Electro-organic Reactions. Part 15.† The Mechanism of Cathodic Cleavage and Elimination from Vicinal Diacetates and an Unusual Cleavage from 9,10-Diacyloxyphenanthrenes

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The products of controlled-potential electrolysis of *cis*- and *trans*-diacetoxystilbene are dependent on solvent composition; in dry dimethylformamide the major product is diphenylacetylene (formed by reductive elimination) whereas in aqueous dimethylformamide hydrogenolysis of one of the acetate groups may be achieved. This trapping of the carbanionic intermediate is compelling evidence for a stepwise mechanism.

In the structurally related 9,10-diacyloxyphenanthrenes elimination is precluded and they are cathodically cleaved in an unexpected fashion. Fission of the acyl–oxygen bonds occurs to give phenanthraquinone radical-anion. After aqueous work-up, phenanthraquinone and the appropriate carboxylic acid are formed. It is suggested that the acid is formed by addition of water to the corresponding keten which, in turn, is probably the product of initial cleavage.

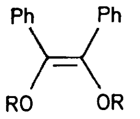
The mechanistic proposals are supported by detailed product analyses, coulometry, and cyclic voltammetric experiments.

CATHODIC cleavage with subsequent elimination is the basis of several useful electrosyntheses. Commonly the starting materials are dihalides and significant examples of their cathodic reactions include the preparation of cyclopropanes [1] (from 1,3-dihalides), alkenes [2] (from vicinal dibromides), the 'propellane' tricyclo[2.2.2.0]-octane from 1,4-dibromobicyclo[2.2.2]octane,[3] and bicyclo[2.2.0]hex-1(4)-ene from 1-bromo-4-chlorobicyclo-[2.2.0]hexane.[4] Reductive elimination is not confined to dihalides; epoxides may be so produced [5] from ditosyloxyalkanes and alkenes from vicinal diacetates.[6]

$$\begin{tikzcd}
R^1CH(X)CH(Y)R^2 \arrow[r, shift left, "e"] & {[R^1CH(X)CH(Y)R^2]^{\overset{\bullet}{-}}} \arrow[l, shift left] \arrow[d, "+e", "-Y^-"'] \\
R^1CH{:}CHR^2 & R^1CH(X)\overset{-}{C}HR^2 \arrow[l, "-X^-"']
\end{tikzcd}$$

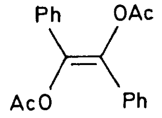
SCHEME 1

The accepted mechanism for these reactions is given (for 1,2-disubstituted compounds), in Scheme 1; for 1,2-dibromides the stereochemistry of the reaction provides good evidence [2] for a carbanionic intermediate although the elimination step is so rapid that the intermediate is not trapped by protonation. Selective cleavage and trapping of the intermediate before elimination would be preparatively useful, particularly in carotenoid chemistry where it would enable for instance the conversion of crustaxanthin derivatives into zeaxanthin or isozeaxanthin derivatives. If successful such trapping would also confirm the intermediacy of discrete carbanions in these reactions and dispel lingering preferences for the alternative concerted mechanism. For these reasons we have investigated factors affecting the cathodic reduction of *cis*- and *trans*-diacetoxystilbene (1) and (2), and various 9,10-disubstituted phenanthrenes, (3) to (6). For the compounds (1) and (2) it has been reported [6a] that, in dry dimethylformamide (DMF), the major product of cathodic reduction is diphenylacetylene. In the presence of an efficient proton donor (*e.g.* phenol) this was further reduced to dibenzyl. It is known [7] for cathodic hydrogenation that, because DMF is a basic solvent, proton donation from added water is inefficient relative, say, to its action in acetonitrile. The products of cathodic reduction of the stilbenediol diacetates in aqueous DMF were therefore studied as a function of water content in the expectation that conditions would be found which were sufficiently protic for the intermediate carbanion to be trapped but insufficiently protic to allow rapid further reduction of the products. The structurally related 9,10-phenanthrene derivatives were included in the study because elimination is unlikely for these compounds. In the event a completely unexpected cleavage reaction was observed for the phenanthrene derivatives.

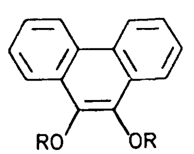


(1)

R = Ac or Bz



(2)



(3) R = Ac
(4) R = Bz
(5) R = n-$C_5H_{11}CO$
(6) R = Me

RESULTS AND DISCUSSION

Voltammetry and Coulometry.—The vicinal diacetates (1) and (2) gave irreversible cyclic voltammetric reduction at scan rates up to 10 V s^{-1}. On extended scan a

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† Part 14, B. Terem and J. H. P. Utley, *Electrochim. Acta*, in the press.

second, quasi-reversible, peak was seen at *ca.* −1.8 V (0.3 V s^{-1}). The conditions and E_p values are given in Table 1.

Controlled-potential coulometry in dry DMF at the first reduction peak potential gave a value of 1.8 F mol^{-1} for the *cis*-diacetoxystilbene. As the peak current for reduction at the first potential diminished that of the second peak remained constant: this identifies the second peak as being due to a product. Voltammetry using diphenylacetylene showed that it gives similar quasi-reversible reduction at E_p −1.89 V (0.2 V s^{-1}), *i.e.* diphenylacetylene is probably the product. These experiments do not, however, provide an unambiguous distinction between cleavage of one acetate or cleavage followed by elimination (each of these would consume 2 F mol^{-1}, see Scheme 1), but it does confirm that further reduction does not take place.

Cyclic voltammetry on 9,10-diacetoxyphenanthrene (3) was more revealing. Using a relatively large vitreous carbon cathode (diameter *ca.* 3 mm) the initial scan was halted at the peak potential (−1.77 V *vs.* Ag/AgI) and held for several minutes before reversal. The reverse scan revealed the appearance of a reversible oxidation peak at E_p −0.2 V. Cyclic voltammetry of 9,10-phenanthraquinone under the same conditions confirmed that the new oxidation–reduction couple was that of the quinone and that the quinone radical-anion was therefore the product of the irreversible reduction at −1.77 V. Similar results were found for cyclic voltammetry on compounds (4) and (5). In each case it was shown that the peak heights for the phenanthraquinone couple grew at the expense of the irreversible reduction peak.

TABLE 1

Cyclic voltammetric peak potentials [a]

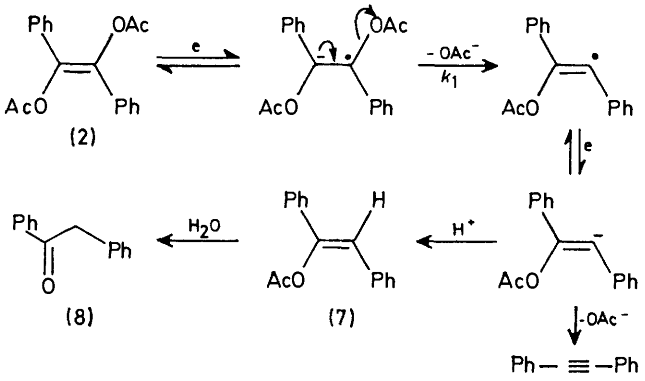
Compound	(1), R = Ac	(1), R = Bz	(2)	(3)	(4)	(5)	(6)
$-E_p$/V *vs.* Ag/AgI	1.60 [b]	1.68 [b]	1.54, 2.00 [b]	1.77	1.65	1.89	1.96

[a] Concentration of substrate *ca.* 10^{-3} mol dm^{-3} in DMF–Bu_4NClO_4 (0.1M); vitreous carbon or Hg drop microelectrode, sweep rate 0.2 V s^{-1}. [b] Sweep rate 0.3 V s^{-1}.

Controlled potential coulometry at the reduction peak potentials gave for compounds (3) and (4) *n* values of 1.50 and 1.54 F mol^{-1}, respectively. A value of 1.3 F mol^{-1} was obtained for (3) from the linear plot of current *vs.* charge in a controlled-potential electrolysis at initial concentration 1.2 mM.

Controlled-potential Electrolysis in DMF of cis- *and* trans-*Diacetoxystilbene.—Dependence of products on water content.* The products of electrolysis to 2 F mol^{-1}, and the relative amounts formed, were markedly sensitive to solvent purity or composition. For reagent grade DMF, used as supplied, the major product of electrolysis [−2.07 V (*vs.* Ag/AgI), Bu_4NClO_4 (0.1M), Hg pool] of *trans*-diacetoxystilbene was the enol acetate (7) identified by g.c.-m.s. and formed in 61% yield. On aqueous work-up the enol acetate was rapidly hydrolysed to deoxybenzoin (8). The other product isolated in a significant amount was *trans*-stilbene (20%). The various pathways under consideration are summarised in Scheme 2; it would appear that the proposed carbanionic intermediate is sufficiently long-lived and sufficiently basic to be protonated efficiently in all but carefully dried DMF.

Treatment of freshly distilled DMF with activated molecular sieve (4A) and the use of Bu_4NI (0.1M) as electrolyte gives a medium in which reduction of *cis*-diacetoxystilbene at −1.5 V gave diphenylacetylene as the major product with, after aqueous work-up, a trace of deoxybenzoin. The choice of electrolyte is important; diphenylacetylene was not detected if Bu_4NClO_4 was used. The ratio of diphenylacetylene : deoxybenzoin was measured by g.l.c. analysis for a series of electrolyses of the *cis*-diacetate for which the water content of the solvent was varied. The results are given in Table 2. Similar electrolysis with added quinol (2 equivalents) as proton donor resulted, according to g.l.c. analysis, in the formation of dibenzyl, deoxybenzoin, and diphenylacetylene in the approximate ratio 1 : 4.5 : 4.5. This result is in accord with the findings of Simonet and his co-workers; [6a] in the presence of the more effective proton donor phenylacetylene is further reduced.



SCHEME 2

TABLE 2

Variation of products of electrolysis of (1; R = Ac) with water concentration [a]

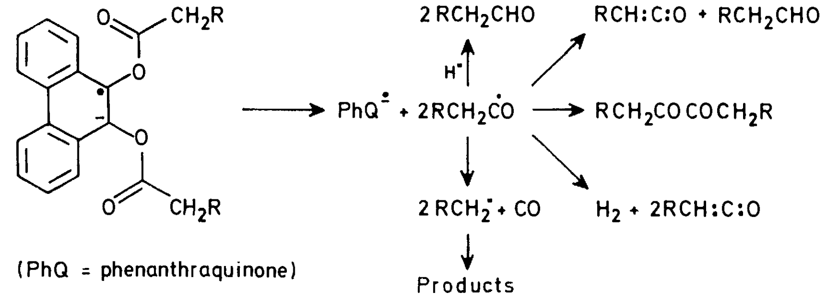
$[H_2O]$/mol dm^{-3}	0.24	0.73	0.97	1.46
$PhCOCH_2Ph$–PhC⋮CPh [b]	0.37	1.98	2.25	9.16

[a] See Experimental section for electrolysis conditions. [b] Ratios determined by g.l.c. analysis with reference to internal standard.

It must be concluded that these experiments support the mechanism given in Scheme 2, *i.e.* with the intermediacy of discrete carbanions. The rate of cleavage (k_1) from the initially formed radical-anion is likely to be considerably slower than similar cleavage [8] from benzylic or allylic positions; the driving force for formation of a vinyl radical will be much less than for formation of benzylic and allylic radicals. Even so the radical-anion was not detected by cyclic voltammetry at scan rates up to 10 V s^{-1}.

It is not likely that the enol acetate (7) arises *via* hydrogen abstraction. Apart from the fact that the coulometric experiments demand the consumption of 2 F mol^{-1} the low yield of enol acetate in dry DMF and high yield in aqueous DMF argues for its formation by an ionic pathway.

Controlled-potential Electrolysis of 9,10-*Diacyloxyphenanthrenes*.—The cyclic voltammetric experiments indicate that the product of electrolysis of these substrates is phenanthraquinone radical-anion (*vide supra*). The cleavage expected from the behaviour of the diacetoxystilbenes is of the carbon–oxygen bonds involving the C(9) or C(10) carbons; instead it appears that an acyl group is removed by cleavage. That there is no intrinsic reason why reductive cleavage is prohibited for bonds at C(9) or C(10) was shown by controlled-potential reduction of 9-bromo-10-methylphenanthrene. Electrolysis in DMF–NaClO$_4$ (0.2M), at the irreversible reduction peak potential found for cyclic voltammetry (—1.8 V, scan rate 0.2 V s^{-1}), consumed 2 F mol^{-1} and gave 9-methylphenanthrene in 69% isolated yield.



Scheme 3

By comparison, controlled-potential reduction of 9,10-diacetoxyphenanthrene (2.5 × 10^{-2} mol) in DMF–Bu$_4$NClO$_4$ (0.1M) at a stirred mercury pool proceeded until 1.5 F mol^{-1} was consumed. Aqueous work-up gave phenanthraquinone in 65% isolated yield; this result is consistent with the initial formation of phenanthraquinone radical-anion with, as is likely, aerial oxidation upon work-up.

Various plausible modes for fragmentation of the radical-anion of the 9,10-diacyloxyphenanthrenes which are consistent with formation of phenanthraquinone radical-anion and the coulometry are represented formally in Scheme 3. At this stage of speculation it is not reasonable to attempt a distinction between stepwise and concerted processes.

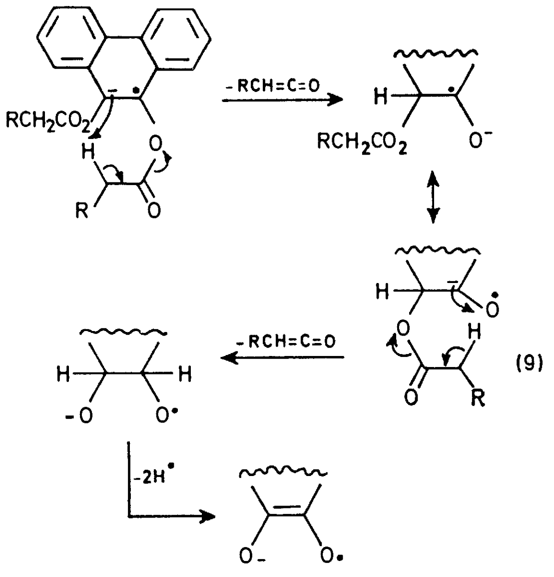
The starting materials were stable over several days in the electrolyte solutions; in addition the possibility of hydrolysis in the basic conditions pertaining at the cathode is at variance with the results of voltammetry in dry DMF and it is very unlikely that such hydrolysis would be significant for the phenanthrene derivatives but not for the analogous stilbene and anthracene derivatives.

Careful attempts were made to identify products additional to phenanthraquinone. For the diacetate the experimental task is not trivial; the likely products are water soluble and/or highly volatile and likely to be lost during work-up. If formed it is probable that, at —1.8 V, biacetyl would be further reduced. Cyclic voltammetry under the same conditions as for the electrolyses showed that biacetyl gave irreversible reduction at E_p — 1.05 V. Despite this probability the catholyte, immediately after reduction of 9,10-diacetoxyphenanthrene, was treated with *o*-phenylenediamine in an attempt to convert any biacetyl present into 2,3-dimethylquinoxaline.[9] No 2,3-dimethylquonixaline was detected by t.l.c. analysis. In a control experiment with added biacetyl it was shown that the amount of biacetyl sought would have reacted and the derivative easily detected by t.l.c. analysis.

Treatment of the catholyte of a freshly electrolysed solution with a few drops of water and then diazomethane, followed by g.l.c. analysis, showed methyl acetate to be present. Comparison with the peak area for an internal standard (*p*-xylene) of known concentration showed that, if it were a product of the electrolysis, acetic acid was produced in 15% yield. This is almost certainly a gross underestimate because separate experiments showed that under the conditions used, the efficiency of conversion of acetic acid into the methyl ester was only *ca.* 30%.

Phenanthrene-9,10-diyl dihexanoate (5) proved to be a more suitable substrate for analysis. In this case the likely products of electrolysis are less water soluble and less volatile than those from the diacetate but sufficiently volatile to be amenable to g.l.c. analysis. Controlled-potential electrolysis at —1.9 V under the conditions used for compounds (3) and (4) consumed 1.8 F mol^{-1} and gave phenanthraquinone in 62% yield. A trace of water was added to the catholyte which was then analysed by g.l.c. There were no detectable amounts of n-$C_5H_{11}CHO$, n-$C_6H_{13}OH$, n-$C_{10}H_{22}$, or n-C_6H_4. At long retention time however a peak was observed corresponding with that of an authentic sample of n-hexanoic acid. In a separate experiment a known weight of an internal standard (n-octanoic acid) was added to the catholyte and g.l.c. analysis showed that hexanoic acid was present in 62.4% yield, *i.e.* equivalent to the phenanthraquinone yield. In this case at least, therefore, the other major product, after the addition of water, is hexanoic acid. It must be presumed that the extra oxygen atoms required are introduced from water. The only plausible route accommodating all of these features is formation of a keten which is hydrolysed rapidly to the carboxylic acid.

The keten intermediate is most probably formed by concerted fragmentation of the radical-anion (Scheme 4). The radical-anion is delocalised and will tend to be planar about the C(9)–C(10) bond. Dreiding models show clearly (and Scheme 4 attempts to portray it), that a 6-membered cyclic transition state is readily accessible. The driving force of quinone radical-anion formation might be held to favour stepwise homolysis (Scheme 3) in which case similar homolysis would be expected from 9,10-diacetoxyanthracene to give anthraquinone radical-anion. A comparison of the behaviour of 9,10-diacetoxyphenanthrene with that of 9,10-diacetoxyanthracene shows that, for the abnormal cleavage under study, it is important that the acetate groups are vicinal. Cyclic voltammetry of 9,10-diacetoxyanthracene, under the conditions used for the phenanthrene diacetate, gave quasi-reversible reduction in the range of scan rates 0.1 to 10 V s^{-1}. At each speed the ratio of the anodic to cathodic peak currents were near unity; *e.g.* at 0.5 V s^{-1}, $E_p(C) = -1.22$ V and $E_p(A) = -1.13$ V with $i_p(A)/i_p(C) \sim 1$. Clearly there is not rapid cleavage as found for the phenanthrene derivatives. Furthermore, Given and Peover [10] have shown that for the 9,10-diacetoxyanthracene, carbon–oxygen cleavage may be achieved only in the presence of effective proton donors. In this case cleavage is 'normal', the leaving group being acetate ion.



$(2\,RCH{=}C{=}O + 2\,H_2O \longrightarrow 2\,RCH_2CO_2H)$

SCHEME 4

If the process were stepwise it might be expected that the intermediate (9) would lose acetate by analogy with the known reductive cleavage of $PhCOCH_2OAc$. That this does not happen argues for the concerted loss of both keten molecules.

For dibenzoate reduction phenanthraquinone was isolated in 66% yield and g.l.c. was used to show that the catholyte of a freshly reduced sample contained no significant amounts of benzaldehyde, or benzyl alcohol (a likely product of further reduction). Benzene and biphenyl were also absent although decarbonylation of an intermediate benzoyl radical is unlikely.[11] Benzil was shown to be absent by t.l.c. analysis and t.l.c. comparison with the product mixture obtained from reduction at -1.66 V of benzil in DMF–Bu_4NClO_4 (0.1M) showed that no reduction products of benzil were formed in the reduction of 9,10-dibenzoyloxyphenanthrene. One possibility for this system is that polymeric, or at least oligomeric, products are formed; this is consistent with the retention of material at the base line during t.l.c. analysis. There is good precedent for the formation of high molecular weight polycyclic products in electrochemical reactions which involve aryl radical intermediates.[12]

Two questions remain unanswered concerning electrolysis of the phenanthrene derivatives. Why does the dibenzoate derivative, for which keten formation is precluded, cleave smoothly and abnormally? And why does controlled-potential coulometry give n values in the range 1.3—1.5? Schemes 3 and 4 demand $n = 1$. The preparative-scale electrolyses consumed between 1.5—1.9 F mol^{-1}. The first question must be shelved until the fate of the lost benzoyl fragment has been established although polymerisation is likely for such a fragment (see above). A possible answer to the second question is that concomitant 2e hydrogenation of the C(9)–C(10) double bond is taking place with the 9,10-dihydrophenanthrene derivative re-oxidising to starting material. Evidence in support of this hypothesis comes from an examination of the cathodic reduction of 9,10-dimethoxyphenanthrene. Controlled-potential electrolysis of this substrate [DMF–Bu_4NClO_4 (0.1M)–HOAc (trace), Hg pool, -1.9 V (*vs.* Ag/AgI)] proceeded smoothly with the consumption of 2.3 F mol^{-1}. After aqueous work-up however the only significant 'product' was starting material 50% of which was recovered.

An alternative explanation of the ambiguous, non-integral, n-values is that the phenanthraquinone radical-anion, which is formed in bulk solution, is itself further reduced to the dianion. In support of this cyclic voltammetry shows that, under the conditions used for preparative-scale electrolysis irreversible reduction to the phenanthraquinone dianion occurs at E_p, -0.85 V (*vs.* Ag/AgI), *i.e.* on the anodic side of the potentials used for electrolysis. Assuming that the irreversibility is caused by rapid protonation the product of further reduction would revert to phenanthraquinone on aqueous work-up in air.

EXPERIMENTAL

Solvents and Materials.—For cyclic voltammetric experiments spectroscopic grade N,N-dimethylformamide (DMF) was used (Hopkin and Williams) after drying over molecular sieves (4A). For preparative-scale electrolyses reagent grade DMF was used as supplied or after fractional distillation and treatment with molecular sieves. Tetra-n-butylammonium iodide (B.D.H. anhydrous grade) was used as supplied and sodium perchlorate ($NaClO_4$, $2H_2O$, AnalaR, B.D.H.,) was dried *in vacuo* at 110 °C; tetra-n-butylammonium perchlorate was prepared by a published method.[13] The following were prepared by reductive acylation of the corresponding dicarbonyl compounds: *cis*- and *trans*-diacetoxystilbene,[14] 9,10-diacetoxyanthracene,[15] and 9,10-diacetoxyphenanthrene.[16] It was found more convenient to prepare the 9,10-phenanthrene derivatives by cathodic reduction at a mercury pool of 9,10-phenanthraquinone at -0.35 V (*vs.* Ag/AgI) in DMF–sodium perchlorate (0.2M) in the presence of an approximately four-fold excess of the appropriate electrophile. The following, previously known, compounds were so prepared (yields and the electrophile used are in parentheses): 9,10-diacetoxyphenanthrene (80%, acetic anhydride); 9,10-dibenzoyloxyphenanthrene (55%, benzoic anhydride); and 9,10-*dimethoxyphenanthrene* (49%, methyl iodide). Phenanthrene-9,10-diyl dihexanoate (76%, hexanoic anhydride) was similarly prepared and obtained as a white solid, m.p. 120 °C; ν_{CO}, 1 745 cm^{-1}; $\delta(CDCl_3)$, 0.42—1.97 (m, 18 H), 2.37—2.82 (m, 4 H), 7.34—8.04 (m, 6 H), and 8.42—8.82 (m, 2 H); *m/e*, 406 (M^+, 25%), 308 ($M - C_6H_{10}O$, 46%), 210 ($M - C_{12}H_{20}O_2$, 100%).

9-Bromo-10-methylphenanthrene was obtained by bromination, in acetic acid, of 9-methylphenanthrene.[17]

Electrochemical Apparatus.—Conventional glass H-cells were used with sintered glass separators. For preparative-scale electrolyses a Chemical Electronics TR2A potentiostat was used; for voltammetry a ' home-built ' potentiostat/sweep unit was used, combined with a Hewlett-Packard 7035B X–Y recorder. The reference electrode was a silver wire coated with silver iodide in DMF solution containing Bu_4NI (0.1M).

Electrolyses.—cis- *and* trans-*diacetoxystilbene*. In a typical experiment the diacetate (0.36 g, 1.2×10^{-3} mol) was electrolysed in DMF–Bu_4HClO_4 (0.1M) [catholyte volume *ca.* 45 cm^3] at a mercury pool cathode (area *ca.* 14 cm^2). The potential was controlled at -1.5 V (*vs.* Ag/Ag I) and 2 F mol^{-1} passed. Dry nitrogen was bubbled through the catholyte during electrolysis. For experiments in the presence of water the appropriate amount was added by microsyringe. A saturated salt solution (*ca.* 40 cm^3) was added to the separated catholyte and the mixture shaken with ether (3×30 cm^3). The combined ether extracts were washed with water (3×25 cm^3) and the ether layer dried (Na_2SO_4) and the ether removed to give a crude product mixture (usually *ca.* 0.35 g). The mixture was analysed either by t.l.c. [silica, light petroleum (85%, b.p. 60—80 °C): acetone (15%)] or g.l.c. [Perkin-Elmer F11, 2½% SE30 column, 160 °C], or both. In each case products were identified by comparison with authentic samples and, for g.l.c., quantified by comparison of peak areas with that of a known amount of added dimethyl phthalate. The appropriate detector response factors were measured for each component with respect to the internal standard. The enol acetate (7) could not be isolated free of substantial contamination with deoxybenzoin, the product of its rapid hydrolysis. From the n.m.r. spectrum of the mixture of (7) and deoxybenzoin the acetate methyl group was identified as a singlet at δ 2.05. The enol acetate was further identified in the gas chromatogram by g.c.-m.s. [m/e = 238 (M^+), 196 ($M - CH_2CO$)], and accurate mass measurement on a g.c. separated sample gave M^+, m/e = 238.100 ($C_{16}H_{14}O_2$ requires 238.110). For g.c.-m.s. experiments a Perkin-Elmer F11 chromatograph was interfaced with an AEI MS902 mass spectrometer.

9-*Bromo*-10-*methylphenanthrene*. This compound was reduced at -1.81 V at a mercury pool in DMF–$NaClO_4$ (0.2M) until 2 F mol^{-1} were consumed. The catholyte (*ca.* 45 cm^3) was added to an equal volume of ether and the mixture washed with water (3×50 cm^3). After drying and removal of solvent 9-methylphenanthrene was isolated in 69% yield.

9,10-*Dibenzoyloxyphenanthrene*. This compound (1.0 g, 2.4×10^{-3} mol) was electrolysed in DMF–Bu_4NClO_4 (0.1M) (catholyte volume *ca.* 45 cm^3) at -1.66 V (*vs.* Ag/Ag I) at a mercury pool cathode (area 13.8 cm^2). After addition of the substrate the current increased from 1.2 to 30 mA. Electrolysis overnight resulted in the consumption of 1.9 F mol^{-1} during which time the current had fallen to *ca.* 1 mA and the colour of the catholyte had changed from pale green to deep red. The catholyte was added to an equal volume of benzene, washed with water (3×40 cm^3), the benzene layer dried (Na_2SO_4), and the solvent removed. The residue was dissolved in chloroform and phenanthraquinone (66%) isolated by column chromatography (silica, elution with benzene–ethyl acetate–ethanol (90 : 5 : 5, v/v). 9,10-Diacetoxyphenanthrene and phenanthrene-9,10-diyl dihexanoate were electrolysed by essentially the same procedure. For g.c. analyses [Perkin-Elmer F11, 20% DEG S column, 150 or 170 °C isothermal], a sample (1 cm^3) was withdrawn after electrolysis to which one or two drops of water were added. T.l.c. analysis [silica plates, benzene–ethyl acetate–ethanol (90 : 7 : 7, v/v)] was performed on part of the residue before column chromatography.

Attempted Trapping of Biacetyl.—A mixture of phenanthraquinone (1 equiv.), biacetyl (1 equiv.), and tetra-n-butylammonium perchlorate in DMF with *o*-phenylenediamine (2 equiv.) was heated on a steam-bath for several minutes. T.l.c. analysis and comparison with authentic samples [silica plates; petroleum (b.p. 60—80 °C)–acetone (80 : 20, v/v)] showed that phenanthrazene [18] and 2,3-dimethylquinoxaline [9] had been formed. Similar treatment and analysis of a freshly electrolysed solution of 9,10-diacetoxyphenanthrene gave no indication of the formation of the 2,3-dimethylquinoxaline.

We are grateful to Mr. D. W. Sopher for miscellaneous voltammetric measurements, to London University (Central Research Fund) for a grant towards the purchase of g.c.-m.s. equipment, and to the S.R.C. for a fellowship (to C. A.).

[9/400 *Received*, 12*th March*, 1979]

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