

condenser. Approximately 50 ml of THF was added to the apparatus and it was heated to a moderate reflux. The solutions of dianion **3** and 1,3-dibromopropane were then added to the Soxhlet extractor *via* stainless steel cannulae at such a rate that one drop of each solution was added to each cycle of the extractor. After the addition was complete, reflux was maintained for several more cycles and the apparatus was allowed to cool before the reaction was worked up as above to give 1.06 g (68%) of distilled methyl 2-oxocyclohexanecarboxylate (**9**, $n = 3$) which was identical to the sample of **9** ($n = 3$) prepared previously. The residue from the distillation was chromatographed on silica gel using chloroform eluent to give 0.15 g (11%) of dimethyl 3,9-dioxoundecanedioate (**10**, $n = 15$).

Methyl 2-(2'-Carbomethoxy-3'-oxocyclohex-1'-enyl)acetate (12). The dianion **3** from 1.16 g (10.0 mmol) of methyl acetoacetate was alkylated with 0.87 g (5.0 mmol) of dibromomethane as in section b of the previous experiment to yield 0.70 g (62%) of distilled **12**: bp 75–78° (0.2 mm); ir (CHCl₃) 3575, 3075, 3010, 2940, 1740, 1735, 1685, 1640, 1445, 1380, 1360, 1340, 1320, 1180, 1080, 1060, 1020, 965, 940, 860, 810 cm⁻¹; nmr (CDCl₃) δ 1.8–2.2 (m, 2 H),

2.3–2.7 (m, 4 H), 3.35 (s, 2 H), 3.75 (s, 3 H), 3.83 (s, 3 H); uv (CH₃-OH) 288 nm (ϵ 1.2 \times 10⁴); mass spectrum m/e (rel intensity) 226 (19), 195 (43), 194 (100), 166 (45), 162 (100), 138 (40), 129 (23), 112 (24), 107 (28), 101 (21), 82 (38), 79 (48), 70 (46), 59 (51), 43 (57).

Dimethyl 3,16-Dioxooctadecanedioate (10, $n = 10$). The dianion **3** from 1.16 g (10.0 mmol) of methyl acetoacetate was reacted with 1.50 g (5.0 mmol) of 1,10-dibromodecane to give a crude product which solidified on standing overnight and was subsequently recrystallized from ether to give 1.52 g (98%) of **10** ($n = 10$): mp 80–82°; ir (CHCl₃) 3090, 3050, 2970, 2900, 1745, 1720, 1640, 1620, 1450, 1420, 1335, 1170, 1030, 940 cm⁻¹; nmr (CDCl₃) δ 1.2 (m, 20 H), 2.43 (t, $J = 6$ Hz, 4 H), 3.27 (s, 4 H), 3.70 (s, 6 H), 4.90 (s);²³ mass spectrum m/e (rel intensity) 370 (10), 339 (13), 338 (12), 320 (16), 296 (24), 265 (18), 256 (17), 255 (100), 237 (21), 223 (14), 205 (22), 195 (11), 181 (23), 178 (14), 163 (27), 158 (12), 143 (9), 129 (71), 116 (90), 101 (51), 69 (58), 59 (95), 43 (65).

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Electrochemical Generation of Carbazoles from Aromatic Amines

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Abstract: It has been found that substituted di- and triphenylamines cyclize to form the corresponding carbazoles in acetonitrile upon anodic oxidation at platinum. The reaction occurs through the dication and will take place only if the cation radical is stable. This same overall process occurs photochemically, and comparisons are made between the two pathways; it was not established that there is common mechanistic ground but some possible parallels are explored. A recent report of the same type of reaction for tetraarylethylenes suggests that this may be a general anodic oxidation pathway for electrolytically generated aromatic dications.

The conversion of aromatic amines to carbazoles *via* an intramolecular cyclization pathway has been effected by a number of chemical methods. Carbazole has been generated from 2-aminobiphenyl by both thermal cyclization^{2,3} and glow discharge⁴ techniques. Photochemical processes involving this same pathway have been shown to lead from *N*-arylenamines to 2,3-dihydroindoles^{5a} and indolines.^{5b} However, most of the photochemical studies have been concerned with the conversion of di- and triphenylamines to the corresponding carbazoles.^{6–13} These latter investigations,

and some additional reports, have been involved with the photochemical mechanism by which this transformation occurs. A good deal of controversy still exists over the kinetics of the process and the nature of the intermediates involved,^{11–16} but it is more or less firmly established that reaction occurs through the amine triplet, which can decay back to the ground state by energy transfer to the solvent or oxygen or it can cyclize to an 11,12-dihydrocarbazole which eliminates hydrogen to form a carbazole (*e.g.*, *N*-phenylcarbazole from triphenylamine). Mass spectrometric data indicate that the 11,12 hydrogens are *trans* to one another in the dihydrocarbazole since they are lost stepwise rather than as molecular hydrogen.^{17,18}

Since some of these reactions have been characterized as being photooxidations, we have been concerned with analogous cyclizations in the electrochemical oxidations of aromatic amines in nonaqueous media. Our primary concern has been with the decomposition pathways of amine cation radicals, and in studying these

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species carbazole formation has not been detected. Although cation radicals have not been implicated in the photochemical mechanisms forwarded, the nature of the intermediates involved in the photooxidations is still somewhat speculative and we have pursued these systems with the expectation that electrochemical studies might shed more light on this remarkable mechanism. The electrochemical conversion of aromatic amines to carbazoles has been accomplished on a limited scale and the results are reported herein.

Experimental Section

All electrolyses were carried out in acetonitrile (MeCN)-tetraethylammonium perchlorate (TEAP) media at platinum. The instrumentation for the electrochemical studies was standard and has been reported previously.¹⁹ Visible spectra were run on a Cary 14 spectrophotometer; solutions of the amines and carbazoles were electrolyzed both externally and *in situ* and similar results were obtained by the two methods. The external electrolyses were carried to completion by controlled-potential oxidation using a Wenking 68 FR0.5 fast-rise potentiostat, and the solutions were transferred to standard cuvettes for the recording of spectra. Some experiments were conducted where the amine cation radical was generated by electrolysis 200 mV past the first anodic wave and its spectrum was subsequently recorded. The electrolysis potential was then moved out to the second anodic wave and the oxidation carried essentially to completion; moderate steady-state background currents were always encountered since these electrolyses were in the region of 1.8–2.0 V. In this way the amine cation radical spectrum could not be confused with that due to the corresponding electrogenerated carbazole radical ion.

In addition, separate experiments were conducted on two of the carbazoles suspected to be products from the corresponding amines. These compounds were electrolyzed at potentials just beyond the primary oxidation waves, where the cation radicals would be generated, as well as at the potential used to convert the amine dications to their respective products. Spectral data on the carbazole cation radicals were readily obtained, since the half-lives of these species are on the order of several minutes. *In situ* electrolyses gave essentially identical results and these experiments clearly established that the species absorbing in the 750–850-nm region are the carbazole cation radicals; the growth and decay patterns of the absorption maxima were also consistent with this assignment. This is further substantiated by a recent survey study covering a large number of substituted carbazoles; in this work it was established that these radicals are moderately stable and characteristically absorb in the 700–850-nm region.²⁰

Thin-layer chromatograms were run using "Bakerflex" alumina paper and benzene-petroleum ether solvent mixtures. Electrolysis mixtures were prepared for chromatography by taking them to dryness and extracting the organic products with benzene. The solutions were concentrated and each mixture was spotted with benzene. The chromatograms were developed with iodine and examined under ultraviolet light; it was found that the fluorescence of the carbazoles was characteristic in these systems relative to the reactants and products present.

Electrolysis of *N*-Ethylbis(*p*-*tert*-butylphenyl)amine. The parent amine (100 mg) was dissolved in acetonitrile-0.1 *F* tetraethylammonium perchlorate (100 ml) and was electrolyzed at a platinum gauze anode (carbon auxiliary in a separate compartment, aqueous sce reference) at a potential of +1.8 V for 20 min; at this point the *n* value for the electrode process was roughly 3 (which would correspond to conversion of the amine to the carbazole cation radical). Appreciable electrolysis current was still passing, indicating that further decomposition reactions were taking place. Following re-reduction at -0.7 V (to reduce off the protons liberated in the coupling reaction), the solvent was stripped off (room temperature) and the residue was partitioned with benzene-9 *M* H₂SO₄. The benzene layer was chromatographed on Woelm neutral alumina and the product was recrystallized from benzene-heptane, mp 149–152°; it was verified as being 3,6-di-*tert*-butyl-*N*-ethylcarbazole by mixture melting point. The yield (15 mg) is quite low but a

concerted effort was not made to maximize electrolysis conditions. The yield is higher in light of the fact that roughly half of the parent amine is recovered from the aqueous layer (during the oxidation process it is protonated and rendered electroinactive), but the presence of considerable side reactions must be acknowledged. From a synthesis standpoint, this is not at present a favorable reaction.

Compound Preparation. Many of the di- and triphenylamines studied had been previously synthesized and reported.^{21,22} Several new compounds were prepared as reported below; the structures were verified by infrared and nmr spectroscopy, as well as by the CHN analyses listed.

***N*-Ethylbis(*p*-*tert*-butylphenyl)amine.** Bis(*p*-*tert*-butylphenyl)amine was synthesized by the method of Walter.²¹ Alkylation was effected with triethyl phosphate by heating in the presence of K₂CO₃; following extraction with benzene the reaction mixture was chromatographed on Woelm neutral alumina. The product was then recrystallized twice from benzene-heptane, mp 87–88°.

Anal. Calcd for C₂₂H₃₁N: C, 85.4; H, 10.1; N, 4.53. Found: C, 85.4; H, 10.0; N, 4.44.

3,6-Di-*tert*-butyl-*N*-ethylcarbazole. *N*-Ethylcarbazole was stirred with an excess of *tert*-butyl chloride and AlCl₃ for 6 hr; the reaction mass was heated for about 30 min toward the end of this time. The mixture was poured on ice and the resulting tar was taken up with benzene and chromatographed on neutral alumina. The product was recrystallized twice from benzene-heptane, mp 151–153°.

Anal. Calcd for C₂₂H₂₉N: C, 85.9; H, 9.53; N, 4.55. Found: C, 85.5; H, 9.47; N, 4.56.

3,6-Dichloro-*N*-*p*-chlorophenylcarbazole. 3,6-Dichlorocarbazole was heated with *p*-chloriodobenzene, copper powder, and potassium carbonate for 16 hr at 210°. The hot reaction mass was extracted twice with benzene and the extract was chromatographed on neutral alumina. The product was then recrystallized twice from benzene-ethanol, mp 175–176°.

Anal. Calcd for C₁₈H₁₀NCl₃: C, 62.4; H, 2.91; N, 4.04. Found: C, 62.8; H, 2.97; N, 3.98.

Results and Discussion

In the photochemical studies previously mentioned, it was found that not all di- and triphenylamines cyclized to generate substituted carbazoles. Appreciable yields were obtained from compounds such as triphenylamine (TPA), tris(*p*-tolyl)amine, and *N*-methyldiphenylamine, but for diphenylamine (DPA) the carbazole yield is relatively low and considerable side reaction occurs.^{8,16} Tris(*p*-carbomethoxyphenyl)amine and *N*-methylbis(*p*-carbomethoxyphenyl)amine, however, have triplet states that do not undergo cyclization but instead phosphoresce back to the ground state.²³ Unfortunately, more molecules have not been studied, but from the available data it appears that only amines with electron-withdrawing substituents will not form carbazoles photochemically.

The electrochemistry of these same molecules is considerably different in that none show the formation of carbazole in the primary oxidation process. In non-aqueous media (acetonitrile), molecules such as TPA, DPA, and *N*-CH₃DPA form the corresponding *p,p*-benzidines in almost quantitative yields upon electrochemical oxidation *via* an intermolecular coupling reaction that has been thoroughly characterized.^{22,24} The electrolysis solutions were vigorously examined for traces of the corresponding carbazoles, but none could be found.

It has been shown that this electrochemical coupling reaction proceeds through a cation radical intermediate formed by removal of one electron from the parent molecule; two of these then couple to form the ben-

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Table I. Electroanalytical Data for Amine Oxidations

Compd	First anodic wave			Second anodic wave		
	$E_{p/2}^a$	$i_p/V^{1/2}C^b$	n value ^c	$E_{p/2}^{a,d}$	$i_p/V^{1/2}C^b$	n value ^f
Tris(<i>p</i> -anisyl)amine	0.52	28.0	1.01	1.21	29.3	1.17
Tris(<i>p</i> -tolyl)amine	0.75	29.4	0.98	1.54	53.3	1.83
Tris(<i>p-tert</i> -butylphenyl)amine	0.76	28.7	0.98	1.56	51.8	1.81
Tris(<i>p</i> -fluorophenyl)amine	0.95	28.5	1.03	1.69	23.8	0.84
Tris(<i>p</i> -chlorophenyl)amine	1.04	30.5	1.02	1.76	56.8	1.87
Tris(<i>p</i> -bromophenyl)amine	1.05	30.0	0.99	1.79	52.6	1.75
Tris(<i>p</i> -iodophenyl)amine	1.01	28.2	0.98	1.67 ^e	55.2	1.96
Tris(<i>p</i> -carbomethoxyphenyl)amine	1.26	26.5	1.02	2.02 ^e	56.2	2.12
Tris(<i>p</i> -acetylphenyl)amine	1.26	27.6	1.04	2.00 ^e	61.4	2.23
Tris(<i>p</i> -benzoylphenyl)amine	1.25	26.4	1.01	2.00 ^e	57.3	
Tris(<i>p</i> -cyanophenyl)amine	1.44	27.1	1.05	2.2 ^e		
<i>N</i> -Ethylbis(<i>p</i> -tolyl)amine	0.74	29.2	1.03	1.61	39.6	1.37
<i>N</i> -Ethylbis(<i>p</i> -anisyl)amine	0.64	28.1	1.00	1.24	19.7	0.70
<i>N</i> -Ethylbis(<i>p-tert</i> -butylphenyl)amine	0.76	28.8	1.01	1.59	51.1	1.78
<i>N</i> -Ethylbis(<i>p</i> -chlorophenyl)amine	0.98	30.8	1.05	1.60 ^e	50.6	1.65

^a In V vs. sce. ^b Average value from linear scan voltammograms taken at scan rates from 33.0 to 500 mV/sec. ^c Coulometric n values from exhaustive electrolyses of approximately 10^{-3} M solutions. ^d Waves are irreversible, $E_{p/2}$ shifts anodic with increasing scan rate. ^e Waves are obscure, data for these systems are highly imprecise. ^f Coulometric n values could not be obtained due to large steady-state currents at the end of the electrolyses; these values are from peak current data and are only for the second waves.

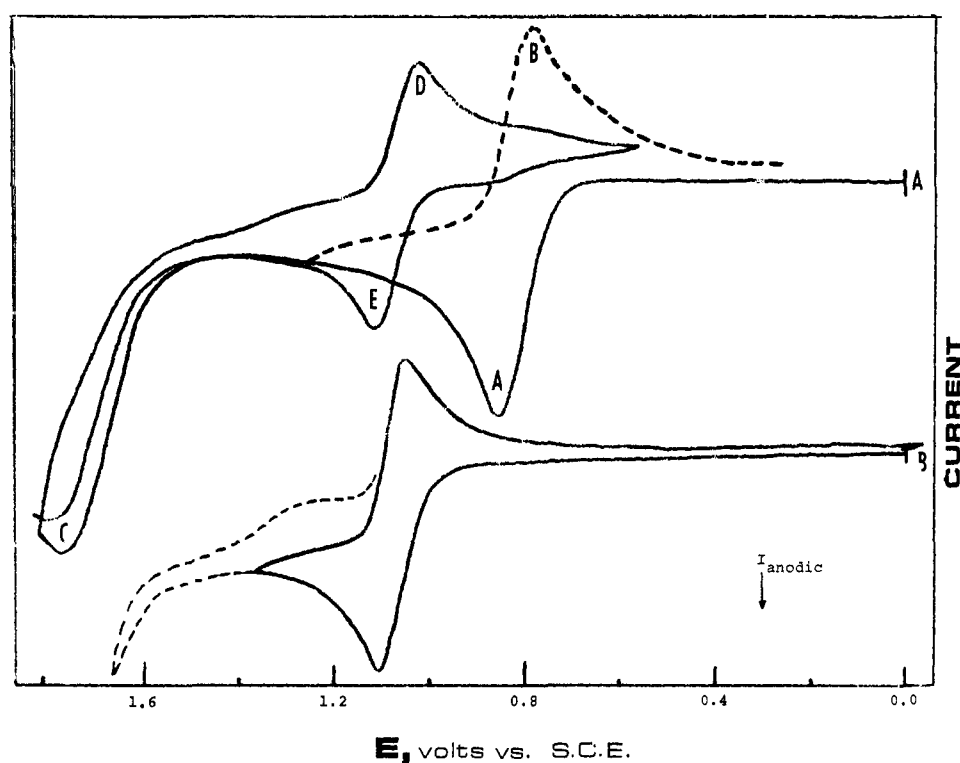


Figure 1. (A) Cyclic voltammogram of *N*-ethylbis(*p*-tolyl)amine in acetonitrile-0.1 *F* tetraethylammonium perchlorate, platinum working electrode, sweep rate = 150 mV/sec. (B) Cyclic voltammogram of 3,6-dimethyl-*N*-ethylcarbazole, same conditions.

zidine. This would seem to indicate that the photochemical mechanism does not involve the cation radical (however, an excited state of the cation radical cannot be excluded) since intermolecular coupling products such as benzidines have not been detected in the irradiation studies. Thus, there appears to be little or no connection between the photochemical and electrochemical mechanisms involving cation radicals for these compounds.

Many other substituted di- and triphenylamines have been studied electrochemically and again no traces of carbazoles have been detected from chemical decomposition of the amine cation radicals.^{25,26} Almost

(25) R. F. Nelson and R. N. Adams, *J. Amer. Chem. Soc.*, **90**, 3925 (1968).

without exception the presence of an open ring position para to the amine nitrogen leads to intermolecular coupling to form a substituted benzidine. However, tri-para-substituted TPA's and di-para-substituted *N*-alkyl DPA's have very stable cation radicals that can readily be generated electrochemically; these neither cyclize nor couple at detectable rates. Electroanalytical data are shown for the various amines studied in Table I. The data for the first oxidation waves are all consistent with what would be expected for a reversible one-electron process. When these molecules are oxidized on to the dications, however, rapid decomposition was found to occur by a number of different pathways.

(26) P. Berkenkotter and R. F. Nelson, unpublished data.

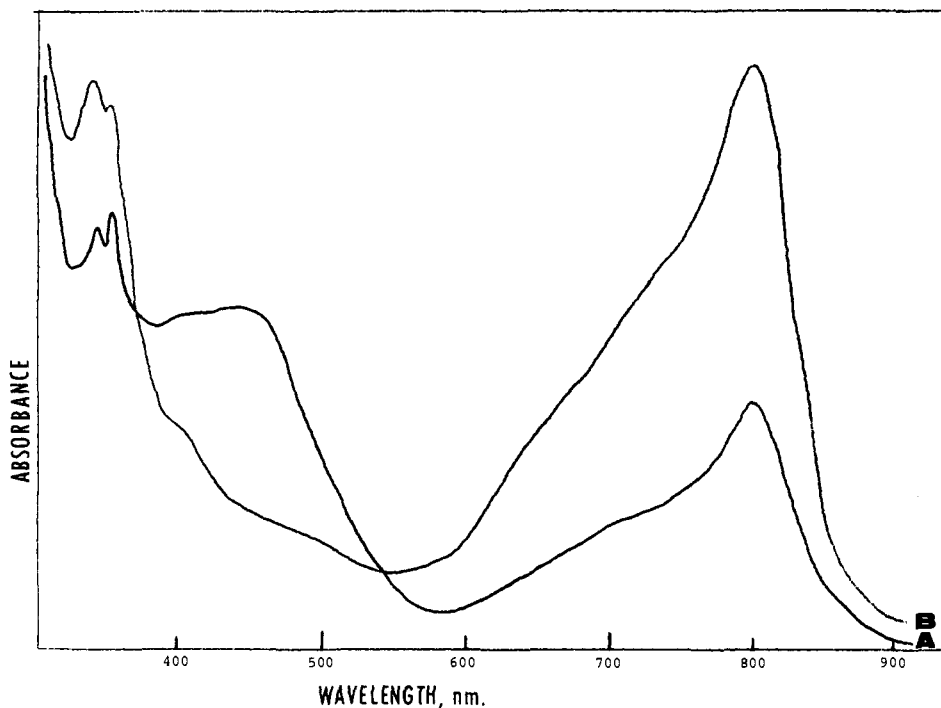


Figure 2. Visible absorption spectra of externally electrolyzed solutions in acetonitrile: (A) tris(*p*-chlorophenyl)amine solution oxidized at the potential of the second anodic wave; (B) 3,6-dichloro-*N*-*p*-chlorophenylcarbazole solution oxidized past its first anodic wave.

Primary among these decomposition reactions in most systems was formation of a reversible redox couple somewhat anodic of the primary amine system, as shown in Figure 1A for *N*-ethylbis(*p*-tolyl)amine. On the first scan the voltage sweep was reversed at 1.3 V and the dotted line shows the reverse peak current obtained for reduction of the cation radical (wave B). Subsequent scans to more anodic potentials show a second oxidation process at about 1.7 V (wave C) which gives rise to a reversible couple around 1.2 V (waves D and E). Since on the first scan this latter couple was absent, the species responsible is clearly being generated by the second anodic process which is seen to be irreversible. A cyclic voltammogram for the corresponding carbazole is shown in Figure 1B; the match-up with waves C and D in the amine system is striking. The carbazole formation was verified in several amine systems using thin-layer chromatography on electrolysis solutions, as well as by matching of cyclic voltammograms and visible absorption spectra of electrolyzed solutions, as shown in Figure 2 for tris(*p*-chlorophenyl)amine and the corresponding carbazole. This system is somewhat complicated, but not atypical, in that the carbazole is not the only decomposition product of the amine dication; in the tris(*p*-chlorophenyl)amine system there is also some halogen elimination and subsequent coupling to form *N,N,N',N'*-tetrakis(*p*-chlorophenyl)benzidine. The broad band at 400–500 nm is due to the oxidized form of the benzidine. The carbazole visible absorption spectra are particularly characteristic in that the peaks are in a wavelength region that is unusual for organic cation radicals; thus, the match-up is more compelling. Further confirmation was obtained by product isolation from controlled-potential electrolyses, as described in the Experimental Section for *N*-ethylbis(*p*-*tert*-butylphenyl)amine.

The electroanalytical data for the second anodic

waves, as shown in Table I, show very little in the way of consistent trends. The precision of the data is very poor due to the proximity of many of the waves to the anodic background of the MeCN–TEAP system. The data are further obscured by the presence of other decomposition pathways competing with the intramolecular cyclizations; primary among these are hydrolysis and substituent elimination. For conversion of the amine parent all the way to the carbazole cation radical three electrons per molecule is required; this is clearly not the case in many of the systems. Nevertheless, there is a general correlation of carbazole yield with *n* value, as seen by a comparison of the electroanalytical data in Table I with the product yield data shown in Table II. The carbazole yields are high (as determined by cyclic voltammetry of roughly millimolar solutions) for those systems not susceptible to hydrolysis or substituent elimination, and the carbazole cation radicals are more stable for those derived from triphenylamines than those from diphenylamines; this latter fact is consistent with data obtained for a number of similarly substituted carbazoles.²⁰

Product isolation was rendered difficult by the previously mentioned parallel decomposition pathways (plus some others not yet delineated) for the amine dications as well as by slow decompositions of the substituted carbazolium radicals. Whereas these latter decomposition reactions are relatively slow on the time scales of the cyclic voltammetric and spectroscopic experiments, they become significant during controlled-potential electrolyses which may take up to an hour to carry out. In addition, at the oxidation potentials used to convert the amines to the corresponding carbazoles these latter species are partially oxidized on to their dications, as shown by the dotted line in Figure 1, curve B.

Thus, yields from preparative-scale electrolyses are

Table II. Product Distributions for Arylamine Dications in Acetonitrile

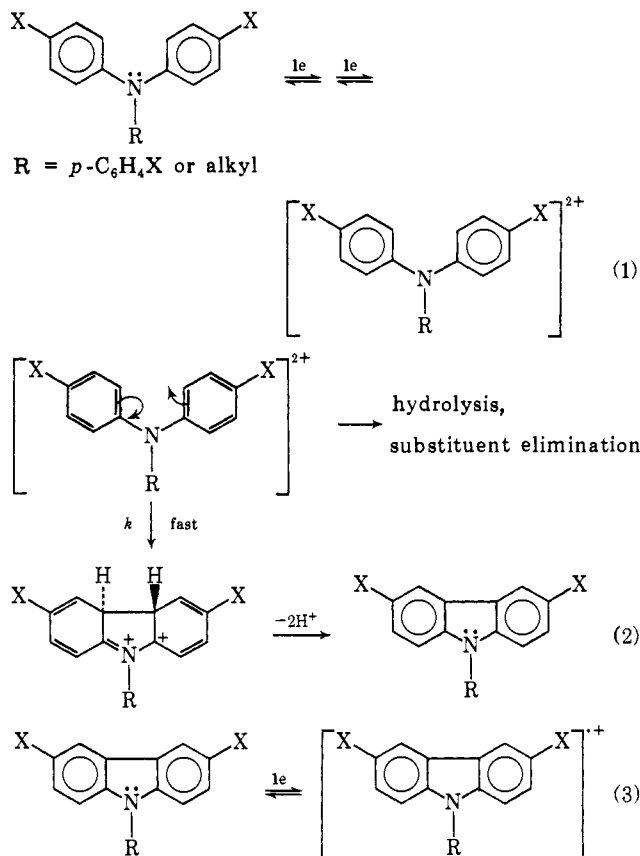
Amine	Carbazole formed ^b	Other products
Tris(<i>p</i> -anisyl)amine	+ ^a	Some hydrolysis occurs
Tris(<i>p</i> -tolyl)amine	++	
Tris(<i>p</i> - <i>tert</i> -butylphenyl)amine	++	
Tris(<i>p</i> -fluorophenyl)amine	+ ^a	
Tris(<i>p</i> -chlorophenyl)amine	+	
Tris(<i>p</i> -bromophenyl)amine	+	<i>N,N,N',N'</i> -Tetrakis- (<i>p</i> -chlorophenyl)- benzidine
Tris(<i>p</i> -bromophenyl)amine	+	
Tris(<i>p</i> -carbomethoxyphenyl)- amine	++	Dication decomposes ex- clusively by hydroly- sis
Tris(<i>p</i> -acetylphenyl)amine	++	
Tris(<i>p</i> -benzoylphenyl)amine	++	
Tris(<i>p</i> -cyanophenyl)amine	++	
<i>N</i> -Ethylbis(<i>p</i> -tolyl)amine	++	
<i>N</i> -Ethylbis(<i>p</i> - <i>tert</i> -butylphenyl)- amine	++	
<i>N</i> -Ethylbis(<i>p</i> -anisyl)amine	-	
<i>N</i> -Ethylbis(<i>p</i> -chlorophenyl)- amine	++	

^a Small amounts (10% or less) of carbazole detected. ^b A “++” represents a relatively higher yield compared to a “+”; a “-” indicates that the corresponding carbazole was not observed on the cyclic voltammogram.

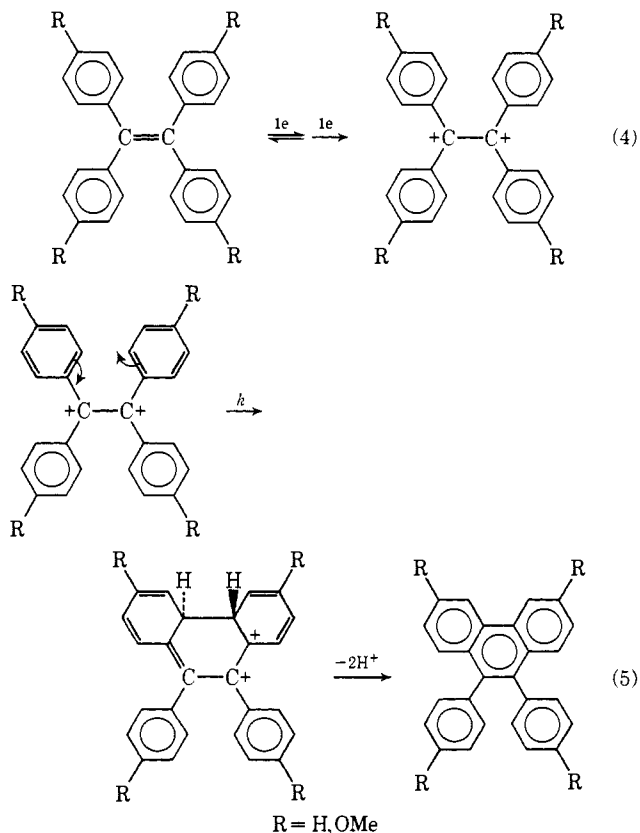
very low as noted in the Experimental Section for *N*-ethylbis(*p*-*tert*-butylphenyl)amine. Better electro-synthesis conditions may raise these yields to an acceptable level but at this time it appears that the photochemical process is far superior in terms of product yields. However, as noted earlier, when the amine molecule contains electron-withdrawing groups, the photocyclization does not occur. In some cases these amines can be cyclized electrochemically; note in particular the tris(*p*-carbomethoxyphenyl)amine which does not cyclize photochemically²³ but does show carbazole formation under electrolysis conditions. In a preparative sense, both methods have advantages and limitations which appear to be generally complementary.

It would be adventuresome to suggest a direct parallel between the photochemical and electrochemical mechanisms since the experimental conditions are so different. The photolyses are usually run in nonpolar solvents and the mechanism involves excited-state species, the key intermediate apparently being the amine triplet. The electrochemical processes are carried out in polar organic solvents containing relatively large amounts of organic salts as supporting electrolytes. The reactive species appears to be the dication of the parent molecule which is generated by discrete removal of two electrons in a stepwise fashion. Thus, a discussion of the electrochemical process will be presented but meaningful comparisons with the photochemical mechanism are not, we feel, warranted at this time.

Due to the fact that the second oxidation steps of the amines are at far anodic potentials (1.7–2.2 V) and the cyclization reactions are extremely rapid, precise quantitative data could not be acquired on these systems. However, it can be ascertained that the oxidation of the amines involves the loss of two electrons. The amine dication is a $4n$ electron system and according to orbital symmetry rules for electrocyclic reactions ring closure



must occur in a conrotatory fashion to achieve proper bonding in the product.²⁷ In the intermediate dihydrocarbazole the hydrogens would be trans to one



(27) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

another and their elimination would lead to the corresponding carbazole. At the applied electrolysis potential the carbazole would be oxidized on to its cation radical, so the overall process has an n value of 3.

It is interesting to note that this type of reaction may be fairly general in organic electrooxidations. It has recently been shown that the electrochemical oxidation of tetraarylethylenes leads to the formation of substituted phenanthrenes.^{28,29} Since the aryethylene dications are isoelectronic with the arylamine dications, the same mechanism may be operative, *i.e.*, a concerted electrocyclic ring closure (eq 4 and 5).

In summary, then, it would appear that these electrochemical data can do relatively little to further clarify the photolytic mechanism. However, the following points can be forwarded.

(1) The photochemical process cannot go through the amine cation radical; according to the electrochemical studies if the cation radical were implicated some benzidines should be found (unless there is a tremendous solvent effect between polar and nonpolar media).

(2) The photochemical process may go through the amine dication, but again the role of solvent has not been clarified.

(3) The cyclization reaction is general for di- and tri-

(28) J. D. Stuart and W. E. Ohnesorge, *J. Electroanal. Chem.*, **30**, App. 11 (1971).

(29) J. D. Stuart and W. E. Ohnesorge, *J. Amer. Chem. Soc.*, **93**, 4531 (1971).

arylamines and is not limited to molecules containing roughly neutral or electron-donating substituents as implied in the collected photochemical studies. However, this is not to say that all the molecules converted electrochemically could also be cyclized photochemically with higher energy radiation.

Extensive electrochemical studies in our laboratory and by others have shown that the following conditions are necessary for the electrochemical cyclization reaction.

(1) Only tertiary aromatic amines can be cyclized where at most one alkyl group can be present and all aromatic rings must be substituted in the positions para to the amine nitrogen. In addition, these substituents must not be susceptible to substitution or elimination.

(2) The reactions must be carried out in nonaqueous media since only here can oxidation potentials be applied such that the amines can be oxidized to the dications.

Further studies are now in progress to achieve better yields in the electrochemical oxidations.

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Intermediates in Nucleophilic Aromatic Substitution. XI.¹ Spiro Meisenheimer Complex of *N,N'*-Dimethyl-*N*-picrylethylenediamine. Partially Rate-Limiting Proton Transfer of Complex Formation. A Temperature-Jump Study

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Abstract: *N,N'*-Dimethyl-*N*-picrylethylenediamine (AH) is in equilibrium with the spiro Meisenheimer complex (XH and X⁻) formed by intramolecular nucleophilic attack on the 1 position of the picryl moiety (eq 1). The rate of equilibration between the starting material and the two forms of the complex, as determined by the temperature-jump technique, not only shows the expected pH dependence but also increases with buffer concentration. The buffer dependence is curvilinear and reaches a plateau at high concentration. This indicates a change from rate-limiting proton transfer at a low concentration to rate-determining nucleophilic attack at high concentration and is a consequence of the unexpectedly high rate constant of $2 \times 10^5 \text{ sec}^{-1}$ for the reversion of the zwitterion (XH) to *N,N'*-dimethyl-*N*-picrylethylenediamine. These results suggest that in some cases general base catalysis in nucleophilic aromatic substitutions by amines is a manifestation of slow proton transfer rather than of sluggish leaving group departure.

In our attempts to deal with the problem of the rates at which intermediates in activated nucleophilic aromatic substitution reactions expel various mobile groups from their sp³ hybridized carbon, we have fre-

quently chosen the reversible interaction of 1,3,5-trinitrobenzene (TNB) with various nucleophiles as a model reaction.³

The choice of TNB as a model substrate offers both

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(2) Alfred P. Sloan Fellow, 1971-1973.

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