ANODIC OXIDATION
OF PENTAPHENYLCYCLOPENTADIENES

TO LENA AND ROSEBELLA

ANODIC OXIDATION OF PENTAPHENYLCYCLOPENTADIENES

By

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ABSTRACT

Cyclic voltammetric oxidation of 1,2,3,4,5-pentaphenylcyclopentadiene has been studied in non-polar chloroalkane solvents (CH_2Cl_2 and CH_2ClCH_2Cl). The oxidation is reversible if tetra-n-butylammonium hexafluorophosphate ($TBA^+PF_6^-$) is used as supporting electrolyte, but irreversible when tetra-n-butylammonium perchlorate ($TBA^+ClO_4^-$) or tetra-n-butylammonium trifluoromethane sulfonate ($TBA^+OT_f^-$) are used, and partially reversible when tetra-n-butylammonium tetrafluoroborate ($TBA^+BF_4^-$) is used. Oxidation of 1,2,3,4,5-pentaphenyl-1-methylcyclopentadiene, which has no relatively acidic protons, was reversible with all four supporting electrolytes.

The criteria for reversibility were observation of cathodic wave on scan reversal, equal anodic and cathodic peak currents, minor dependence of peak potentials on scan rate, υ, and linearity of anodic peak current, i_{pa} with the square root of scan rate, $\upsilon^{1/2}$, corresponding to Randles-Sevcik equation for reversible processes.

It is proposed that perchlorate (ClO_4^-) and triflate (OT_f^-) anions are sufficiently basic to accept a proton from 1,2,3,4,5-pentaphenylcyclopentadiene cation-radical intermediate, while tetrafluoroborate (BF_4^-) and particularly hexafluorophosphate (PF_6^-) are less basic, and therefore less reactive.

Controlled potential electrolysis of 1,2,3,4,5-pentaphenylcyclopentadiene with tetra-n-butylammonium perchlorate as supporting electrolyte affords the cation, which is consistent with an ECE mechanism in which the chemical step is proton loss.

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a	hyperfine coupling constant
A	surface area
Amp	amphere
μA	microamphere
Ar	aryl group
bp	boiling point
c	concentration
C	coulomb
^{o}C	degree celsius
cm	centimeter
cm^{-1}	reciprocal centimeters
D	diffusion coefficient
e^{-}	electron
esr	electron spin resonance
E	potential
ECE	chemical reaction coupled between two charge transfers
EEC	chemical reaction following two successive charge transfers
E_{pa}	anodic peak potential
E_{pc}	cathodic peak potential
gm	gram
hν	light
i_{pa}	anodic peak current
iR	ohmic resistance

ID	internal diameter
k	rate constant
Kcal	kilocaloric
K	equilibrium constant
K_{diss}	dissociation constant
Lit	literature
m/e	mass to charge ratio
mg	milligram
min	minute
ml	milliliter
mm	millimeter
mmol	millimole
mM	millimolar
mp	melting point
mV	millivolt
M^{n+}	metal ion
n	number of electrons
nm	nanometer
nmr	nuclear magnetic resonance
Nu	nucleophile
ppm	parts per million
R	alkyl group
SCE	saturated calomel electrode
$TBA^+BF_4^-$	tetra-n-butylammonium tetrafluoroborate

$TBA^+ClO_4^-$	tetra-n-butylammonium perchlorate
$TBA^+NO_3^-$	tetra-n-butylammonium nitrate
$TBA^+OT_f^-$	tetra-n-butylammonium trifluoromethanesulfonate
$TBA^+PF_6^-$	tetra-n-butylammonium hexafluorophosphate
UV	ultra violet
ν	voltage scan rate
V	voltage
Δ	heat
λ_{max}	wavelength of maximum absorbance
*	excited state

INTRODUCTION

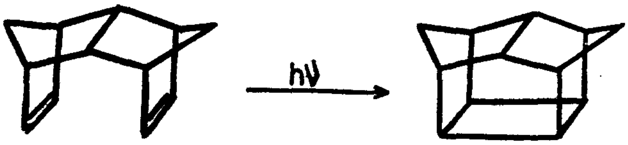
A. Cation radicals for the past few decades have received a lot of attention. Recent reviews[1-3] recognize that electron-transfer plays important roles in diverse homogeneous reactions of organic compounds. They are generated by removing an electron from a neutral, electron-paired molecule and thus have both a positive charge and an unpaired electron. Methods for generating these reactive intermediates can be photochemical[4-7] or reaction with ground state oxidizing agents[2,4,8-12] or electrochemical oxidation.[3,13-16] In principle, therefore, the intermediate cation radical generated by any of the mentioned methods can be symbolized as:

$$A \quad \underset{+e}{\overset{e-}{\rightleftharpoons}} \quad A^{+\cdot}$$

where A is a neutral molecule, and $A^{+\cdot}$ is the reactive cation radical intermediate.

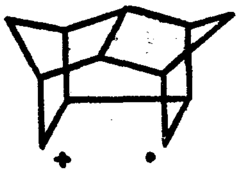
i) Photochemical Methods

The methods were recognized back in the early 1940's by Lewis and Lipkin[17] when they irradiated triphenylamine in ether-isopentane-ethanol mixture at liquid-air temperature and noticed that it gave cation radicals. On warming, the cation radicals disappeared and they concluded that the ejected electron was trapped in the frozen mixture and was recaptured by cation radical when the temperature was raised. They called this photoionization. Electron ejection from systems having π-electrons on irradiation occurs quite readily especially in polar solvents, e.g., acetonitrile. As a result of the high quantum yields observed in many photo-induced reactions, Jones and co-workers[7] concluded that cation radicals are involved in such reactions. The example they had was 1,4,4a,5,8,8a-hexahydro-1,4,5,8-dimethanonaphthalene, 1, which isomerized to



1 2

2 on sensitization in acetonitrile. This isomerization is believed to occur via cation radical 3 which is capable of propagating the reaction by attacking 1 hence starting a chain



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process. The mechanistic details for photo-ionization are quite complicated because they may involve one or two-photon processes. For a one-photon process (monophotonic), the quantum yields are a maximum for irradiation at shorter wavelengths and are markedly dependent on solvent and temperature. Most of the monophotonic reactions are carried out in halogenated solvents and an example of an aromatic substrate in chloroform is shown in Scheme I.

Scheme I

$$\mathrm{ArH} + h\nu \longrightarrow {}^{1}\mathrm{ArH}^{*} \qquad (1)$$

$${}^{1}\mathrm{ArH}^{*} + \mathrm{CHCl_3} \longrightarrow \mathrm{ArH}^{+\bullet} + \mathrm{Cl}^{-} + \mathrm{CHCl_2} \qquad (2)$$

$$\mathrm{ArH,\ CHCl_3} + h\nu \longrightarrow \mathrm{ArH}^{+\bullet} + \mathrm{Cl}^{-} + \mathrm{CHCl_2} \qquad (3)$$

The electron transfer may occur from the excited aromatic singlet to ground state solvent (stages (1) and (2)) or within charge-transfer complex (stage (3)). In either case, halide ion ejection is the driving force in promoting the transfer, and this explains the process being dependent on solvent. The temperature also dictates the stability of the cation radical intermediate, $\mathrm{ArH}^{+\bullet}$.

For two-photon processes, the sequence is shown in Scheme II.

Scheme II

$$\mathrm{ArH} + h\nu \longrightarrow {}^{1}\mathrm{ArH}^{*} \qquad (1)$$

$${}^{1}\mathrm{ArH}^{*} \longrightarrow {}^{3}\mathrm{ArH}^{*} \qquad (2)$$

$${}^{3}\mathrm{ArH}^{*} + h\nu \longrightarrow \mathrm{ArH}^{**} \qquad (3)$$

$$\mathrm{ArH}^{**} \longrightarrow \mathrm{ArH}^{+\bullet} + e^{-} \qquad (4)$$

The ejection of the electron in this process depends on the energy of the second photon which causes the triplet-triplet transition (stage (3)).

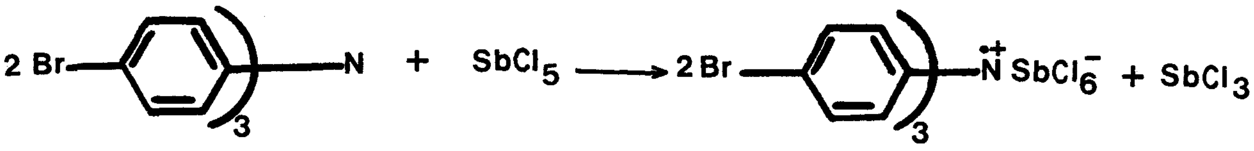
ii) Chemical Oxidation Methods

Oxidation of organic compounds to their cation radicals can be done in various ways. The conventional method of using concentrated sulphuric acid has been used since the early period of esr spectroscopy[5], when it was realized that the oxidized substance was paramagnetic. This was due to the generated cation radicals and although the actual mechanism of oxidation of aromatic hydrocarbons by sulphuric acid is not known, a complete general equation for the reaction can be written as:

$$2ArH + 3H_2SO_4 \longrightarrow 2ArH^{+\cdot} + 2H_2O + SO_2 + 2HSO_4^-$$

Other Bronsted acids which have found useful applications in the generation of cation radicals are trifluoromethane sulphonic acid, CF_3SO_3H[10] and trifluoroacetic acid, CF_3COOH[11].

On the other hand, Lewis acids have found an important role too. Ledwith[4] found that molecules containing 'lone pair' atoms such as oxygen, nitrogen and sulphur are prone to lose an electron readily to suitable Lewis acids. Tris(p-bromophenyl)-aminium ion 5 formed readily from the amine, 4 in presence of antimony pentachloride;



4 5

The aminium ion 5 which has oxidizing power was found to be stabilized by the hexachloroantimonate ion ($SbCl_6^-$) against any thermal or photochemical decomposition.

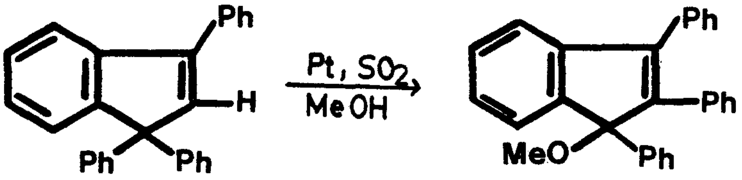
A variety of organic compounds have been found to be easily oxidized by inorganic one-electron oxidants[4,8-10] like iron(III), cerium(IV), copper(II) and cobalt(III) which all undergo a reaction of the form:

$$ArH + M^{n+} \longrightarrow ArH^{\dot{+}} + M^{(n-1)+}$$

Unlike the Lewis acids which form stable cation radicals, the polyvalent metal salt oxidants form short-lived cation radicals because they usually involve further oxidation and, also, nucleophilic attack by the anions of the metal salts.

iii) Electrochemical Methods

An electrode is fundamentally an electron transfer agent, so that, given the proper solvent system and electrolyte, anodic oxidation allows formation of cation radicals without any associated proton or other atom transfer and without the formation of a reduced form in the immediate vicinity of the cation radical. Moreover, because the potential of the electrode can be adjusted precisely, its oxidizing power can be controlled and further oxidation of the cation radical can often be avoided. Due to this, many physical organic chemists have become interested in these reactions. Miller[15], while investigating the rearrangement of 1,1,3-triphenylindene, 6 to the methoxy derivative of 1,2,3-triphenylindene, 7 in sulphur dioxide containing 0.2% methanol realised that the rearrangement was slowed down considerably at low temperatures (-70°C) and also by higher concentrations of methanol. This was due to slow destruction of the cation radical intermediates at low temperature and nucleophilic attack by a higher concentration of methanol. Parker[3] has observed that the anodic oxidation reaction of 9,10-diphenylanthracene, 8 occurs



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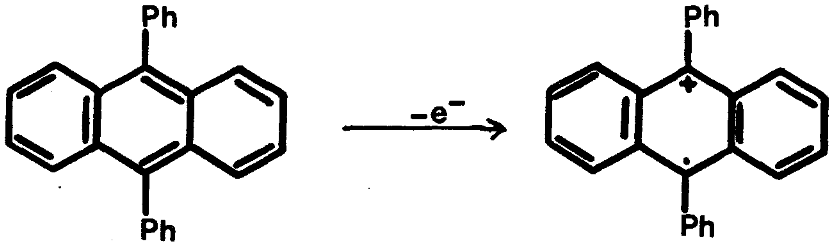


8 9

via formation of a cation radical, 9 which can undergo various reactions depending on the medium.

Other methods of generating cation radicals are oxidation by halogens[18] and formation on catalytic surfaces.[19]

B. Detection Techniques

Cation radicals have been shown kinetically and spectroscopically to be intermediates in many oxidation processes of organic compounds. In some cases of hetero-aromatic species especially those containing sulphur atoms, the positive identification has been possible.[20] Particularly in aprotic solvents, some of these intermediates were found to have lifetimes long enough to permit assignment through direct observation of physical or chemical parameters. Often, however, the radical character and short lifetimes of these species prevent unambiguous identification especially in polar solvents like water.

The present highly time-resolved detection such as rapid-mixing pulse radiolysis and flash (laser) photolysis has enabled the detection of species with lifetimes below a microsecond.[21]

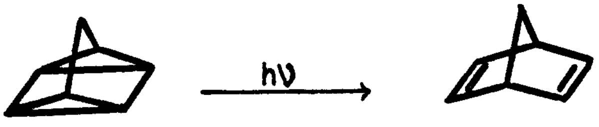
Other techniques generally used for investigating the nature of these intermediates are esr[22], photoelectron spectroscopy[23] and cyclic voltammetry.[24] Magnetic susceptibility measurement was a useful technique but now it is obsolete because it required relatively high concentrations of the intermediate.

C. Reactions

a) Isomerization

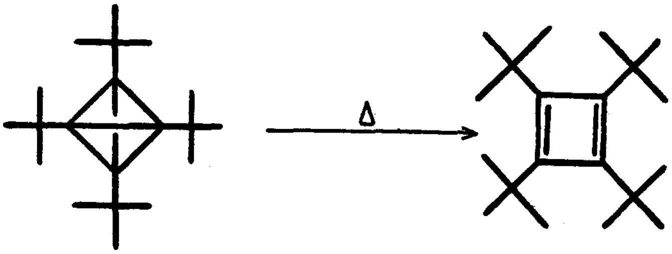
i) Isomerization of Strained Molecules

Strained ring molecules have been shown to be of high reactivities and this was attributed to the nature of the chemical bonds. Due to violation of 'normal' bond angles, molecules of this class are as a rule, thermodynamically unstable and considerable energy is released during intramolecular conversion to less strained isomers. Kabakoff and co-workers[25] found that in quadricyclane, 10, the strain energy is 96kcal mol^{-1}, of which 27 kcal mol^{-1} is released during the rearrangement to norbornadiene, 11[26].



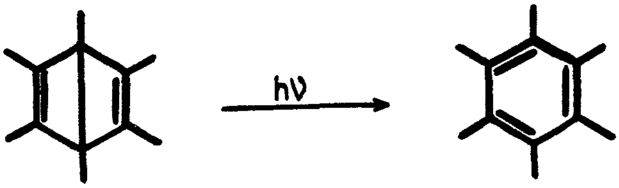
10 11

However, in spite of the intrinsic instability of these strained ring molecules, many of them show slow isomerization and the reason could be inhibition by a barrier imposed by orbital symmetry and also the substituents e.g., t-butyl, may sterically hinder the conversion. A useful illustration of this point is observation reported by Maier and co-workers[27] who found that isomerization of tetra-t-butyltetrahedran, 12 to tetra-t-butylcyclobutadiene, 13 does not occur below



12 13

135°C because of the repulsion between the bulky t-butyl groups. The thermal stability of these polycyclic molecules is in sharp contrast to the fast isomerization that is observed during photolysis. This, along with the recognition that cation radicals may be formed during photolysis provided the background for the now accepted cation radical chain mechanism for photoisomerization. Work reported by Jones and coworkers[16] indicated that the conversion of hexamethyldewarbenzene, 14 to hexamethylbenzene, 15 occurred readily on irradiation.

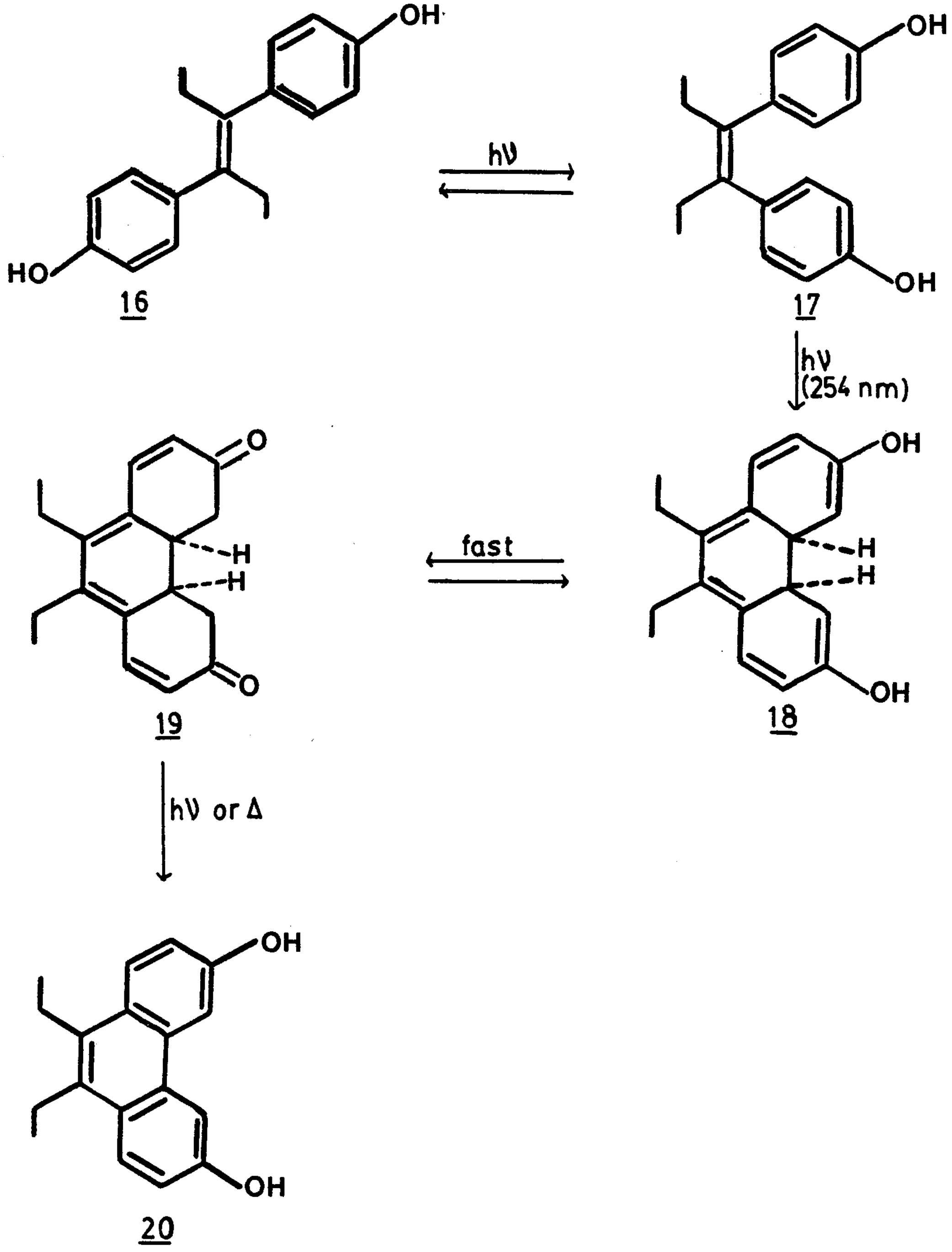


14 15

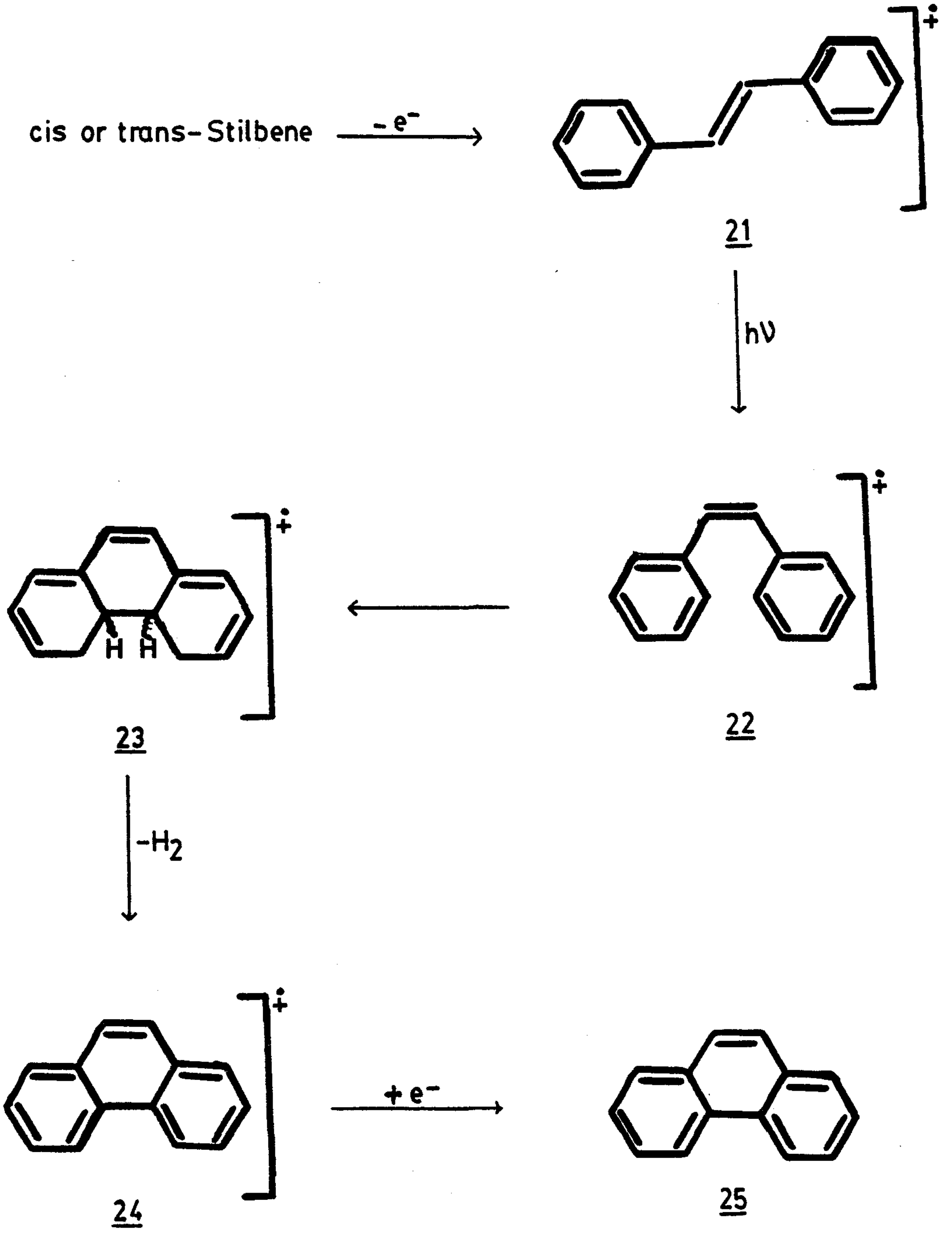
The same conversion was noticed earlier by Evans and co-workers[28] when they oxidized 14 anodically in acetonitrile and observed no other detectable product except 15.

ii) Isomerization Of Unstrained Molecules

Although the photo-oxidation cyclization of stilbenes to phenanthrene is a reaction of remarkable generality and synthetic utility, definitive mechanistic studies have been thwarted by the difficulty in isolating the intermediate proposed to be dihydrophenanthrene. In an attempt to isolate this intermediate, Doyle and co-workers[29] irradiated diethylstilbestrol, 16 at 254nm and were able to isolate the photoproduct 19 with little difficulty.


OH
16
HO
hν
OH
17
OH
hν
(254 nm)
O
H
H
O
19
fast
OH
H
H
OH
18
hν or Δ
OH
OH
20

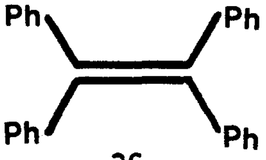
This reaction provided a definitive clue towards the cyclization pathway of stilbenes. Work done later by Gooden and Brauman[30] on fragmentation of stilbene cation radical, 21 generated by electron impact of either cis- or trans-isomer using ion cyclotron resonance was in favour of the following mechanism:



Low energy electron impact of either cis- or trans-stilbene produces predominantly the trans-product 21 which photoisomerizes to the cis-product 22, which then cyclizes to the dihydrophenanthrene cation radical, 23. Depending on the geometry and excess energy, 23 may fragment to 24 on concerted loss of H_2 or other cations such as $C_{14}H_{11}^+$ and $C_{13}H_9^+$ on loss of $H^\bullet$ and $CH_3^\bullet$ respectively. Dehydrogenation of 23 to give 24 occurs only in the presence of oxygen or iodine.[31]

Recently, Lewis and co-workers[32] reported a nearly quantitative isomerization of cis-stilbene to the trans-isomer when irradiated in the presence of a sensitizer (9,10-dicyanoanthracene). In this investigation, the cyclization product, phenanthrene, was detected at trace levels even in the presence of oxygen. This indicated that cyclization of cis-stilbene cation radical to dihydrophenanthrene cation radical either does not compete with isomerization to trans-stilbene cation radical or occurs reversibly under the mentioned conditions. In all, the isomerization and/or cyclization of stilbenes can occur via the formation of cation radicals.[30]

Tetraphenylethylene (TPE), 26 has also been shown to



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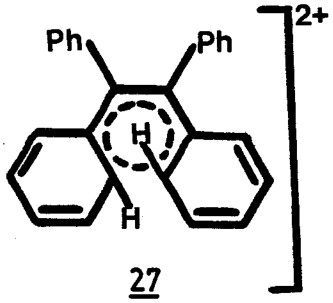
cyclize to 9,10-diphenylphenanthrene (DPP), and several mechanistic schemes have been reported[33,34] like in Scheme III.

Scheme III

$$\text{TPE} \xrightarrow{e^-} \text{TPE}^{+\bullet} \qquad (1)$$

$$2\text{TPE}^{+\bullet} \longrightarrow \text{DPP} + \text{TPE} + 2\text{H}^+ \qquad (2)$$

The tetraphenylethylene cation radical, $\text{TPE}^{+\bullet}$ disproportionates to a dication 27 which then undergoes cyclization after the



27

loss of two protons to form 9,10-diphenylphenanthrene (DPP) as shown in stage (2) of Scheme III.

iii) cis-trans-Isomerization

In the course of investigating the formation and decay of trans-stilbene radical ions, Lewis and co-workers[32] observed that electron-transfer quenching of singlet 9,10-dicyanoanthracene (DCA) by trans-stilbene (t-S) resulted in inefficient isomerization, whereas quenching by cis-stilbene (c-S) resulted in a nearly quantitative isomerization to t-S in acetonitrile. Further studies on this unusual one-way photoisomerization process indicated that it occurred via a cation radical chain mechanism in which the activation energy for cation radical isomerization is substantially lower than that for neutral c-S. The isomerization steps are as shown in Scheme IV.

Scheme IV

$$\mathrm{DCA} + h\nu \longrightarrow {}^{1}\mathrm{DCA}^{*} \qquad (1)$$

$$ {}^{1}\mathrm{DCA}^{*} + \text{c-S} \longrightarrow \mathrm{DCA}^{\bar{\bullet}} + \text{c-S}^{\dot{+}} \qquad (2)$$

$$\text{c-S}^{\dot{+}} \longrightarrow \text{t-S}^{\dot{+}} \qquad (3)$$

$$\text{t-S}^{\dot{+}} + \text{c-S} \longrightarrow \text{t-S} + \text{c-S}^{\dot{+}} \qquad (4)$$

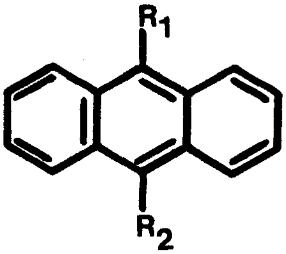
$$\mathrm{DCA}^{\bar{\bullet}} + \text{t,c-S}^{\dot{+}} \longrightarrow \mathrm{DCA} + \text{t,c-S} \qquad (5)$$

The above scheme was further confirmed when two radical ions were observed by transient absorption[35] and by resonance Raman spectroscopy[36] in acetonitrile. They were believed to be 9,10-dicyanoanthracene anion radical and stilbene cation radical; the occurrence of which was due to electron transfer from cis- or trans- stilbene to singlet 9,10-dicyanoanthracene. This being an exothermic process it occurs spontaneously.

In presence of molecular oxygen, the cation radical isomerization process is inhibited and the photooxygenation process reported by Foote and Eriksen[37] gives benzaldehyde as the major product, trans-isomer (1-2%), benzil and epoxidation stereoisomers, presumably formed from cis- and trans-stilbene cation radicals.

b) Reaction with Nucleophiles

Cation radicals of most organic compounds react so rapidly that it is not possible to prepare solutions of the intermediates for kinetic and mechanistic studies at ambient temperatures. There are exceptions, and compounds having structures 28 and 29, where X and Y are O, S or N-R are transformed upon oxidation in solvents such as acetonitrile to reasonably stable cation radicals.



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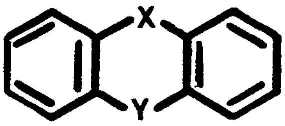

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By virtue of the fact that initial reaction between a cation radical and a nucleophile produces an unstable radical intermediate, the reactions are inevitably complex. Further electron-transfer reactions with nucleophiles are necessary in order to reach a stable product. All these processes depend on conductivity, oxidizability and nucleophilicity of the solvent/ electrolyte system being used. In a strictly non-aqueous system, solvents used are polar aprotic such as acetonitrile and dimethylformamide non-polar aprotic such as methylene dichloride and 1,2-dichloroethane, or protic solvents like methanol, trifluoroacetic acid and sulfonic acids. Factors which dictate the choice of solvents to be used in electrochemical work are that they should be electroinactive, that is to say they should have a wide oxidation window and they should be of low nucleophilicity. The anions of the supporting electrolytes commonly used are also those which are quite electroinactive such as perchlorates (ClO_4^-), tetrafluoroborates (BF_4^-), hexafluorophosphates (PF_6^-), nitrates (NO_3^-), aromatic sulfonates (RSO_3^-), carboxylate ions ($RCOO^-$), tetraethylaluminate ($AlEt_4^-$), and tetraphenylborate (BPh_4^-). Their corresponding cations in practice are usually alkali and alkaline earth metals ions together with ammonium (NH_4^+) and tetraalkylammonium (R_4N^+) ions.

There are <u>three</u> mechanisms which have been believed to describe the reaction pathways of cation radicals with nucleophiles. They are designated Disproportionation, Complexation and Half-regeneration.[38] The most important difference between Disproportionation and the other two is that the <u>dication</u>, rather than the cation radical is the species reacting with the nucleophile. The primary difference between Complexation and the Half-regeneration mechanism is that in the former, the initial interaction results in the formation of a π-complex and covalent bonding does not occur until the dication stage, while in the latter, the bond formation takes place in the first step. Illustrative Schemes V - VII are as shown below, where A is the substrate and X is a nucleophile which could be the solvent, electrolyte anion or any other added nucleophile.

Scheme V Disproportionation

$$A \xrightleftharpoons[k_{-1}]{k_1} A^{+\cdot} \qquad (1)$$

$$2A^{+\cdot} \xrightleftharpoons[k_{-2}]{k_2} A^{2+} + A \qquad (2)$$

$$A^{2+} + X \xrightarrow{k_3} \text{products} \qquad (3)$$

Scheme VI Complexation

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^{+\cdot} \qquad (1)$$

$$A^{+\cdot} + X \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (A/X)^{+\cdot} \qquad (2)$$

$$(A/X)^{+\cdot} + A^{+\cdot} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} (A/X)^{2+} + A \qquad (3)$$

$$(A/X)^{2+} \xrightarrow{k_4} \text{products} \qquad (4)$$

Scheme VII Half-regeneration

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^{+\cdot} \qquad (1)$$

$$A^{+\cdot} + X \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \overset{\bullet}{A}-X^{+} \qquad (2)$$

$$\overset{\bullet}{A}-X^{+} + A^{+\cdot} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} A^{+}-X^{+} + A \qquad (3)$$

$$A^{+}-X^{+} \xrightarrow{k_4} \text{products} \qquad (4)$$

Disproportionation to a dication and a neutral parent compound has always been a distinct possibility during radical ion reactions. The dication would invariably be more reactive towards nucleophiles than the corresponding cation radical and the likelihood that such reactions would follow the disproportionation pathway depends upon three factors in Scheme V.

i) k_2/k_1, the relative rate constants for the reactions of the two species i.e., stages (1) and (2)

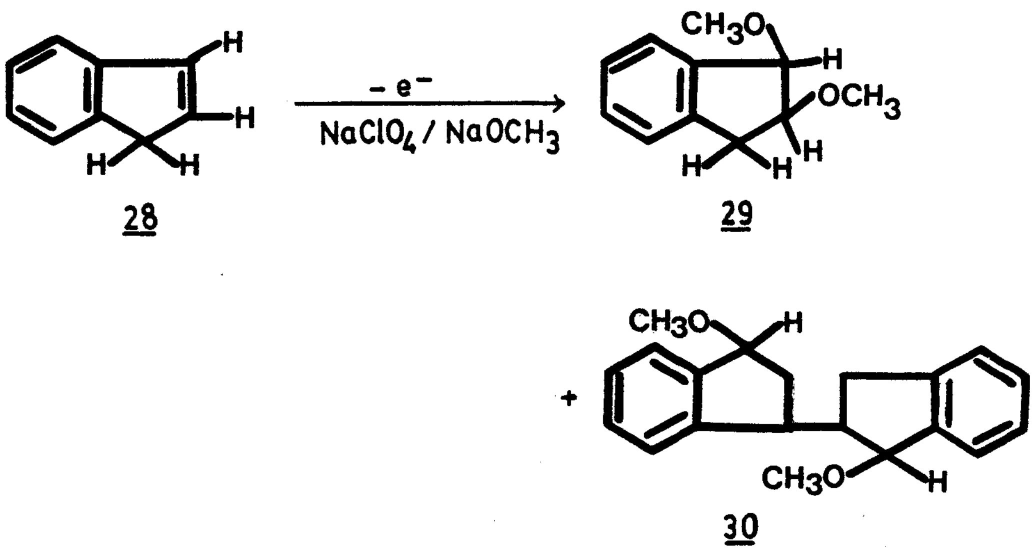
ii) the magnitude of k_2, the rate constant of disproportionation in stage (2)

iii) the magnitude of the disproportionation equilibrium constant, K_{disp} in stage (2)

Cation radicals of most aromatic compounds in solvents such as acetonitrile have very small values for their disproportionation equilibrium constants, this being attributed to the reactivity of the dications formed. Measurements made in solvents containing strong mineral acids[39] or even in neutral solvents which are nucleophile-free[40] gave values less than 10^{-9}. So, the feasibility of the disproportionation mechanism can only be tested by comparing the observed rate constants with the maximum possible predicted values of established reactions.[41]

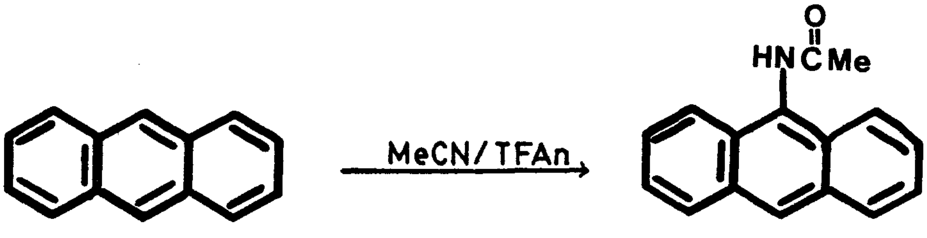
For complexation mechanism to be favourable relative to disproportionation, the formation of the complexed cation radical must be accompanied by a significant lowering of the oxidation potential. Since this can be counteracted by a low equilibrum concentration of the complex, the complexation mechanism via the dication is not favourable. This means that if the complex has another favourable reaction pathway, this would compete, making it impossible to distinguish between complexation and half-regeneration mechanisms by kinetic measurements.

A specific example which illustrates the reaction of cation radicals with nucleophiles is the work reported by Engels and co-workers[42] on the electrolysis of indene, 28 in methanolic solution of sodium perchlorate/sodium methoxide. Two major products; 45% 1,2-dimethoxyindane, 29 and 26% 1,1'-dimethoxy-2,2'-biindane, 30, were observed.



The mechanism is believed to involve a cation radical which is attacked by the methoxy anion to form a neutral radical which can either dimerize to form 30 or lose another electron followed by another methoxy anion attack to form 29. The higher yield of 29 demonstrates the ease at which the neutral radical gets oxidized as compared to the parent compound 28.

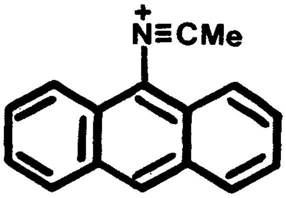
Work reported by Hammerich and Parker[43] on anodic acetamidation of anthracene, 31 in presence of trifluoroacetic acid anhydride as a water-scavenger (to make acetonitrile solvent 'super-dry') illustrates reaction of cation radicals



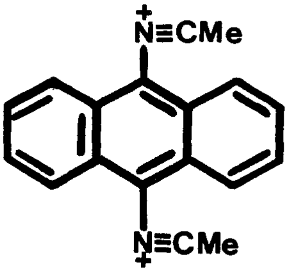
31

34(82%)

with solvents which can act as nucleophiles. Cyclic voltammetric scans showed two irreversible 2e-oxidation peaks at +1.24V and +1.69V (Potentials quoted versus SCE unless stated otherwise) were attributed to the involvement of ECE reaction of 31 to produce 9-anthranylnitrilium ion, 32 (first wave) and further oxidation to 9,10-anthranyldinitrilium ion, 33, (second wave).

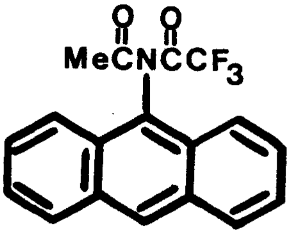


32



33

From the shape of the waves, it was revealed that species 32 was unstable because the wave decayed and a new quasi-reversible wave was formed at +1.54V which was attributed to the formation of a new product, 35, during electrolysis and its structure was determined to be as shown below:

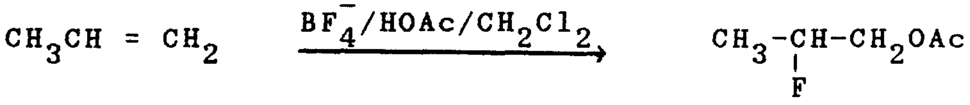


35

This was formed as a result of trifluoroacetic acid anhydride attacking the acetamide, 34 followed by a loss of a proton. Preparative scale oxidation of anthracene, 31 in acetonitrile-trifluoroacetic acid anhydride (25:1) resulted in 82% yield of the acetamide, 34 and was very much dependent on the quality of acetonitrile used.

When the same electrolysis was done using acetonitrile dried over alumina, the same cyclic voltammetric scan waves were observed, and this served as a clue to the fact that acetamidation can occur at high yields only in presence of ‘adventious water’, which is present in anhydrous solvents.

In cases where the solvent is less susceptible to attack by cation radicals, the electrolyte anion or any other added nucleophile would be attacked. Clark and co-workers[44] while investigating the effect of various aprotic solvents on the electrolytic products of propylene, <u>36</u> found that when the process was carried out in methylene chloride containing tetraethylammonium tetrafluoroborate ($Et_4N^+BF_4^-$) and 2% acetic acid, fluorinated product, <u>37</u> was isolated in significant quantities.

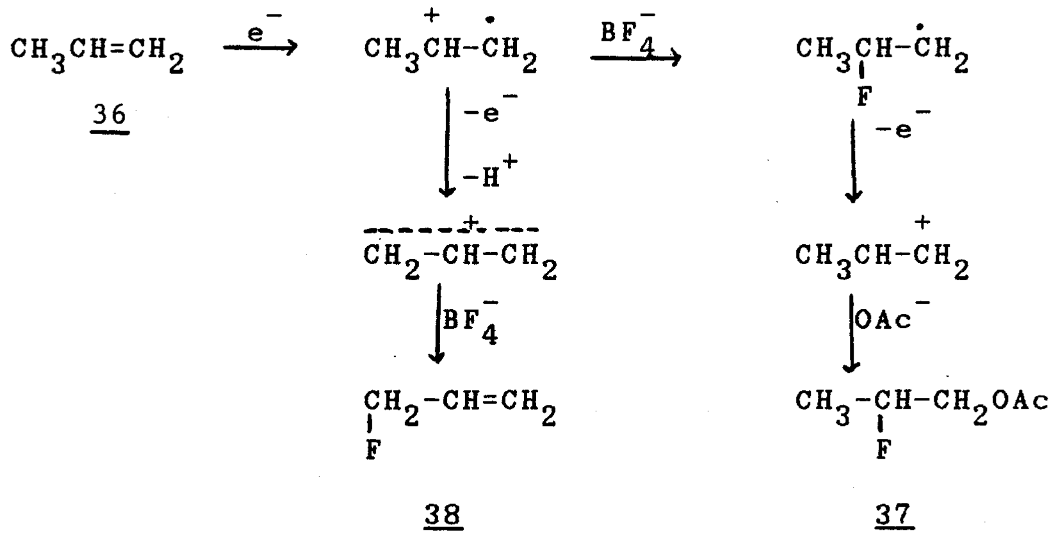


$$CH_3CH = CH_2 \xrightarrow{BF_4^-/HOAc/CH_2Cl_2} CH_3-\underset{\overset{|}{F}}{C}H-CH_2OAc$$

<u>36</u> <u>37</u>

Some traces of allyl fluoride <u>38</u> were also detected; both products were believed to have formed according to the steps shown in Scheme VIII.

Scheme VIII



When the solvent was changed to a more polar one like propylene carbonate, a drastic reduction of the fluorinated product was observed, and when nitromethane was used, none of the fluorinated product was detected. Since it is the basicity of the solvent which determines the stability of the cation radical of propylene towards deprotonation, methylene chloride is expected to be less basic than propylene carbonate and nitromethane and thus cannot compete with tetrafluoroborate or acetate anions towards cation radical attack hence fluorinated products were observed.

C. Dimerization

Anodic oxidation of aromatic compounds leads to formation of cation radicals, the fate of which is dependent on four factors:

i) The substituent at the double bond will determine not only the ease of oxidation of the neutral compound to a cation radical but also the stability of this intermediate by charge delocalization.

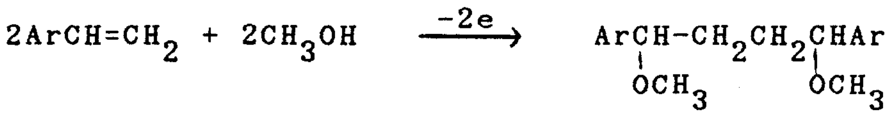
ii) The electrolysis medium i.e., the solvent and/or the supporting electrolyte anions, depending on their nucleophilicity, may react with the cation radicals.

iii) The anode electrode material can have influence on the reaction of the cation radicals.

iv) The anode potential may determine if the cation radical will be further oxidized to a dication.

In the case of a medium of low nucleophilicity, anodic oxidation would lead to formation of dimeric products often with incorporation of nucleophiles from the medium. For most compounds, the mechanisms have been referred to commonly as radical-radical dimerization (RRD) and radical-substrate coupling (RSC).[45] Kinetic investigation on these mechanisms have revealed a complex rate law with reaction orders changing with the initial substrate concentration. Competing mechanisms were proposed with RRD dominating at high substrate concentrations and RSC taking over at low substrate concentrations.[46]

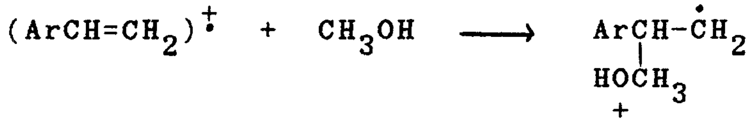
An illustrative example for these two mechanisms is the valuable synthetic process for additive dimerization of cation radicals of arylolefins and related substances in the presence of nucleophiles, developed by Schafer and co-workers.[47]



$$2ArCH{=}CH_2 + 2CH_3OH \xrightarrow{-2e} Ar\underset{OCH_3}{CH}{-}CH_2CH_2\underset{OCH_3}{CH}Ar$$

Three initial reaction <u>steps</u> are plausible for this reaction:

i) nucleophilic attack on the chain radical by the nucleophile,



$$(ArCH{=}CH_2)^{+\cdot} + CH_3OH \longrightarrow Ar\underset{\underset{+}{H}OCH_3}{CH}{-}\overset{\bullet}{C}H_2 \qquad (1)$$

This step is quite unlikely for a number of reasons. Firstly, a less stable cation radical is formed and secondly, if this cation radical were formed in low concentration, it would not be expected to undergo selectively second order dimerization or reaction with substrate without interference from hydrogen abstraction reactions.

ii) radical-substrate coupling step (RSC),

$$(ArCH{=}CH_2)^{+\cdot} + ArCH{=}CH_2 \longrightarrow Ar\overset{\bullet}{C}HCH_2CH_2\overset{+}{C}HAr \qquad (2)$$

iii) radical-radical dimerization step (RRD),

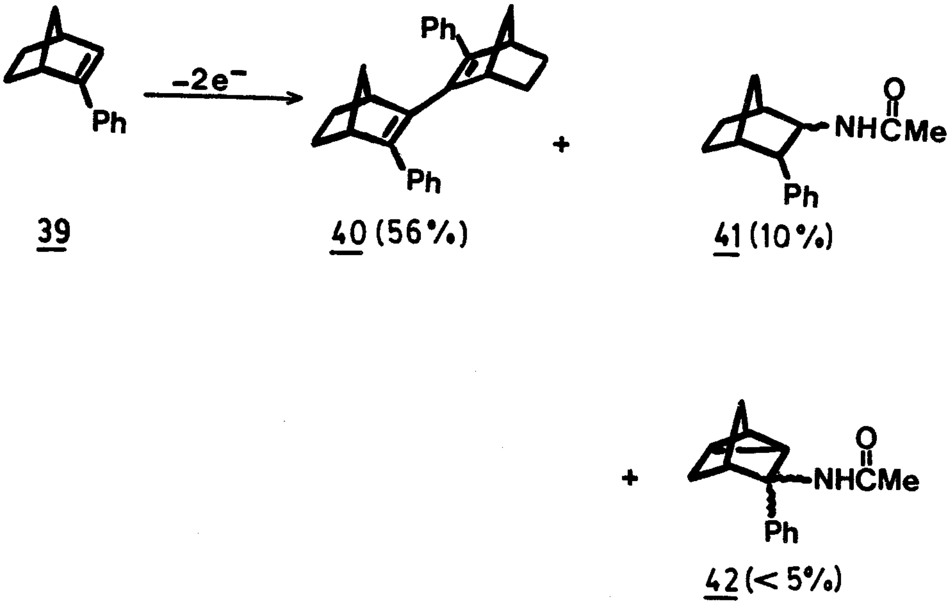
$$2(ArCH{=}CH_2)^{+\cdot} \longrightarrow Ar\overset{+}{C}HCH_2CH_2\overset{+}{C}HAr \qquad (3)$$

The competitive nature of the two mechanisms, RRD and RSC have been studied using theoretical working curves,[48] which have revealed that the rate constant for RRD (step (3)) is three times that of the RSC (step (2)).

A more recent study[49] indicated that the coupling mechanism of a radical cation is much more complex than previously thought and it appeared that the primary reaction is an attack of the cation radical on the substrate i.e., RSC step. The question arises as to why this reaction is faster relative to radical-radical dimerization (RRD). In considering this, the author[49] looked at rates rather than rate constants for the reaction and argued that even though the rate constant for radical-radical dimerization (RRD) is greater, the average concentration ratio of substrate to radical cation in the reaction layer can be quite large and the radical-substrate coupling (RSC) should predominate.

So the question as to which mechanism predominates at what concentration and whether rates, rather than rate constants should be used is still subject to criticism.

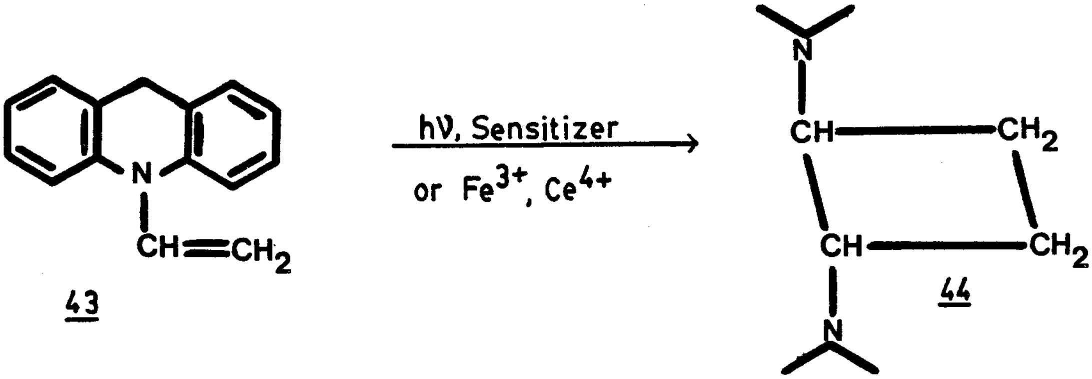
The fate of the initial cation radical formed would also depend on whether intramolecular rearrangements[50] might be kinetically competitive with intermolecular reaction and/or deprotonation. One example which illustrates an intermolecular reaction leading to dimeric product, with no incorporated nucleophiles is work reported by Fox and Akaba[51] on the electrolysis of 2-phenylnorbonene, 39 in acetonitrile containing tetra-n-butylammonium perchlorate.

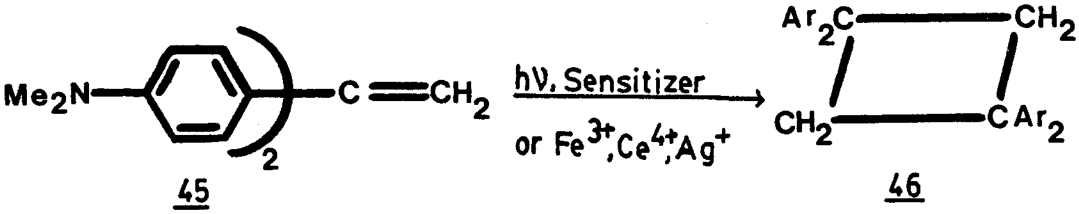


39 40 (56%) 41 (10%) 42 (< 5%)

The major product, 40, is predicted to be formed via mechanisms mentioned earlier[45,46] with a loss of two protons to give the neutral dimer. Slow formation of 42 clearly indicates that intramolecular rearrangements could not compete kinetically with intermolecular reaction.

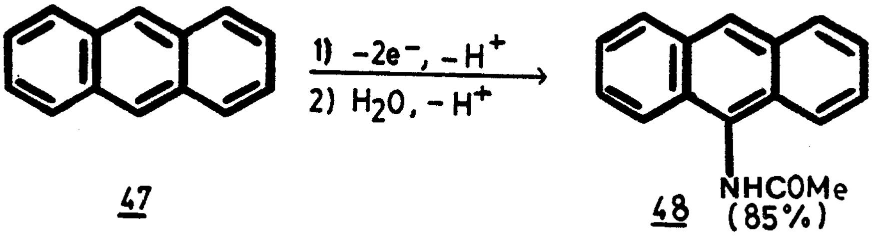
Cyclodimerization of certain vinyl-substituted aromatic amines to cyclobutanes occurs under photosensitized[52] or catalytic oxidation by suitable inorganic one-electron oxidants[53] such as iron (III), cerium (IV) and copper (II). Of the enamines, N-vinylcarbazole, 43, and 4,4'-dimethylamino-1,1'-diphenylethylene, 45 are most available and have been used extensively for the study of mechanistic pathways.

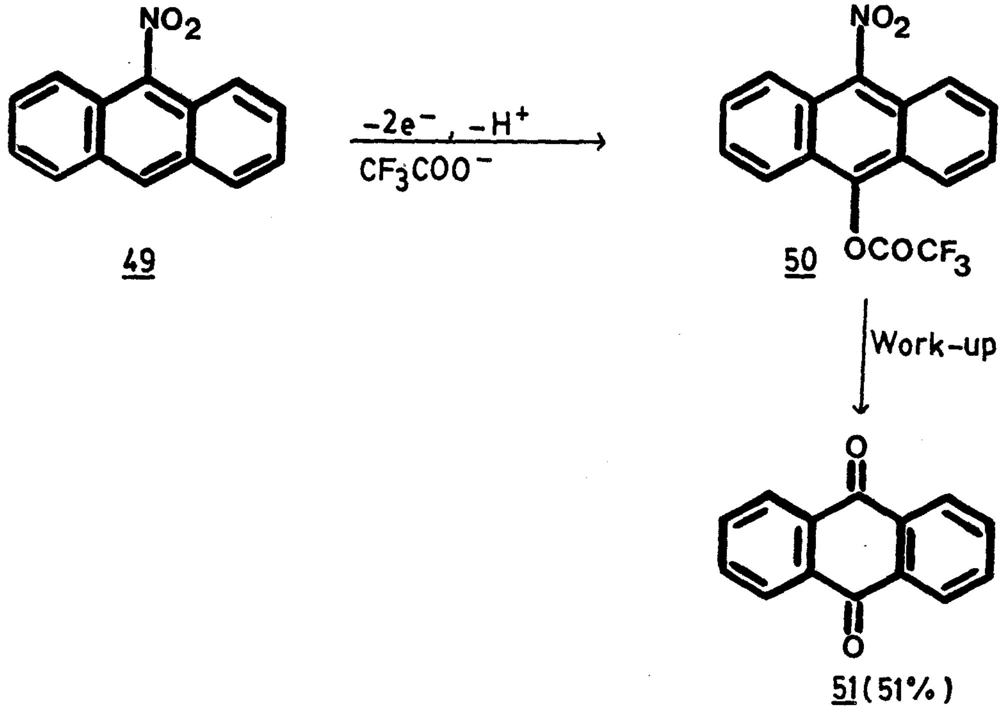


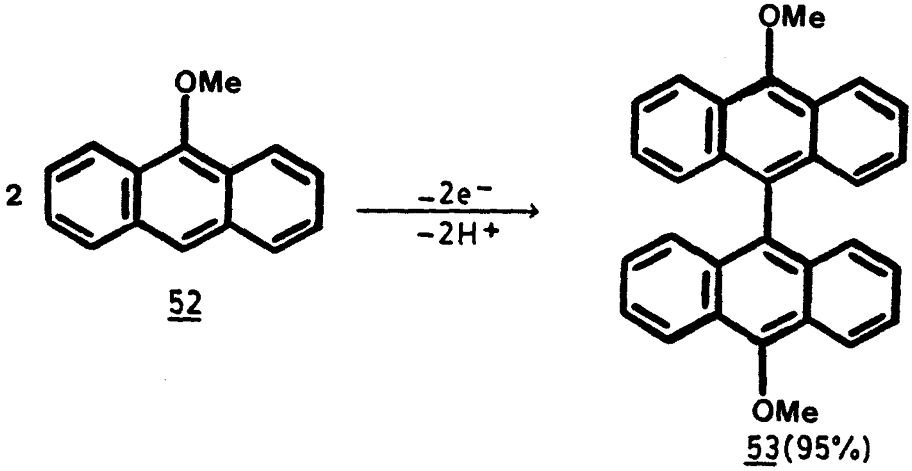


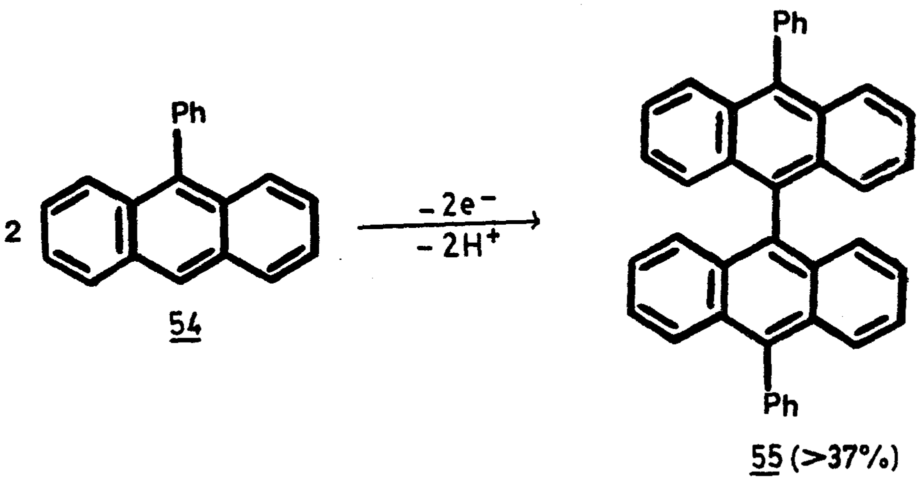
The intermediate in each case is a cation radical which cyclizes head-to-head for amine 43 and head-to-tail for 45. The reason is not quite clear although steric effects might play a role in these orientations.

Hammerich and Parker[54] studied a series of 9-substituted anthracene cation radicals in acetonitrile with the objective of determining the effect of the substituent on reaction mechanism and products. The following results were the outcome of their study:



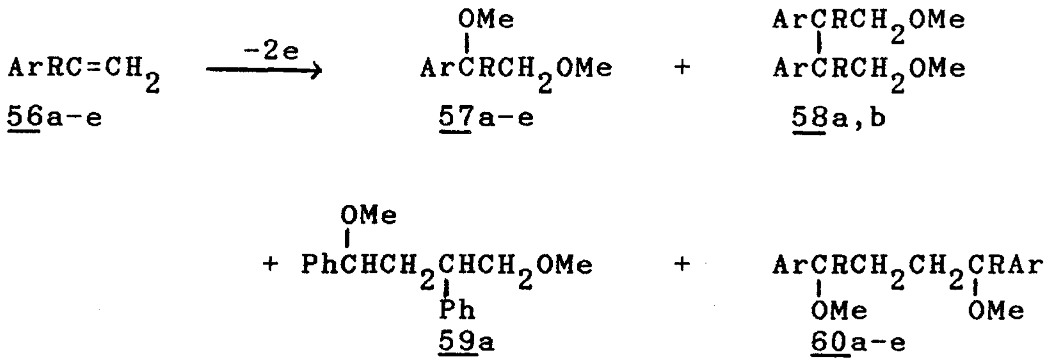

NO2
-2e⁻ , -H⁺
CF3COO⁻
49
NO2
50
OCOCF3
Work-up
O
O
51(51%)


OMe
2
52
-2e⁻
-2H⁺
OMe
OMe
53(95%)


Ph
2
54
-2e⁻
-2H⁺
Ph
Ph
55 (>37%)

Thus, under essentialy the same conditions, in acetonitrile containing trifluoroacetic acid, 9-substituted anthracene cation radicals undergo three distinctly different reactions; dimerization, acetamidation or trifluoroacetoxylation. Dimerization predominates when the 9-substituent is phenyl or methoxy. Both of these substituents strongly stabilize the charges in the 10,10'-positions of the initially formed dimer dication. Formation of the dimer dication is highly unfavourable with the electron-withdrawing nitro group and this explains the failure of 9-nitroanthracene, 49 to dimerize; instead it reacted with trifluoroacetate ion to give the neutral adducts, 50.

In electrochemical oxidation of aromatic olefins, the structure of the olefin and the nature of the anode material have great influence on the reaction pathways and/or products. Kojima and co-workers[55] have shown that when a series of substituted styrenes, 56a-e are oxidized in methanol in presence of sodium methoxide using platinum anode, dimethoxylated monomers, 57 a-e are the major products, together with one or more of the three types of dimethoxylated dimers, 58a,b (αα-dimer), 59a (αβ-dimer) and 60 a-e (ββ-dimer).



$$\underset{\underline{56}\text{a-e}}{\mathrm{ArRC{=}CH_2}} \xrightarrow{-2e} \underset{\underline{57}\text{a-e}}{\mathrm{Ar\overset{OMe}{\overset{|}{C}}RCH_2OMe}} + \underset{\underline{58}\text{a,b}}{\begin{matrix}\mathrm{ArCRCH_2OMe}\\ |\\ \mathrm{ArCRCH_2OMe}\end{matrix}}$$

$$+ \underset{\underline{59}\text{a}}{\mathrm{Ph\overset{OMe}{\overset{|}{C}}HCH_2\underset{Ph}{\underset{|}{C}}HCH_2OMe}} + \underset{\underline{60}\text{a-e}}{\mathrm{Ar\underset{OMe}{\underset{|}{C}}RCH_2CH_2\underset{OMe}{\underset{|}{C}}RAr}}$$

a: Ar=Ph, R=H b: Ar=p-ClC_6H_4, R=H

c: Ar= R=Ph d: Ar=p-MeC_6H_4, R=H

e: Ar=p-$MeOC_6H_4$, R=H

On the other hand, when a graphite anode is used, dimethoxylated dimers, <u>60</u>a-e (ββ-dimer) are the major products, together with dimethoxylated monomers, <u>57</u>a-e. The difference in electrooxidation products from the two anode materials is due to the fact that graphite electrode generally adsorbs the substrate more strongly than platinum. Therefore, the results with graphite anode can be accounted for by strong adsorption of the olefins and their cation radicals on the electrode at their β-carbon atoms. This would mean higher concentration of these two species near the electrode surface and will affect their facile combination subsequently, leading to ββ-dimer as a major product.

d) Proton Loss in Cation Radical Reactions

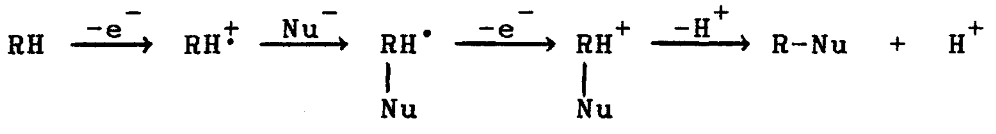
In an anodic oxidation of hydrocarbons, the initial electron-transfer generates a cation radical. This species can transfer a proton to a suitable base in the system to form a radical which subsequently can lose another electron to form a cation. In this case, the reaction is termed ECE.

$$\mathrm{RH} \xrightarrow{-e^-} \mathrm{RH}^{+\bullet} \xrightarrow{-\mathrm{H}^+} \mathrm{R}^{\bullet} \xrightarrow{-e^-} \mathrm{R}^+ \longrightarrow \text{products} \qquad (1)$$

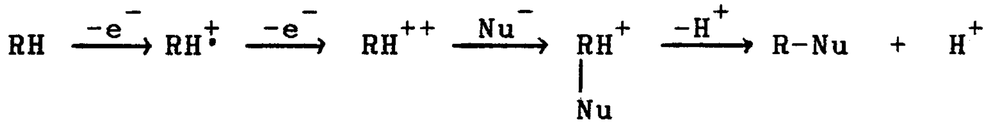
Alternatively, the cation radical can lose a second electron to form a dication which undergoes loss of a proton to form a cation. This mechanism is termed EEC.

$$\mathrm{RH} \xrightarrow{-e^-} \mathrm{RH}^{+\bullet} \xrightarrow{-e^-} \mathrm{RH}^{++} \xrightarrow{-\mathrm{H}^+} \mathrm{R}^+ \longrightarrow \text{products} \qquad (2)$$

For cases like these where the overall reaction requires the transfer of two electrons, the question as to the timing of these two-electron transfers relative to the proton transfer and the attack by the nucleophiles have to be resolved. In such cases, reactions may occur as shown below:



$$\mathrm{RH} \xrightarrow{-e^-} \mathrm{RH}^{+\bullet} \xrightarrow{\mathrm{Nu}^-} \underset{\mathrm{Nu}}{\underset{|}{\mathrm{RH}^{\bullet}}} \xrightarrow{-e^-} \underset{\mathrm{Nu}}{\underset{|}{\mathrm{RH}^{+}}} \xrightarrow{-\mathrm{H}^+} \mathrm{R{-}Nu} + \mathrm{H}^+ \qquad (3)$$



$$\mathrm{RH} \xrightarrow{-e^-} \mathrm{RH}^{+\bullet} \xrightarrow{-e^-} \mathrm{RH}^{++} \xrightarrow{\mathrm{Nu}^-} \underset{\mathrm{Nu}}{\underset{|}{\mathrm{RH}^{+}}} \xrightarrow{-\mathrm{H}^+} \mathrm{R{-}Nu} + \mathrm{H}^+ \qquad (4)$$

In all cases, the rate of deprotonation is dependent on the oxidation potential of the hydrocarbon[12], the strength of the base used[15] and the nature of bonding protons have in the compound i.e., whether they are acidic, allylic or benzylic or whether they are aliphatic.

The electrode studies of the mechanism of deprotonation of a number of arenemethyl cation radicals have been done. Spectroelectrochemical data obtained in acetonitrile during the oxidation of a number of methylbenzenes indicated that the reactions are <u>first order</u> in cation radical and an ECE mechanism involved is as shown in Scheme IX.

<u>Scheme IX</u>

$$\mathrm{Ar{-}CH_3} \xrightarrow{-e^-} \mathrm{(Ar{-}CH_3)^{+\bullet}} \tag{1}$$

$$\mathrm{(Ar{-}CH_3)^{+\bullet}} \longrightarrow \mathrm{Ar{-}CH_2^{\bullet}} + \mathrm{H^+} \tag{2}$$

$$\mathrm{Ar{-}CH_2^{\bullet}} + \mathrm{(Ar{-}CH_3)^{+\bullet}} \longrightarrow \mathrm{Ar{-}CH_2^{+}} + \mathrm{Ar{-}CH_3} \tag{3}$$

$$\mathrm{Ar{-}CH_2^{+}} + \mathrm{Nu} \longrightarrow \text{products} \tag{4}$$

Reaction step (2) was considered the rate determinig step which is chemical step (deprotonation) and is either reversible or irreversible[56] depending on the base present. But, when Barek and co-workers[57] investigated the deprotonation of hexamethylbenzene cation radical in <u>acidic</u> methylene chloride, they noticed that the reaction was <u>second</u>

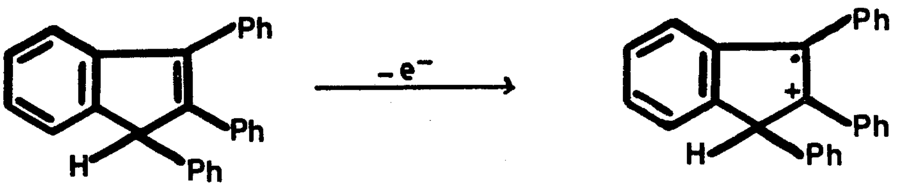
order in cation radical and suggested that the electron-transfer reaction step (3) was the rate-determining step and that reaction step (2) was reversible under acidic conditions. These results prompted Baumberger and Parker[58] to reinvestigate the same reaction in acidic and in neutral acetonitrile and the results indicated a much more complex situation than previously believed. The reaction order in cation radical was observed to be 2 under all conditions and this clearly showed that the mechanism is much more complex than the simple ECE mechanism predicted earlier. It is most likely that the mechanism proposed earlier could still be correct except that in some cases, depending upon the conditions, the electron-transfer step (3) can be rate-determining. In this particular result from Baumberger and Parker's investigation,[58] the use of acetonitrile containing trifluoroacetic acid, or over neutral alumina, ensured that the strongest nucleophile in solution is the solvent (acetonitrile) and it is quite unlikely for reaction step (4) to contribute to the overall rate of reaction.

A further examination of the deprotonation mechanism of hexamethylbenzene by Parker[59] showed that the rate constant is dependent on the substrate concentration and that it increases with concentration. Kinetic data performed on the same substrate indicated an increase in rate constant with decreasing temperature. The same trend was observed when the substrate was fully deuterated.

Illustrative examples showing the rate dependence of deprotonation of the arenemethyl groups on oxidation potential are hexamethylbenzene (E_{ox}=1.52V) and durene (E_{ox}=1.62V) cation radicals. Measurement of these oxidation potentials (versus SCE) was done in acetic acid containing 0.5M sodium acetate. The rate of deprotonation of durene cation radical has been shown to be five times faster than that of hexamethylbenzene.[12] This can be attributed to the stabilization of the cation radical by six methyl groups in the case of hexamethylbenzene as compared to four in durene. For the same reason, mesitylene cation radical (E_{ox}=1.90V) deprotonates much faster than pentamethylbenzene (E_{ox}=1.62V). Thus, the relative rate of deprotonation of arenemethyl cation radicals is in their order of increasing oxidation potentials:

hexamethylbenzene < pentamethylbenzene < durene < mesitylene

In this laboratory, McCullough and Yeroushalmi[15] while investigating the lifetimes of indene cation radical, $\underline{61}^{+\cdot}$ using cyclic voltammetry found that they were dependent on the electrolyte anion especially in non-polar solvents.

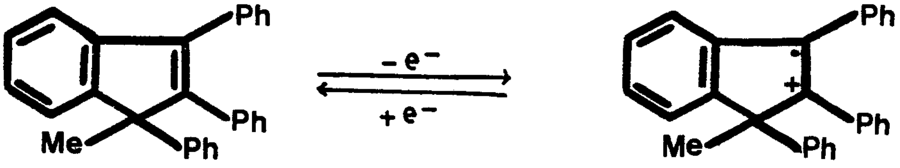


61

$61^{+\cdot}$

The mechanism proposed was that the cation radical, $\underline{61}^{+\cdot}$ loses protons, especially the acidic type, to the electrolyte anion and the rate was dictated by the base strength of these anions. For instance, in 1,2-dichloroethane containing 0.1M perchlorate or triflate anions, the rate of proton loss was faster than when hexafluorophosphate anions were used, as the cyclic voltammetric scans showed irreversibility and reversibility respectively.

A further investigation on the fate of indene cation radicals, $\underline{61}^{+\cdot}$ by the same authors[15] showed that in the absence of acidic proton i.e., when the acidic proton is substituted with a methyl group, $\underline{62}$, the electrode reactions were reversible in both perchlorate and hexafluorophosphate anions.



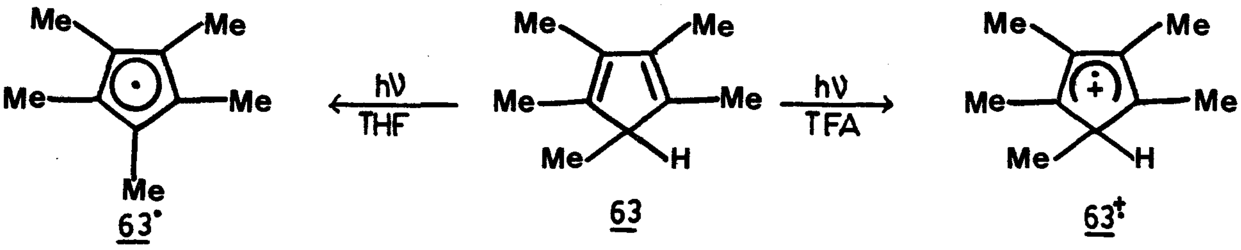
$\underline{62}$ $\underline{62}^{+\cdot}$

On the basis of this observation, the authors[15] proposed that the cation radical, $\underline{62}^{+\cdot}$ was stable in both perchlorate and hexafluorophosphate during the time necessary for cyclic voltammetric scan reversal; and that the rate of deprotonation of $\underline{62}^{+\cdot}$ was reduced considerably compared to $\underline{61}^{+\cdot}$ which possesses acidic protons that can be abstracted easily.

Schlesener and co-workers[12], in their detailed paper on rates and mechanism of proton transfer from transient cation radicals reported that the rate of deprotonation is dependent on the base strength, as well as on the cation radical stability. This was revealed by the results from oxidation of various methylbenzenes in acetonitrile solution containing 0.1M lithium perchlorate and 0.1mM tris(phenanthroline)iron(III) complex. When various substituted pyridines were added as proton acceptors, the rate of deprotonation was observed to increase with increasing strength of the pyridine bases. For instance, the rate of deprotonation of hexamethylbenzene cation radical was found to be faster in 4-methyoxypyridine ($k=22$ $M^{-1}s^{-1}$) than in 3-cyanopyridine ($k=13$ $M^{-1}s^{-1}$). This is in keeping with the fact that 4-methoxypyridine is a stronger base due to the methoxy group which donates the electrons to the ring, creating a higher electron density around the nitrogen, whereas in 3-cyanopyridine, the cyano group withdraws electrons rendering it less basic.

Besides the strength of the pyridine bases, the same authors[12] found that the positions of the substituent on the pyridine ring played a role in the rate of deprotonation of methylbenzene cation radicals. For instance, hexamethylbenzene cation radical deprotonates faster in 4-methylpyridine ($k=16$ $M^{-1}s^{-1}$) than in 2-methylpyridine base ($k=12$ $M^{-1}s^{-1}$). This may be attributed to the fact that the nitrogen atom, which plays an important role in the abstraction of the protons, suffers more steric effect in 2-methyl than in 4-methyl-substituted pyridines and hence is less basic.

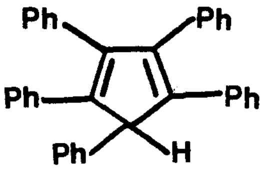
Compounds such as pentamethylcyclopentadiene, 63, when irradiated with U.V. light in liquid solution result in homolysis of the C-H bond to give the pentamethylcyclopentadienyl radical, 63$^{\bullet}$, and molecular hydrogen. Davies and Lusztyk[60] reported an esr spectrum of 63$^{\bullet}$ to consist of 14 of the 16 predicted lines due to proton couplings; the other two lines (first and last) could not be observed due to low intensity.



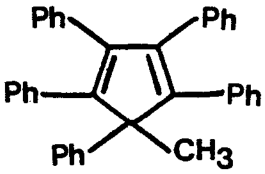
More recently, Courtneidge and coworkers[61] reported that when 61 was irradiated with U.V. light (unfiltered, or filtered through pyrex glass) using trifluoroacetic acid as solvent at -10°C, a different species which also exhibited an esr spectrum was observed. The spectrum was simulated using the hyperfine coupling constants a(6H) 15.0, a(6H) 4.0, a(1H) 1.6, a(3H) 0.8 Gauss and this was assigned to pentamethylcyclopentadiene cation radical, 63$^{+\bullet}$. This spectrum was found to be similar to esr spectrum of cyclopentadiene cation radical obtained from γ-radiolysis of cyclopentadiene in a matrix of trichlorofluoromethane.[62] So most organic cation radicals can be regarded as the conjugate acids of neutral radicals which are usually more familiar and the equilibrium can be expressed as follows:

$$R^{\bullet} + H^{+} \rightleftharpoons RH^{+\bullet}$$

In order to further investigate the dependence of reaction pathways of aromatic olefins on the strength of the electrolyte anions and on the kind of protons present in the compound, it was decided the electro-oxidation of 1,2,3,4,5-pentaphenylcyclopentadiene, 64 and 1,2,3,4,5-pentapheny-l-methylcyclopentadiene, 65 in non-polar aprotic solvents be investigated, and the electrolysis products be identified as evidence for the reaction mechanism.



64



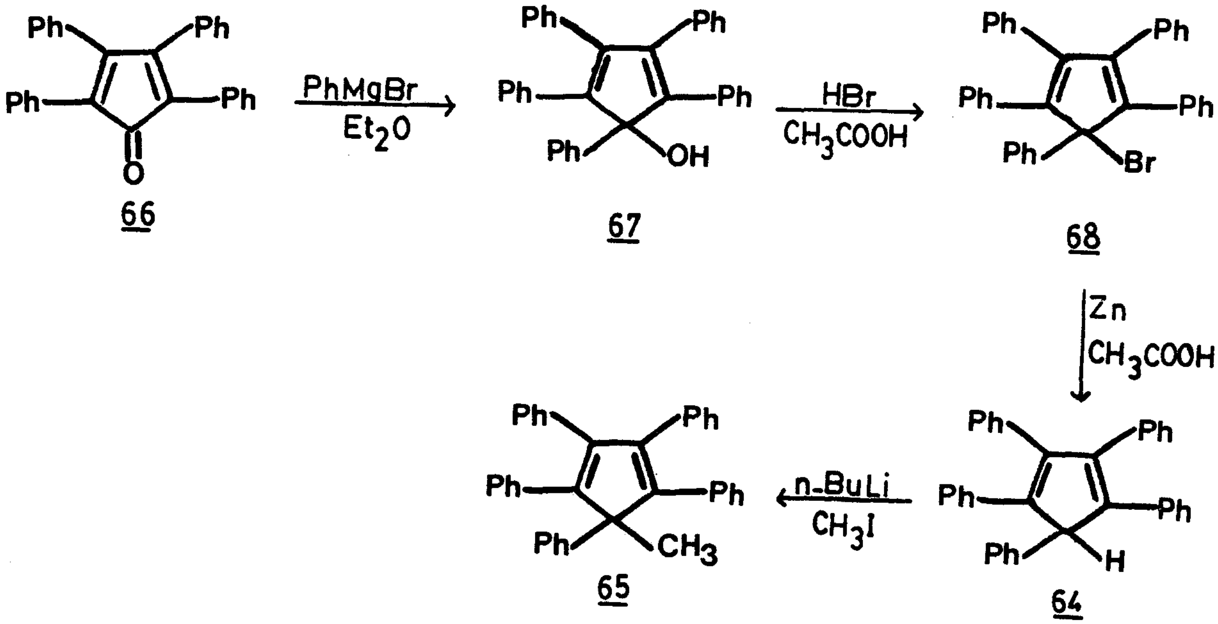
65

II RESULTS

A. Synthesis of 1,2,3,4,5-pentaphenylcyclopentadiene, 64 and 1,2,3,4,5-pentaphenyl-1-methylcyclopentadiene, 65

The two hydrocarbons of interest, 64 and 65 were synthesized from tetraphenylcyclopentadienone, 66 according to the following synthetic scheme (Scheme X)

Scheme X



i) Conversion of tetraphenylcyclopentadienone, 66 to 1,2,3,4,5-pentaphenylcyclopentadienol, 67

The procedure followed was similar to that described by Kieslich and Kurreck[63] and by Ziegler and Schnell.[64] Treatment of tetraphenylcyclopentadienone, 66, with phenylmagnesium bromide (Grignard reagent) resulted in the formation of light yellow crystals of 1,2,3,4,5-pentaphenylcyclopentadienol, 67 in a 93.2% yield. A melting point, 174-175°C was comparable to that reported by Ziegler and Schnell[64] (175-176°C) and the infra red spectrum showed evidence for an O-H bond with an absorption band at 3600cm^{-1}, which is characteristic of a tertiary alcohol, normally around 3620cm^{-1}.[65] The absence of an absorption band at 1675cm^{-1} [65] was a clear indication that there was no residual precursor, 66, in the product.

A ^{1}H nmr exhibited a singlet at 2.44 ppm corresponding to a resonance signal of a proton attached to oxygen, which generally absorbs in the 0.5-5.0 ppm region[65] and two complex multiplets enveloped at 6.9-7.65 ppm region.[65]

A mass spectrum, m/e = 462 corresponded to molecular formula, $C_{35}H_{26}O$.

ii) Conversion of 1,2,3,4,5-pentaphenylcyclopentadienol, 67 to 1,2,3,4,5-pentapenylcyclopentadienyl bromide, 68

Treatment of 1,2,3,4,5-pentaphenylcyclopentadienol, 67 with hydrogen bromide in glacial acetic acid resulted in the formation of orange yellow crystals of 1,2,3,4,5-pentaphenylcyclopentadienyl bromide, 68 in a 91.7% yield. The crystals turned lemon-yellow upon recrystallization from benzene-petroleum ether. A melting point, 186-188°C corresponded quite closely to that reported by Ziegler and Schnell[64] (188-189°C) and the absence of an O-H absorption band around 3600cm^{-1} in the infrared spectrum was a clear indication that there was no precursor alcohol, 67 in the product.

A ^1H nmr exhibited only two complex multiplets enveloped in the 6.8-7.5ppm region corresponding to phenylic proton resonances normally at 6.5-8.3ppm region.[65]

A mass spectrum, m/e=524 and elemental analysis (C, 80.05%; H, 5.01%; Br, 15.4%) was in agreement with molecular formula, $C_{35}H_{25}Br$. An earlier attempt to prepare the bromide, 68 by dissolving the alcohol, 67 in benzene instead of ethyl acetate before treating with hydrogen bromide in glacial acetic acid was unsuccessful. No crystals were formed even after stirring overnight and chilling. Apparently, if benzene is to be used as solvent, gaseous hydrogen bromide should be used instead of hydrogen bromide solution in glacial acetic acid.

iii) Conversion of 1,2,3,4,5-pentaphenylcyclopentadienyl bromide, 68 to 1,2,3,4,5-pentaphenylcyclopentadiene, 64

The procedure followed for reducing the bromide, 68 to the hydrocarbon 64 was similar to that described by Ziegler and Schnell.[64] The reaction involved treatment of 1,2,3,4,5-pentaphenylcyclopentadienyl bromide, 68 with hot glacial acetic acid in presence of zinc dust, and on filtration of the hot solution to remove excess zinc, pale yellow crystals precipitated upon cooling. A yield of 35.4% was rather low and attempts to improve it by heating the contents for a longer period were fruitless. No attempt was made to use stronger reducing agents such as lithium aluminium hydride ($LiAlH_4$) or sodium borohydride ($NaBH_4$).A melting point, 251-253°C corresponded quite well with that reported by Breslow and co-workers[66], and although Ziegler and Schnell[64] reported a melting point which was rather low (244-246°C), all the other experimental evidences were in agreement with the structure of the compound of interest.

A ^1H nmr exhibited two resonance signals, a singlet at 5.07ppm which is characteristic of allylic proton resonance, and a complex multiplet at 7.0-7.5ppm corresponding to phenylic proton resonances.A mass spectrum, m/e=446 and elemental analysis (C, 93.78%; H, 6.18%) were in agreement with the molecular formula, $C_{35}H_{26}$, corresponding to 64.

iv) Conversion of 1,2,3,4,5-pentaphenylcyclopentadiene, 64 to 1,2,3,4,5-pentaphenyl-1-methylcyclopentadiene, 65

The procedure used was similar to that described by Giuseppe and co-workers[67] which involved treatment of 1,2,3,4,5-pentaphenylcyclopentadiene, 64 with n-butyllithium to generate an anion of 64 resulting from the loss of the acidic proton. This was then quenched with methyl iodide and after work-up, the product was chromatographed (silica gel-petroleum ether/benzene) and recrystallized from absolute ethanol to give white crystals; yield, 81.1% and melting point, 157-158°C. A ^1H nmr exhibited four resonance signals, a singlet at 1.43ppm which corresponded to aliphatic proton resonance (CH_3) and three multiplets at 6.65-6.8, 6.81-7.12 and 7.13-7.33 ppm regions which corresponded to three kinds of phenylic proton resonances. Unlike the precursor hydrocarbon, 64, the phenylic proton resonances were found at higher field and their equivalence had been reduced; both factors being attributed to the introduction of the methyl group. A mass spectrum of the parent ion at m/e=460 and elemental analysis (C, 93.8%; H, 6.1%) were in agreement with the molecular formula, $C_{36}H_{28}$, which corresponded well with hydrocarbon 65.

B. Electrochemical Oxidation of 1,2,3,4,5-pentaphenylcyclopentadiene, 64

The electrochemical oxidation mechanism of 1,2,3,4,5-pentaphenylcyclopentadienyl 64, was studied using a Cyclic Voltamograph (CV-27) and a three-electrode cell equipped with a platinum bead (working electrode), a platinum wire (auxilary electrode) and a standard calomel (mercury/mercurous chloride) reference electrode. The current-voltage measurements which were recorded on a X-Y recorder were used directly, due to inavailability of positive feed-back device to compensate for ohmic resistance (iR) of the solution, and the only precaution taken was to place the working electrode as close as possible to the reference electrode. Since all the measurements were done at room temperature, the ohmic drop is expected to be quite significant especially in non-polar solvents such as 1,2-dichloroethane. This is in contrast with low temperature (-70°C) cyclic voltammetry which can be done without any compensation yet no significant ohmic drop is observed.[68]

When cyclic voltammetric oxidation of 1,2,3,4,5-pentaphenylcyclopentadiene, 64 was performed in anhydrous 1,2-dichloroethane containing 0.1M tetra-n-butylammonium hexafluorophosphate ($TBA^+PF_6^-$), anodic waves (+1.30 - +1.36V) and correspondingly, upon scan reversal, cathodic waves (+1.12 - +1.17V) were observed when the scan rates were varied over a wide range (50-1000 mV/sec). No reversal cathodic waves were observed for scan rates less than 30 mV/sec, instead, a new small cathodic wave was observed around 0.0V region (Fig. I).

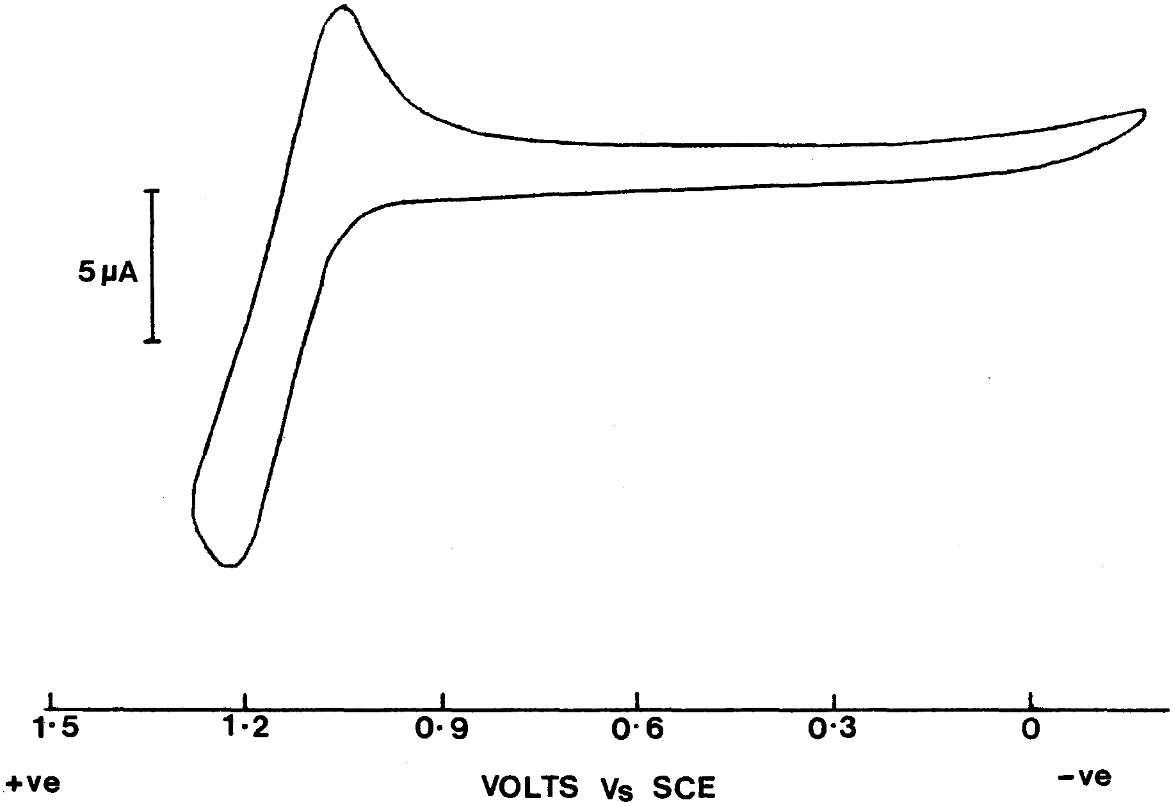


Figure I. Cyclic voltammetric wave of 1,2,3,4,5-pentaphenylcyclopentadiene (1.5mM) in deoxygenated 1,2-dichloroethane containing tetra-n-butylammonium hexafluorophosphate (0.1M), scanned positive first from -0.2V, at 500 mV/sec. Anodic current is shown as negative peak, and 1cm represents 2.5μA in the vertical scale.

The anode peak current, i_{pa} was observed to increase with scan rate and the peak potentials, E_{pa} and E_{pc} showed some slight dependence on the scan rate. The results of cyclic voltammetric oxidation of 1,2,3,4,5-pentaphenylcyclopentadiene, <u>64</u> in 1,2-dichloroethane containing $TBA^+PF_6^-$ (0.1M) are as shown in Table 1.

<u>Table 1</u>

Scan rate, ν, mV/sec	$\nu^{1/2}$, $(V/sec)^{1/2}$	i_{pa}, Amp.x10^{-5}	E_{pa}, V vs SCE	E_{pc}, V vs SCE
1000	1.00	2.09	1.36	1.12
500	0.71	1.60	1.33	1.14
200	0.45	1.13	1.31	1.16
50	0.22	0.70	1.30	1.17
25	0.16	0.63	1.28	-

Under the conditions for a single reversible electrode process and semi-infinite linear diffusion to a planar electrode of constant surface area, the instantaneous current is given by the Randles-Sevcik equation.[69]

$$i_p = 2.69 \times 10^5 \, n^{3/2} \, A \, C \, D^{1/2} \, \nu^{1/2}$$

This equation shows that the peak current, i_p of a reversible process is directly proportional to the square root of the potential scan rate. When this plot was done for the results in Table I, a straight line with a correlation coefficient of unity and an intercept of 0.334 x 10^{-5} amp was obtained as shown in Figure II.

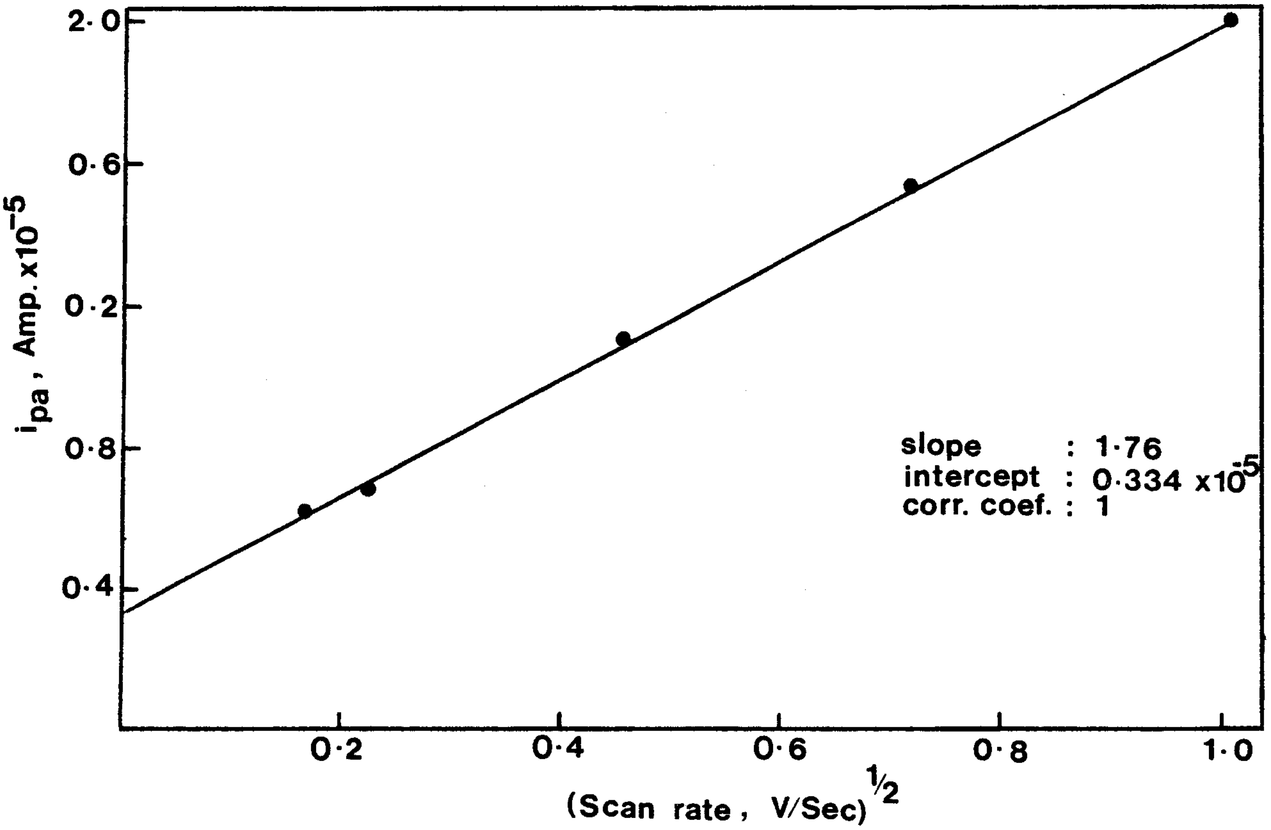


Figure II Plot of anodic peak current, i_{pa} versus square root of potential scan rate, $\nu,^{1/2}$ for 1,2,3,4,5-pentaphenylcyclopentadiene, 64, (1.5mM) in 1,2-dichloroethane containing tetra-n-butylammonium hexafluorophosphate (0.1M).

Another useful diagnostic phenomenon for a revesible process is that the peak potentials, E_{pa} and E_{pc} should not be dependent on voltage scan rate.[69] From the results in Table I, some slight change in peak potentials of the order of 60mV was observed over a 20-fold increase in scan rate.

In order to further investigate this slight dependence of peak potential on the scan rate, a study of 9,10-diphenylanthracene, which has been established to undergo single reversible process,[78] was done under the same conditions and concentration and the results are as shown in Table II.

Table II

Scan rate, ν, mV/sec	ν, $^{1/2}$ $(V/sec)^{1/2}$	i_{pa}, Amp.x10^{-5}	E_{pa}, V vs SCE	E_{pc}, V vs SCE
1000	1.00	2.00	1.32	1.09
500	0.71	1.55	1.30	1.10
200	0.45	1.05	1.28	1.11
50	0.22	0.55	1.25	1.13
25	0.16	0.44	1.24	1.14

Anodic waves (+1.24 - +1.32V) and corresponding cathodic waves (+1.09 - +1.14V) were observed over a wide range of scan rates (Fig. III), and no cathodic wave around 0.0V was observed even at scan rates less than 25mV/sec.

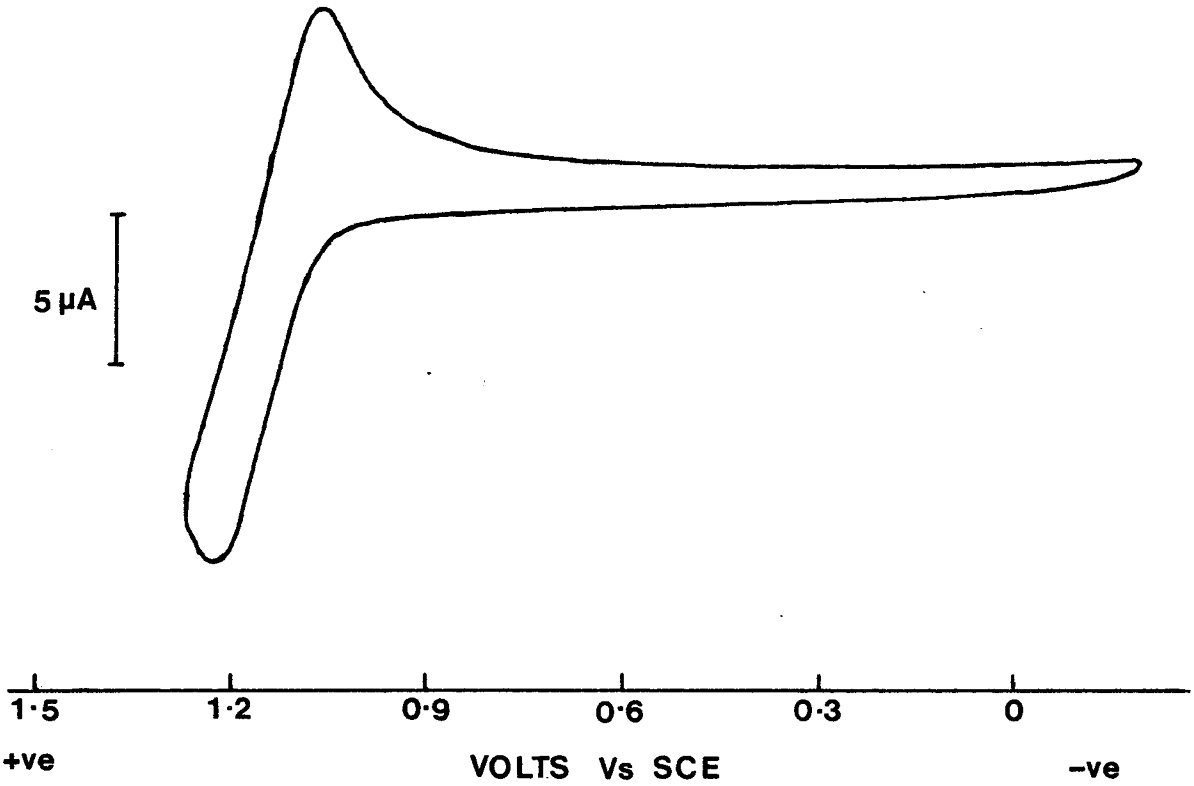


Figure III. Cyclic voltammetric wave of 9,10-diphenylanthracene (1.5mM) in deoxygenated 1,2-dichloroethane containing tetra-n-butylammonium hexafluorophosphate (0.1M) scanned positive first from −0.2V at 500 mV/sec. Anodic current is shown as negative peak, and 1cm represents 0.5μA in the vertical scale.

A plot of anodic peak current, i_{pa} versus square root of voltage scan rate gave a straight with correlation coefficient of 0.999 and an intercept of 0.106×10^{-5} amp which was in agreement with Randles-Sevcik equation[69] for a single reversible process. A slight change in peak potentials of the order of 70mV was observed over a 20-fold increase in scan rate, and this was comparable with that observed for 1,2,3,4,5-pentaphenylcyclopentadiene, 64. These two results suggest that the electrode processes of 64 in 1,2-dichloroethane containing tetra-n-butylammonium hexafluorophosphate are similar to those of 9,10-diphenylanthracene and are reversible especially at scan rates greater than 30mV/sec.

However, when cyclic voltammetric oxidation of 1,2,3,4,5-pentaphenylcyclopentadiene, 64, was done in anhydrous 1,2-dichloroethane containing tetra-n-butylammonium perchlorate ($TBA^+ClO_4^-$) or tetra-n-butylammonium trifluoromethanesulfonate ($TBA^+OT_f^-$), anodic waves at +1.31 - +1.51V region were observed and the reversal cathodic waves were either very small or completely absent. Instead, new cathodic waves around 0.0V appeared when the scan rates were varied over a wide range (Figure IV).

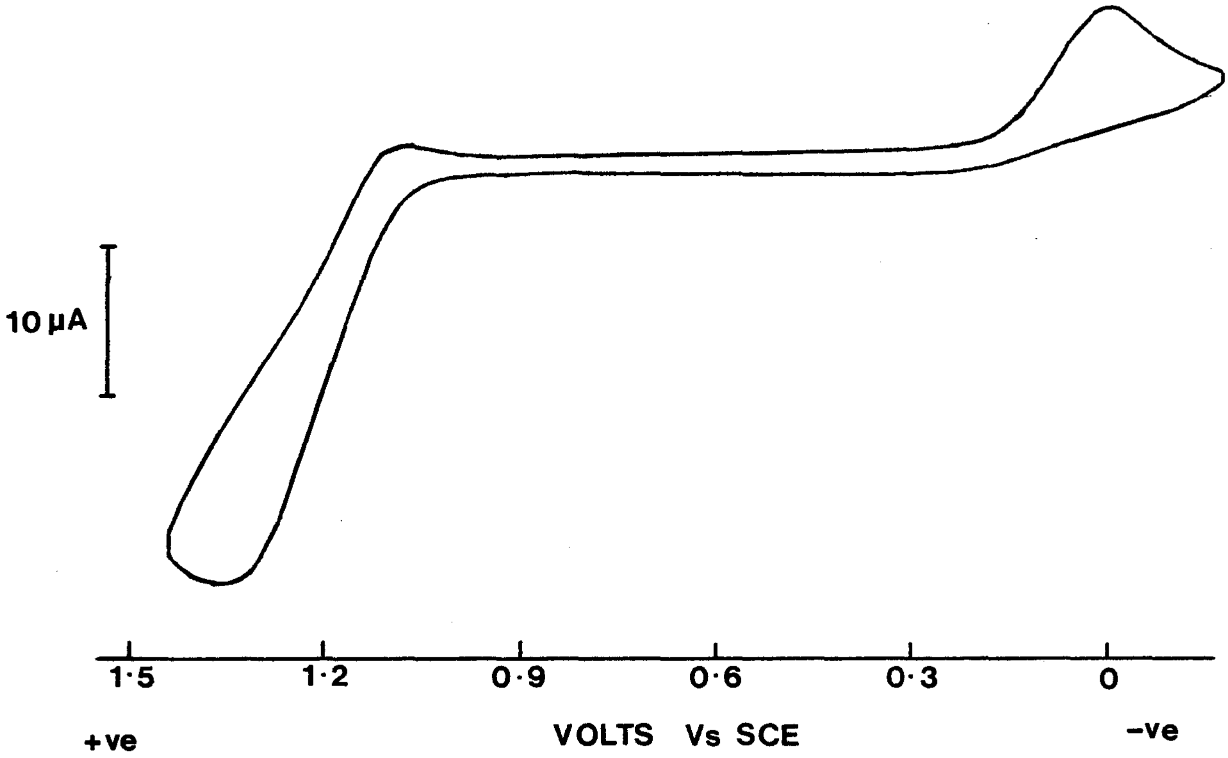


Figure IV. Cyclic voltammetric wave of 1,2,3,4,5-pentaphenylcyclopentadiene (1.5mM) in deoxygenated 1,2-dichloroethane containing tetra-n-butylammonium perchlorate (0.1M) scanned positive first from -0.2V at 500mV/sec. Anodic current is shown as negative peak, and 1cm represents 5μA in the vertical scale.

For a totally irreversible process, there is no direct relationship between anodic peak current, i_{pa} and the scan rate, ν corresponding to the Randles-Sevcik equation,[69] and also the anodic peak potential, E_{pa} is dependent on the scan rate. The results for 1,2,3,4,5-pentaphenylcyclopentadiene, 64 in anhydrous 1,2-dichloroethane containing tetra-n-butylammonium perchlorate ($TBA^+ClO_4^-$) are as shown in Table III.

Table III

Scan rate, ν, mV/sec	$\nu^{1/2}$, $(V/sec)^{1/2}$	i_{pa}, Amp.x10^{-5}	E_{pa}, V vs SCE
1000	1.00	3.75	1.51
500	0.71	3.25	1.40
200	0.45	2.50	1.38
50	0.22	1.40	1.31

When anodic peak current, i_{pa} was plotted versus square root of voltage scan rate, a curve (Figure V) was obtained.

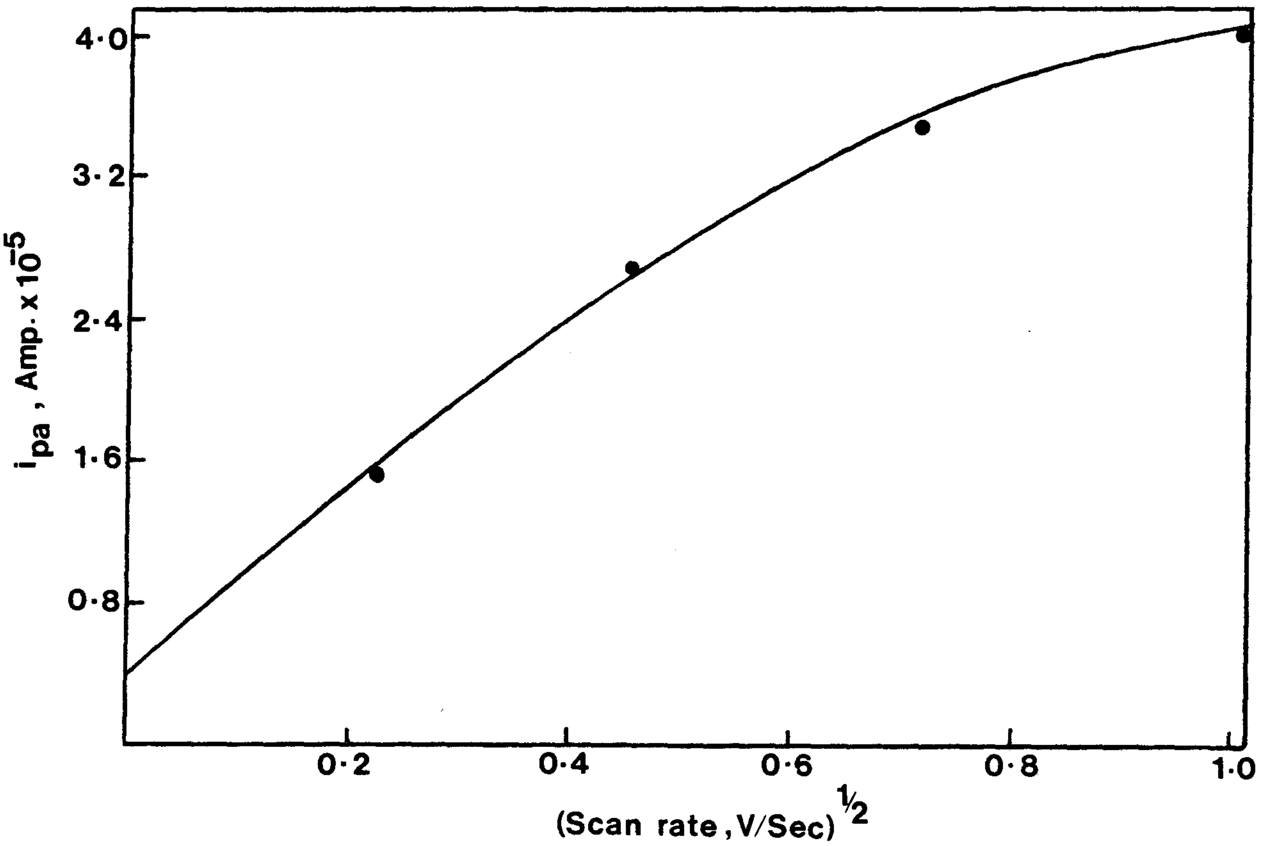


Figure V Plot of anodic peak current, i_{pa} versus square root of potential scan rate, $\nu^{1/2}$ for 1,2,3,4,5-pentaphenylcyclopentadiene, 64 (1.5mM) in 1,2-dichloroethane containing tetra-n-butylammonium perchlorate (0.1M).

This indicated that there is no direct relationship between anodic peak current and square root of potential scan rate. The anodic peak potential, E_{pa} was observed to change considerably with voltage scan rate, and for a 20-fold increase in scan rate, this change in anodic peak potential was of the order of 200mV, while the peak potential of the wave at 0.0V shifted to more negative potential. These results suggest an irreversible electrode oxidation.

When cyclic voltammetric oxidation 1,2,3,4,5-pentaphenylcyclopentadiene <u>64</u> was done in 1,2-dichloroethane containing tetra-n-butylammonium tetrafluoroborate ($TBA^{+}BF_{4}^{-}$), anodic waves (+1.43 - +1.52V) and correspondingly, upon scan reversal, cathodic waves (+1.23 - +1.27V) were observed when the potential scan rates were varied over a wide range (50-1000mV/sec). These cathodic waves were smaller (lower cathodic peak current) than when tetra-n-butylammonium hexafluorophosphate ($TBA^{+}PF_{6}^{-}$) was used. Small cathodic waves were also observed around 0.0V (Figure VI).

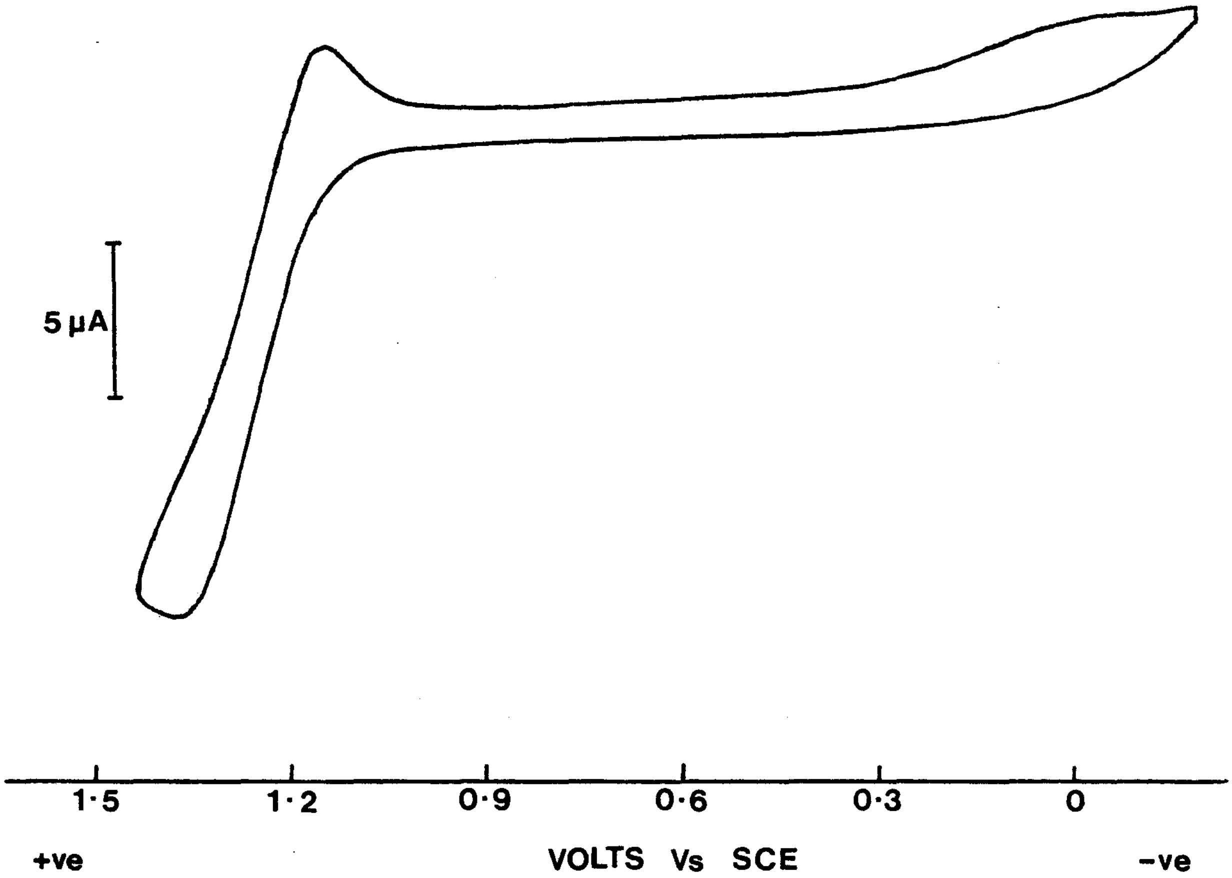


Figure VI

Cyclic voltammetric wave of 1,2,3,4,5-pentaphenylcyclopentadiene (1.5mM) in deoxygenated 1,2-dichloroethane containing tetra-n-butylammonium tetrafluoroborate (0.1M) scanned positive first from -0.2V at 500mV/sec. Anodic current is shown as negative peak, and 1cm represents 2.5μA in the vertical scale.

The results are shown in Table IV.

Table IV

Scan rate, ν, mV/sec	$\nu,^{1/2}$ $(V/sec)^{1/2}$	i_{pa}, Amp.x10^{-5}	E_{pa}, V vs SCE	E_{pc}, V vs SCE
1000	1.00	2.25	1.52	1.23
500	0.21	2.00	1.50	1.25
200	0.45	1.58	1.48	1.26
50	0.22	1.05	1.43	1.27
25	0.16	0.80	-	-

For an irreversible or quasi-reversible oxidation process, there is no direct relationship between anodic peak current, i_{pa} and the square root of voltage scan rate corresponding to Randles-Sevcik equation[69], and the peak potentials vary significantly with scan rate.

When anodic peak current, i_{pa} was plotted versus square root of scan rate, $\nu,^{1/2}$ it gave a curve (Figure VII).

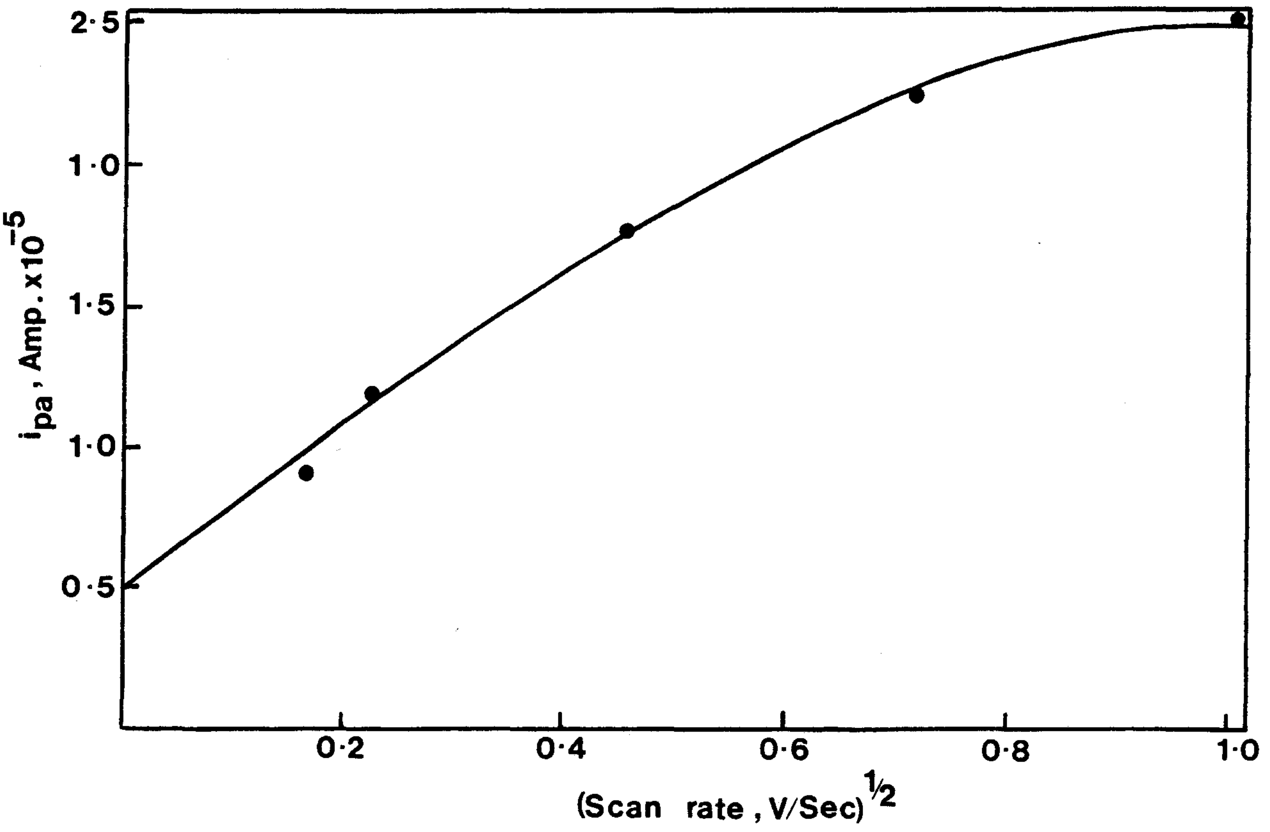


Figure VII

Plot of anodic peak current, i_{pa} versus square root of potential scan rate, ν,$^{1/2}$ for 1,2,3,4,5-pentaphenylcyclopentadiene, 64 (1.5mM) in 1,2-dichloroethane containing tetra-n-butylammonium tetrafluoroborate (0.1M).

The anodic peak potential, E_{pa} was observed to increase by about 100mV for a 20-fold increase in the voltage scan rate. These two results suggest an irreversible or guasireversible electrode process, but the fact that the cathodic waves were smaller than their corresponding anodic waves and not completely absent indicates that the oxidation is guasi-reversible.

However, when cyclic voltammetric oxidation of 1,2,3,4,5-pentaphenylcyclopentadiene, 64 was carried out in anhydrous acetonitrile containing any of the four electrolytes viz., tetra-n-butylammonium perchlorate ($TBA^+ClO_4^-$), teta-n-butylammonium trifluoromethanesulfonate ($TBA^+OT_f^-$), tetra-n-butylammonium tetrafluoroborate ($TBA^+BF_4^-$) and tetra-n-butylammonium hexafluorophosphate ($TBA^+PF_6^-$), the results were all similar. Anodic waves were observed with complete absence of the reversal cathodic waves. The cathodic waves around 0.0V were also observed in all cases and these suggest irreversible oxidation processes for all four supporting electrolytes in acetonitrile.

When cyclic voltammetric oxidation of 1,2,3,4,5-pentaphenyl-1-methylcyclopentadiene, 65 was investigated in anhydrous 1,2-dichloroethane containing any of the four supporting electrolytes viz., $TBA^+ClO_4^-$, $TBA^+OT_f^-$, $TBA^+BF_4^-$ or $TBA^+PF_6^-$, the scan waves were all similar. When $TBA^+PF_6^-$ was used, anodic waves (+1.27 - +1.36V) and correspondingly, upon scan reversal, cathodic waves (+1.12 - +1.17V) were observed when the scan rates were varied over a wide range (25-1000mV/sec), and no cathodic waves around 0.0V were observed even at scan rates lower than 25mV/sec (Fig.VIII).

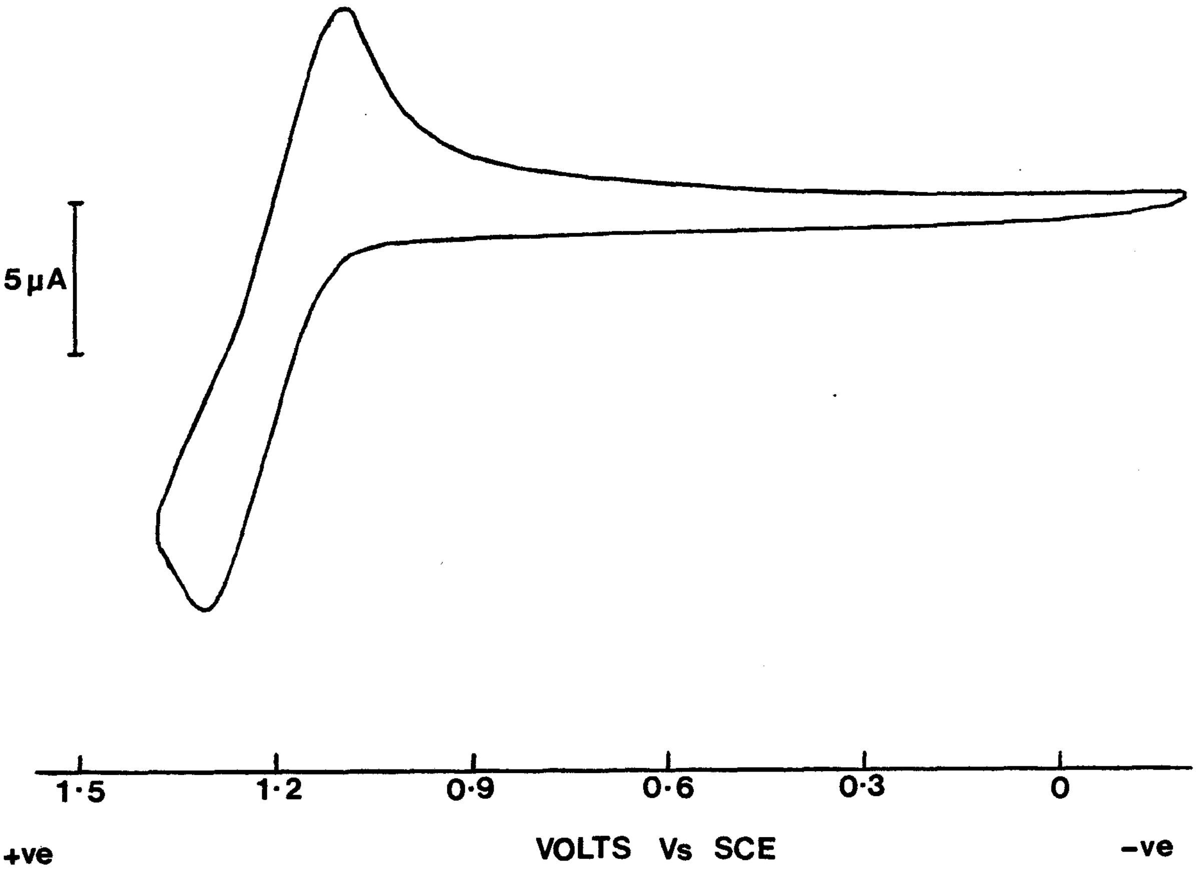


Figure VIII

Cyclic voltammetric wave of 1,2,3,4,5-pentaphenyl-1-methylcyclopentadiene, 65 (1.5mM) in deoxygenated 1,2-dichloroethane containing tetra-n-butylammonium hexafluorophosphate (0.1M) scanned positive first from -0.2V at 500mV/sec. Anodic current is shown as negative peak, and 1cm represents 2.5μA in the vertical scale.

The results are shown in Table V.

Table V

Scan rate, ν, mV/sec	$\nu^{1/2}$, (V/sec)$^{1/2}$	i_{pa}, Amp.x10^{-5}	E_{pa}, V vs SCE	E_{pc}, V vs SCE
1000	1.00	2.14	1.36	1.12
500	0.71	1.61	1.34	1.13
200	0.43	1.08	1.31	1.15
50	0.22	0.58	1.28	1.17
25	0.16	0.43	1.27	1.17

A plot of anodic peak current, i_{pa} versus square root of scan rate, $V^{1/2}$, gave a straight line with correlation coefficient of 0.999 and an intercept of 0.133 x 10^{-5}amp. which was in agreement with Randles-Sevcik equation[69] for reversible processes.

A slight change in peak potential of about 80mV for a 20-fold increase in scan rate was comparable to that obtained for 9,10-diphenylanthracene, which was investigated under similar conditions, and these results suggest that the electrode processes of 1,2,3,4,5-pentaphenyl-1-methylcyclopentadiene, 65 in any of the four mentioned electrolytes, are reversible.

When anhydrous acetonitrile was used as a solvent, the cyclic voltammetric scans of <u>65</u> in any of the four electrolytes (TBA^+ClO_4, $TBA^+OT_f^-$, $TBA^+BF_4^-$ or $TBA^+PF_6^-$) were similar to those obtained for 1,2-dichloroethane. This indicated that even in a strongly polar solvent such as acetonitrile, the electrode processes of <u>65</u> in all four supporting electrolytes are reversible.

On the other hand, cyclic voltammetric oxidation of 1,2,3,4,5-pentaphenylcyclopentadiene, <u>64</u> and 1,2,3,4,5-pentaphenyl-1-methylcyclopentadiene, <u>65</u> in anhydrous 1,2-dichloroethane containing tetra-n-butylammonium nitrate ($TBA^+NO_3^-$) did not show any difference in their reaction pathways. Both showed anodic waves with complete absence of reversal cathodic waves. Figure IX shows cyclic voltammetric oxidation wave of <u>65</u>.

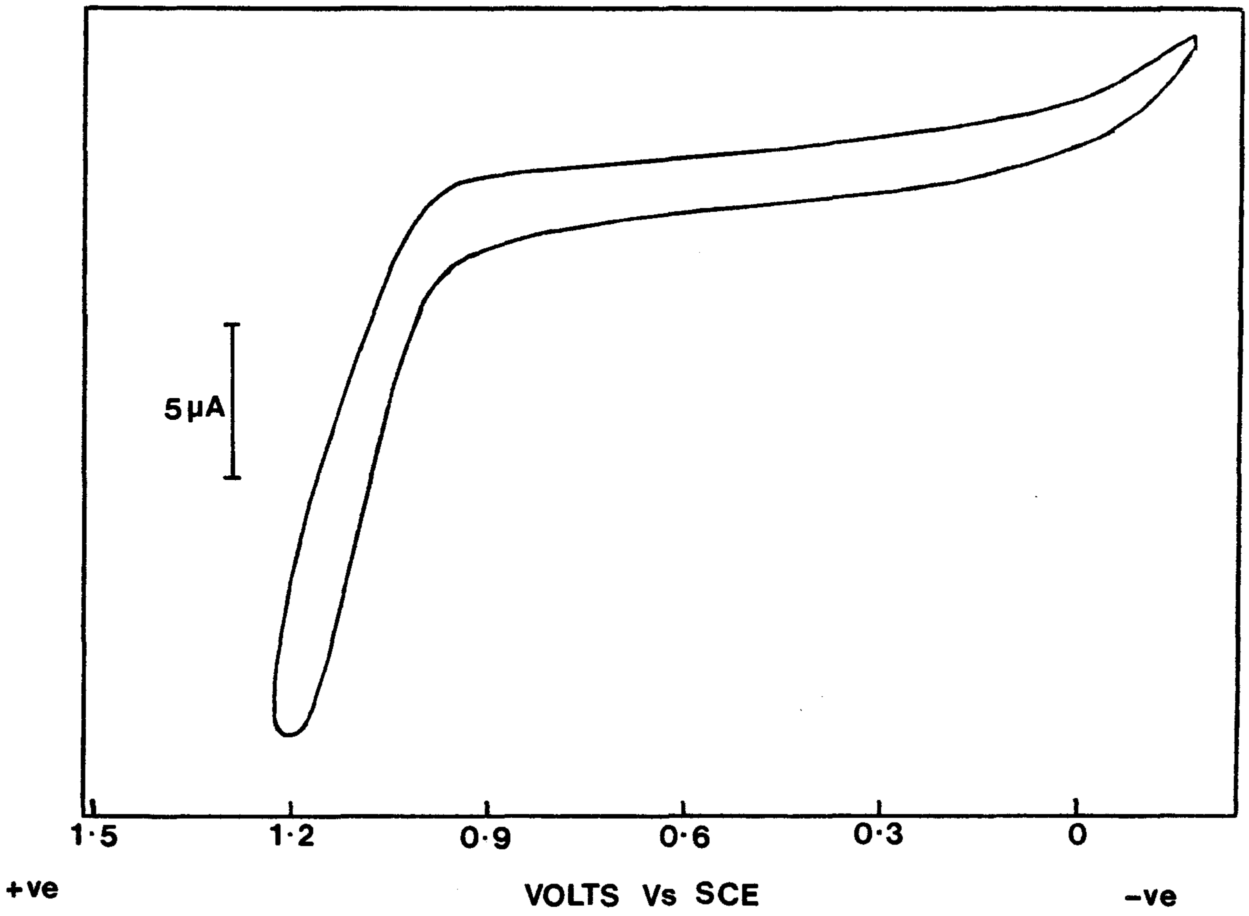


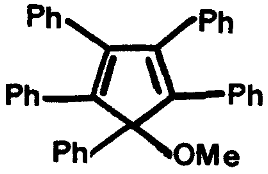
Figure IX

Cyclic voltammetric wave of 1,2,3,4,5-pentaphenyl-1-methylcyclopentadiene (1.5mM) in deoxygenated 1,2-dichloroethane containing tetra-n-butylammonium nitrate (0.1M) scanned positive first from -0.2V at 500mV/sec. Anodic current is shown as negative peak and 1cm represents 2.5μA in the vertical scale.

This result suggests an irreversible electrode process and it probably means that the nitrate anion is acting as a nucleophile rather than a base.

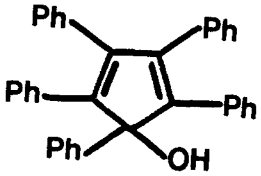
C. Controlled Potential Electrolysis of 1,2,3,4,5-pentaphenylcyclopentadiene, 64

Controlled potential electrolysis of 64 at 1.42V in anhydrous 1,2-dichloroethane containing tetra-n-butylammonium perchlorate ($TBA^+ClO_4^-$) under argon gave a reddish solution (λ_{max} 530nm) after a charge equivalent to 2 faradays had been passed through. When this solution was immediately quenched with anhydrous methanol, it afforded methyl ether 69 as the major product.



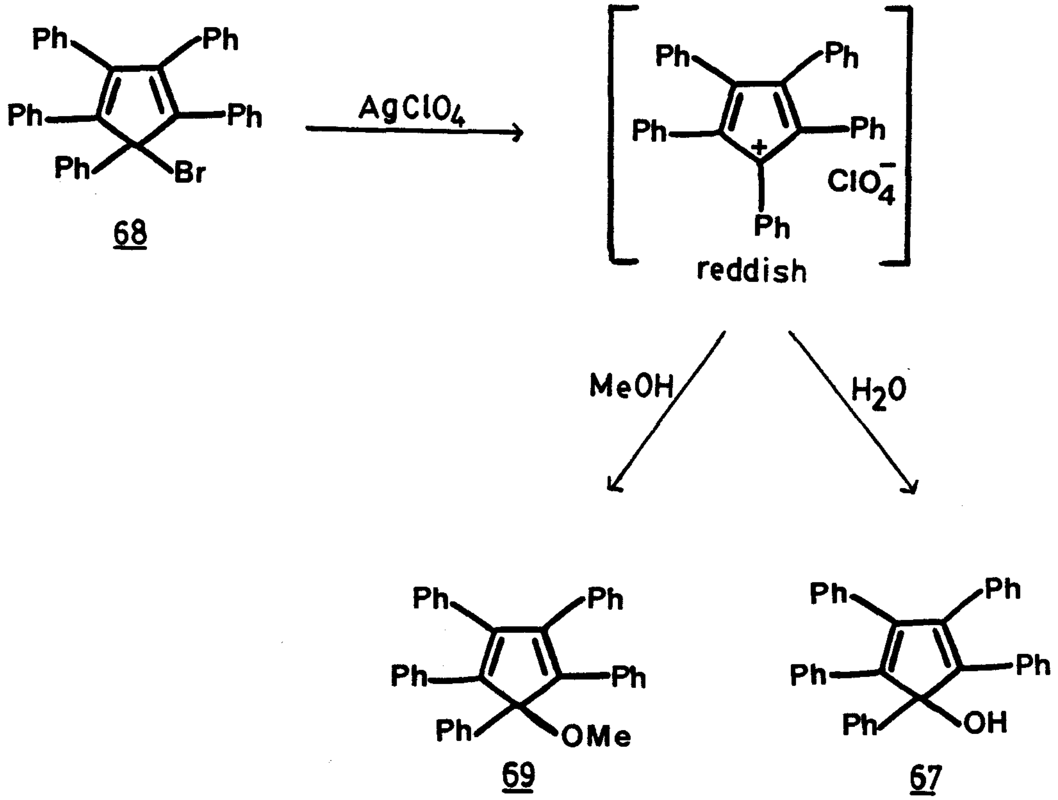
69

This was identified by mass spectrum which showed a parent ion at m/e=476, corresponding to molecular formula, $C_{36}H_{28}O$, and by HPLC comparison with an authentic sample. No dimers nor other significant products were observed. When water was used to quench similar reddish electrolyzed liquor of 64, the only significant product isolated was alcohol, 67.



67

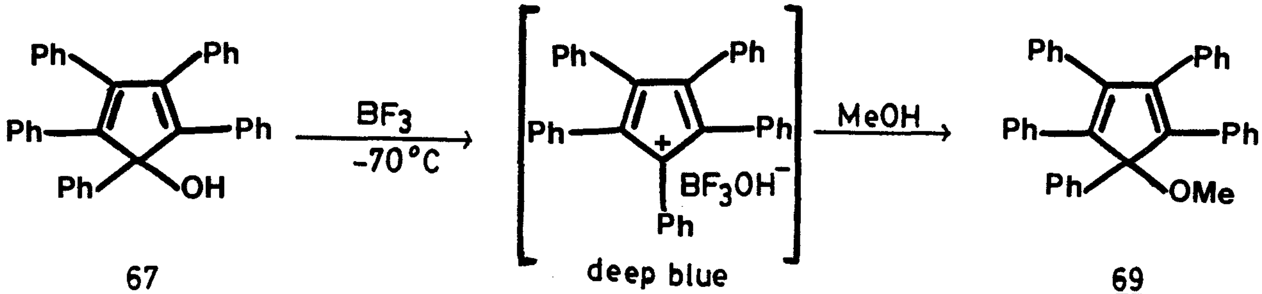
This was identified by infrared and HPLC comparison with an authentic sample and by mixed melting point. The products isolated from the two quenching experiments suggest the reactive species in the reddish solution to be a cation, from the way it reacted with methanol and water. In order to confirm it, a different chemical approach to generate the cation was employed. A solution of 1,2,3,4,5-pentaphenylcyclopentadienyl bromide, 68, in anhydrous 1,2-dichloroethane was treated with silver perchlorate ($AgClO_4$) in anhydrous benzene under dry nitrogen and in presence of excess tetra-n-butylammonium perchlorate ($TBA^+ClO_4^-$). After filtering the precipitate of silver bromide, the reddish cationic solution which fades quite fast at ordinary atmospheric conditions or in absence of excess perchlorate anions, was immediately quenched with anhydrous methanol. The only significant product isolated was methyl ether, 69 which was identified by means mentioned earlier.



When a similar reddish cation solution was quenched with water, it subsequently afforded alcohol, 67 as the only significant isolated product.

These results suggest that the reddish electrolyzed liquor of 64 was cationic intermediate which was only stable under inert environment (argon) and in presence of excess perchlorate anions.

When a solution of 1,2,3,4,5-pentaphenylcycyopentadienol, 67 in anhydrous methylene chloride at $-70^{o}C$ was treated with gaseous boron trifluoride, a deep blue solution was obtained.



67

69

Although the colour of the cation solution obtained in this experiment was deep blue as compared to the reddish electrolyzed liquor, it still afforded methyl ether, 69 as the major product when it was quenched with precooled anhydrous methanol. When the deep blue solution was left to warm to room temperature in an inert environment and in the presence of excess perchlorate anions, no methyl ether, 69 was detected upon quenching the warm solution with anhydrous methanol. Instead, some polar compounds were observed by HPLC and no attempts were made to identify any of them. This was in agreement with the earlier report by Breslow and co-workers[66] who suggested the compounds to be some fluorinated materials. This result indicated that, in the presence of boron trifluoride, the cation solution in methylene chloride is not stable at room temperature even in the presence of excess perchlorate anions and under inert atmosphere.

Controlled potential electrolysis of 1,2,3,4,5-pentaphenyl-1-methylcyclopentadiene, 65 in anhydrous 1,2-dichloroethane containing tetra-n-butylammonium perchlorate ($TBA^+ClO_4^-$) under argon, gave navy blue solution after several minutes and turned greenish brown after a charge equivalent to 2 faradays had been passed through. When this was quenched with sodium methoxide, it gave several products which were more polar than the precursor compound as observed by HPLC. Similar products were also observed when water was used for quenching, and this indicated that the reaction processes were more complicated and might have involved some reactions with either the solvent or the supporting electrolyte. No dimers were observed. Attempts to identify some of these products by mass spectrometry were unsuccessful and were discontinued.

III EXPERIMENTAL

A.a) Materials

1,2,3,4,5-tetraphenylcyclopentadienone, 66 was obtained from Aldrich Chemical Co., and was used directly without further crystallization. All the other organic and inorganic reagents were purchased from various Chemical Suppliers and were used directly without further purification.

Supporting Electrolytes: Preparation and Crystallization

i) Tetra-n-butylammonium trifluoromethanesulfonate ($TBA^+OT_f^-$)

A solution of 16.19gm (25mmol) of aqueous 40% tetra-n-butylammonium hydroxide (BDH Chemicals Ltd.) in 20ml of water was rapidly stirred while 3.75gm (25mmol) of trifluoromethane sulfonic acid was slowly added. After cooling to room temperature, the mixture was filtered and the residue was washed with water until the washings were neutral. The crude product was left to dry in air and recrystallized two times from methylene chloride-ether and dried at 60°C under vacuum to yield 8.8gm (22.5mmol), 90% of the pure product, m.p. 110-112°C (Lit.[70] 111-112.5°C)

ii) Tetra-n-butylammonium tetrafluoroborate ($TBA^+BF_4^-$)

A solution of 16.19 gm (25mmol) of aqueous 40% tetra-n-butylammonium hydroxide in 30mls of water was treated with 3.6ml (26mmol) of aqueous 48-50% fluoroboric acid. The resulting mixture was stirred at room temperature for 1-2 min. and the crystalline salt was collected on a filter paper, washed with water until the washings were neutral and left to dry in air. The crude salt was recrystallized three times from ethyl acetate-pentane and dried at 60°C under vacuum to yield 6.0gm (18.3mmol), 73.4% of pure product, m.p. 161-162°C (Lit.[71] 162-162.5°C).

iii) Tetra-n-butylammonium hexafluorophosphate ($TBA^+PF_6^-$)

A solution of 19.43 gm (30mmol) of aqueous 40% tetra-n-butylammonium hydroxide in 30 mls of water was rapidly stirred while 5.05gm (30mmol) of sodium hexafluorophosphate in 20ml of water was slowly added. The solid was collected on a filter paper, washed with water and left to dry in air. Crystallization (three times) from ethylacetate-pentane and drying at 60°C under vacuum yielded 10.3gm (26.6mmol), 89% of the pure product m.p. 246-247°C (Lit.[72] 247°C).

iv) Tetra-n-butylammonium perchlorate ($TBA^+ClO_4^-$)

This was obtained from Pfaltz and Bauer Inc. and was recrystallized two times from ethyl acetate-pentane and dried at 60°C under vacuum to give white needle-like crystals, m.p. 211-212°C.

v) Tetra-n-butylammonium nitrate ($TBA^+NO_3^-$)

This also was obtained from Pfaltz and Bauer Inc., and was recrystallized two times from ethyl acetate-pentane and dried at 60°C under vacuum to give white crystals, m.p. 121-122°C.

b) Solvents

i) 1,2-Dichloroethane and acetonitrile

Both solvents were 99+% Gold Label grade supplied by Aldrich Chemical Co., and stirred with basic alumina, Brockman Activity I, 80-200 mesh, for 24 hours and distilled over calcium hydride under dry nitrogen.

ii) Benzene

This was supplied by J.T. Baker Chemicals Co., and was distilled over phophorus pentoxide under dry nitrogen and kept in a brown bottle containing molecular sieves, 8-12 mesh. It was always kept in a nitrogen bag.

iii) Tetrahydrofuran (THF)

This was obtained from Fischer Scientific Co., and was distilled over benzophenone-sodium under dry nitrogen. It was always used immediately after distillation.

iv) Methanol

This was supplied by Caledon Laboratories Ltd. and was distilled over magnesium, Grignard reagent grade, activated by iodine, 99.9%, under dry nitrogen.

B. Instruments for Compound Identification

Melting points were determined using a Kofler hot stage microscope (Reichert Instruments, Austria) and were reported uncorrected. Infrared spectra were run on a Perkin Elmer 283 using carbon tetrachloride as solvent and were calibrated with the 1601.8 band of polystyrene film.

The ultra-violet (UV) spectra were obtained with Hewlett Packard 8451A Diode Array spectrophotometer and the proton nmr spectra were obtained on a Varian EM-390 using deuterated chloroform as solvent. All chemical shifts (δ) were reported as parts per million (ppm) downfield from tetramethylsilane (TMS) used as an internal standard. Mass spectra were obtained with a VG Micromass 7070F instrument using perfluorokerosene (PFK) as reference calibrant.

Analytical and semi-preparative liquid chromatography were performed on a HPLC system which used Model AA-94 pump (Eldex Laboratories Inc.) and an ISCO UA-5 Absorbance/Fluorescence detector with a 254nm filter. The analytical column was RP-18 (C-18 chain, 10μm spherical) 4.6mm ID x 220 mm while the semi-preparative column was RP-18 (C-18, monofunctional, 5μm spherical) 4.6mm ID x 250mm. The mobile phase was glass-distilled acetonitrile (BDH Chemicals Ltd.) and filtered distilled water, in the ratio 9:1. All elemental analyses were determined by Guelph Laboratories Ltd., Guelph, Ontario.

C. Syntheses

i) Synthesis of 1,2,3,4,5-pentaphenylcyclopentadienol, 67

The procedure followed was similar to that described by KieslicH and Kurreck[63] and by Ziegler and Schnell[64]. In a dry 500ml two-way round bottomed flask equipped with a condenser and a 125ml addition funnel, 1.37gm (56.3mmol) of dry magnesium was introduced, warmed with a hot air drier and flushed with dry nitrogen. After allowing to cool, 5-10ml anhydrous ether and a small crystal of iodine were introduced with constant stirring. From the addition funnel, 12.24gm (78mmol) of bromobenzene diluted with 20-30ml of anhydrous ether, was added dropwise to the mixture which was stirred constantly. After the addition, the funnel was rinsed with 2-3ml of anhydrous ether and added to the reaction mixture. Stirring was continued until all the magnesium had dissolved. 10gm (26mmol) of 1,2,3,4-tetraphenylcyclopentadienone, 66 in 100ml of anhydrous benzene was then added dropwise to the reaction mixture, after which the contents were refluxed for 2 hours and allowed to cool. This was neutralized with cold dilute hydrochloric acid, extracted with ether (3x20ml), washed with water and dried over anhydrous magnesium sulphate. The solvent was evaporated and the crude product crystallized from benzene-petroleum ether to yield 11.2gm (24.2mmol), 93.2% of pale yellow crystals, m.p. 174-176°C. Infrared spectrum (CCl_4) showed a characteristic absorption band at 3600cm^{-1} plus many other bands in the finger-print regions while the proton nmr exhibited a singlet resonance signal at 2.44ppm at two complex multiplets at 6.9-7.65ppm region measured in $CDCl_3$ using TMS as an internal standard. Mass spectrum showed a parent ion at m/e = 462 corresponding to molecular formula, $C_{35}H_6O$.

ii) Synthesis of 1,2,3,4,5-pentaphenylcyclopentadienyl bromide, 68

The method used was similar to that described by Ziegler and Schnell[64]. In a 250ml round bottomed flask equipped with a condenser, a solution of 10gm (21.6mmol) of 1,2,3,4,5-pentaphenylcyclopentadienol, 67 in 50ml of ethyl acetate was introduced and 3ml (23.2mmol) solution of 45% hydrogen bromide in glacial acetic acid (BDH Chemicals Co.) was added while the contents were stirred. Orange-yellow crystals which were observed after 2-3min was left stirring overnight, filtered and washed with petroleum ether, bp 35-60°C, to remove excess hydrogen bromide. Recrystallization from benzene-petroleum ether afforded lemon-yellow crystals, 10.4gm (19.8mmol), 91.7% m.p. 186-188°C.

A proton nmr spectrum ($CDCl_3$) exhibited only two complex multiplets enveloped in the 6.8-7.5ppm region measured against TMS as internal standard. Infrared spectrum did not show any absorption band at 3600cm^{-1} which indicated that there was no precursor alcohol, 67 in the product. Elemental analysis (C, 80.05%; H, 5.01%; Br, 15.4%) corresponded to a molecular formula, $C_{35}H_{25}Br$.

iii) Synthesis of 1,2,3,4,5-pentaphenylcyclopentadiene, 64

The procedure followed was that described by Ziegler and Schnell[64]. To a hot solution of 1,2,3,4,5-pentaphenylcyclopentadienyl bromide, 68 (2gm, 3.8mmol) in 30ml of glacial acetic acid, 3gm (45.9mmol) of zinc dust was added slowly and carefully to avoid frothing while the contents were stirred slowly with a glass rod. Then it was boiled until the lemon-yellow colour varnished, and filtered while hot through sintered glass crucible (medium porocity) to remove excess zinc. Upon cooling the filtrate, the pale yellow crystals which precipitated were filtered and washed with petroleum ether to remove excess acetic acid. A yield of 0.6gm (1.3mmol), 35.4% was obtained, m.p. 251-253°C. A proton nmr spectrum ($CDCl_3$) exhibited two resonance signals; a singlet at 5.07ppm and a complex multiplet at 7.0-7.5ppm region measured against TMS as internal standard.

Mass spectrum showed a molecular ion at m/e=446 and elemental analysis (C, 93.78%; H, 6.18%) corresponded to molecular formula, $C_{35}H_{26}$.

iv) Synthesis of 1,2,3,4,5-pentaphenyl-1-methylcyclopentadiene, 65

The procedure followed was similar to that described by Giuseppe and co-workers.[67] In a 250ml two-way round bottomed flask equipped with a condenser connected to a nitrogen supply, 3gm (6.7mmol) of 1,2,3,4,5-pentaphenylcyclopentadiene, 64 in 50ml of anhydrous tetrahydrofuran (THF) was introduced and 3.2ml (7.1mmol) solution of n-butyllithium (2.6M) in hexane (Aldrich Chemical Co.) was added dropwise from a syringe, through a septum, to the contents which were stirred constantly.

After 4-5min, a fluorescent greenish-yellow colour developed and stirring was continued for 30 min. 1gm (7.1mmol) of methyl iodide in 5ml of anhydrous THF was added and the mixture was stirred for 1 hour. The contents were neutralized with dilute hydrochloric acid and the organic matter extracted with ether (3x10ml). The combined ether extracts were washed with water and dried over anhydrous magnesium sulphate. After evaporating the solvent, the crude product was chromatographed on silica gel 60-200 mesh, eluted with petroleum ether-benzene (8:1) and recrystallized from absolute alcohol (ethanol) to yield white crystals, 2.5gm (5.4mmol), 81.1%, m.p. 157-158°C.

Proton nmr spectrum ($CDCl_3$) exhibited four resonance signals; a singlet at 1.43ppm and three multiplets at 6.56-6.8, 6.81-7.12, 7.13-7.33ppm measured against TMS as internal standard.

Mass spectrum showed a parent ion at m/e=460 and elemental analysis (C, 93.8%; H, 6.1%) corresponded to molecular formula, $C_{36}H_{28}$.

v) <u>Synthesis of 1,2,3,4,5-pentaphenyl-1-methoxycyclopentadiene, 69</u>

In a 250ml two-way round bottomed flask equipped with a condenser and nitrogen supply, 0.5 (1.08mmol) of 1,2,3,4,5-pentaphenylcyclopentadienol, <u>67</u> in 20ml anhydrous tetrahydrofuran was introduced and 0.5ml (1.12mmol) solution of n-butyllithium (2.6M) in hexane was added dropwise from a syringe through a septum, to the contents, with constant stirring. A dark greenish colour developed immediately and stirring was continued for 15 min. At this point was added 0.16gm (1.12mmol) of methyl iodide in 3ml of anhydrous tetrahydrofuran. The contents were stirred for 1 hour, neutralized with dilute hydrochloric acid and the organic solution extracted with ether (3x10ml). The total ether extracts were washed with water and dried over anhydrous magnesium sulphate. The ether was evaporated and the crude product recrystrallized from benzene-petroleum ether to yield biege crystals, 0.2gm (0.42mmol), 38.9%, m.p. 196-197°C (Lit.[73] 197-198°C). Proton nmr spectrum ($CDCl_3$) exhibited two resonance signals; a singlet at 3.45ppm (corresponding to methoxy protons which generally appear at 3.3ppm[65]) and a complex multiplet enveloped in the 6.9-7.4ppm region (corresponding to phenylic protons which normally appear at 6.5-8.3ppm region[65]) measured against TMS as internal standard.

Mass spectrum showed a parent ion at m/e=476 corresponding to molecular formula, $C_{36}H_{28}O$.

D. Cyclic Voltammetric Oxidation and Controlled Potential Electrolysis

i) Cyclic voltammetric Set-up

Cyclic voltammetric oxidation was performed on a CV-27 Cyclic Voltamograph using an Omnigraph 2000 X-Y recorder for current-voltage measurements. The sample cell was a 20ml glass vial and Micro-V magnetic stirrer (Cole-Parmer) was used as a stand. The reference electrode was typically a saturated calomel, SCE (Metrohm AG, Switzerland) which was isolated from the substrate solution by placing it in a glass frit to prevent contamination by leakage of the aqueous internal solution of the reference electrode. The working electrode was platinum bead (0.03cm^2) embedded on a cobalt glass seal, while the auxiliary electrode was platinum wire (diameter, 0.42mm). A typical set-up is as shown on Figure X.

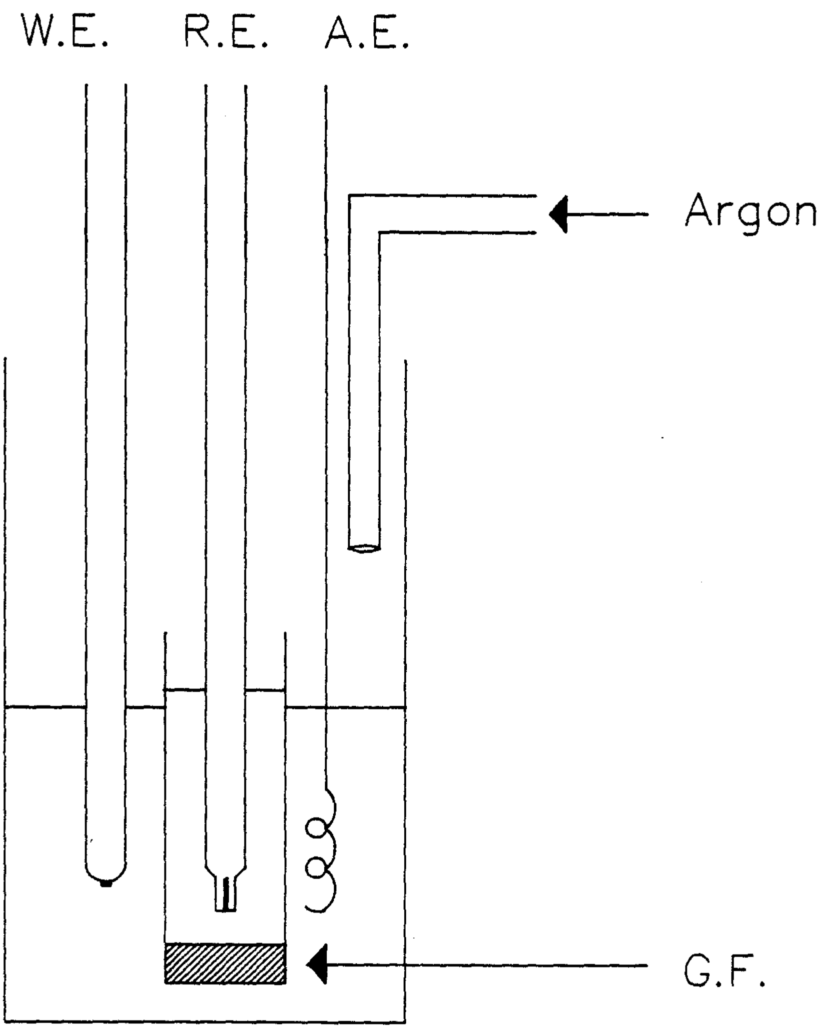


Figure X

Experimental set-up for cyclic voltammetry.

A.E - auxiliary electrode
G.F - glass frit
R.E - reference electrode
W.E - working electrode

ii) Cyclic Voltammetric Measurements

A solution of the supporting electrolyte (0.1M) contained in 3ml of anhydrous 1,2-dichloroethane was introduced into the sample cell and deoxygenated with dry argon. The electrodes were rinsed with acetone, then with methylene chloride and wiped dry before placing them close together in the solution so as to minimize the ohmic resistance (iR) which was not compensated. In all cases, a background scan (solvent plus supporting electrolyte) was run over the scan range -0.2V - +1.8V, to ensure no oxidizable impurities were present. The sample was dissolved in the same solution to make 1-2mM substrate concentration, deoxygenated and scanned. Then the positive potential limit was adjusted such that the scan reversal (switching potential) occurred just after the first maximum anode peak corresponding to one electron-transfer, and scan rates were varied over a wide range (25-1000mV/sec).

The supporting electrolytes used were tetra-n-butylammonium perchlorate ($TBA^+ClO_4^-$), tetra-n-butylammonium trifluoromethane sulfonate ($TBA^+OT_f^-$), tetra-n-butylammonium tetrafluoroborate ($TBA^+BF_4^-$) and tetra-n-butylammonium hexafluorophosphate ($TBA^+PF_6^-$). Beside the non-polar and non-nucleophilic solvent (1,2-dichloroethane), acetonitrile was used for comparative purposes. The electrode processes of

1,2,3,4,5-pentaphenylcyclopentadiene, 64 and 1,2,3,4,5-pentaphenyl-1-methylcyclopentadiene, 65 were also investigated in anhydrous 1,2-dichloroethane containing tetra-n-butylammonium nitrate (see results section).

iii) Controlled Potential Electrolysis

Controlled potential electrolysis also used the CV-27 Cyclic Voltamograph and a three-compartment electrolytic cell containing 50ml of solution, where the working compartment, the auxiliary-electrode compartment and reference-electrode compartment were separated by glass frits. The reference-electrode compartment was constructed such that it was at the core of the working electrode (Figure XI).

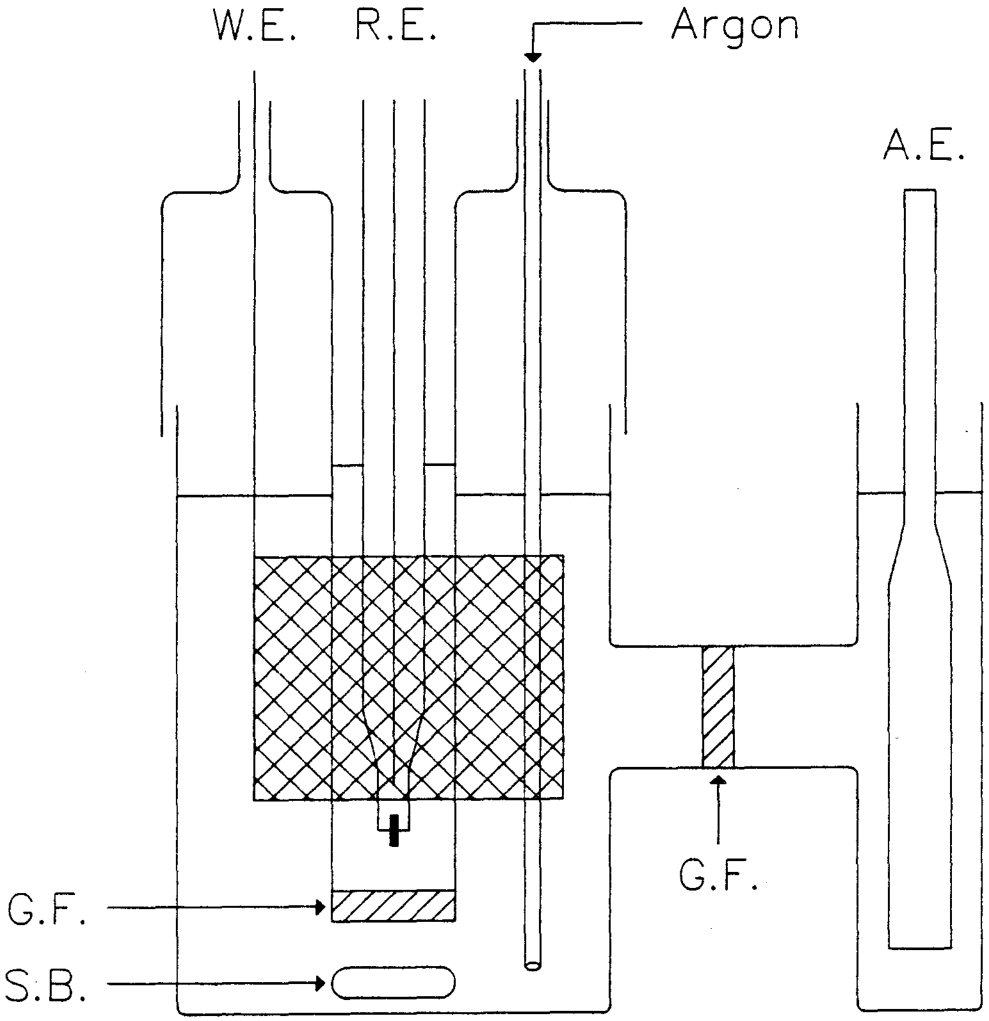


Figure XI

Experimental set-up for controlled potential electrolysis.

A.E - auxiliary electrode
G.F - glass frit
R.E - reference electrode
S.B - stirring bar
W.E - working electrode

The working electrode was a cylindrical platinum gauze (25mm ID x 50mm), the auxiliary electrode was a nickel spatula (8mm x 0.5mm) and the reference was a typical saturated calomel electrode (SCE).

A solution of tetra-n-butylammonium perchlorate (0.1M) in 50ml of anhydrous 1,2-dichloroethane was introduced to all compartments and 100mg (0.22mmol) of 1,2,3,4,5-pentaphenylcyclopentadiene, 64 was added to the solution in the main cell compartment, and was stirred until it all dissolved. A slow stream of dry argon was passed throughout the course of the experiment. The electrodes were rinsed with 1,2-dichloroethane and introduced to their respective compartments, the electrolysis potential set (1.42V) and the solution was electrolyzed until a charge equivalent to 2 faradays (43.3C) had been passed through. The resulting reddish solution (λ_{max} 530nm) was quenched immediately with anhydrous methanol and it afforded methyl ether, 69 as the major product. This was identified by proton nmr, mass spectrometry and by HPLC comparison with an authentic sample.

In a similar experiment, the electrolyzed solution was quenched with water and afforded alcohol, 67 as the major product, which was identified by HPLC, infrared spectrum comparison with an authentic sample, and by mixed melting point.

E. Alternative Methods of Generating 1,2,3,4,5-Pentaphenylcyclopentadienyl Cations.

i) Reaction of 1,2,3,4,5-pentaphenylcyclopentadienyl bromide 68 with silver perchlorate

To a deoxygenated solution of 1,2,3,4,5-pentaphenylcyclopentadienyl bromide 68 (200mg) in 30ml of anhydrous 1,2-dichloroethane containing 1.02gm of tetra-n-butylammonium perchlorate, 79mg of silver perchlorate in 20ml of anhydrous benzene was added under dry nitrogen. The reddish solution which developed immediately was shaken for 2-3min and filtered directly into a flask containing anhydrous methanol. The major product isolated after this quenching was methyl ether, 69. In a similar experiment where water instead of anhydrous methanol was used for quenching, the only isolable product was alcohol, 67.

ii) Reaction of 1,2,3,4,5-pentaphenylcyclopentadienol, 67 with boron trifluoride.

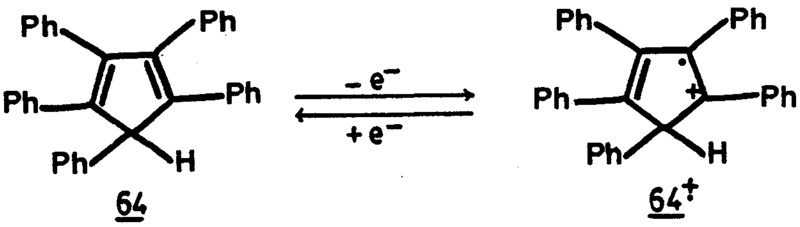
1,2,3,4,5-pentaphenylcyclopentadienol, 67 (100mg) was dissolved in 20ml of anhydrous methylene chloride; the solution was purged with dry argon and cooled to -70°C. Gaseous boron trifluoride (Canadian Liquid Air Ltd.), was passed through the cold solution which turned deep blue. This was quenched with cold deoxygenated anhydrous methanol and the major product isolated was methyl ether, <u>69</u>. When the deep blue solution was allowed to warm to room temperature in the presence of excess tetra-n-butylammonium perchlorate, it turned wine-red, but when this solution was quenched with anhydrous methanol, no methyl ether, <u>69</u> was detected.

IV. DISCUSSION AND CONCLUSION

The use of 1,2-dichloroethane which is essentially a non-basic and non-nucleophilic solvent enables the study of electro-generated cation radical intermediate of 1,2,3,4,5-pentaphenylcyclopentadiene, 64 in various supporting electrolytes using cyclic voltammetry. These studies have shown with reasonable certainty that a cation radical is formed by electron-transfer from the olefinic linkage, and its fate is dictated by the nature of the electrolyte anions, namely; perchlorate (ClO_4^-), triflate (OT_f^-), tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-) and nitrate (NO_3^-).

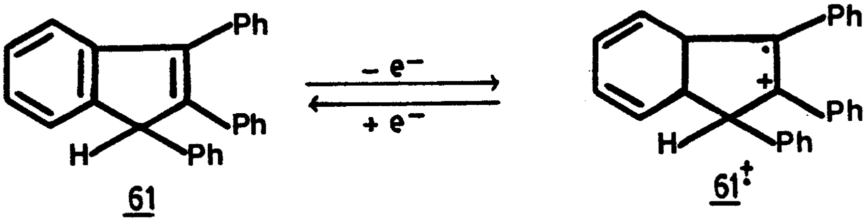
The general behaviour of 1,2,3,4,5-pentaphenylcyclopentadiene cation radical, $64^{+\cdot}$ in anhydrous 1,2-dichloroethane containing tetra-n-butylammonium hexafluorophosphate ($TBA^+PF_6^-$) can be characterized by the direct relationship between anodic peak current, i_{pa} and the square root of potential scan rate, $\nu^{1/2}$ corresponding to the Randles-Sevcik equation[69] for reversible processes (Figure II), essentially equal anodic (i_{pa}) and reversal cathodic (i_{pc}) peak currents (Figure I), slight dependence of anodic peak potential, E_{pa} on the scan rate (change of the order of 60mV for a 20-fold increase in scan rate) and a peak separation, E_{pa} and E_{pc} of 130-240mV. The latter two parameters does not seem to fit well to a reversible one-electron transfer process of which the anodic peak potential, E_{pa} and E_{pc} should theoretically be 57mV.

As a matter of comparison, the behaviour of 9,10-diphenylanthracene, which has been established to undergo reversible one-electron transfer,[78] was studied under similar conditions and the results were quite similar to those obtained from 64 (Figure III). The slight dependence of anodic peak potential, E_{pa} on scan rate and the peak separation were of the same magnitude. This was evident that a reversible one-electron transfer must have occurred from the parent hydrocarbon, 64 to form a cation radical intermediate, $64^{+\cdot}$ which was stable during the time necessary for scan reversal in the presence of hexafluorophosphate anions.



The reason for the observed wide peak separation and the slight dependence of anodic peak potential on scan rate is attributed to ohmic resistance[34] which was not compensated, and concentration of the supporting electrolyte which was not high enough to facilitate the conductivity especially in such a non-polar solvent like 1,2-dichloroethane.

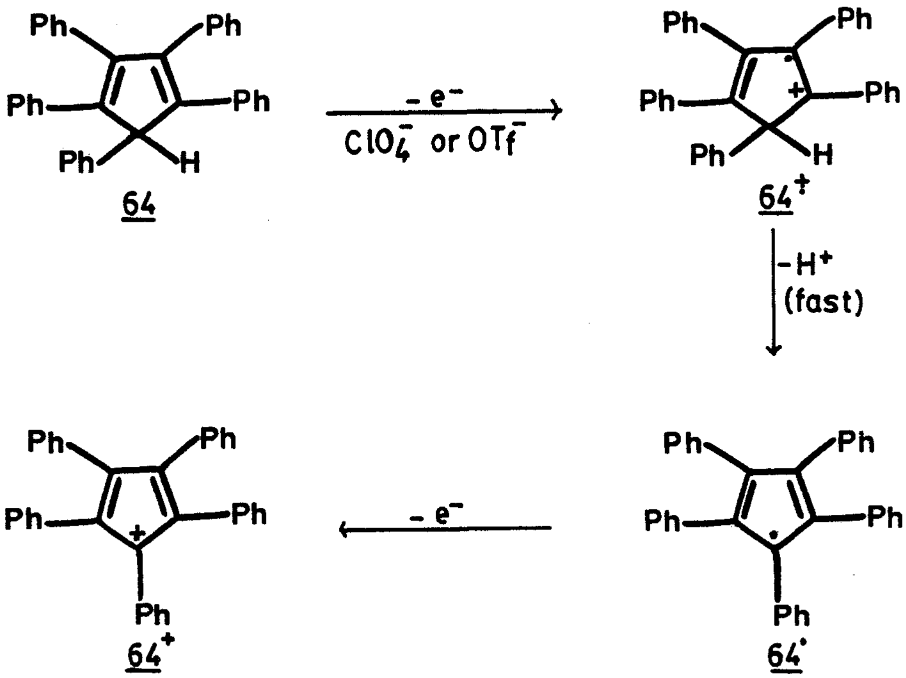
In this laboratory,[13] similar results were obtained from cyclic voltammetric oxidation of 1,2,3-triphenylindene, 61 in anhydrous 1,2-dichloroethane containing tetra-n-butylammonium hexafluorophosphate. It was observed that the cation radical intermediate, $\underline{61}^{+\cdot}$ was stable during the scan time.



These observations led to the conclusion that hexafluorophosphate anion (PF_6^-) is a weak nucleophile because it does not attack the intermediate, $\underline{61}^{+\cdot}$ and it is also a weak base because it does not abstract the ionizable proton from the intermediate, $\underline{61}^{+\cdot}$ in the time necessary for scanning.

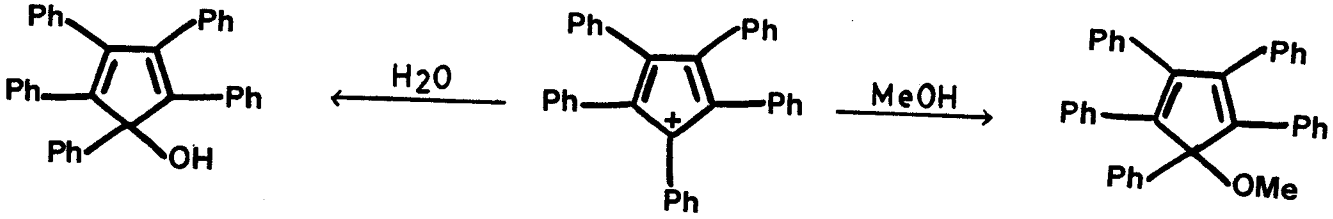
In contrast, cyclic voltammetric oxidation of 64 in the same solvent (1,2-dichloroethane) containing tetra-n-butylammonium perchlorate ($TBA^+ClO_4^-$) or tetra-n-butylammonium trifluoromethane sulfonate ($TBA^+OT_f^-$) showed no direct relationship between anodic peak current, i_{pa} and the square root of scan rate i.e., it did not obey Randles-Sevcik equation[69] for reversible processes (Figure V). It also showed significant variation of anodic peak potential,

E_{pa} with scan rate (a change of about 200mV for a 20-fold increase in scan rate), and cathodic waves were either very small or absent on scan reversal (Fig. IV). The anodic peak current, i_{pa} was twice in magnitude as compared to that observed when hexafluorophosphate (PF_6^-) was used as supporting electrolyte. This suggested that two electrons were involved during the oxidation of 64 in presence of $TBA^+ClO_4^-$ or $TBA^+OT_f^-$ and that the cation radical intermediate, $\underline{64}^{+\cdot}$ was unstable in these two electrolytes during the time necessary for scan reversal. A proposed mechanism is as shown below:



Due to the cation radical intermediate, $\underline{64}^{+\cdot}$ being unstable in presence of perchlorate anions (ClO_4^-), it undergoes fast chemical reaction (deprotonation) to give a stable[74,75] neutral radical $64^{\bullet}$, which has a lower oxidation potential than the parent compound 64 hence it subsequently loses the unpaired electron to form cation 64^{+}. The overall reaction involves loss of two electrons and this explains the magnitude of anodic peak current, i_{pa} which was observed to be twice that obtained when hexafluorophosphate (PF_6^-) was used.

The presence of a cation intermediate, 64^{+} was further confirmed by controlled potential electrolysis of 64 in anhydrous 1,2-dichloroethane containing perchlorate anions (ClO_4^-). After consumption of charge equivalent to 2 faradays, methyl ether, 69 and alcohol, 67 were isolated as major products after immediate quenching of the reddish electrolyzed liquor (λ_{max} 530nm) with anhydrous methanol and water respectively.

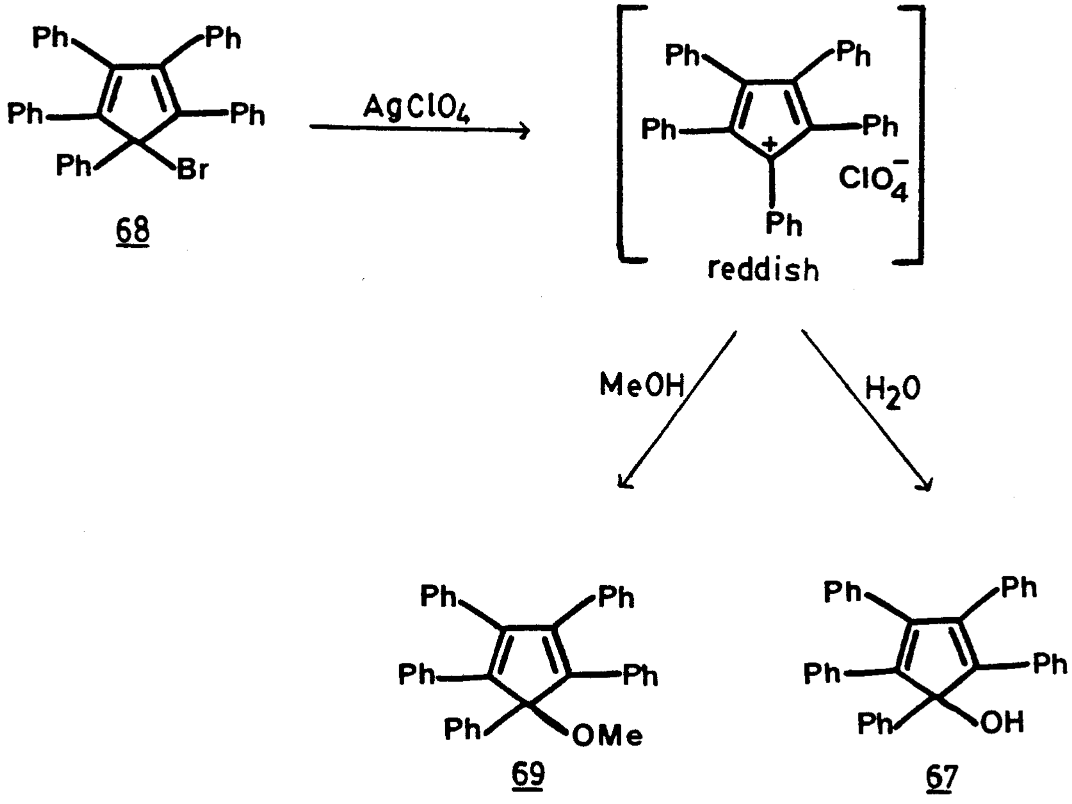


67

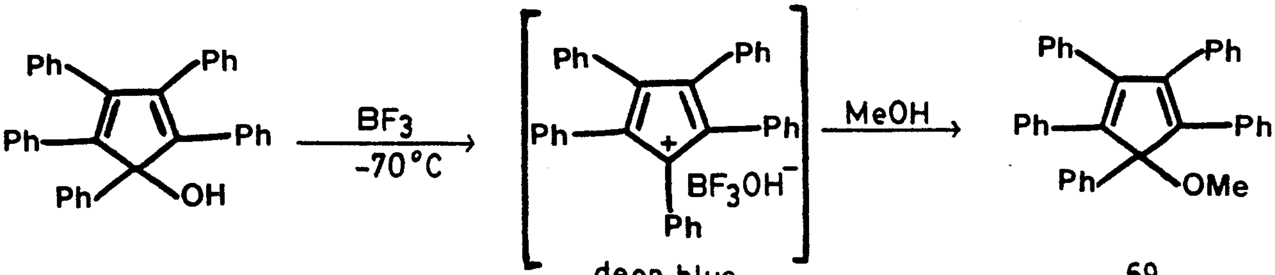
64^{+} (reddish)

69

No dimers were observed, and this was in agreement with the earlier report by Kurreck and Broser[74] and by Kurreck[75] that the neutral radical intermediate, $64^{\bullet}$ is quite stable in an inert atmosphere and does not dimerize. The same cation intermediate, <u>64</u>$^+$ was generated chemically by treatment of 1,2,3,4,5-pentaphenylcyclopentadienyl bromide, <u>68</u> with silver perchlorate ($AgClO_4$) in the presence of excess perchlorate anions (ClO_4^-). It gave a reddish solution which was similar to the electrolyzed liquor and afforded methyl ether, <u>69</u> and alcohol, <u>67</u> as major products upon immediate quenching with anhydrous methanol and water respectively.



The cation intermediate <u>64</u>$^+$ was also generated by treatment of the alcohol, <u>67</u> with boron trifluoride at low temperature (-70°). A deep blue solution was obtained which, upon quenching, while cold, with anhydrous methanol afforded

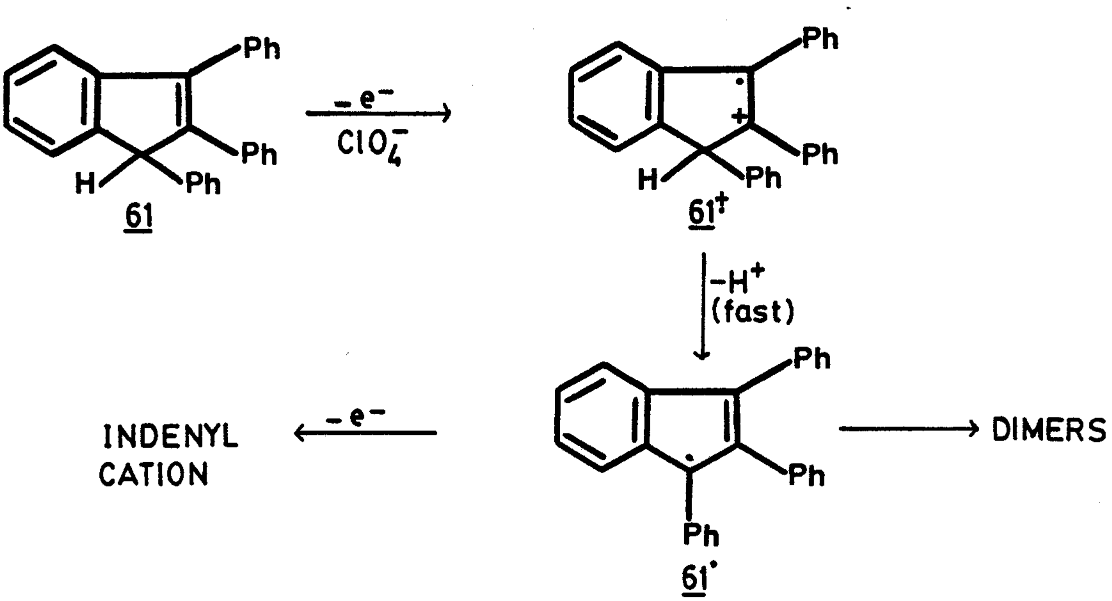


<u>67</u> <u>69</u>

methyl ether, <u>69</u> as a major product. When the deep blue solution was left to warm to room temperature in the presence of excess perchlorate anions (ClO_4^-), and under inert atmosphere, the colour faded and no methyl ether, <u>69</u> was detected upon quenching with anhydrous methanol. This was in agreement with the earlier report by Breslow and co-workers[66] who suggested that the cation intermediate, <u>64</u>$^+$ was unstable at room temperature in the presence of boron trifluoride and may react to form fluorinated materials.

The presence of irreversible cathodic waves around 0.0V region (Figure IV) can be attributed to either the reduction of the protons[76,77] abstracted from cation radicals or the reduction of the cation itself.[13] No further attempts were made in identifying the species responsible for these reduction waves.

In this laboratory[13], similar results were observed when the authors investigated cyclic voltammetric oxidation of 1,2,3-triphenylindene, <u>61</u> in anhydrous 1,2-dichloroethane containing tetra-n-butylammonium perchlorate ($TBA^+ClO_4^-$) and reported that the chemical reaction step (deprotonation) following the electro-transfer process was fast, to give the neutral radical, <u>61</u>$^\bullet$

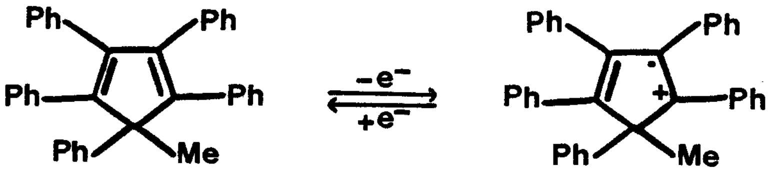


Unlike 1,2,3,4,5-pentaphenylcyclopentadiene radical, <u>64</u> which does not dimerize due to its stability, 1,2,3-triphenylindene radical, <u>61</u>$^\bullet$ undergoes competitive reaction between dimerization and loss of the unpaired electron to form indenyl cation. Both of these products were detected when the reddish electrolyzed liquor (λ_{max} 450nm) of <u>61</u> was quenched with anhydrous methanol or water.

These results suggest that 1,2,3,4,5-pentaphenylcyclopentadiene cation radical, $\underline{64}^{\ddagger}$ which is stable in the presence of hexafluorophosphate anions (PF_6^-), is quite unstable in the presence of perchlorate (ClO_4^-) or triflate (OT_f^-) anions; both behave as strong bases and are able to abstract the ionizable proton faster than the time necessary for scanning.

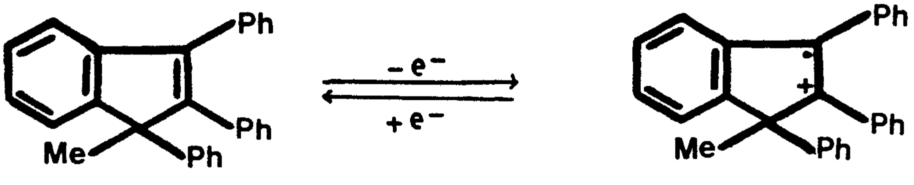
Although cyclic voltammetric oxidation of 1,2,3,4,5-pentaphenylcyclopentadiene, $\underline{64}$ in anhydrous 1,2-dichloroethane containing tetra-n-butylammonium tetrafluoroborate ($TBA^+BF_4^-$) showed some reversibility, the cathodic wave was smaller than the anodic wave (Figure VI). There was no direct relationship between anodic peak current, i_{pa} and the square root of scan rate i.e., the process did not obey Randles-Sevcik equation[69] for reversible processes (Figure VII). The anodic peak potential, E_{pa} varied significantly with the scan rate (change of about 90mV for a 20-fold increase in scan rate), and a peak separation, E_{pa} and E_{pc} of 160-290mV, both do not agree, in magnitude, with the figures obtained from a reversible process using 9,10-diphenylanthracene. The appearance of small cathodic waves around 0.0V region which could be attributed to either the reduction of the protons[76,77] abstracted from the cation radical intermediates, or of the cation intermediates.[13] These led to a conclusion that the reaction between 1,2,3,4,5-pentaphenylcyclopentadiene cation radical, $\underline{64}^{\ddagger}$ and tetrafluoroborate anions (BF_4^-) is quasi-reversible and that the abstraction of the ionizable proton from the intermediate, $\underline{64}^{\ddagger}$ is not fast enough compared to the time necessary for scanning.

In order to confirm that the reaction between the cation radical intermediate, $\underline{64}^{+\cdot}$ and the electrolyte anions was via the abstraction of the ionizable proton from the intermediate and not a nucleophilic attack, a controlled reaction was conducted using 1,2,3,4,5-pentaphenyl-1-methylcyclopentadiene, $\underline{65}$ as a model compound which does not have ionizable protons. Its cyclic voltammetric oxidation in anhydrous 1,2-dichloroethane containing perchlorate (ClO_4^-), triflate (OT_f^-), tetrafluoroborate (BF_4^-) or hexafluorophosphate (PF_6^-) were all characterized by Randles-Sevick equation[69] for reversible processes, and by the usual criteria[78], to be reversible and also were similar to the results obtained from cyclic voltammetric oxidation of 9,10-diphenylanthracene under similar conditions. This leads to a conclusion that the cation radical intermediate, $\underline{65}^{+\cdot}$ is stable in all the four electrolyte anions during the scan time.



$\underline{65}$ $\underline{65}^{+\cdot}$

Similar results were obtained in this laboratory.[13] Cyclic voltammetric behaviour of 1,2,3-triphenyl-1-methylindene, <u>62</u> in anhydrous 1,2-dichloroethane containing perchlorate (ClO_4^-), triflate (OT_f^-) or hexafluorophosphate (PF_6^-) anions were studied, and it was observed that the processes were all reversible by usual criteria.[78]



<u>62</u> $\qquad$ <u>62</u>$^{+\cdot}$

In contrast, the cyclic voltammetric oxidation of 1,2,3,4,5-pentaphenylcyclopentadiene, <u>64</u> and 1,2,3,4,5-pentaphenyl-1-methylcyclopentadiene, <u>65</u> in anhydrous 1,2-dichloroethane containing tetra-n-butylammonium nitrate ($TBA^+NO_3^-$) showed irreversibility in both cases (Figure IX). This indicated that unlike the other four electrolyte anions which behaved more-or-less like bases, the nitrate anion seems to be acting as a nucleophile which attacks the cation radical intermediates.

Proton loss from cation radical $\underline{64}^{+\cdot}$ is apparently rapid when electrolyte anions perchlorate (ClO_4^-), triflate (OT_f^-) are used, but relatively slow when hexafluorophosphate (PF_6^-) is present. With the latter anion, $\underline{64}^{+\cdot}$ is formed reversibly in C.V. experiments, if chloroalkane solvents are used. The reactivity of these anions to $\underline{64}^{+\cdot}$ parallels their basicities.

$$PF_6^- < BF_4^- < ClO_4^- \approx CF_3SO_3^- <<< NO_3^-$$

This trend is supported by the results from dissociation constants of their corresponding acids in glacial acetic. Engelbrecht and Rode[79] reported dissociation constants of nitric acid, HNO_3 ($K_{diss}=10^{-10.1}$), perchloric acid, $HClO_4$ ($K_{diss}=10^{-4.87}$) and triflic acid, CF_3SO_3H ($K_{diss}=10^{-4.7}$). This indicates that perchloric and triflic acids are strong acids, hence the anions are weak bases while nitric acid is a weaker acid, hence nitrate ion is a stronger base. Although the quantitative values for tetrafluoroboric (HBF_4) and hexafluorophosphoric (HPF_6) acids were not available, they are expected to be stronger than triflic acid, hence the anions should be weaker bases. A similar trend was observed by Eberson and Nyberg[80] when they showed qualitatively the increasing degree of resistance towards anodic oxidation for a series of anions, viz.,

$$NO_3^- <<< ClO_4^- < CF_3SO_3^- < BF_4^- \approx PF_6^-$$

such that, those anions which are easily oxidized such as ClO_4^- are strong bases and accept protons readily while those which resist oxidation, such as PF_6^- are very weak bases and do not accept protons readily.

These results may also be of value in the quantitative determination of arenes by electrochemical oxidation, since reversible oxidation is preferrred for this kind of work.

APPENDIX I

In most cyclic voltammetry, the potential of the working electrode is changed linearly with time.[81,82] Therefore,

$$E = B - \alpha t \qquad (1)$$

where E is the working electrode potential, and B and α are constants.

Also, at the electrode surface, we have

$$\frac{RT}{nF} \ell n \frac{C_s{}^+}{C_s} = \alpha(t-t_o) \qquad (2)$$

where C_s and $C_s{}^+$ are the concentrations of neutral (sample molecules and oxidized molecules. Activities are assumed equal to concentrations.

It is also assumed that the current is controlled by diffusion to the electrode. Therefore, for diffusion to a planar surface,

$$\frac{\delta C}{\delta t} = D \frac{\delta^2 C}{\delta x^2} \qquad (3)$$

where C is the concentration of diffusion substance at any point, x the distance from the surface, and t the time. D is the diffusion coefficient. Solution of equation (3) with the surface conditions of equation (2) gives the Randles-Sevcik equation (4) at 25°C.

$$i_p = 2.69 \times 10^5 \ n^{3/2} \ A \ C \ D^{1/2} \ \nu^{1/2} \qquad (4)$$

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