 2-TrOAc the 69 % component is shown to correspond to this compound. Since 9-TrOAc can be analyzed by GLC (0.5 % of the monoacetate mixture) it is evident that the 31 % component must be 1-TrOAc.

Anodic oxidation of triphenylmethane (2). A solution of triphenylmethane (3.0 g) and potassium acetate (2.0 g) in acetonitrile (20 ml) – acetic acid (20 ml) was oxidized anodically at a carbon anode (anode potential 1.6 V vs. SCE) until 0.9 F mol⁻¹ had been passed through the solution. After work-up as described above the

product mixture was analyzed by GLC/MS, comparing with authentic specimens of all possible monoacetates. GLC analysis (2 m × 0.3 mm 3 % OV-101 on Chromosorb W column, 139−270 °C/6 °C min^{-1}) established the $\alpha{:}o{:}m{:}p$ proportion to be 66:15:8:11. The current yield was 50 % (2,2′,4,4′,6,6′-hexamethylbiphenyl as internal standard) and the monoacetate/higher acetates ratio 98:2.

Anodic oxidation of fluorene (3). A solution of fluorene (1.66 g) in HOAc/1 M NaOAc (50 ml) was oxidized anodically at a platinum anode at 1.6 V *vs.* SCE until 0.2 F mol^{-1} of 3 had been passed through the solution. After the usual work-up the product mixture was chromatographed on a silica gel column, using (1) pentane and (2) pentane-diethyl ether (1:1) as eluents. The separation process was followed by GLC analysis (2 m × 0.3 mm 5 % neopentylglycol succinate on Chromosorb W column at 200 °C; pentamethylbenzyl acetate as internal standard). The current yields of 2-acetoxyfluorene, 9-acetoxyfluorene, and 1-/3-/4-acetoxyfluorene were 14, 0.5 and 0.5 %, respectively. With tetrabutylammonium tetrafluoroborate as supporting electrolyte only the 9-isomer was obtained (0.5 % current yield).

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