Electrochemical Oxidation of Iminobibenzyl and Related Compounds

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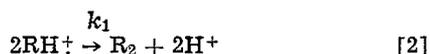*Donnan Laboratories, University of Liverpool, Liverpool L693BX, England*

ABSTRACT

Electrochemical oxidation of iminobibenzyl and several related compounds has been investigated in acetonitrile. The mechanism of the oxidation is best described by an ECE process with coupling of the product of an initial one-electron oxidation in a subsequent but very fast reaction to form a dimeric compound that is further oxidized by an over-all two-electron process at potentials more negative than those required for oxidation of the parent compounds. The electrochemistry of these compounds is complicated by the release of protons during the oxidation which protonate the starting materials and the neutral dimerized products rendering them electrochemically inactive. Differences in the electrochemistries of the various coupled products are discussed in terms of structural variations.

In recent years considerable effort has been expended in elucidating the mechanisms of electrolytic oxidation of heterocyclic nitrogen and amine compounds as well as other nitrogen containing species. [See Ref. (1) and (2) for reviews of the work in this area.] One of the prominent characteristics of aromatic amines is oxidative coupling to form a variety of dimerized derivatives of the original parent compounds. Certain heterocyclic nitrogen compounds such as carbazole which may be considered as being derived from diphenylamine also undergo a similar coupling process on oxidation (3).

The present investigation was initially undertaken to compare the electrochemistry of imipramine hydrochloride, a widely prescribed antidepressant drug, with the electrochemical behavior of the structurally similar but physiologically less active iminobibenzyl and 5-methyliminobibenzyl. We also felt it worthwhile to compare the electrochemistry of these compounds with that of the related carbazoles (I) whose primary structural difference with the above compounds is the nature of the biphenyl linkage.

The homogeneous oxidation of most of the present compounds along with a number of carbazoles with chemical oxidants (*e.g.*, 2,3-dichloro-5,6-dicyano-p-benzoquinone) has shown recently (4) that all of the compounds undergo oxidative coupling with ultimate formation of the cation radical salt of the coupled product. The electrochemical coupling of the carbazoles has been previously investigated by Ambrose and Nelson (3) who showed that the neutral coupled products can be oxidized to corresponding cation radicals and dications at potentials negative of those for the oxidation of the parent compounds. The electrochemical behavior of the carbazoles was consistent with an ECE mechanism with oxidative peak heights of the potential sweep voltammograms being twice those expected for a 1-electron process (3). Controlled potential electrolysis also gave an n value of 2. Ambrose and Nelson (3) proposed the following mechanism for the oxidative coupling of the carbazoles (3).

$$RH - e \leftrightarrows RH\overset{+}{\cdot} \qquad [1]$$

$$2RH\overset{+}{\cdot} \xrightarrow{k_1} R_2 + 2H^+ \qquad [2]$$

$$R_2 - e \leftrightarrows R_2\overset{+}{\cdot} \qquad [3]$$

$$R_2\overset{+}{\cdot} - e \leftrightarrows R_2^{2+} \qquad [4]$$

* Electrochemical Society Active Member.
Key words: cyclic voltammetry, coulometry, oxidative coupling, imipramine, 5-methyliminostilbene.

The chemical reaction in Eq. [2] is undoubtedly very rapid, since under no circumstances was it possible to observe the reduction of the radical cation of the oxidized parent (RH$\overset{+}{\cdot}$). In neither study (3, 4) were the investigators able to determine if the protons are lost before or after coupling.

We report here the electrochemical oxidation of iminobibenzyl(**II**), 5-methyliminobibenzyl (**III**), imipramine·HClO$_4$(**IV**) and 5-methyliminostilbene(**V**), and the electrochemical behavior of the products of the oxidation
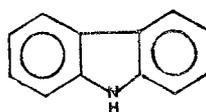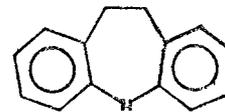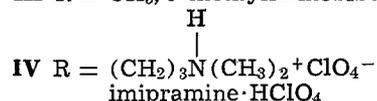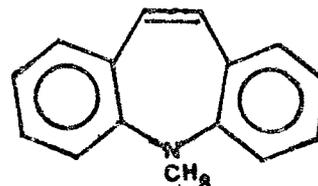

I Carbazole   **II** R = H, iminobibenzyl

III R = CH$_3$, 5-methyliminobibenzyl

IV R = (CH$_2$)$_3$N(CH$_3$)$_2$$^+ClO_4$$^-$
imipramine·HClO$_4$

V 5-methyliminostilbene

Experimental

The preparation of the compounds used in this study has been described (4). Tetrabutylammonium perchlorate (TBAP), the supporting electrolyte in all experiments, was of polarographic grade and purchased from Southwestern Analytical Chemicals. The TBAP which is contaminated with water was dried under vacuum at about 100°C for 24 hr. All other chemicals were of reagent grade quality and used without further purification.

Acetonitrile used as the solvent in these experiments was prepared from spectrograde acetonitrile by vacuum distillation from P$_2$O$_5$ at room temperature. The distillation was repeated at least three times with periodic freeze-pump-thawing to remove air.

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Table I. $i_p/Cv^{1/2}$ ratios and oxidation and reduction peak potentials for parent and product of the oxidation of parent

Compound	$i_p/Cv^{1/2}$ [a] Parent	E_p ox[b] Parent	E_p ox[b] Product	E_p red[b] Product
Carbazole[3]		+0.86	0.86, 0.56	0.8, 0.5
Iminobibenzyl	17.9	+0.48	0.42, 0.24	0.36, 0.18
5-Methyliminobibenzyl	18.3	+0.61	0.48	0.40
Imipramine HClO$_4$[c]	17.7	+0.75	0.61	0.55
5-Methyliminostilbene	17.9	+0.58	−0.27	−0.30
10-Methylphenothiazene[d]	16.1			

[a] i_p in μA, C in mM, v in V/sec. Within experimental error the $i_p/Cv^{1/2}$ values were independent of sweep rate between 0.2 and 10 V/sec.

[b] Sweep rate = 0.2 V/sec. E_p vs. Ag/0.1M AgNO$_3$.

[c] Imipramine hydrochloride was converted to the perchlorate by passing an aqueous solution through an anion exchange column in the perchlorate form and freeze drying the eluent.

[d] A standard one-electron oxidant of similar geometric size to the compounds under investigation. Due to the similarity in size the diffusion coefficients should be nearly the same for all compounds.

The cell used in this study for coulometric and electrochemical characterizations was of conventional design (5). The working electrode for coulometry was a platinum gauze. The working electrode for cyclic voltammetry was a small platinum disk electrode sealed in glass (~0.013 cm²) and was polished before each use with 0.5μ alumina polishing powder. The auxiliary electrode was a platinum wire and the reference electrode a silver wire which for certain experiments was in contact with a solution of 0.1M AgNO$_3$ in acetonitrile; the potential of this electrode was +0.333V vs. an aqueous SCE. All potentials are reported vs. this Ag/Ag$^+$ electrode.

All electrochemical experiments were carried out under an inert helium atmosphere in a Vacuum/Atmospheres Corporation (Hawthorne, California) dry box. A PAR Model 170 electrochemical system (Princeton Applied Research Corporation, Princeton, New Jersey) was used for the electrochemical experiments.

Infrared measurements were made with a Beckman Model IR5A spectrophotometer (KBr pellets). Mass spectra were obtained on a Bell & Howell Model 21-491 low resolution mass spectrometer.

Results

Iminobibenzyl.—At a voltammetric sweep rate of 0.2 V/sec iminobibenzyl shows an oxidation wave with E_{pa} at +0.48V vs. the Ag/0.1M Ag$^+$ electrode. The height of this peak corresponded to that for a one-electron process by calibration against the peak height for the known one-electron oxidation of 10-methylphenothiazene (Table I). This result contrasts with the two-electron peak height previously observed for the carbazoles (3). On sweep reversal two reduction peaks were observed with E_{pc}'s at +0.36 and +0.18V (Fig. 1). Upon repeated cycling two new oxidation peaks were evident at +0.42 and +0.24V. The peak potentials for iminobibenzyl and the other compounds in this study are summarized in Table I.

Table II. Coulometric n_{app} values for parent compounds and the products of a controlled potential oxidation of the parent compounds

Compound[a]	n_{app} ox Parent	n_{app} red Product	n_{app} ox of red product	n_{app} red of H$^+$
Iminobibenzyl	2.02	0.96	0.94	0.95
5-Methyliminobibenzyl[b]	1.0	0.5	0.5	0.5
	2.2	0.93	0.9	0.98
Imipramine HClO$_4$	0.92	0.45	0.44	1.5
5-Methyliminostilbene	0.95	0.45	0.43	0.47

[a] The concentration of compound ~1 mM in all coulometric experiments.

[b] The two values listed correspond to the two breaks observed in the Q-t curve.
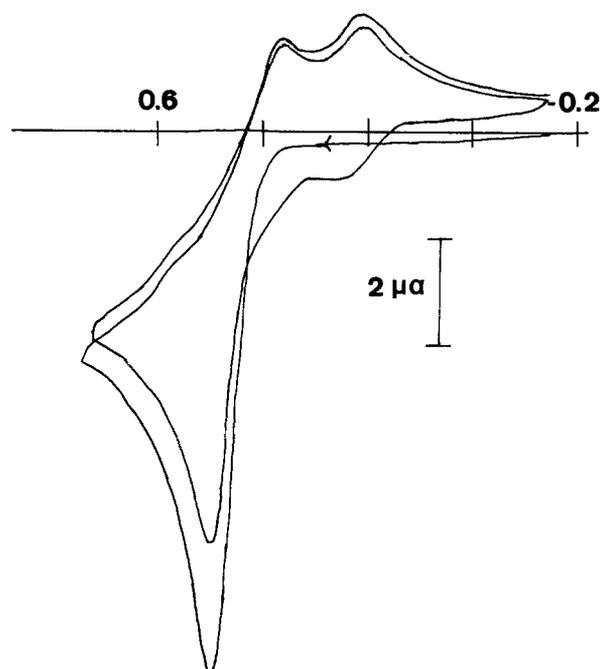

Fig. 1. Cyclic voltammogram of 1.25 mM iminobibenzyl. Conditions: sweep rate = 0.2 V/sec; 0.1M TBAP supporting electrolyte; X-axis is E, V, vs. Ag/0.1M Ag$^+$ reference electrode.

Controlled potential electrolysis at +0.85V gave an n_{app} value of 2 (where n_{app} represents the coulombs of electricity per mole of electroactive compound) (Table II) which is twice the value indicated by the voltammetry results. The oxidized solution had an intense blue color. Cyclic voltammetry of the solution following oxidation showed a redox couple centered at about +0.5V (Fig. 2) and a hydrogen ion reduction wave commencing at about −0.5V. Controlled potential coulometry of this solution indicated that the product of the initial oxidation could be reduced (at E = +0.2V) and then reoxidized again (at E = +0.85V) with an n_{app} = 1. Controlled potential reduction at −1.3V (following the oxidation at +0.85V) showed the release of one H$^+$ per parent molecule oxidized (i.e., n_{app} = 1.0) during the initial oxidation at +0.85V. After the reduction of the protons only the two redox couples observed after repeated cycling of a solution of unoxidized parent were present (Fig. 3). There was no evidence of any
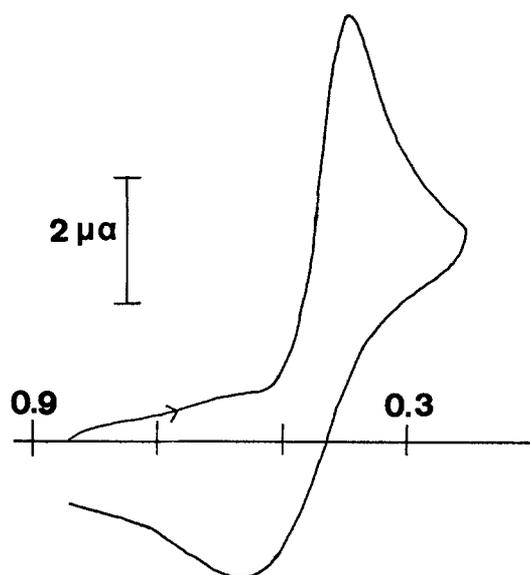

Fig. 2. Cyclic voltammogram of 1.25 mM iminobibenzyl after oxidative electrolysis at +0.85V. Conditions: Same as Fig. 1.
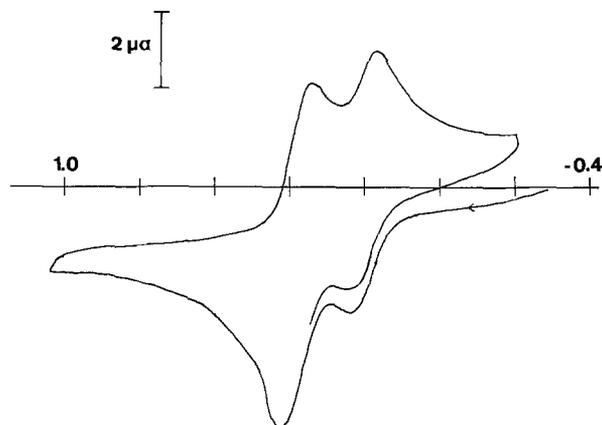
Fig. 3. Cyclic voltammogram of 1.25 mM iminobibenzyl following electrolysis at +0.85 and at —1.3V. Conditions: Same as Fig. 1.

remaining parent or the couple observed at +0.5V following the initial oxidation at +0.85V. The separation between E_{pa} and E_{pc} for each couple was 60 mV and indicates that each couple corresponds to a one-electron process. Coulometry demonstrated that a total of one electron was necessary to oxidize and then reduce both couples. In the absence of protons the product of the oxidation of parent at +0.85V behaved electrochemically in an entirely analogous manner to the carbazole products where two one-electron couples were also seen. In fact, except for the anomalous voltammetric peak height observed for the parent and the electrochemical behavior of the product of the oxidation of iminobibenzyl in the presence of protons, the electrochemistry is similar to that for the carbazoles. It seems likely therefore that a similar mechanism is operative in the case of iminobibenzyl with ultimate formation of a product (**VI**) which, by analogy with homogenous studies (4), probably arises by coupling at the 2-position

VI
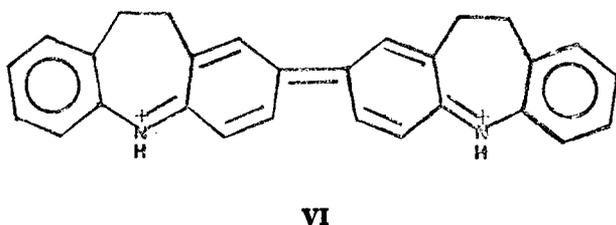
The rate of the coupling reaction is fast because no evidence was obtained for reduction of the parent radical cation during the voltammetry experiments.

In order to confirm that **VI** is indeed the major product of the oxidation at +0.85V, an attempt was made to isolate the neutral analog of **VI** prepared by a controlled potential reduction of a solution of **VI**. At the relatively high solution concentrations necessary to isolate a reasonable quantity of material ($\geq$ 20 mM), the electrochemistry of iminobibenzyl was not as clean as observed at lower concentrations ($\sim$ 1 mM). This is probably because of precipitation of the electrolysis products onto the working electrode. At these concentrations it was not possible to carry the oxidations or reductions to theoretical completion before the electrolysis currents decayed to very small values. The solutions that resulted upon reduction of an oxidized solution of iminobibenzyl contained significant quantities of unreduced material as indicated by an intense bluish-green color. Removing the acetonitrile solvent after reduction on a vacuum line followed by dissolution of the solid in benzene to separate the neutral from most of the charged products and extraction of the benzene solution with water to remove most of the remaining charged species re-

sulted on freeze-drying in a brown solid with a slight violet tinge. Infrared spectra of this material showed a strong absorption at 805 cm^{-1}. This is the same absorption expected for the iminobibenzyl dimer with coupling at the 2-position (4). The parent peak of a mass spectrum of this compound occurred at a molecular weight of 388 the same as the bibenzyl dimer. The mass spectrum also indicated the presence of minor amounts of higher molecular weight materials.

Possible complications due to the presence of H$^+$ that may explain the anomalous behavior of the coupled product and one electron peak height of the parent will be discussed later.

5-Methyliminobibenzyl.—Investigations of the homogeneous oxidation of 5-methyliminobibenzyl have demonstrated a similar coupling process as was found for iminobibenzyl with coupling also taking place at the 2-position (4). In view of this and the strong supporting evidence presented above demonstrating that the homogeneous and electrochemical oxidations of iminobibenzyl result in the same reaction product, it is assumed that the product of the electrolytic oxidation of 5-methyliminobibenzyl is structurally similar to **VI**.

5-Methyliminobibenzyl also had a voltammetric peak height on oxidation the same as that expected for a 1-electron process (See Table I). On sweep reversal, a reduction peak approximately one-half the height of the oxidation peak was observed (Fig. 4). The ratio of the two peak heights was independent of sweep rate up to 10 V/sec. At a sweep rate of 0.2 V/sec E_{pa} and E_{pc} were 0.61 and 0.40V, respectively. If cycling was continued, a new oxidation peak develops at about +0.48V.

A number of controlled potential electrolysis experiments were performed with 5-methyliminobibenzyl. Q-t curves for electrolysis at +0.8V showed a sharp break at an n_{app} value of 1. The oxidized solutions were an intense blue color. The slope of the Q-t curves after this break was small but definitely larger than the slope usually found after complete electrolysis. On continuing the electrolysis, another break in the Q-t curves was observed at an n_{app} value of 2-2.2. If the electrolysis was stopped after the first break ($n = 1$) and a cyclic voltammogram obtained, a redox couple was seen centered at +0.44V (Fig. 5). There was no evidence for the original peak at +0.61V. When the scan was continued to negative enough potentials, a number of irreversible and distorted peaks corresponding to proton reduction was seen between —0.3 and —1.2V. When the electrolysis was continued until $n_{app} = 2$, cyclic voltammetry (with the initial potential at the potential of the electrolysis) showed only the reduction peak at +0.4V. There were no oxidation peaks at +0.48 or 0.61V. Stopping the electrolysis at +0.8V at any stage and electrolyzing at
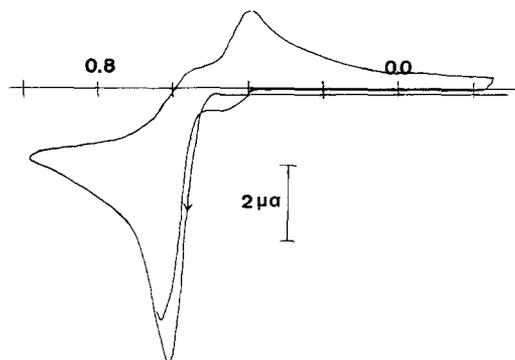

Fig. 4. Cyclic voltammogram of 0.85 mM 5-methyliminobibenzyl. Conditions: Same as in Fig. 1.
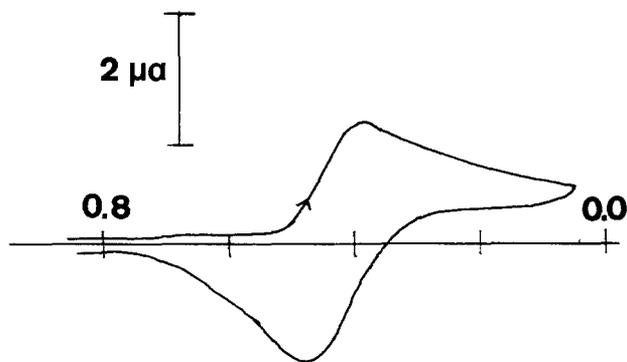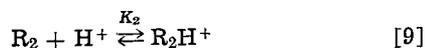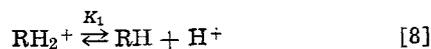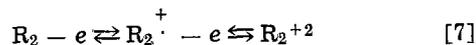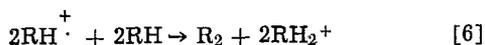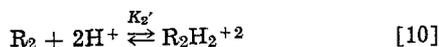
Fig. 5. Cyclic voltammogram of 0.85 mM 5-methyliminobibenzyl after one electron of electrolysis at +0.8V. After two electrons of electrolysis the oxidation peak is not observed. Conditions: Same as in Fig. 1.

+0.2V always resulted in half of the number of coulombs for reduction as had been passed during oxidation at +0.8V. The number of electrons obtained in reduction at −1.3V after electrolysis at +0.2V was the same as the number that had been obtained at +0.2V. Cyclic voltammetry following this reduction at −1.3V showed oxidation waves at +0.48 and +0.61V (Fig. 6), unless a complete electrolysis had been carried out at +0.8V ($n_{app} = 2$) at which time the +0.61V peak was absent.

A mechanism consistent with the above results is

$$RH - e \rightleftharpoons \overset{+}{RH} \cdot \tag{5}$$

$$2\overset{+}{RH} \cdot + 2RH \rightarrow R_2 + 2RH_2{}^+ \tag{6}$$

$$R_2 - e \rightleftharpoons \overset{+}{R_2} \cdot - e \rightleftharpoons R_2{}^{+2} \tag{7}$$

$$RH_2{}^+ \overset{K_1}{\rightleftharpoons} RH + H^+ \tag{8}$$

$$R_2 + H^+ \overset{K_2}{\rightleftharpoons} R_2H^+ \tag{9}$$

and/or

$$R_2 + 2H^+ \overset{K_2'}{\rightleftharpoons} R_2H_2{}^{+2} \tag{10}$$

Equation [6] above implies no mechanistic interpretation since it cannot be ascertained whether coupling occurs before or after loss of a proton from the
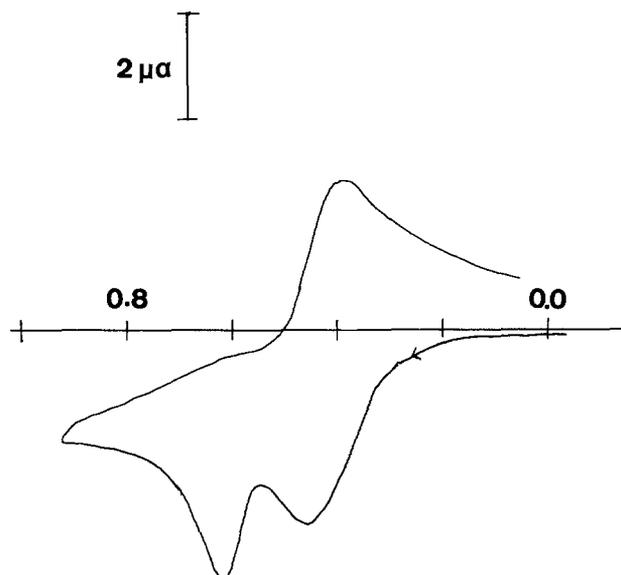

Fig. 6. Cyclic voltammogram of 0.85 mM 5-methyliminobibenzyl after one electron of electrolysis at +0.8V followed by electrolysis at −1.3V. After two electrons of electrolysis, the oxidation peak at 0.61V is not observed. Conditions: Same as in Fig. 1.

cation radical. The proposed mechanism is the same as that for carbazole except for the protonations of the neutral parent and coupled product. The chemical reactions in Eq. [6] are undoubtedly very rapid as demonstrated by the absence of a reverse reduction peak accompanying the oxidation peak at +0.61V. The reduction peak at +0.40V and the oxidation peak at +0.48V correspond to the redox processes of Eq. [7]. Both redox processes occur at similar potentials since only one peak is observed. The apparent total one-electron oxidation of the 5-methyl parent plus coupled product; whereas two would be expected by analogy to carbazole, comes about because of the protonation of the parent molecule in Eq. [6] which renders the parent molecule electrochemically inactive. By the time half the parent has become oxidized the remaining parent is protonated. The small residual slope of the Q-t curves after one electron of oxidation is due to the oxidation of the small amount of parent that can remain in equilibrium with protons and protonated parent, Eq. [8]. If the resulting dication is now reduced, the neutral dimer itself can be protonated and rendered inactive to oxidation, Eq. [9]. This mechanism is consistent with the fact that 5-methyliminobibenzyl is a stronger base than the related carbazoles (*vide infra*) where protonation of parent introduced no complications.

In an attempt to verify the role of protons, several experiments were carried out in the presence of the nucleophile pyridine in the hope of scavenging protons. When a large excess of pyridine was present (>10:1), cyclic voltammograms indicated that two electrons were transferred. Controlled potential electrolysis, however, showed that eventually in excess of four electrons were transferred. Pyridine apparently attacks the dication dimer forming a species that is oxidized further. The rate of the attack cannot be too rapid or else the voltammetry and electrolysis would have indicated the same number of electrons. Cyclic voltammetry showed no evidence of the couple at +0.44 following an oxidation with a large excess of pyridine. Also, the solution did not attain the intense blue color found after electrolysis performed without pyridine. If the electrolysis was carried out until the first break in the Q-t curves with a somewhat less than stoichiometric amount of pyridine followed by a reductive electrolysis at +0.2, the yield of the neutral dimerized product was 30% greater than was found in the absence of pyridine ($n_{app} = 0.65$ *vs.* 0.5, the time of the oxidative electrolysis was about the same). Some proton scavenging is apparently taking place. Interestingly, pyridine acted only as a proton scavenger in the electrolysis of carbazoles (3).

Experiments were also performed with added acid. According to the proposed mechanism, the acid should protonate the parent and no oxidation should be observed. Addition of equivalent amounts of acetic acid resulted in no change in the electrochemical behavior. However, when acetic acid was in large excess (100:1), the peak height of the +0.61V oxidation was somewhat diminished. At these concentrations of acetic acid a new smaller peak approximately 100 mV positive of the main oxidation appeared. With equivalent amounts of H_2SO_4, the +0.61V peak was absent and the new peak at ∼ +0.7V attained its maximum development, about one-third the peak height of the original oxidation. Further addition of H_2SO_4 resulted in the disappearance of this peak also. The results suggest that acetic acid is too weak an acid to protonate the 5-methyliminobibenzyl parent. Blank experiments where only supporting electrolyte and acid were present showed oxidative currents in the region of the peak observed above at +0.7V. These currents are probably due to added impurities such as water which undergoes a pH dependent oxidation in this region.

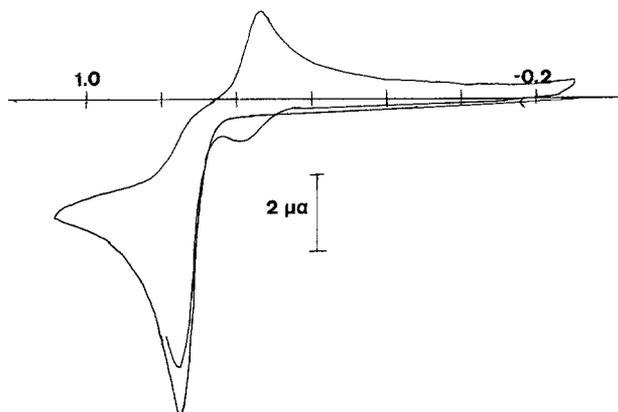*Imipramine · HClO4.*—A number of electrochemical experiments were also performed on the $HClO_4$ salt of

Fig. 7. Cyclic voltammogram of 1.0 mM imipramine HClO₄. Conditions: Same as in Fig. 1.

imipramine. After reduction of the proton of the tertiary amine group, the tertiary amine probably serves as a base for scavenging protons. The electrochemistry of the protonated imipramine was in all ways similar to 5-methyliminobibenzyl. An apparent one-electron oxidation was observed at $+0.75V$ and an apparent one-half electron reduction at $+0.55V$ (Fig. 7). These ratios and numbers were confirmed with controlled potential oxidations and reductions. Reduction of the amine proton ($-1.2V$) apparently activated the amine group which was oxidized before 0.75V. Controlled potential electrolysis at $+0.9V$ indicated that considerably more than two electrons were necessary for complete oxidation. The mechanism, however, appeared to be complicated and was not pursued further.

5-Methyliminostilbene.—Homogeneous oxidations of 5-methyliminostilbene (4) have shown that the coupling process may be more complicated than with the related bibenzyl compounds. A possibility of coupling at both the 2 and 10 positions was postulated (4). Electrochemical oxidation might then be expected to result in a more complex product distribution than was observed with the above compounds.

Cyclic voltammograms of 5-methyliminostilbene were characterized by two oxidation peaks at $+0.58$ and $+1.0V$ at 0.2 V/sec (Fig. 8). The height of the 0.58V peak corresponded to 1 electron (Table I). The peak at $+1.0V$ was more rounded and corresponded to about 0.2 electrons. On sweep reversal a new redox couple was observed at $-0.28V$ (peak separation = 30 mV). There was no evidence for reduction of the oxidized parent (radical cation). Coulometry at $+0.7V$ resulted in an initial $n_{app} = 1$. The oxidized solution (with a yellow color) had a reduction peak at -0.30 and an accompanying oxidation peak at -0.27 (Fig. 9). No evidence was seen of the original oxidation peaks at $+0.58$ and $+1.0V$ suggesting that the $+1.0V$ peak may be oxidation of the parent or a species formed at

$+0.58V$. Close inspection of the region around $-0.28V$ showed evidence of another redox couple at somewhat more positive potentials suggesting that at least two products may result from the oxidation at $+0.7V$. Controlled potential reductions and oxidations of the couples in the $-0.28V$ region showed that one-half the number of electrons are required as are initially consumed at $+0.7V$. Reduction of protons at -1.3 suggest that one proton is liberated per parent molecule oxidized. Reduction of protons results in the reappearance of the $+0.58$ and $+1.0V$ peaks (Fig. 10) which are about one-half of their original height. The mechanism of oxidative coupling of 5-methyliminostilbene at $+0.7V$ appears similar to 5-methyliminobibenzyl except more coupling positions are available.

An apparent change in mechanism occurs when the oxidation is performed at a potential positive of the $+1.0V$ peak. Performing such an electrolysis resulted in an n_{app} of about 1.85 and the product distribution appears to be much more complicated. The resulting products are reduced with one-half of the number of electrons required for the oxidation. Electrolysis at $-1.3V$ requires the same number of electrons as required for reduction of the products of the oxidation.

Discussion

The general oxidative behavior of all of the above compounds is probably similar. The likely initial step in the oxidation is the formation of a cation radical of the parent compound. In a very fast follow-up reaction the cation radicals couple at the 2-position (except possibly for iminostilbene where more coupling modes are possible) with the loss of one proton per parent. The proposed mechanism now deviates from the carbazole mechanism in that the parent and neutral coupled product may be protonated by the protons released during coupling and become electrochemically inactivated. A similar inactivation by released protons has been proposed for the anodic oxidation of N-alkylanilines (6).

Differences in electrochemical behavior between the compounds may in part be explained by differences in basicity of the parents. A relatively minor decrease in basicity of iminobibenzyl as compared to 5-methyliminobibenzyl would probably not increase the concentration of unprotonated parent that can remain in equilibrium with protons enough to have an easily measurable effect on the height of the oxidation wave. Because of the difference in time scale between potential sweep and coulometric experiments, this relatively small increase in unprotonated parent could have a significant effect on the shape of the Q-t curve. What might be expected would be a more drawn out Q-t curve with a less well-defined break. This is in fact the case with iminobibenzyl and supports the contention that iminobibenzyl is less basic than the 5-methyl analogue. Protonation of the neutral iminobibenzyl dimer might well be responsible for the merging and shifting of the two product couples observed in cyclic
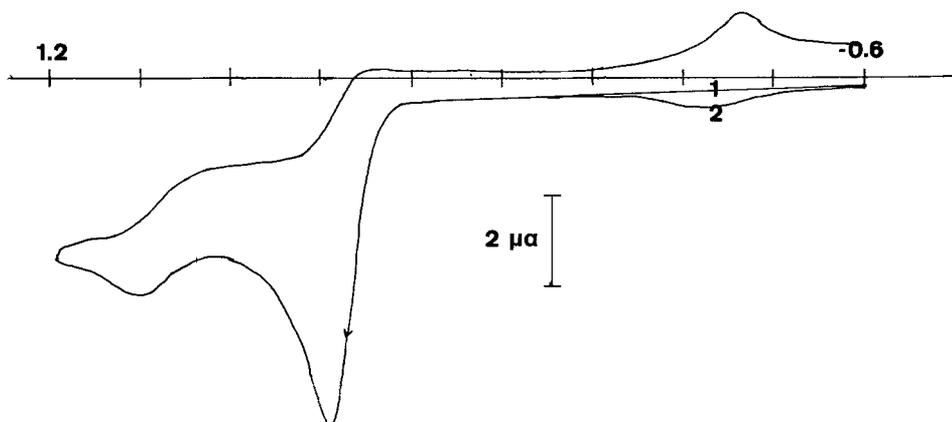

Fig. 8. Cyclic voltammogram of 1.0 mM 5-methyliminostilbene. 1, 1st sweep; 2, 2nd sweep. Conditions: Same as in Fig. 1.
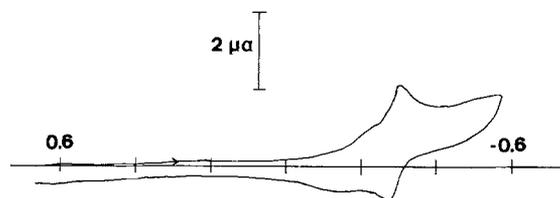
Fig. 9. Cyclic voltammogram of 1.0 mM 5-methyliminostilbene after electrolysis at +0.7V. Conditions: Same as in Fig. 1.
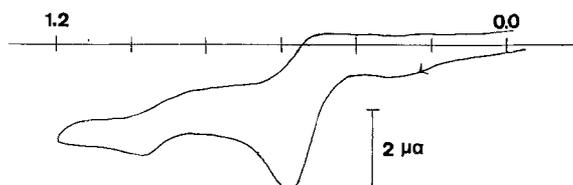

Fig. 10. Cyclic voltammogram of 1.0 mM 5-methyliminostilbene after electrolysis at +0.7V followed by electrolysis at −1.3V.

voltammetry of the parent compound as indicated by the reappearance of these couples upon reduction of protons.

The difference in basicities between the present compounds and the carbazoles can be explained in terms of structural considerations. The planar structure of the carbazoles permits the interaction of the lone pair of electrons on the nitrogen with the pi-electrons of the benzene rings making the lone pair less nucleophilic and very much less basic. X-ray structures of imino-bibenzyl-type compounds of interest in this study have not been obtained. However, x-ray studies of related compounds (7) and other considerations (8) indicate that the ethylene bridge of iminobibenzyl, 5-methyl-iminobibenzyl, and imipramine prevents easy attainment of a planar structure thus making the nitrogen lone pair more available. Although some increase in planarity is expected for 5-methyliminostilbene due to the unsaturated nature of the ethylene linkage, consideration of molecular models indicates that this bridge is highly strained and some rotation out of the plane is expected with a subsequent increase in basicity as compared to carbazole.

The subtle variation in basicities among the studied compounds is not as easily explained. The greater basicities of the N-substituted iminobibenzyls may partly result from the electron-donating properties of the aliphatic substituents on the nitrogens. Comparisons of the changes in basicity that result from substituting an aliphatic chain for hydrogen in a variety of amine compounds [e.g., pK_a's for anilinium and N,N-dimethylanilinium are 4.63 and 5.15, respectively (9)] indicate that the effect may not be large.[1] However, it may be that only small effects are necessary to explain the observed differences. An attractive aspect of this explanation is that it may explain why 5-methyliminostilbene is apparently a stronger base than iminobibenzyl even though it should be more planar. Arguments are presented below that suggest that iminobibenzyl is more planar, and therefore less basic, than 5-methyliminobibenzyl, perhaps because of some nonbonding interaction between the nitrogen methyl group and the benzene rings (9). Steric hindrance around the nitrogen atom of iminobibenzyl is well established from N-alkylation studies (10). Several attempts were made at determining the pK_a's for these compounds by titration of the base-forms in acetonitrile with perchloric acid (made anhydrous by addition of an excess of acetic anhydride). However, the basicity of these compounds (less than that of acetate

ion) was too small to show glass electrode responses larger than the drifts we observed for this electrode in changing from one calibration solution to another (up to 100 mV). Moreover, to account quantitatively for the differences in these compounds, differences in the acidity of the very unstable radical cations would also have to be considered.

Differences in planarity should also have some effect on the redox potentials of these compounds. Unfortunately, the irreversible nature of the following chemical reaction prevents using peak potentials as a reliable guide as to the ease of oxidation of the parent compounds although where known the differences in potentials correlate with the differences in ionization potentials (11). For the most part the redox processes of the coupled products are reversible or nearly so. Inspection of Table I shows that no real trend exists for the redox potentials of the coupled products, and it is likely that a number of effects such as the relative stabilization of reduced and oxidized forms by delocalization and conformational effects may play important roles. Related substituent effects are apparent in the anodic oxidation of N-akyl anilines (6).

Deserving special note, though, is the unusual ease with which the 5-methyliminostilbene dimer may be oxidized. A reasonable explanation is that the major product of the 5-methyliminostilbene oxidation is a dimer coupled at the 10-position rather than the 2-position as is the case for the other compounds. A structure VII reminiscent of a

VII
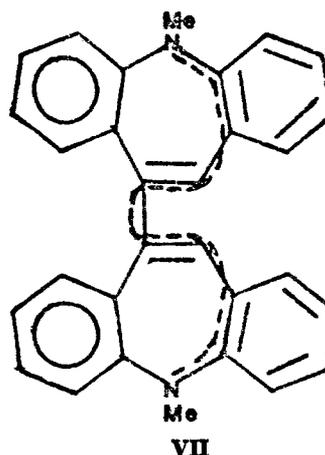
diamiminobutadiene results (dotted line outlines the butadiene backbone). Compounds such as this are known to be exceedingly easy to oxidize (12). One might also consider VII to be related to the dihydro forms of bipyridylium dications which are very easily oxidized (13). VII cannot be isolated in the presence of atmospheric oxygen because of its low oxidation potential. Attempts at isolating the dication salt of VII after bulk electrolysis were unsuccessful.

If the parent molecules are sufficiently nonplanar, the two parent moieties of the dimers are effectively electronically decoupled. Removing an electron results in most of the positive charge residing on one of the parent moieties. Removing the second electron should then not be much more difficult than the first. The oxidation peaks for the two processes would then appear close together. This appears to be the case for 5-methyliminobibenzyl and imipramine. The two oxidation peaks observed for iminobibenzyl suggests on the basis of the above argument that iminobibenzyl is more planar than the 5-methyl analogue.

Since the coupled 5-methyliminostilbene also has only one oxidation peak, one might be tempted to suggest that a reaction scheme analogous to that of 5-methyliminobibenzyl was occurring. However, the peak separation between the oxidation is 30 mV and it is, therefore, not possible to ascertain whether these peaks correspond to two 1-electron processes occurring at the same potential or one 2-electron process.

A nuance of the 300 mV separation between the two oxidations of bicarbazoles is that any neutral bicarbazole formed as a transient in the oxidation of carbazole can react with dication to yield the radical cation. A measurable ESR signal might be expected during electrolysis. Such an ESR signal was observed for carbazole (3). The closeness of the two oxidations for the dimeric 5-methyliminobibenzyl make the driving force for such a reaction sequence much smaller. Accordingly, the probability of producing a sufficient number of free radicals to observe during an electrolysis in an ESR cavity is much less. In line with this reasoning, an *in situ* electrolysis of 5-methyliminobibenzyl in an ESR (14) cavity resulted in no ESR signal.

Acknowledgment

REFERENCES

1. "Organic Electrochemistry: An Introduction and Guide," M. M. Baizer, Editor, Marcel Dekker, Inc., New York (1973).
2. C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems," Marcel Dekker, Inc., New York (1970).
3. J. F. Ambrose and R. F. Nelson, *This Journal,* **115,** 1159 (1968).
4. P. Beresford, D. H. Iles, L. J. Kricka, and A. Ledwith, *J. Chem. Soc. Perkin I,* 276 (1974).
5. W. V. Childs, J. T. Maloy, C. P. Keszthelyi, and A. J. Bard, *This Journal,* **118,** 874 (1971).
6. R. L. Hand and R. F. Nelson, *J. Am. Chem. Soc.,* **96,** 850 (1974).
7. L. J. Kricka and A. Ledwith, *Chem. Rev.,* **1,** 101 (1974).
8. J. R. Huber and J. E. Adams, *Ber. Bunsenges. Phys. Chem.,* **78,** 217 (1974); R. J. Abraham, L. J. Kricka, and A. Ledwith, *J. Chem. Soc. Perkin II,* In press.
9. Handbook of Chemistry and Physics, 51st ed., The Chemical Rubber Co., P D120, (1970); "Determination of Organic Structures by Physical Methods," E. H. Braude and F. C. Nachod, Editors, p. 567, Academic Press, New York (1955).
10. L. J. Kricka and A. Ledwith, *J. Chem. Soc. Perkin I,* 2292 (1972).
11. H. J. Haink, J. E. Adams, and J. R. Huber, *Ber. Bunsenges. Phys. Chem.,* **78,** 436 (1974).
12. J. M. Fritsch, H. Weingarten, and J. D. Wilson, *J. Am. Chem. Soc.,* **92,** 4038 (1970).
13. E. Steckhan and T. Kuwana, *Ber. Bunsenges. Phys. Chem.,* **78,** 253 (1974).
14. I. B. Goldberg and A. J. Bard, *J. Phys. Chem.,* **75,** 3281 (1971).