Anal. Calcd for $C_{22}H_{36}$: C, 87.92; H, 12.08. Found: C, 87.98; H, 12.10.

The cumulene was obtained in 18% yield using lithium piperidide as base but could not be obtained from the acetylenic ester with sodium hydride in glyme.

1-*tert*-Butoxy-3-*tert*-butyl-4,4-dimethyl-1,2-pentadiene (6). The methanol filtrate from the preparation of the hexapentaene was distilled through a microcolumn to give 1.29 g (19%) of the alkoxyallene: bp 57° (0.4 mm); $n^{25}D$ 1.4624; ir max 3.39, 5.11, 5.17, 9.0 μ; nmr ($CDCl_3$) δ 1.20, 1.26 (s, s, 27), 6.25 (s, 1).

Anal. Calcd for $C_{15}H_{28}O$: C, 80.27; H, 12.58. Found: C, 80.31; H, 12.65.

Tetrakis(di-*tert*-butylvinylidene)cyclobutane (8). A sample of 0.30 g of tetra-*tert*-butylhexapentaene was immersed in an oil bath at 200° for 15 min. After cooling pentane was added and the suspension was filtered to give 0.27 g (90%) of the dimer, mp 350–360°. Recrystallization from xylene gave white crystals: mp 361°; uv max (tetrahydrofuran) 316, 298, 268, 258, 250 nm (ϵ 2040, 1720, 13,200, 16,300, 15,800); ir max 3.37, 3.43, 3.47, 5.12, 5.19 μ; nmr ($CDCl_3$) δ 1.20 (s).

Anal. Calcd for $C_{44}H_{72}$: C, 87.92; H, 12.08; mol wt, 601. Found: C, 88.05; H, 12.02; mol wt 595 (ebullient in benzene).

1,2-Bis(di-*tert*-butylvinylidene)-3,3,4,4-tetrafluorocyclobutane (9). A Carius tube containing 0.92 g of tetra-*tert*-butylhexapentaene, 7.5 g of tetrafluoroethylene, and 20 ml of benzene was sealed and heated at 200° for 6 hr. The solvent was removed and the residue was crystallized from methanol to give 0.93 g (70%) of the cycloadduct, mp 128–130°. An analytical sample was recrystallized from methanol: mp 129.5–130.5°; ir max 3.35, 3.46, 5.12, 7.17, 7.31, 7.5–9.0 μ; ^{1}H nmr ($CDCl_3$) δ 1.24 (s); ^{19}F nmr ($CDCl_3$) +112 ppm (s).

Anal. Calcd for $C_{24}H_{36}F_4$: C, 71.97; H, 9.06; F, 18.97. Found: C, 71.90; H, 8.98; F, 18.79.

1,2-Bis(trifluoromethyl)-3,4-bis(di-*tert*-butylvinylidene)cyclobutene (10). A mixture of 1.47 g of tetra-*tert*-butylhexapentaene, 12 g of hexafluoro-2-butyne, and 10 ml of benzene was heated at 190° in a Carius tube for 2 hr. The tube was cooled and opened, the solvent was evaporated, and the crude solid was sublimed at 100° (0.5 mm) to give 0.30 g of the cycloadduct: mp 135.5–137°; uv max (EtOH) 270 nm (ϵ 11,100); ir max 3.39, 3.40, 3.45, 5.05, 5.10, 6.07, 7.25, 8–9 μ.

Anal. Calcd for $C_{26}H_{36}F_6$: C, 67.50; H, 7.85; F, 24.65. Found: C, 67.16; H, 7.92; F, 25.07.

3,10-Di-*tert*-butyl-2,2,11,11-tetramethyl-6,6-bis(trifluoromethyl)-3,4,5,7,8,9-dodecahexaene (11). The sublimate bottom from the above reaction was recrystallized from ethanol to give the dodecahexene (0.30 g) as lemon yellow crystals: mp 158–159°; uv max (EtOH) 377, 355 sh, 330, 243 nm (ϵ 76,300, 46,700, 119,000, 3840); ir max 3.35, 3.41, 3.46, 4.84, 7.16, 7.31, 8–9 μ; ^{1}H nmr ($CDCl_3$) δ 1.30 (s); ^{19}F nmr ($CDCl_3$) +74.6 ppm (s).

Anal. Calcd for $C_{26}H_{36}F_6$: C, 67.50; H, 7.85; F, 24.65. Found: C, 67.15; H, 7.91; F, 25.13.

Formation of 11 from 10. A solution of 0.20 g of **10** in 20 ml of diphenylmethane was heated at 220° under nitrogen for 4 hr. The mixture was cooled and filtered to give 0.13 g of yellow **11**, mp 156–158°. After recrystallization from ethanol the material melted at 158–159° and had an ir spectrum identical with that of **11**.

1,2-Bis(diphenylmethylene)-3,3,4,4-tetrafluorocyclobutane (12). A mixture of 3.0 g of tetraphenylbutatriene, 21 g of tetrafluoroethylene, and 40 ml of benzene was heated at 200° for 6 hr in a Carius tube. The mixture was cooled and filtered to return 0.22 g of unreacted butatriene. From the filtrate there was obtained 0.80 g of crude cycloadduct, mp 184–195°. Recrystallization from hexane gave yellow crystals: mp 195–196°; ir max 3.24, 6.25, 6.35, 6.67, 7.5–9 μ; ^{19}F nmr ($CDCl_3$) +109.6 ppm (s).

Anal. Calcd for $C_{30}H_{20}F_4$: C, 78.93; H, 4.42; F, 16.65. Found: C, 79.17; H, 4.31; F, 16.26.

3,6-Di-*tert*-butyl-4,5-dichloro-2,2,7,7-tetramethyl-3,5-octadiene (13). A solution of 40 g of 3,6-di-*tert*-butyl-2,2,7,7-tetramethyl-4-octyne-3,6-diol in 300 ml of dioxane was added dropwise to a stirred solution of 400 ml of concentrated hydrochloric acid and 200 ml of acetic acid. The mixture was stirred 4 hr at room temperature. The product precipitated and was filtered, washed with water, and dried to give 43 g (96%) of solid, mp 99–105°. Recrystallization from acetonitrile gave solid: mp 113–114°; uv no absorption maxima; ir max 3.36, 6.10, 7.17, 7.30, 12.9 μ; nmr ($CDCl_3$) δ 1.40 (s).

Anal. Calcd for $C_{20}H_{36}Cl_2$: C, 69.13; H, 10.45; Cl, 20.42. Found: C, 69.14; H, 10.52; Cl, 20.35.

3,6-Di-*tert*-butyl-2,2,7,7-tetramethyl-3,4,5-octatriene (Tetra-*tert*-butylbutatriene) (14). A mixture of 15.5 g of 3,6-di-*tert*-butyl-4,5-dichloro-2,2,7,7-tetramethyl-3,5-octadiene, 6 g of zinc dust, and 125 ml of acetonitrile was heated at reflux for 3 hr. The hot mixture was filtered, and the butatriene crystallized in the filtrate. Sublimation of the crude solid at 80° (0.5 mm) gave 5.58 g (45%) of the butatriene, mp 135°. Recrystallization from acetonitrile gave white crystals: mp 135–137°; uv max 300, 264, 228 nm (ϵ 3150, 32,400, 9050); ir max 3.38, 3.43, 7.20, 7.33 μ; nmr ($CDCl_3$) δ 1.32 (s).

Anal. Calcd for $C_{20}H_{36}$: C, 86.87; H, 13.13. Found: C, 86.68; H, 13.23.

Electrochemical Oxidation of Phenylethylenes. I. Conversion of Tetraphenylethylene to 9,10-Diphenylphenanthrene[1a]

James D. Stuart[1b] and William E. Ohnesorge*

Contribution from the Department of Chemistry, Lehigh University, Bethlehem, Pennsylvania 18015. *Received October 30, 1970*

Abstract: Electrochemical oxidation of tetraphenylethylene in acetonitrile solution at *ca.* +1.3 V *vs.* (aqueous) sce produces high yields of 9,10-diphenylphenanthrene. Cyclic voltammetry indicates that the detailed mechanism is rather complicated and involves several electrode (E) and follow-up chemical (C) reactions.

The initial step in the electrochemical oxidation of many organic compounds is the loss of a π electron to form a (monovalent) carbonium ion radical. Follow-up chemical reactions often involve attack by a nucleophile; if approach to the reactive site(s) on the carbonium ion is relatively unhindered and the species is not stabilized, *e.g.*, by a high degree of charge delocalization, these reactions occur rapidly. Moreover, additional reactions may follow so that the overall electrochemical oxidation is a very complicated process involving a variety of electrode (E) and chemical (C) steps—sometimes occurring in parallel as well as in series.[2] Therefore, it is usually not possible to de-

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(1) (a) Presented in part at the May 1969 meeting of The Electrochemical Society, New York, N. Y. (b) Based on the Ph.D. Thesis of J. D. S., Lehigh University, 1969.

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termine unequivocally all details of the numerous steps involved. A summary has recently been given by Adams.[3]

Results of a study of the electrochemical oxidation of tetraphenylethylene (TPE) to form 9,10-diphenylphenanthrene (DPP) are presented. The same transformation can be effected chemically and by photolysis, although different mechanisms and intermediates are involved.[4,5] Addition of acetate, methoxy, ethoxy, fluoride, and pyridine across olefinic bonds upon electrochemical oxidation of phenylethylenes has been reported.[6] Although the mechanism of acetoxylation has been described,[7,8] all details of the other processes are not known.

Experimental Section

Apparatus. Infrared and uv-visible spectra were recorded on commercial instruments. Conventional electrochemical equipment was used for dc polarography, cyclic voltammetry,[9,10] and controlled potential electrolysis (Wenking No. 61 fast rise model potentiostat). Electrodes were properly placed to achieve uniform electrode potential distribution and positive feedback was used to compensate for the *iR* drop.[11,12] Cell resistances were *ca.* 2000 ohms between the working and auxiliary electrodes. The total current was determined by the gain in weight of the silver cathode (auxiliary electrode) or by (graphic) current–time integration.

The solutions to be electrolyzed (*ca.* 175 ml) were contained in a jar covered with a tightly fitting Teflon top. The working electrode for coulometry and for preparative electrolysis was a platinum mesh electrode (5.0 × 3.0 cm). The auxiliary electrode was either a silver wire (coiled into a helix of *ca.* 2 cm diameter) or a platinum mesh electrode (5.0 cm × 2.5 cm) isolated from the working electrode by a (4–8 μ) fritted disk.

The platinum working electrodes in all voltammetric experiments were cleaned by washing (in the order listed) with: concentrated nitric acid, acidified ferrous sulfate, distilled water, and acetonitrile before recording each current–potential curve. For dc polarograms the working electrode (rotated at 600 rpm) was either a platinum wire (24 gauge) sealed in 6-mm glass tubing (the exposed wire area, *ca.* 0.0075 cm^2, was polished with fine emery cloth and jewelers rouge until the wire was flush with the surface of the glass) or a rotating platinum bulb electrode (Sargent, Catalog No. S-30420). For cyclic voltammetry the working electrode was a stationary platinum disk electrode (platinum inlay electrode Beckman, Catalog No. 39273). The auxiliary electrode for voltammetric studies was a platinum wire immersed directly in the cell solution, *ca.* 75 ml, but spatially removed from the working electrode.

Two kinds of reference electrodes were used. (1) For voltammetric studies an aqueous sce was isolated from the electrolysis solution by a three-compartment salt bridge; the reference side was filled with saturated aqueous potassium chloride, the middle compartment with 0.5 *M* aqueous sodium perchlorate, and the other with a solution having the same composition of supporting electrolyte and solvent as that in the electrolysis cell. (2) A silver wire immersed in an acetonitrile solution containing 0.1 *M* silver perchlorate and 0.1 *M* tetraethylammonium perchlorate was used as the reference electrode during long-term electrolysis; it was isolated from the electrolysis solution by a salt bridge filled with a solution having the same composition of supporting electrolyte and solvent as that in the electrolysis cell. Potentials are given *vs.* the aqueous sce reference electrode; those measured against the Ag/Ag$^+$ reference electrode were converted by adding +0.30 V to the measured value.[13]

Reagents and Solutions. Tetraethylammonium perchlorate (TEAP) (Eastman) was recrystallized twice from distilled water, air dried on top of a 110° oven, and finally dried over phosphorus pentoxide in an evacuated drying pistol at 100°.

Sodium perchlorate (G. Frederick Smith) was dried in an oven at 230° and stored above magnesium perchlorate which had been activated at 230° for 24 hr. Silver perchlorate was prepared as described previously.[14]

Tetraphenylethylene (Aldrich), mp 224.0–225.0° (lit. 223–224°) was used as obtained.

9,10-Diphenylphenanthrene (DPP) was prepared by large-scale controlled potential electrolysis of tetraphenylethylene and recrystallized five times from methanol and sublimed; mp 239.5–241.0° (lit. 239–240°); the ultraviolet absorption spectrum in *n*-hexane also agreed with the published spectrum.[15]

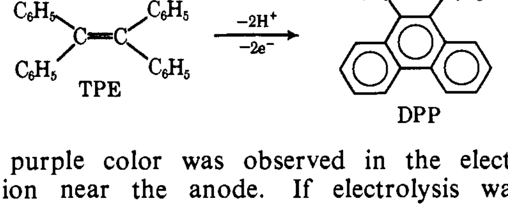
Acetonitrile (Fisher, Practical Grade) was purified by distillation from sodium hydride, phosphorus pentoxide, and calcium hydride.[16,17] Under voltammetric conditions the platinum working electrode limits of this solvent containing 0.2 *M* TEAP as the supporting electrolyte were +2.7 and −1.9 V. Analysis by Karl Fischer titration[14] showed water content to be generally 3–10 m*M*. Commonly an increase of 10–30 m*M* in water content was observed over a period of 6–12 hr during the electrolysis. When 0.5 *M* sodium perchlorate was used as supporting electrolyte, analysis showed initial water content generally 11–30 m*M*.

Procedures. The solutions were preelectrolyzed to a constant residual current level prior to adding the electroactive material. (Bubbling prepurified nitrogen, which had passed through freshly distilled acetonitrile, had no noticeable effect on the products.) After completion of the electrolysis the anolyte was transferred to a 250-ml one-necked flask and the solvent removed in a vacuum Roto-Vap at temperatures below 40°.

The residues were extracted several times with acetone. The acetone extractions were chromatographed on an activated silica gel (0.2–0.5 mm, Brinkman Instruments) or activated aluminum oxide (Baker) column, 25 cm long and 2 cm wide. (Better separations were obtained with the silica gel column.) The column was developed and eluted with the following solvents (in the order listed): petroleum ether (bp 30–60°), benzene, ethyl ether, methanol, and acetone. A better separation was achieved by using the gradient elution technique; the eluting agent was progressively enriched in the more polar solvent. The order of elution of products was: unreacted TPE, DPP, yellow oil, and/or carbonyl compounds. Product identifications were based on melting points, ultraviolet-visible, and infrared absorption spectra.

Results

Controlled Potential Electrolysis. When solutions of tetraphenylethylene (TPE) were exhaustively oxidized electrochemically (+1.3 V), 9,10-diphenylphenanthrene (DPP) was obtained and isolated in high yield (*ca.* 75%). Addition of up to 200 m*M* water to the initial electrolysis solution had no noticeable effect on the yield of DPP. Coulometry showed that there were 2.10 ± 0.10 electrons lost per TPE molecule in the electrode process(es).



A purple color was observed in the electrolysis solution near the anode. If electrolysis was discontinued after a 30-sec generation period, this color

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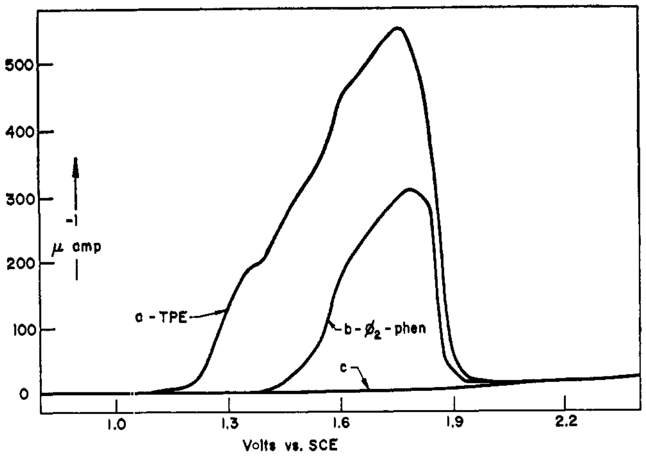

Figure 1. Dc polarograms in acetonitrile, 0.2 *M* in TEAP: curve a, 1.0 m*M* TPE; curve b, 1.0 m*M* DPP; curve c, residual current (scan rate 3.3 mV/sec).

disappeared within *ca.* 60 sec. In a solution that was 0.5 *M* in water with a generation period of 30 sec, the purple color disappeared within 30 sec. A visible absorption spectrum of the purple-colored solution generated during the controlled potential electrolytic oxidation of TPE resembled the spectrum of the TPE cation radical, *i.e.*, a strong absorption band at 480 nm and a weaker band at 600 nm.[18–20]

Dc Polarography. Figure 1 shows a dc polarogram of TPE in acetonitrile solution 0.2 *M* in TEAP. The supporting electrolyte is discharged at potentials more anodic than *ca.* +2.5 V.

The increase in current at potentials more anodic than *ca.* +1.45 V was due to the oxidation of DPP. Solutions of DPP showed anodic currents with the same shoulder and peak potentials as well as the sharp maximum and rapid subsequent current decay that were observed in the TPE polarogram, Figure 1, curve b. Phenanthrene oxidation products (and those of many other polynuclear aromatic hydrocarbons) polymerize on a platinum anode.[21]

The limiting currents in Figure 1 were compared to the limiting polarographic currents of two other compounds under similar electrolysis conditions: (1) the first anodic wave of 9,10-diphenylanthracene (K and K Laboratories), which results from a reversible one-electron oxidation process[22,23] (on this basis the first anodic shoulder (+1.33 V) in the dc polarogram of TPE corresponded to the loss of 1.0 electron; the shoulder at +1.45 V to the loss of approximately 0.6 electron); (2) the (reversible) two-electron oxidation of tetrakis(*p*-methoxyphenyl)ethylene in acetonitrile.[24–26] The shoulder at +1.33 V corresponded to the loss of 1.2 electrons, the +1.45-V shoulder to the loss of an additional 0.8 electron. The shoulder at +1.60 V corresponded to the loss of 1.0 additional electron in agreement with the cyclic voltammetric data that showed a one-electron, nearly Nernstian oxidation of DPP at +1.60 V to form what is suspected to be its (monovalent) cation radical. Because of the similarity in molecular dimensions of TPE and tetrakis(*p*-methoxyphenyl)ethylene, one would expect that the diffusion coefficient of TPE would be closer to the diffusion coefficient of TAE than to that of 9,10-diphenylanthracene.

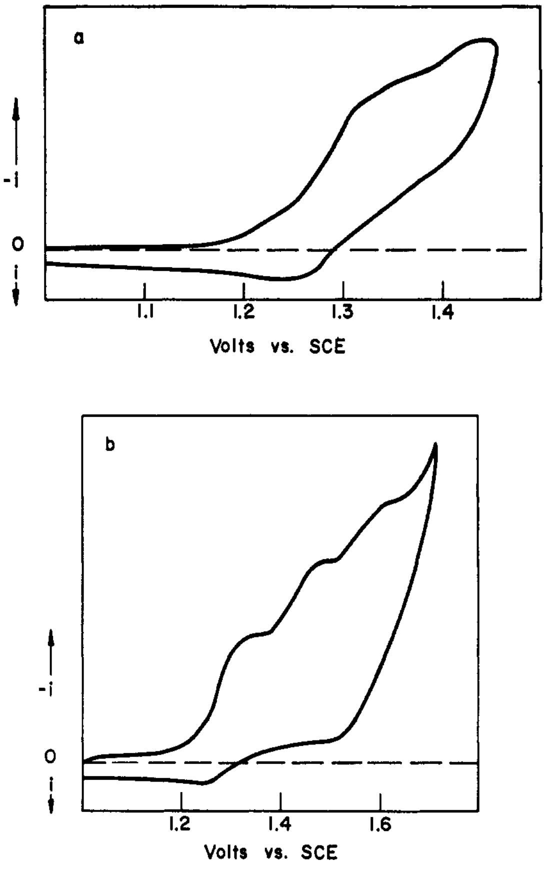

Figure 2. Cyclic voltammograms of 0.5 m*M* TPE in acetonitrile solution 0.2 *M* in TEAP: curve a, scan rate 1.0 V/sec; curve b, scan rate 2.5 V/sec.

Cyclic Voltammetry. Single-sweep cyclic voltammetry at scan rates from 0.01 to 20.0 V/sec was used in diagnosing the mechanism of the electrochemical process. The potential region +1.0 to *ca.* +1.5 V (corresponding to the two-electron oxidation of TPE) was extensively studied.

At low-scan rates (less than 0.40 V/sec) only one anodic wave was observed; its height indicated the loss of *ca.* two electrons. A small cathodic wave, $E_{\mathrm{pk}_{\mathrm{C}\text{-}1}}$ = 1.20–1.25 V, was associated with this anodic wave.

At scan rates greater than 0.40 V/sec there were two separated, but closely spaced, anodic waves of unequal height. [Figure 2, curve b, also includes the first (reversible) anodic wave of DPP at +1.6 V.]

Data obtained by single-sweep cyclic voltammetry on a 0.5 m*M* solution of TPE in acetonitrile are summarized in the following. The height of the second (more anodic) wave increased rapidly with increasing scan rate; at a rate of 20.0 V/sec the second peak height was approximately one-third that of the first peak.

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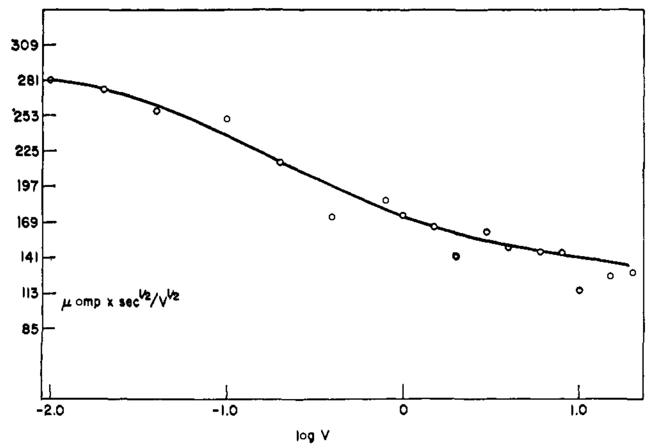


Figure 3. Peak current function for the first anodic wave of 0.5 mM TPE in acetonitrile solution 0.2 M in TEAP (V = voltage scan rate in volts/second).

The total current function for both the first and second anodic waves, $(i_{\mathrm{pk}_{\mathrm{A}\text{-}1}} + i_{\mathrm{pk}_{\mathrm{A}\text{-}2}})/v^{1/2}$,[27] remained approximately constant and was independent of the scan rate (0.1–20 V/sec). The current function for the first peak $(i_{\mathrm{pk}_{\mathrm{A}\text{-}1}}/v^{1/2})$ decreased continually with increasing scan rate, Figure 3. Thus, the first electrode process underwent a transition from an apparent loss of two electrons at low scan rates to the loss of only one electron at high scan rates.

Each oxidation wave shifted anodic with increased scan rate. A cathodic wave, $E_{\mathrm{pk}_{\mathrm{C}\text{-}1}}$, at +1.25 V, associated with the first of the (separated) anodic waves, became discernible at scan rates greater than 0.10 V/sec. Its height increased with increasing scan rate, although the cathodic peak potential was not affected by the scan rate. There was no cathodic wave associated with the second TPE oxidation wave ($E_{\mathrm{pk}_{\mathrm{A}\text{-}2}}$ at *ca.* +1.45 V) up to scan rates of 40 V/sec. The reduction of the proton(s), as CH_3CNH^+ or H_3O^+, liberated upon the oxidation of TPE was observed as cathodic waves at *ca.* 0.0 V.[28]

Similar cyclic and dc voltammetric data for TPE were observed in methylene chloride and in nitrobenzene solutions. The cation radicals are usually more stable in these solvents than they are in acetonitrile.[29]

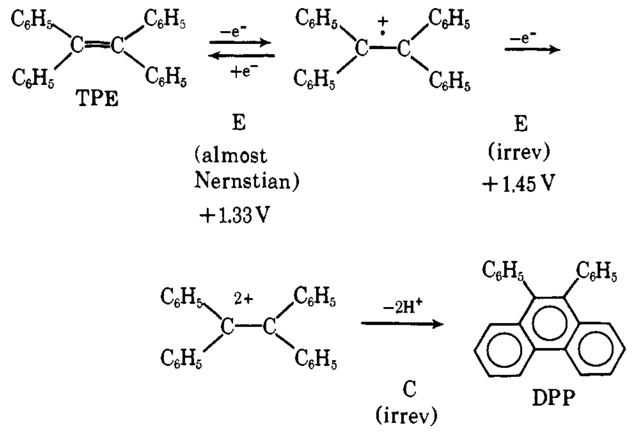
Discussion

The results of the large-scale controlled potential electrolysis of tetraphenylethylene defined the stoichiometry of the over-all two-electron oxidation at +1.3 V of TPE to 9,10-diphenylphenanthrene. The cyclic and slow-scan dc voltammetric data give some insight into the mechanism for the electrochemical conversion of TPE to DPP.

Shain and others[30–32] have considered various electrochemical reaction schemes and have given several diagnostic criteria for assigning electrochemical mechanisms from cyclic voltammograms based generally upon observing the effect of scan rate on the number, height, and position (on the voltage axis) of the voltammetric wave(s).

The interpretation of the effect of scan rate on the shape of polarograms was restricted in the present work by several factors. (1) Only cases in which the electron transfer was either Nernstian or totally irreversible have been considered. (2) The uncertainty in potential measurements from the oscilloscope trace was of the order of 0.01 V for a 1-V scan and limited the quantitative interpretation of shifts in peak potentials. (3) Because of the small separation between the successive anodic waves, the peak current for the second wave could not be accurately measured from the projected (descending) current line of the first wave. (4) The charging current was determined at each scan rate over the potential range of interest from polarograms obtained on solutions containing the solvent and supporting electrolyte alone; subtraction of the charging current at the location of each E_{pk} introduced a rather large error in the peak current measurements. Consequently, a spread of data points was obtained and only trends were considered. As usual, unequivocal assignment of a mechanism is not possible for a complex multistep electrochemical system.

However, several mechanisms can be written which are consistent with the data for the electrochemical oxidation of TPE to DPP. A simple scheme would be an EEC reaction sequence.



There were two oxidation waves at nearly the same potential, *ca.* +1.33 and +1.45 V. However, a reduction wave was associated only with the first; the first E step appeared to have some Nernstian character. The second E step was non-Nernstian and was probably coupled to an irreversible chemical reaction. The continuous shift of the anodic waves with increasing scan rates to more positive potentials and the absence of a cathodic peak associated with the second wave are consistent with these assignments.

It has been established that the first anodic charge transfer from an aromatic compound and other compounds with extensively delocalized π electrons usually involves the removal of an electron from the highest energy molecular orbital occupied. The somewhat reversible character of the first anodic wave and observation of a purple color whose visible absorption bands matched those previously reported upon chemical oxidation of TPE to the cation radical (which

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(27) The currents for the first anodic and cathodic peaks, $i_{\mathrm{pkA}\text{-}1}$ and $i_{\mathrm{pkC}\text{-}1}$, were measured from the zero current line after subtracting the approximate residual current. The currents for the second and third anodic waves were measured from the maximum current of the preceding peak.

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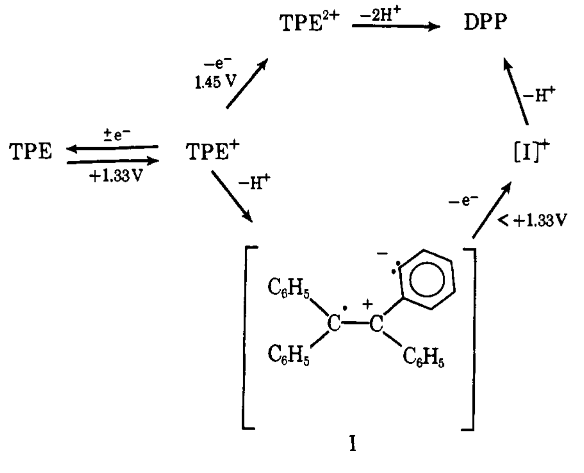
produced resolved esr spectra[33,34]) provide strong evidence for the involvement of the TPE cation radical as an intermediate species. The lifetime of this cation radical was approximately 1 sec, estimated by varying the cyclic voltammogram scan rate until the cathodic wave corresponding to the reduction of the cation radical was barely perceptible.

The second electrooxidation, occurring at approximately +1.45 V, was non-Nerstian and there was no reduction wave associated with this anodic wave. Although the irreversibility may have resulted from slow electron transfer, irreversible chemical reactions, preceding or following the charge transfer, must have occurred in order to give the final product, DPP.

If the C process(es) take place *after* the second charge transfer, three subsequent chemical steps (although not necessarily in this order) must have occurred. (1) The divalent cation of TPE would have to assume a planar configuration; the phenyl groups of TPE are rotated about 35° out of the plane of the ethylenic bond.[35] (2) The species must undergo intramolecular coupling at the ortho positions of the two *cis*-phenyl groups to form a 4a,4b-dihydrophenanthrene-type intermediate. (3) Two protons must be lost to form the product, DPP.

One or more of these chemical reactions, however, may have occurred *before* the second charge transfer. This scheme would be an ECE(C) reaction sequence similar to a mechanism suggested by Gatzke, *et al.*, who studied the oxidation of TPE by chromyl chloride.[4] Their alternate mechanism involved electron transfer from TPE to chromyl chloride, giving a radical cation in the initial step, followed by rotation of two phenyl groups into a planar configuration, coupling by nucleophilic attack of the adjacent phenyl group upon the positive charge at the ortho position directly attached to the carbonium ion center, and loss of a proton to give a radical that was easily oxidized and then lost a (second) proton to form DPP.



The first C step(s) of the ECE(C) and the second E step of the EEC reaction sequences may occur simultaneously (a concerted process) or may be in competition. In the latter case branching mechanisms may be involved. The dominant reaction sequence would then depend on the voltage scan rate.

Two branching schemes, similar to those suggested by others for different systems, appear appropriate. The following is patterned after the one proposed by Aikens, *et al.*,[36] for the electrochemical oxidation of 1,5-dichloroanthracene. It involves competition between the loss of the second electron and the loss of a proton from the monovalent TPE carbonium ion radical. Note that oxidation of I, the conjugate base of TPE⁺, would occur at potentials less than +1.33 V.

A second branching reaction sequence that is also consistent with the voltammetric data involves disproportionation of the monovalent cation radical intermediate at slow scan rates as has been suggested for the electrochemical oxidation scheme for tetrakis-(dimethylamino)ethylene.[37] The initial E process

$$\mathrm{TPE} \underset{\substack{+\mathrm{e}\\ +1.33\ \mathrm{V}}}{\overset{-\mathrm{e}}{\rightleftarrows}} \mathrm{TPE}^{+}$$

was followed at slow scans by

$$2\mathrm{TPE}^{+} \xrightarrow{\text{slow}} \mathrm{TPE} + \mathrm{TPE}^{2+}$$

but at fast scans by

$$\mathrm{TPE}^{+} \xrightarrow[+1.45\ \mathrm{V}]{-\mathrm{e}} \mathrm{TPE}^{2+}$$

TPE molecules formed by disproportionation in slow scan experiments would be reoxidized immediately at the anode to give increased current on the first anodic wave. Thus, the first anodic cyclic voltammetric peak at +1.33 V was larger than the second anodic peak at +1.45 V, particularly at slow scan rates.

The most direct evidence for a branching mechanism is the dependence of the current functions, $i_{\mathrm{pk}_\mathrm{A}}/V^{1/2}$, on the voltage scan rate for each of the anodic peaks. The transition of the first peak from a *ca.* two-electron process at low scan rates to nearly a one-electron process at high scan rates may indicate a change in the principal reaction sequence as the scan rate is increased. At low scan rates there is sufficient time for almost complete chemical reaction of the monovalent cation radical before the potential becomes sufficiently anodic to remove the second electron; this would account for the overall two-electron oxidation of TPE to the phenanthrene at +1.3 V using slow scan rates as well as exhaustive controlled potential electrolysis.

Using fast scans there is insufficient time to complete the intermediate chemical reactions and the second electron is lost from TPE⁺ at *ca.* +1.45 V. The overall electrode reaction for the first anodic wave thus undergoes transition from an apparent two-electron ECEC sequence at slow scan rates to one in which the electrons are lost in two one-electron steps (at different anode potentials) at fast scans. The significant increase in the current function for the second peak, which was imperceptible at scan rates less than 0.40 V/sec, but grew to one-third the height of the first peak at a 20 V/sec scan rate may reflect these changes.

Although the same major product was obtained from electrochemical and photochemical oxidations of TPE, the mechanisms of the reactions are quite different.

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The photochemical reaction involves the lowest energy TPE excited singlet state whereas the more energetic carbonium ion(s) intermediates are involved in the electrochemical oxidation. Despite different intermediates there were no differences apparent in the overall stoichiometry for the major TPE reaction. However, intramolecular coupling reactions are much less important (and in some cases did not occur) when similar compounds giving carbonium ion radicals that are less stable than TPE$^+$, *e.g.*, triphenyl- and diphenylethylenes, were electrolyzed under the same conditions described above.[38]

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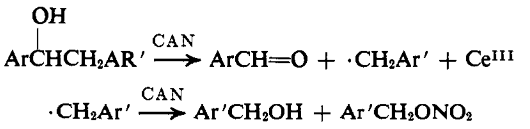
Oxidation of Organic Compounds with Cerium(IV). XI. Oxidative Cleavage of 1,2-Diarylethanols and 1-Aryl-2,3-diphenylpropan-2-ols by Cerium(IV) and Chromic Acid[1,2]

Paul M. Nave[1d] **and Walter S. Trahanovsky***[1e]

Contribution from the Department of Chemistry,
Iowa State University of Science and Technology,
Ames, Iowa 50010. *Received June 16, 1970*

Abstract: The cerium(IV) oxidation of 1,2-diarylethanols in 75% aqueous acetonitrile and 85% aqueous acetic acid is shown to give only products of oxidative cleavage. Relative rates of oxidation of a series of 2-aryl-1-phenylethanols which were determined by competition experiments are reported. Plots of the log of these rates against σ^+ for the substituent of the 2-aryl group give ρ values of -2.00 ± 0.02 in 75% aqueous acetonitrile and -2.01 ± 0.04 in 85% aqueous acetic acid. Radical trapping experiments show that the benzyl radical is an intermediate in the reaction, and these results and the ρ values characterize the oxidative cleavage as a one-electron oxidation. Oxidations of 1-aryl-2,3-diphenylpropan-2-ols with either cerium(IV) or chromic acid are shown to give benzyl phenyl ketone and the substituted benzyl phenyl ketone, the expected products of oxidative cleavage. From the relative yields of the two ketones, the relative rates of cleavage of substituted benzyl radicals were obtained. These rates are correlated with the σ^+ for the substituent and give ρ values of -1.91 ± 0.01 and -1.01 ± 0.01 for the cerium(IV) and chromic acid oxidations, respectively. The latter ρ value compares well with the previously reported ρ value of -0.96 for the oxidative cleavage of 2-aryl-1-phenylethanols by chromic acid. These results indicate that these oxidative cleavages are one-electron oxidations and are consistent with our assumptions for the 2-aryl-1-phenylethanol series that the substituent effect on the equilibrium of alcohol–metal complex formation is very small and that for both oxidants, equilibrium complex formation is attained. That a free alkoxy radical is not formed in these oxidations is shown by the magnitude of the ρ values and their difference for the two oxidants. The different ρ values for the two oxidants must reflect differences in the transition state of the decomposition of the alcohol–metal complexes. Analysis of existing data suggests that for secondary alcohols the oxidative cleavage reaction is normally a one-electron oxidation and ketone formation is normally a two-electron oxidation.

In a preliminary communication[2a] we have shown that the oxidative cleavage of 1,2-diarylethanols by ceric ammonium nitrate (CAN) is a one-electron process since the intermediate benzyl radical could be trapped, and the ρ for the reaction was -2.0, which is closer to the range of ρ's reported for benzyl radical reactions, -0.3 to -1.5,[3] than the -4.5 to -6.5 range[4] reported for benzyl cation processes. Part of this publication is devoted to further details of this study. From a similar study of the oxidation of 1,2-diarylethanols by chromic acid, we concluded that the oxidative cleavage reaction brought about by chromic acid is also a one-



$$\text{Ar}\overset{\text{OH}}{\text{C}}\text{HCH}_2\text{AR}' \xrightarrow{\text{CAN}} \text{ArCH{=}O} + \cdot\text{CH}_2\text{Ar}' + \text{Ce}^{\text{III}}$$

$$\cdot\text{CH}_2\text{Ar}' \xrightarrow{\text{CAN}} \text{Ar}'\text{CH}_2\text{OH} + \text{Ar}'\text{CH}_2\text{ONO}_2$$

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