THE ELECTROOXIDATION OF PYRROLE, INDOLE, CARBAZOLE, AND THEIR DERIVATIVES

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Abstract -- The electrooxidations of pyrrole, indole, carbazole and a number of their substituted and partially reduced derivatives are described. The overall mechanistic aspects are summarized and discussed. Certain aspects of indole alkaloid biosynthesis involving oxidation are considered. The experimental conditions used in a number of reactions are summarized.

INTRODUCTION

In an earlier review article on the electrooxidation of phenolic isoquinolines,[1] we presented a general introduction to electrooxidation and discussed some of the advantages and disadvantages of the technique. Specifically, we pointed out that it was possible to control the amount of oxidizing power (potential) applied to a given substrate, thus minimizing overoxidation of easily oxidized materials. We summarized our attempts to carry out biomimetic oxidations in the isoquinoline alkaloid series. In this article, we will summarize the electrooxidations of another group of heterocyclic compounds which are easily oxidized, specifically pyrrole and its benzoderivatives, indole and carbazole.

Pyrrole and its derivatives are quite similar to the phenols in their general degree of reactivity, their degree of acidity, and their ease of oxidation. Furthermore, parallel biosynthetic roles are played by the phenolic amino acid tyrosine and the indolic amino acid tryptophane. These two amino acids, through a series of oxidations and ring closures, give rise to the isoquinoline and indole alkaloids, respectively. Considering the importance of the pyrrole system, its relative ease of oxidation and the desirability of preventing "overoxidation", it is remarkable that relatively few electrooxidation studies have been carried out.

The half-wave potentials of some pyrrole systems are given in Table I along

with some reference compounds of interest. The actual values of the potentials differ depending upon the substituents present and the conditions of the measurements. However, the relative order of reactivity is valid. Pyridine is much more difficult to oxidize than any of the five-membered systems and is sometimes used as a solvent for electrooxidations. The half-wave potentials for the pyrroles and phenols are strongly dependent upon pH, being more easily oxidized in base (as long as the pyrrole is unsubstituted on nitrogen).

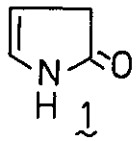
Table I. Oxidation Potentials of Some Pyrrole Derivatives and Reference Compounds

Compound	*Half-wave potentials, V. vs. S.C.E.*	*Ref.*
pyrrole	1.08	2
indole	0.94	3
carbazole	1.18	2
1,2,3,4-tetrahydro-carbazole	0.66	3
1,2,3,4-tetrahydro-β-carboline	0.70	3
pyridine	2.22	2
phenolic 1,2,3,4-tetra-hydroisoquinolines and phenols	0.7 - 1.2	2, 4

PYRROLE

There are at least four reports on the electrooxidation of unsubstituted pyrrole. Lund[5] found that pyrrole oxidation rapidly coated the anode with a polymer which stopped the reaction. This polymerization reaction has been used recently[6] to prepare a polymer coated electrode. The coating is reported to be a "strongly adhered durable film with enhanced conductivity and good electrode properties." The electrode was used to study the cyclic voltammetry of several substrates, but no catalytic effects were noted, and no preparative reactions were carried out.

Pyrrole has been oxidized in the presence of benzaldehyde to give porphines in low yields.[7] However, the actual electrooxidation is probably that of a partially reduced porphine formed from pyrrole and benzaldehyde rather than an oxidation of pyrrole itself. Finally, the electrooxidation of pyrrole in base has been shown to produce compounds 1, 2, and 3 in unspecified yield.[8] Possible mechanisms for this reaction are considered below.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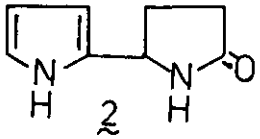
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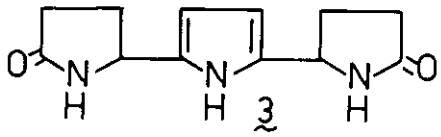
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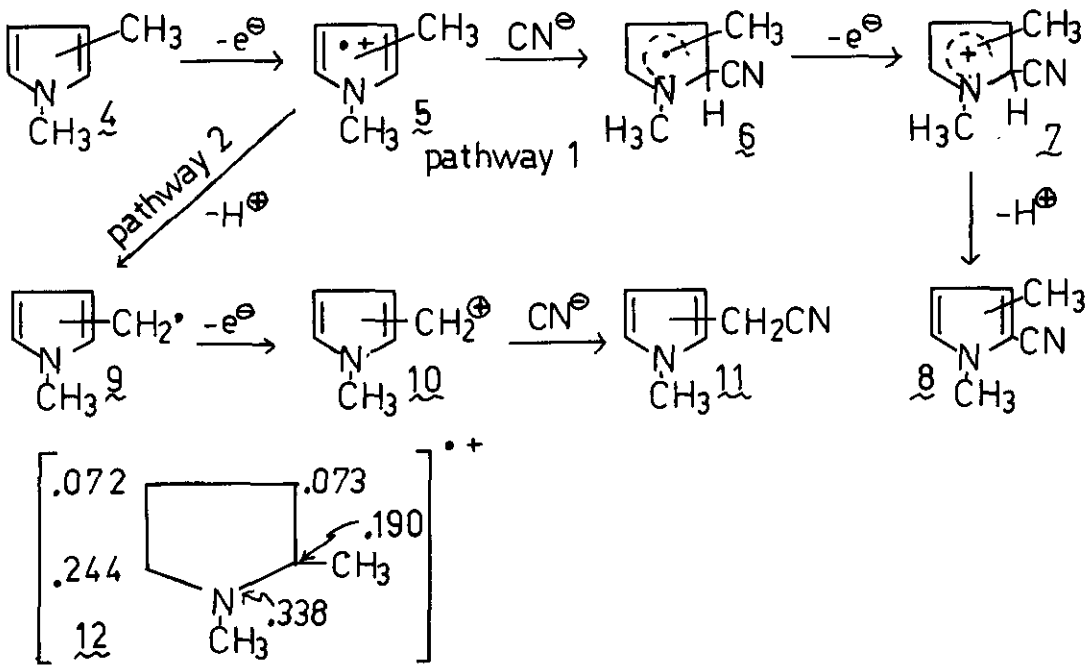
When the nitrogen in pyrrole is blocked with a methyl group, polymerization appears to be retarded, and oxidation products can be obtained. The brief communication of Yoshida[9] provides some elegant examples of electrochemical synthesis as well as a mechanistic framework for the presentation of this article. A series of N-substituted pyrroles and indoles were oxidized in methanolic sodium cyanide to yield two types of products. Most of the products contained a cyano group on the aromatic ring, but in a few cases, side chain cyanation occurred. Scheme I, as drawn out for a methyl N-methylpyrrole (4), illustrates the mechanistic possibilities. These possibilities correspond to the classical mechanisms proposed for oxidative substitution on aromatic systems *vs.* oxidative substitution on side chains.[10] In pathway 1, the initially formed cation radical (5) may react with $CN^{\ominus}$ to give the radical (6) which subsequently loses another electron and proton to give a ring substituted product (8). In pathway 2, 5 may lose a proton to form a benzyl type radical (9) which loses a second electron to give 10 which reacts with $CN^{\ominus}$ to yield a side chain substitution product (11). Yoshida carried out a molecular orbital calculation on the radical cation of 1,2-dimethylpyrrole which showed the positive charge distribution given in 12.

From 12, it is obvious that ring cyanation would go first to the 2 and 5 positions if they are vacant. This is in accord with the experiments. If the 2 and 5 positions are occupied by methyl groups, reaction appears to take the second pathway leading to side chain cyanation. In only one case, 2,5-dimethyl-1-phenylpyrrole, was any 3-substitution obtained, and this was in low yield (5%). The products observed from pyrrole itself (1,2 and 3)[8] can be explained by similar reasoning. The radical cation which would be derived from pyrrole (corresponding to 5) could react with $OH^{\ominus}$ to yield, after loss of a second electron and a proton, 2-hydroxypyrrole which is a tautomer of 1. Compound 1 is an enamide which would be expected to undergo a non-oxidative nucleophilic

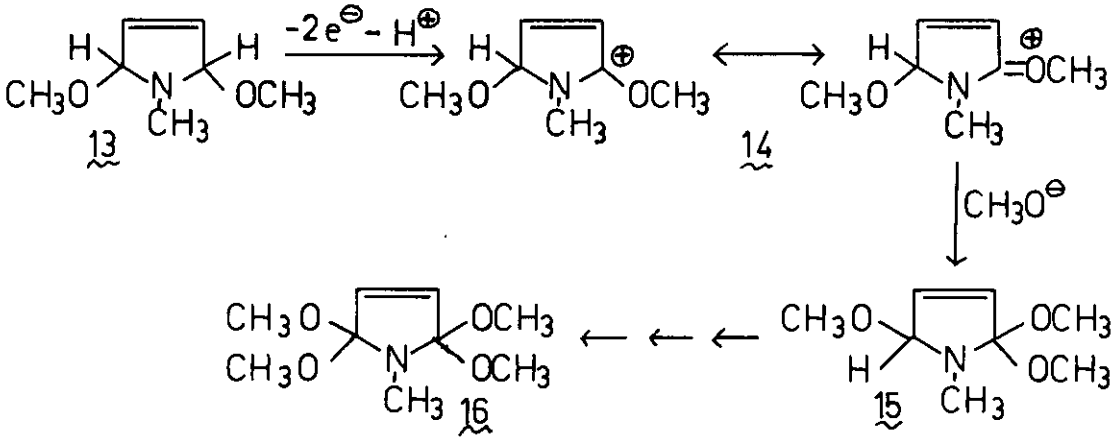
Scheme I



attack by an electron-rich pyrrole to give 2. A similar reaction of 2 with a second molecule of 1 would produce 3.

In an earlier work, Weinberg and Brown[11] oxidized N-methylpyrrole to give a 64% yield of 2,2,5,5-tetramethoxy-N-methylpyrrole (16). Although a mechanism involving a dication was proposed by the authors, the reaction can be easily explained by a Yoshida type pathway. A radical cation derived from N-methylpyrrole and analogous to 5 could react with $CH_3O^{\ominus}$ to give a radical which could lose a second electron to give a cation analogous to 7. If 7 reacts with $CH_3O^{\ominus}$ instead of losing a proton, 2,5-dimethoxy-3-pyrroline (13) is obtained. If 13 undergoes similar oxidation at the oxygen-activated allyl position, the resonance hybrid (14) would be obtained. Further reaction of 14 with $CH_3O^{\ominus}$ would yield 15 which, by a similar process could yield product (16). It is noteworthy that various electrooxidations of thiophene and furan in the presence of nucleophiles tend to stop at the intermediate disubstituted, dihydro stage corresponding to 13 rather than being further oxidized.[12]

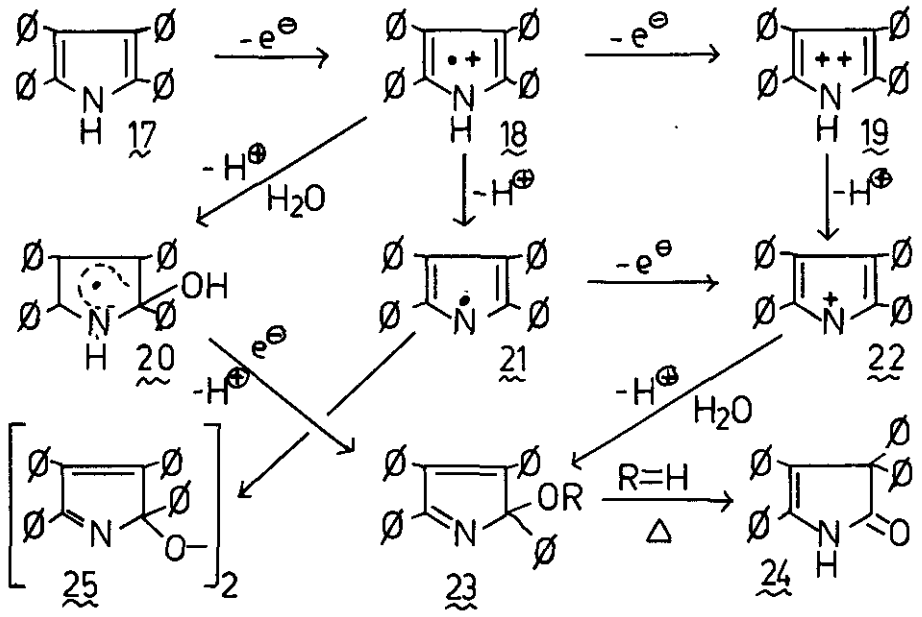
When the four carbons of pyrrole are substituted by aromatic groups,



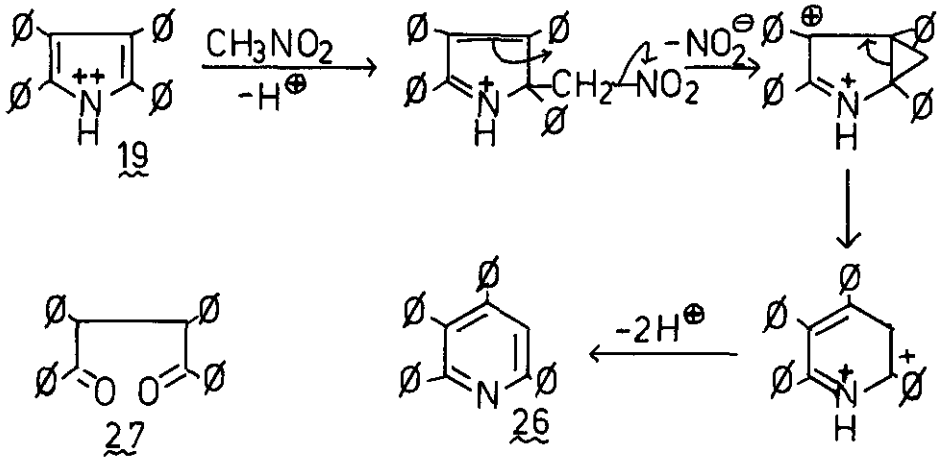
pathway 2 in Scheme 1 is blocked and pathway 1 cannot be completed. Caullet and his coworkers have investigated an extensive series of these compounds and found that the ultimate products depend upon the solvent and temperature.[13] In neutral solution, all of the compounds studied showed two waves which are thought to correspond to the sequential formation of the radical cation (18) and the dication (19) (Scheme II for 2,3,4,5-tetraphenylpyrrole, 17). In base, only one wave was observed corresponding to the two electron pathway through 18 and 21 to the cation (22). At 0°C, in nitromethane or acetonitrile containing traces of water, 23 (R=H) was obtained in yields of about 60%. In methanol and ethanol, the corresponding ethers (23, R=CH_3 and CH_3CH_2) were obtained. Compound 23 could be formed by several routes: nucleophilic attack by water (or alcohol) on the cation radical (18) to give 20 followed by loss of another electron and a proton; nucleophilic attack by water on the cation 22 followed by loss of a proton; or, as the authors prefer, attack of water on the dication (19) followed by the loss of two protons. The same product was obtained when the reaction was carried out at the first or second wave. The authors present evidence that the radical cation (18) disproportionates to starting material and 19 when the reaction is carried out at the first wave, thus explaining the products through dication 19. When 23 (R=H) was heated, it rearranged to 24.

When the reaction was carried out at higher temperature (> 40°) in CH_3CN, 24 was obtained along with 23. In the presence of air, the peroxide (25) was obtained, presumably from a radical such as 21. At higher temperatures in nitromethane, an interesting reaction occurred in which the carbon from the nitromethane was incorporated into a pyridine ring. It was proposed that the

Scheme II



dication (19) reacted as shown to yield 26. Similar and perhaps more plausible mechanisms could be written involving other intermediates in Scheme II. In many cases, traces of the dibenzoylstilbene (27) were isolated and are thought to arise from oxidation of 23, perhaps with $NO_2^{\ominus}$ formed as shown in 19 to 26.



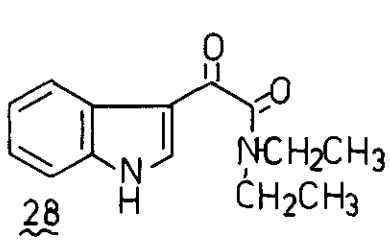
In all, five tetraarylpyrroles were investigated; tetraphenyl, tetra-p-

tolyl, tetra-p-anisyl, tetra-p-chlorophenyl, and tetra-p-biphenyl. The ease of oxidation of the various compounds was correlated with Taft σ^* values,[13d] and the more electron rich systems were found to be more easily oxidized. The more electron rich systems were also found to give the more stable cation radicals (18). A recent analytical study of a series of tetrasubstituted pyrroles supports the formation of the cation radicals and dications described in Scheme II.[14] However, no preparative reactions were carried out.

When all five atoms of pyrrole are substituted with aromatic groups, the reactions of Scheme II are blocked, and relatively stable cation radicals are obtained.[15] The cation radicals were characterized spectrometrically, but no products were isolated from the reactions. In his studies on the electrooxidation of amino acids, Takayama oxidized pyrrolidine-2-carboxylic acid (proline)[16a] and 5-carboxy-2-pyrrolidone.[16b] From proline, he obtained pyrrolidine, succinimide, succinic acid, CO_2, and NH_3. From 5-carboxy-2-pyrrolidone, he obtained succinimide, succinic acid and CO_2. The reactions were not potential controlled and should be repeated using modern methods.[44]

INDOLE

Indole itself, like pyrrole, produces an electrode fouling on oxidation which makes product isolation difficult.[3] However, when the oxidation was carried out using a graphite cloth anode (which was replaced several times during the reaction) in the presence of tetraethylammonium perchlorate in acetonitrile, it was possible to isolate about 15% of 28.[17] The extra atoms appear to have come from the electrolyte, but the mode of formation is not known. In light of the results given below for the cyanation of indole, it is remarkable that reaction has occurred at the 3-position of the indole.



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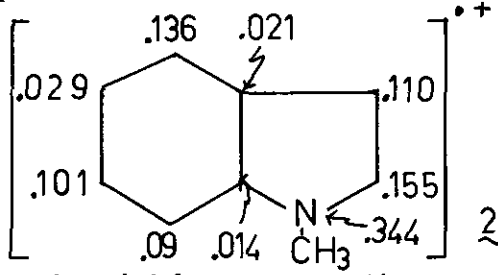

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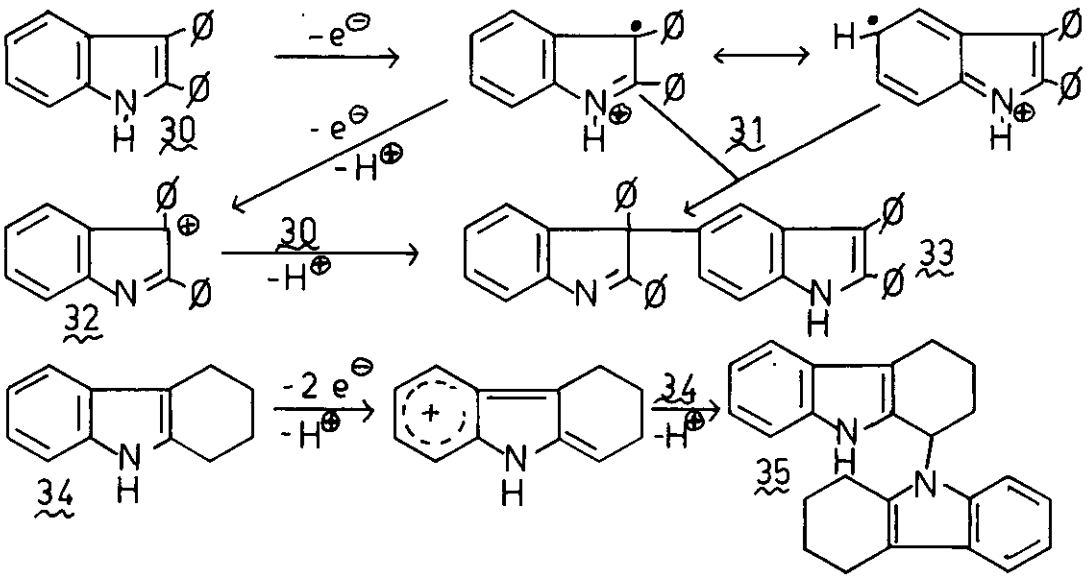
Yoshida[9] has also cyanated various indoles. The reaction was more successful when the nitrogen was methylated, although a 16% yield of 2-cyano-3-methylindole was obtained from 3-methylindole. N-Methylindole gave 50% of the 2-cyano derivative and 9% of the 3-cyano derivative, thus indicating that the

indole cation radical (analogous to 5) is more reactive at the 2-position. This is in contrast to the Nelson work[17] and the normal ground-state behavior of indole. It is, however, in accord with the results of a molecular orbital calculation on the cation radical of indole as shown in 29.[18] When position 2 was occupied, cyanation took place at the 3-position. The mechanism of this reaction is similar to pathway 1 in Scheme I. No side chain cyanation was noted.

When positions 2 and 3 of indole are blocked, dimerization reactions take place. Thus, 2,3-diphenylindole (30) gives a 90-95% yield of 33.[19] This dimerization can take place by at least two mechanisms. The first of these is proposed by the authors and involves a radical pairing of the two resonance forms of the indole cation radical (31) followed by a loss of two protons to give 33. A second or ionic pathway would involve the loss of two electrons and a proton from 30 to give a cation (32). This cation could then attack another molecule of 30 to give 33 after proton loss. This is almost a classic case of contrasting radical and ionic mechanisms which must be considered in any electrochemical dimerization reaction, and it is extremely difficult to distinguish between them. Analytical evidence is presented in favor of a cation radical formation followed by a rapid second order reaction, thus corresponding to a radical mechanism. However, the isolation of a single unsymmetrical dimer would appear to be evidence in favor of an ionic mechanism. It is difficult to see why two identical resonance forms of 31 should not couple to give, for example, a 5,5' dimer as is observed in the carbazole series shown below. We have observed [3,20] the electrooxidative dimerization of 1,2,3,4-tetrahydrocarbazole (34) to the known dimer (35)[21] and have suggested the ionic mechanism shown below. Aiura and Kanaoka[21] have shown that an ionic mechanism best accounts for the peroxide oxidation of 34 to 35.

Sainsbury and Wyatt[22] have investigated the intramolecular coupling of a number of compounds containing two easily oxidizable portions, an indole or a partially reduced indole and a dimethoxybenzene. Several interesting results were obtained, but it is not easy to decide which of the two portions was oxidized first to bring about reaction. The results are sketched out in Scheme IV. The oxidation of 36 to 37 is thought to take place through an intermediate dienol as shown since the methoxy group at position 6 on the indoline is lost

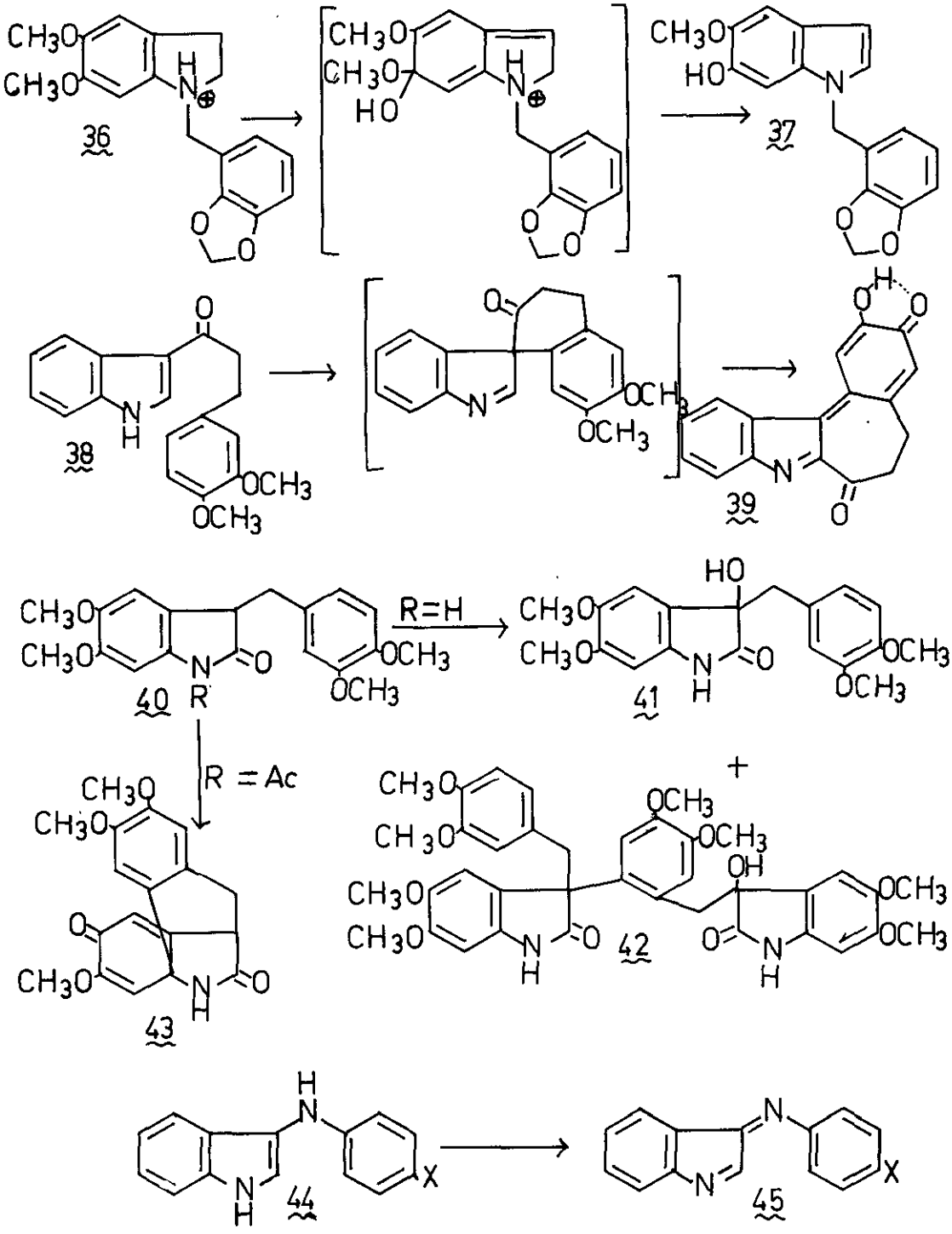
Scheme III



and since reaction does not take place when the two methoxy groups on the indoline are replaced by a methylenedioxy group. The oxidation of 38 to 39 takes place in 68% yield and could involve an initial oxidation in either the indole or the benzene ring to give an intermediate as shown. The intermediate was not isolated but is thought to rearrange and yield 39 after further oxidation. The oxidation of 40 produces two products, depending upon whether the nitrogen is acetylated or free. When the nitrogen is free, reaction appears to take place through the oxindole ring leading to the 3-hydroxyoxindole (41) and a dimer (42). The dimer could result from the acid catalyzed dimerization of 41 or from one of the electrolysis intermediates. When nitrogen is acetylated, the reaction is best visualized as the oxidation of the benzene ring to give a positive species which attacks the indole at the 7a position to cause a loss of the methoxy group at 5 and dienone formation (43). The intramolecular coupling of 40 to 43 is similar to the intramolecular coupling observed in the isoquinoline series by Miller and Stermitz[23] and in the lycorine alkaloid series by Tobinaga and his coworkers.[24]

The oxidation of a series of 3-arylaminoindoles (44) has been studied analytically and preparatively.[25] The products are iminoindoles such as 45, and the

Scheme IV



reaction is thought to take place by a cation radical mechanism.

ELECTROOXIDATION AND THE INDOLE ALKALOIDS

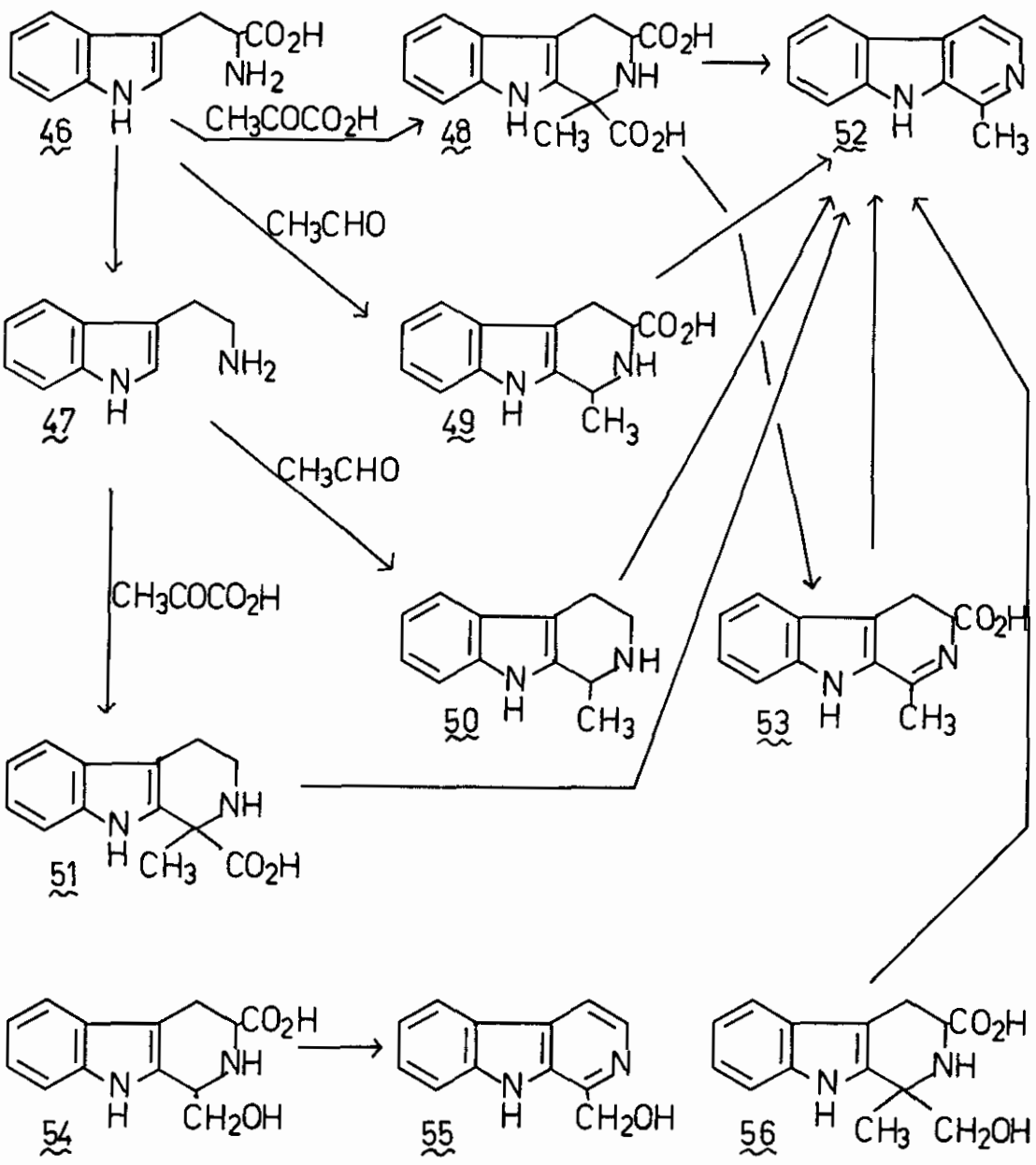
The indole alkaloids are derived from the amino acid tryptophane (46) by a complex series of enzyme mediated ring closures, rearrangements and oxidations.[26] Frequently, indole alkaloids contain an oxygen function such as a hydroxyl or a methoxy group in the benzene ring. This oxygen may be added as the first oxidation step as is probably the case in the isoquinoline alkaloids[1] or at a later stage. The biomimetic oxidation of tryptophane has been studied intensively,[27] but the electrooxidation has been studied only briefly under fairly uncontrolled conditions. The only products isolated were ammonia and carbon dioxide.[28] The problem should be reinvestigated using a controlled potential.

The next step in indole alkaloid biosynthesis involves the formation of a β-carboline ring from tryptophan and some fragment which will give carbon 1 of the β-carboline ring. In the case of harman (52) this fragment provides carbon 1 and a methyl group. The general routes from 46 to 52 are shown in Scheme V. There are two points of variation in different routes. The first point is whether 46 is decarboxylated to tryptamine (47) before ring closure or not. Since some indole alkaloids retain the tryptophane carboxyl group,[26c] it would appear that some β-carboline-3-carboxylic acids such as 48 or 49 are involved in some biosyntheses at least. The second point of variation concerns the fragment which yields carbon 1 of the β-carboline. The fragment could be acetaldehyde (46 to 49 to 52 and 47 to 50 to 52) or pyruvic acid (46 to 48 to 52 and 47 to 51 to 52). This controversy has been summarized for a similar situation in isoquinoline alkaloid biosynthesis, which appears to follow the pyruvate pathway.[29]

For the more complex indole alkaloids, carbon 1 of the β-carboline is part of a monoterpene unit derived from the iridoid loganin. The final elaboration of the complex alkaloids involves a number of oxidation steps,[26d] some of which seem to involve an oxidative decarboxylation of a β-carboline-3-carboxylic acid.[30]

In the biomimetic conversion of tryptophane to harman, there are essentially three problems; the loss of the carboxyl group at carbon 1, the loss of the carboxyl group at carbon 3, and the aromatization of the ring. We postulated that these conversions might all take place through a controlled electrooxidation of the easily oxidized indole portion of the various intermediates. We found

Scheme V



that similar reactions occur in the isoquinoline series.[31] Actually, the loss of carboxyl from carbon 1 is not so much a problem since it decarboxylates easily in acid without oxidation.[32] Furthermore, chemical oxidations of the carboxylic acids constitute a known synthetic route to aromatic β-carboline

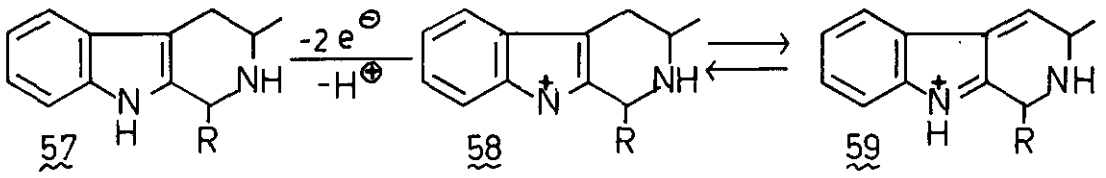
systems.[33] In order to test our hypothesis, we prepared samples of 48, 49, 50, and 51 as well as some other reference compounds.[3]

At about the discharge potential of the indole ring, as determined from indole and 1,2,3,4-tetrahydrocarbazole, all of the carboxylic acids are oxidatively decarboxylated and the rings are aromatized to give harman (52) in good yield. Furthermore, the conversion of 48 to 52 appears to take place via 1-methyl-3,4-dihydro-β-carboline-3-carboxylic acid (53) which was also prepared and investigated. The conversion of 49 to 52 appears to go through a 1,2-dihydro-β-carboline although such an intermediate could not be isolated (such 1,2-dihydro-β-carbolines have never been isolated). The conversion of 51 to 52 did take place through a 3,4-dihydro-β-carboline which could be isolated. In addition, two compounds containing a 1-hydroxymethyl group were prepared, 54 and 56. Compound 54 gave the natural product (55) in good yield on oxidation, and 56 was converted to 52 with the loss of the hydroxymethyl group. 1,2,3,4-Tetrahydro-β-carboline, 1-methyl-1,2,3,4-tetrahydro-β-carboline (50), indole, 1,1-dimethyl-1,2,3,4-tetrahydro-β-carboline-3-carboxylic acid, and the N-acetyl derivatives of 1,2,3,4-tetrahydro-β-carboline and its 1-methyl derivative all gave electrode fouling and no isolable products.

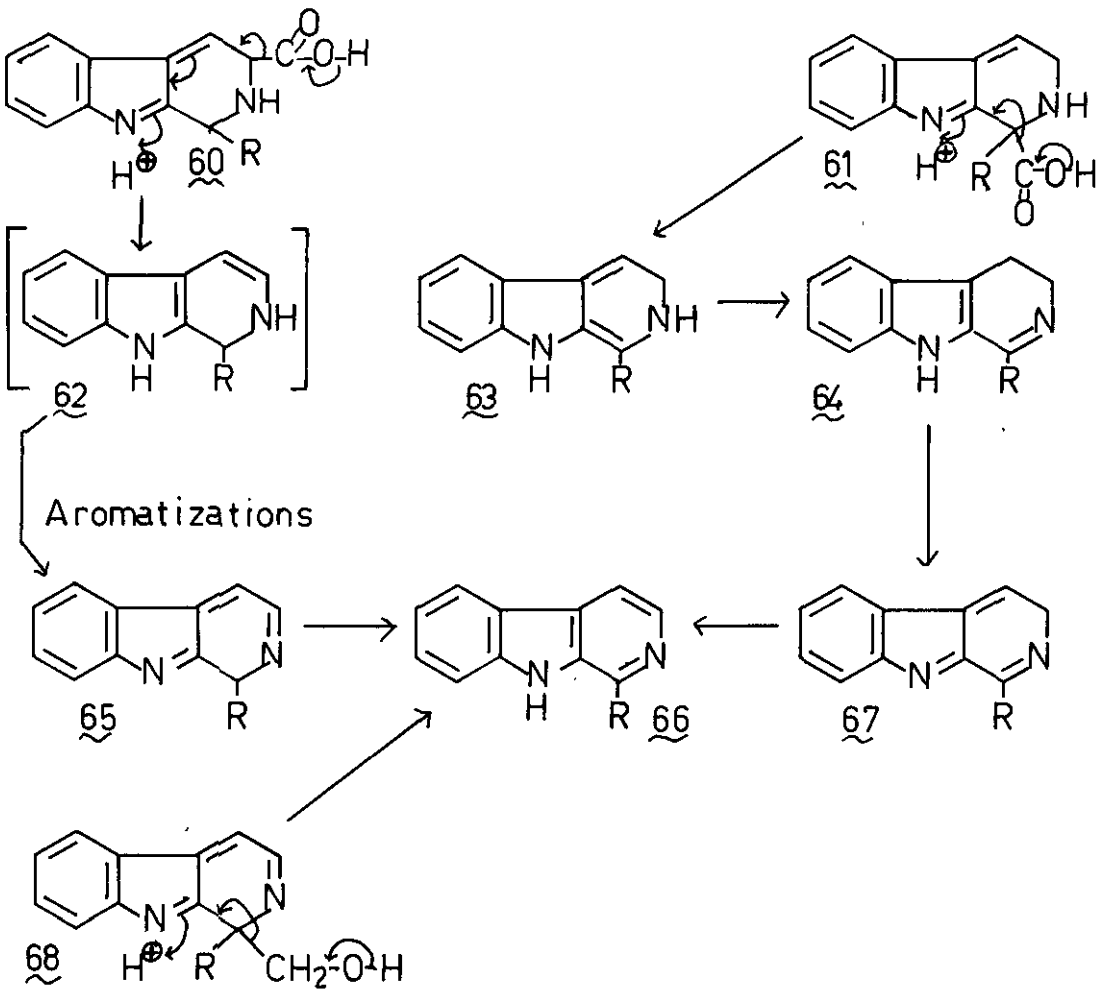
Five different reactions appear to take place in Scheme V. These are oxidative decarboxylation of a 1-carboxylic acid and a 3-carboxylic acid, dehydrogenation between C-1 and nitrogen and between C-3 and C-4, and the loss of the hydroxymethyl group. The last three are probably driven partially by formation of an aromatic ring. These reactions can all be visualized as taking place through a positively charged intermediate similar to 10, 22, and 32 as given above. *Possible mechanisms are given in Scheme VI.* A general structure (57) could lose two electrons and a proton to give a cation which can be written in a number of ways, two of which are 58 and 59. If 59 is further deprotonated and drawn with the carboxyl groups in place as in 60 and 61, the decarboxylations can take place by conventional paths to give the intermediate dihydro derivatives (62 and 64) respectively. Compound 62 was not isolated, but 64 was. The oxidation of the dicarboxylic acid (48) would involve both reactions. If 62 were further oxidized to 65, and 64 were oxidized to 67 by routes similar to those in 57 to 58, 59, compounds 65 and 67 would result. Both could tautomerize to the observed aromatic product (66). If 65 were visualized with a $-CH_2OH$ group in place as in 68, the loss of the group as formaldehyde can be rationalized.

Scheme VI

Initial Oxidation (R=CH_3)



Decarboxylations



These facile decarboxylations triggered by oxidation of an aromatic ring are reminiscent of the "pseudo Kolbe" reactions proposed by Coleman and Eberson.[34b] In this specific example,[34a] phenylacetic acids were oxidatively decarboxylated to give benzyl carbonium ions. In our oxidative decarboxylations of 1,2,3,4-tetrahydroisoquinoline-1-carboxylic acids[31] the reaction was again that of a substituted phenyl acetic acid. In the β-carboline systems, the decarboxylations involve both a phenyl acetic acid system and a phenyl propionic acid system. Indole-3-acetic acid has been shown to undergo a typical Kolbe radical dimerization to 1,2-bis(3-indolyl)ethane in low yield.[35]

The voltammetry of a number of indole alkaloids was studied by Allen and Powell.[36] They concluded that the loss of one electron from the indole was the rate controlling step in acid but that a two-electron reaction occurred under neutral conditions. These observations are in accord with the mechanistic views in this review. However, no products were isolated, and preparative experiments in this series would be interesting.

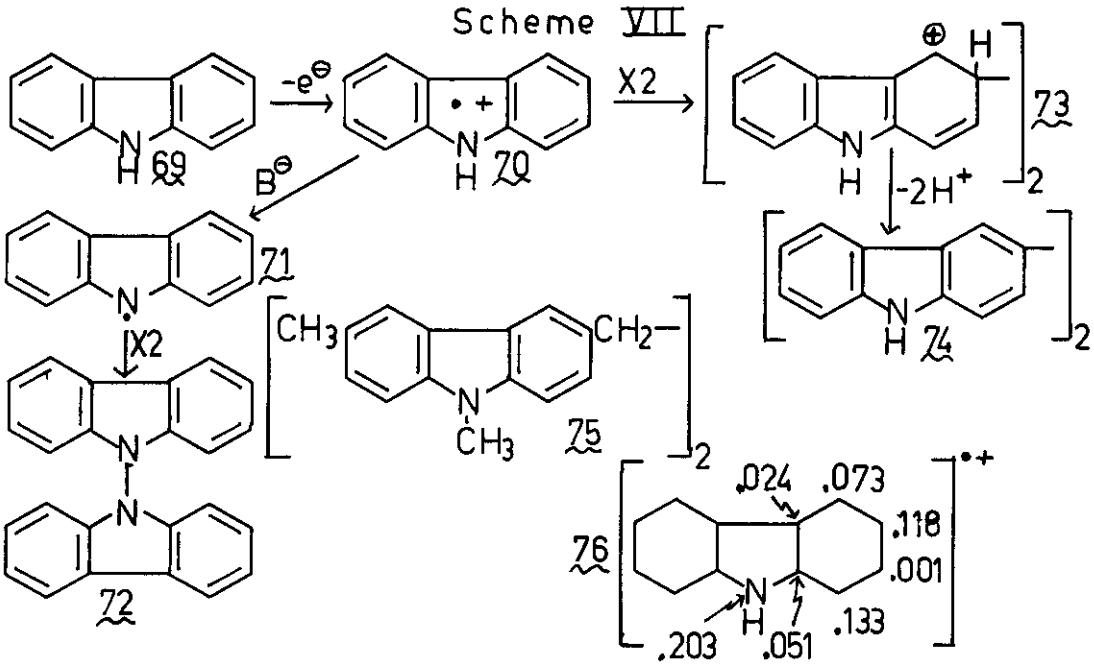
CARBAZOLE

In the various oxidations described above, the electron-rich nitrogen ring is the initial site of oxidation, and the various products result from a nucleophilic attack on the ring or from reactions taking place on aliphatic carbons attached to the ring. In carbazole, most of these reactions are blocked by the fused benzene rings. However, the radical character of the initially formed species is spread over the entire system, giving rise to quite a different reactivity.

Carbazole (69) and 71 of its substituted derivatives have been oxidized by Nelson and his coworkers.[37] The products were isolated in most cases, and the mechanism was carefully investigated. The products are symmetric carbon-carbon (3, 3') and nitrogen-nitrogen (9,9') dimers like 72 and 74 in Scheme VII. The oxidation of 3,6,9-trimethylcarbazole was postulated to give the dimer (75) although the product was not isolated. It is interesting to note that no unsymmetrical dimers were isolated in this study whereas the dimerizations of the various indoles gave only unsymmetrical dimers.

The distribution of the unshared electron or radical character of the carbazole cation radical was calculated to be as shown in 76. Note that the numbers in 76 refer to radical character whereas the numbers previously noted for pyrrole (12) and indole (29) refer to positive charge. The reaction is visualized to

Scheme VII



take place through the cation radical (70). In neutral solution, 70 dimerizes to the dication 73. Loss of two protons leads to the 3, 3'-dimer (74) in moderate yields. In base (2,4,6-trimethylpyridine), 70 is deprotonated to the radical (71) which dimerizes to the 9,9'-dimer(72) in almost quantitative yield. When a substituent is present on nitrogen, the 3,3'-dimer is obtained. When substituents are present on nitrogen and in the 3-position, a 6,6'-dimer results. When the nitrogen and both positions 3 and 6 are substituted, a fairly stable cation radical is obtained. These cation radicals were characterized by ultraviolet-visible spectroscopy and by electron paramagnetic resonance.

When the carbazole contained amino groups or dimethylamino groups in the 3-position, the behavior was comparable to that of p-phenylenediamines with the derived cation radicals having an enhanced stability. Similarly substituted cation radicals have been obtained from carbazoles by Lamm, Pragst, and Jugelt.[38]

EXPERIMENTAL CONDITIONS

In an electrooxidation, the initially formed cation radical can undergo essentially three reactions; loss of a proton to give a radical, reaction with a nucleophile, and dimerization to a dication. In such reactions the solvent and the electrolyte play major roles. A basic solvent or one containing a base will promote proton loss; a nucleophilic solvent will promote nucleophilic reactions; and a neutral and non-nucleophilic solvent will produce dimerizations. Examples

of all of these reactions have been given.

The solvent, in particular, is a problem. It must be sufficiently polar to dissolve an electrolyte to conduct a current, but it must be sufficiently non-polar to dissolve organic compounds. A polar solvent generally has some nucleophilic properties, and such common solvents as water and alcohol generally produce nucleophilic reactions. In recent years, much work has been done in non-aqueous solvents. An elegant discussion of such systems is given by Mann.[39] For preparative purposes, a solvent should have a low boiling point so that the products can be easily isolated. The preferred non-aqueous solvent is surely acetonitrile when one is trying to avoid nucleophilic reactions of solvent, although, under some conditions, acetonitrile does behave as a nucleophile, giving rise to acetamido substituents.

The preferred electrolytes seem to be salts of the tetraalkylammonium ion such as tetraethyl- or tetra-n-butylammonium perchlorate or fluoroborate. A study of a number of these salts as well as directions for their preparation are given by House.[40] When a base is needed in the system, one of the sterically hindered pyridines such as 2,4,6-trimethylpyridine will usually serve. It does not react as a nucleophile, but will remove a proton.

Three anodic materials, platinum, carbon, and lead dioxide, are in common use, and instructions for their preparation and use are available.[41] Platinum is probably the easiest to use, but carbon is available in more forms and is much less expensive. We favor the use of graphite or carbon felts or cloth[42] which have a large surface area and are inexpensive enough to be disposable after one use. The cathode is generally platinum or nickel.

Cell design varies widely from elaborate custom-made glass systems to open beakers. Only two aspects are really important. One is whether the system is closed or open to air, and the second is whether the anode and cathode are separated by a membrane or not. In most cases, it is advisable to conduct reactions under nitrogen, at least in initial experiments until it can be shown that air is not a factor in the reaction. Most organic oxidations are not reversible reactions and do not need to be carried out in membrane divided cells. However, because it is customary, most reactions are carried out in such systems. The DuPont Nafion membranes make ideal dividers for most reactions.[43]

Some of the experimental conditions used in the work reported in this review are given in Table II. The solvents or electrolytes which participated in the

reactions are designated with an astrisk (*).

Table II. Experimental Conditions for Preparative Oxidations

Cmpd.	Solvent	Electrolyte	Potential V. vs. S.C.E.	Anode	Ref.
PYRROLES					
pyrrole	CH_3CN (99%)	Et_4NBF_4	?		6
4 and similar cmpds.	CH_3OH	NaCN*	1.0	Pt	9
4	CH_3OH	KOH	constant current	Pt	11
17 and similar cmpds.	a. CH_3CN b. CH_3NO_2* c. CH_3OH*	$LiClO_4$	a. 1.0 b. 1.2-1.4 c. 0.4	Pt	13
INDOLES					
indole	CH_3CN	Et_4NClO_4*	1.4	C cloth	17
N-substituted indoles	CH_3OH	NaCN*	1.0	Pt	9
30	CH_3CN	Et_4NClO_4	1.1	Pt	19
34	CH_3CN-H_2O, 9:1	$LiClO_4$	0.7	C felt	3, 20
36, 38, 40	CH_3CN	$NaClO_4$	1.1-1.3	Pt and C felt	22
48, 49, 51, 54, 56	CH_3OH-H_2O (1:1) buffered to pH 7	KH_2PO_4 K_2HPO_4	0.7-0.9	C felt	3
44	CH_3CN	Et_4NClO_4	0.8-0.95	Pt	25
CARBAZOLES					
69 and derivatives	a. CH_3CN b. CH_3CN + 2,4,6-trimethyl-pyridine*	Et_4NClO_4	1.1-1.5	Pt	37

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42. A large variety of these materials are available from the Carbon Products Division, Union Carbide Corp., New York, 10017.

43. Nafion 425 membrane is available from the Plastics Dept., E. I. Dupont De Nemours and Co., Wilmington, Del. 19898.

44. After this manuscript was prepared, we became aware of the work of Okita, Wakamatsu and Ban (M. Okita, T. Wakamatsu and Y. Ban, J. Chem. Soc., Chem. Comm. 1979, 749). N-Substituted 2-pyrrolidones were oxidized to 5-hydroxy-2-pyrrolidones and succinimides in reasonable yields.

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