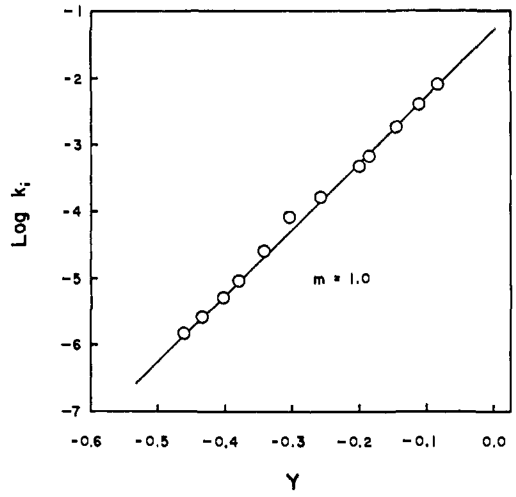

Figure 4. Plot of log k_i for **1** against Y, m = 1.0.

A plot of log k_i against Y deduced earlier for LPDE solutions is given in Figure 4. A linear plot of slope m = 1.0 is obtained. The intercept represents the value of k_i in pure ether. Valkanas and Waight[10a] have compared the rate constant for rearrangement of **1** at 25.0° in the dioxane–water range of 90–60% using the Y scale and also found a linear relationship of slope m = 1.0. The fact that LPDE solutions also gave a value of m = 1 shows LPDE solutions are consistent with the well-studied dioxane–water solutions.

We have previously reported[1] that the ionization rate constant of triphenylmethyl chloride (TCl) in LPDE solutions showed in the lower limit a second-order dependence on [$LiClO_4$]. Plotting log k_1 for the ionization of TCl against our Y scale for LPDE solutions gives a curved line, Here it should be noted that the limiting stoichiometric composition of the transition state associated with the ionization of TCl in LPDE solutions (<1 M) is TCl,2($Li^+ClO_4^-$). In general, when lithium perchlorate ion pairs or higher aggregates are participating in the ionization process of RX by multiple interaction mechanisms, a linear free energy relationship in terms of the Y values derived above would not be expected to hold. In this case, a more helpful approach is to delineate the catalytic efficiency of LPDE solutions in terms of extended parametric equations characterized by two or more interaction mechanisms. The applicability of such extended parametric equations to delineate electrostatic catalysis by ionic aggregates will be considered in future publications from this laboratory.

Electrolytic Oxidations of Organic Compounds. II. N,N-Dimethylaminoalkenes[1]

John M. Fritsch,[2] Harold Weingarten, and James D. Wilson

Contribution from Monsanto Co., Central Research Department, St. Louis, Missouri 63166. *Received August 18, 1969*

Abstract: Dimethylamino-substituted alkenes very readily undergo electrochemical oxidation, the multisubstituted examples being among the most easily oxidized neutral organic compounds known. Generally the initial oxidation products are the monocation radicals. Esr studies show that unpaired electrons polarize *away* from the dimethylamino groups in these species. Factors affecting the oxidation potentials of the aminoalkenes and the lifetimes and fates of the cation radicals produced are considered.

Many studies have been made of the electrooxidation of organic compounds,[3,4] but our understanding of this area is still far from perfect. The subject is complicated, largely because of the rapidity and complexity of reactions following the initial charge transfer. Recently several studies of general classes of compounds[3–7] have succeeded in establishing some of the basic features of electrooxidations, *e.g.*, that the initial step is a one-electron transfer, and what the effect of reactive-site blocking is on the lifetime of the radical cations. Developments in electroanalytical chemistry, both in theory and in technique, have greatly helped these studies.[3]

We have studied the chemical and electrochemical oxidations of a variety of dimethylamino-substituted alkenes (also called vinylamines or enamines) and report here in detail[1] the results of the electrochemical studies. The results of the chemical oxidations will be reported separately.[8]

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[1] (a) Presented at the Electrochemical Society Meeting, New York, N. Y., May 1969. (b) Part I: J. M. Fritsch and H. Weingarten, *J. Amer. Chem. Soc.*, **90**, 793 (1968).

[2] Author to whom correspondence should be addressed at: Computer Systems Laboratory, Washington University, St. Louis, Mo. 63110.

[3] (a) R. N. Adams, "Electrochemistry at Solid Electrodes," Marcel-Dekker, New York, N. Y., 1969; (b) R. N. Adams, *Accounts Chem. Res.*, **2**, 175 (1969).

[4] N. L. Weinberg and H. R. Weinberg, *Chem. Rev.*, **68**, 449 (1968).

[5] (a) E. T. Seo, R. F. Nelson, J. M. Fritsch, L. S. Marcoux, D. W. Leedy, and R. N. Adams, *J. Amer. Chem. Soc.*, **88**, 3498 (1966); (b) R. F. Nelson and R. N. Adams, *ibid.*, **90**, 3925 (1968).

[6] J. F. Ambrose and R. F. Nelson, *J. Electrochem. Soc.*, **115**, 1159 (1968).

[7] (a) M. E. Peover and B. S. White, *J. Electroanal. Chem.*, **13**, 93 (1967); (b) J. Phelps, K. S. V. Santhanam, and A. J. Bard, *J. Amer. Chem. Soc.*, **89**, 1752 (1967); (c) L. S. Marcoux, J. M. Fritsch, and R. N. Adams, *ibid.*, **89**, 5776 (1967).

[8] H. Weingarten and J. S. Wager, *Tetrahedron Lett.*, 3267 (1969); H. Weingarten and J. S. Wager, *J. Org. Chem.*, **35**, 1750 (1970).

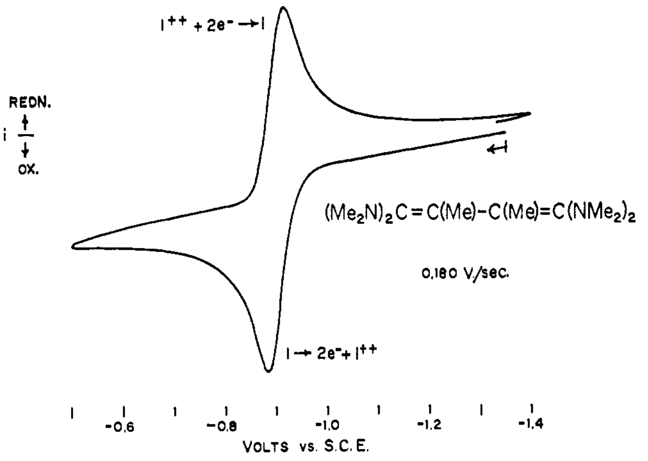

Figure 1. Cyclic polarogram of 1,1,4,4-tetrakis(dimethylamino)-2,3-dimethylbutadiene (I) at mercury.

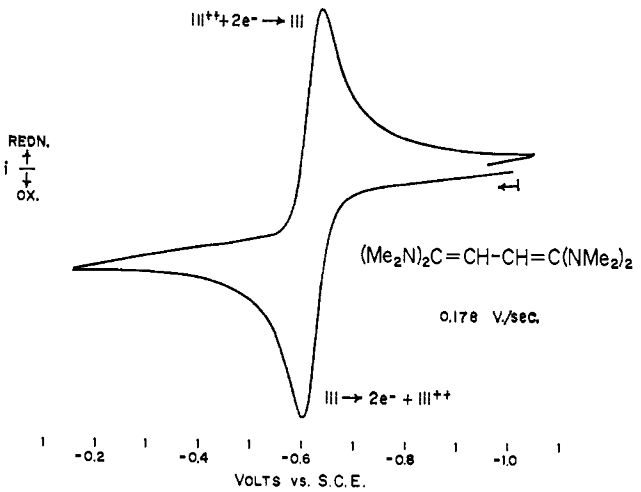

Figure 2. Cyclic polarogram of 1,1,4,4-tetrakis(dimethylamino)-butadiene (III) at mercury.

Results and Discussion

Oxidation Potentials. Table I lists the aminoalkenes whose electrochemistry was studied, together with their oxidation potentials and half-lives for decomposition in the medium employed, dry acetonitrile containing 0.1 *M* tetraethylammonium perchlorate (TEAP). The potentials were measured or estimated from the cyclic polarograms of *ca.* 1 m*M* solutions of substrate. In equating the measured "half-wave" potentials to the formal potentials we assume the diffusion coefficients of reactants and products to be roughly equal, which is a reasonable assumption to make for most organic compounds.[3a]

The aminoalkenes all oxidize very readily. The neutral molecules studied oxidize at potentials smaller than that of N,N-dimethylaniline ($E_{ox}{}^{o\prime} = +0.7$ V *vs.* sce),[5a] a favored subject for electrochemical oxidation studies, and the oxidation potential of I may be the most negative ever recorded for a neutral organic molecule. As a class the polyaminoalkenes are the strongest neutral organic electron donators known.

The ease of oxidation seems to be dependent, primarily, on the number of amino groups substituted on the double bonds; the potential decreases with each additional amino group capable of conjugating with the π system. Beyond this, the extent of the π system, the degree of alkyl or aryl substitution, and steric interactions affect the potential. Substitution of alkyl for hydrogen lowers the potential considerably, as would be expected, but substitution of aryl groups makes a lesser change (*cf.* the potentials of IX and XI, for example). Presumably aryl substitution stabilizes by resonance the neutral species about as much as the cationic species. Nonbonded interactions between C-methyls and N-methyls are probably responsible for large potential differences between I and III. Since probably only the cation radical gains much stabilization from delocalization over the *entire* molecule, steric repulsion between the C- and N-methyl groups will destabilize it with respect to the neutral and dicationic species, which can adopt sterically more favorable, nonconjugated configurations without suffering energetically. This will reduce the potential for the oxidation of mono- to dication, and, since in I and III the observed potential is the average of potentials of two steps (see below), this reduces the potential observed. A similar argument can be used to rationalize the relatively low potential of XII compared to XVI, although we recognize that inductive effects are working in the same direction. The large stabilization to be gained when charge can be spread out over an extensive π system is illustrated by the low potential of VI, 0.9 V more negative than that of XXI. Our data can give no conclusive answer to the interesting question of the relative abilities of *gem*- and *vic*-diamino groups to lower the oxidation potential.

Note that those compounds which can delocalize charge over a large number of atoms (polyamino monoenes and dienes) exhibit two oxidations at relatively low potentials. The ability of these systems to stabilize two positive charges makes the second unpaired electron extremely easily removed.

Redox Chemistry of Compounds I–IV and VI. These five aminoalkenes of Table I form an interesting (and instructive) set. All five compounds are oxidized readily, ultimately giving up two electrons. For each compound, both monocation and dication, as well as the neutral molecule, are stable in the absence of oxygen and water (except for disproportionation reactions; see below). The separations of the first and second oxidation potentials vary from <-0.24 V for I (*i.e.*, the cation radical of I is more easily oxidized than the neutral molecule by at least 0.24 V) to $+0.23$ V for IV.

Compounds I and III. Cyclic polarograms of these two substrates are shown in Figures 1 and 2. For both of these, a mercury-coated platinum working electrode[9] was used instead of the normal pure Pt disk, which gave distorted polarograms (see below). Both exhibit, within experimental error, cyclic polarograms typical of ideal, *reversible two*-electron oxidations.[3a,10] The anodic and cathodic peaks are separated, respectively, by 32 and 30 mV (theoretically 29 mV for a two-electron process). The anodic peak and half-peak potentials are separated by 31 and 29 mV, respectively (theory: 28.5 mV). Cyclic controlled-potential cou-

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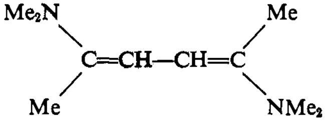
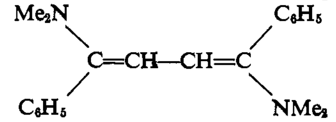
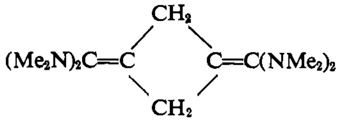
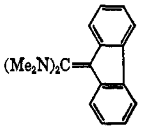
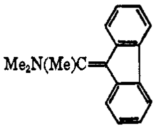
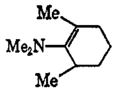
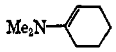
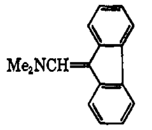
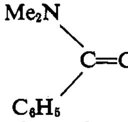
(9) L. Ramaley, R. L. Brubaker, and C. G. Enke, *Anal. Chem.*, 35, 1088 (1963).

(10) D. S. Polcyn and I. Shain, *ibid.*, 38, 370 (1966).

Table I. The Oxidation Potentials and Radical Cation Lifetimes

No.	Compd	E_{oxid}°′ (V *vs.* sce)[a]		$(t_{1/2})_R$ (sec)[b]
I	$(Me_2N)_2C{=}C(Me){-}C(Me){=}C(NMe_2)_2$	−0.901[c]	(−0.901)[d,e]	*f*
II	$(Me_2N)_2C{=}C(NMe_2)_2$	−0.77 −0.75[g]	(−0.65)[e] (−0.61)[e,g]	(∞)[h]
III	$(Me_2N)_2C{=}CH{-}CH{=}C(NMe_2)_2$	−0.615[i]	(−0.615)[e,j]	(∞)[h]
IV	$(Me_2N)_2C{=}CH(NMe_2)$	−0.40	(−0.17)[e]	(∞)[h]
V		−0.36	(−0.18)[e]	150[k]
VI		−0.20	(+0.02)[e]	(∞)[h]
VII		0.00		<0.005
VIII	$(Me_2N)_2C{=}CH{-}CH_2{-}CH{=}C(NMe_2)_2$	0.00		<0.005
IX	$(Me_2N)_2C{=}CMe_2$	0.05		0.025
X	$(Me_2N)_2C{=}CHMe$	0.23		<0.005
XI		0.24		(∞)[h]
XII		0.32		0.1
XIII		0.38		0.003
XIV		0.42		<0.005
XV	$(Me_2N)_2C{=}CH_2$	0.48		<0.005
XVI		0.48		<0.005
XVII	$(Me_2N)_2C{=}CCl_2$	0.52		250
XVIII	$H_2C{=}C(NMe_2){-}C(NMe_2){=}CH_2$	0.58	(1.10)[e]	<0.005
XIX	$C(NMe_2)_4$	0.65		<0.005
XX	$(Me_2N)_2C{=}CF_2$	0.7		<0.005
XXI		0.70		<0.005
XXII	$Me_2N(Me)C{=}CH{-}C(Me){=}\overset{+}{N}Me_2$	1.30[e]		0.6[l]

[a] Formal potential: measured (for reversible oxidations) or estimated from the cyclic polarograms in acetonitrile–0.1 *M* TEAP using the potential at which the oxidation current had reached 85% of its peak value (R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964)) (taking the formal potential as being essentially equal to the polarographic half-wave potential). For the irreversible oxidations this measurement was made at a *ca.* 0.1 V/sec scan rate (the dependence on scan rate was small: Nicholson and Shain). [b] Half-life of the monocation radical (see text). [c] Experimental value at a mercury electrode. Actual value is > −0.78 V (see text). [d] Experimental value at a mercury electrode. Actual value is < −1.02 V (see text). [e] Oxidation to the dication. [f] Monocation quantitatively disproportionates (see text). [g] From K. Kuwata and D. H. Geske, *J. Amer. Chem. Soc.*, **86**, 2101 (1964). [h] Half-life of at least several days in the medium employed (free from oxygen and water). [i] Experimental value at a mercury electrode. Actual value is −0.58 V (see text). [j] Experimental value at a mercury electrode. Actual value is −0.66 V (see text). [k] The dication has a lifetime of *ca.* 10 sec. [l] A dication radical.

lometry[11] verified the reversible two-electron process in both cases.

Solutions of both I and III were coulometrically half-oxidized, *i.e.*, one electron per molecule was removed. The solution containing I remained colorless and exhibited no esr signal, but the solution of III became red and showed an esr signal which was con-

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(11) Cyclic controlled-potential coulometry is a coulometric oxidation (or reduction) followed by a coulometric reduction (or oxidation) at potentials such that these electrolytic steps should go to completion. Hence all of the electroactive material is returned to the original state for a reversible redox couple involving a stable product. See A. J. Bard and S. V. Tatwawadi, *J. Phys. Chem.*, **68**, 2676 (1964).

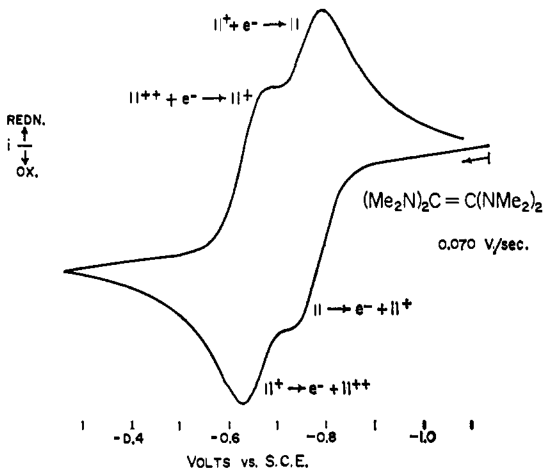

Figure 3. Cyclic polarogram of tetrakis(dimethylamino)ethylene (II) at platinum.

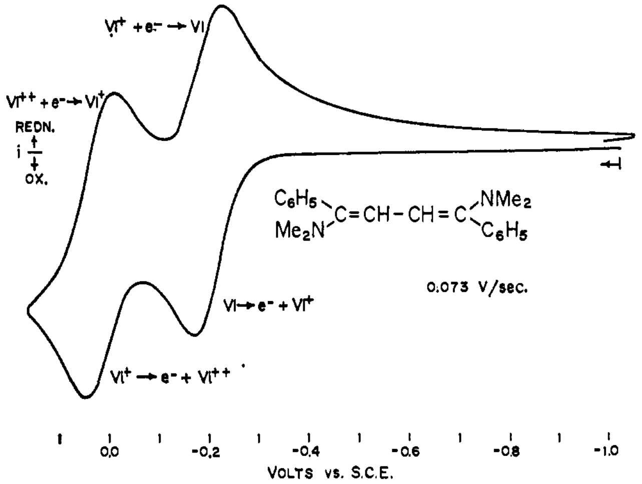

Figure 4. Cyclic polarogram of 1,4-bis(dimethylamino)-1,4-diphenylbutadiene (VI) at platinum.

sistent with about 10% of the substrate's being present as cation radical.

These data indicate that the cation radicals of I and III disproportionate into their respective neutral and dipositive species, I, completely. These two compounds alone lose two electrons in a concerted process. Their cation radicals oxidize more readily than the initial species and thus appear as exceptions to the rule that organic compounds normally oxidize and reduce in discrete one-electron steps. From the esr results, estimates can be made of the magnitude of the disproportion constant for the reaction $2A^+ \rightleftharpoons A + A^{2+}$, $K_{\text{disp}} = [A][A^{2+}]/[A^+]^2$. The coulometrically half-oxidized solution of I was originally 10^{-3} *M;* assuming that 10^{-6} *M* cation radical could have been detected, this implies that at equilibrium $[I^+] < 10^{-2}[I]$ and thus $K_{\text{disp}} > 10^4$. For III, the concentration of cation radical found by esr implies that $K_{\text{disp}} \approx 25$. From these data, approximate values for the separation, $E_2{}^{o\prime} - E_1{}^{o\prime}$, of the second and first oxidation potentials can be calculated for I and III through eq 1, and these results are listed in Table II along with the disproportionation constants of II, IV, V, and VI. Now,

Table II. Disproportionation Constants for Cation Radicals of I–VI

Compd	$E_2{}^{o\prime} - E_1{}^{o\prime}$, V	K_{disp}
I	[<−0.24][a]	>10⁴
III	[−0.08][a]	*Ca.* 25
II	0.12	9.4 × 10⁻³
	0.14[b]	4.3 × 10⁻³ [b]
V	0.18	9.1 × 10⁻⁴
VI	0.22	1.9 × 10⁻⁴
IV	0.23	1.3 × 10⁻⁴

[a] Calculated from an independently estimated (from esr plus coulometry) value of K_{disp} (see text). [b] See Table I, footnote *g*.

$$\log K_{\text{disp}} = (E_2{}^{o\prime} - E_1{}^{o\prime})/-0.0592 \qquad (1)$$

since both of the oxidation steps are fully reversible, the actual values of $E_1{}^{o\prime}$ and $E_2{}^{o\prime}$ can be obtained from $(E_2{}^{o\prime} - E_1{}^{o\prime})$ and the measured value of $E_{A \rightleftharpoons A^{2+}}{}^{o\prime}$ which equals $(E_1{}^{o\prime} + E_2{}^{o\prime})/2$.[10,12]

The relationships among the mono- and dications of I and III are completely analogous to those among certain metals, *e.g.*, Cu, for which $E_2{}^o - E_1{}^o = -0.337$ V and $K_{\text{disp}} = 2 \times 10^6$ in water.[13a]

Compounds II, IV, and VI. The cyclic polarograms of these compounds are reproduced in Figures 3–5. Each polarogram shows two resolvable, fully reversible one-electron oxidations. Geske and Kuwata[13b] previously showed II to exhibit this kind of behavior and our results confirm theirs entirely. In each case the anodic and cathodic waves are separated by potentials within experimental error of the theoretical value, 58 mV,[3a,10] and similarly the anodic peak and half-peak potentials (theoretical 57 mV). Cyclic coulometry confirmed the two one-electron steps.

(12) Given the potentials of these three electrode reactions

$$A^{2+} + e^- \rightleftharpoons A^+ \qquad E_2{}^{o\prime}$$
$$A^+ + e^- \rightleftharpoons A \qquad E_1{}^{o\prime}$$
$$A^{2+} + 2e^- \rightleftharpoons A \qquad E^{o\prime}$$

Then, using the free-energy changes

$$\Delta F = -nFE$$

or

$$\Delta F_2{}^{o\prime} = -n_2FE_2{}^{o\prime} = -FE_2{}^{o\prime}$$
$$\Delta F_1{}^{o\prime} = -n_1FE_1{}^{o\prime} = -FE_1{}^{o\prime}$$

and

$$\Delta F^{o\prime} = -nFE^{o\prime} = -2FE^{o\prime}$$

But

$$\Delta F^{o\prime} = \Delta F_1{}^{o\prime} + \Delta F_2{}^{o\prime}$$
$$= -FE_1{}^{o\prime} - FE_2{}^{o\prime}$$
$$= -F(E_1{}^{o\prime} + E_2{}^{o\prime})$$

or

$$-2FE^{o\prime} = -F(E_1{}^{o\prime} + E_2{}^{o\prime})$$

Thus

$$E^{o\prime} = (E_1{}^{o\prime} + E_2{}^{o\prime})/2$$

(13) (a) W. M. Latimer and J. H. Hildebrand, "Reference Book of Inorganic Chemistry," 3rd ed, MacMillan and Co., New York, N. Y., 1957, p 528; Table I, footnote *g*.

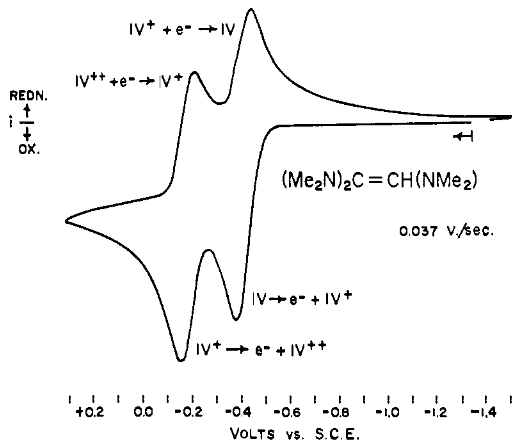

Figure 5. Cyclic polarogram of tris(dimethylamino)ethylene (IV) at platinum.

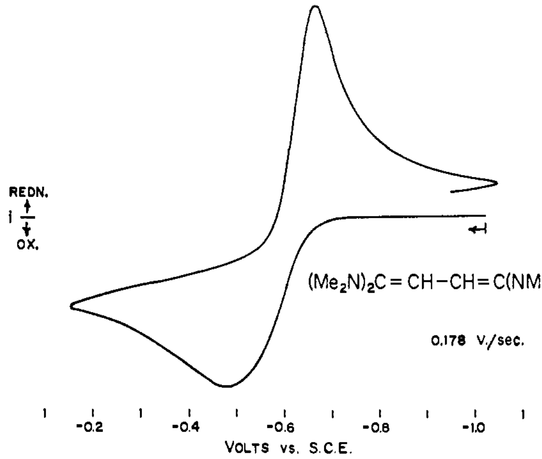

Figure 6. Cyclic polarogram of 1,1,4,4-tetrakis(dimethylamino)-butadiene (III) at platinum.

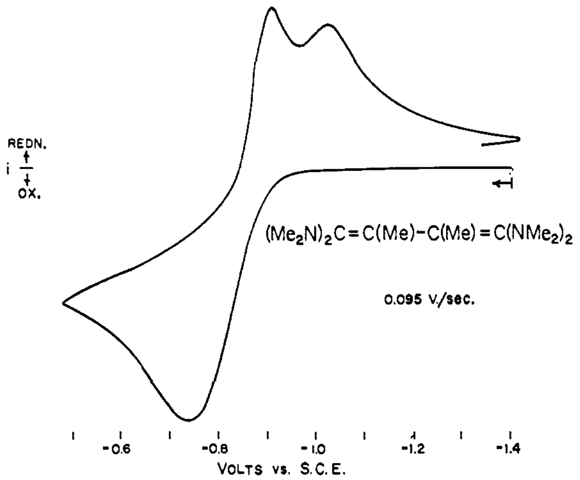

Figure 7. Cyclic polarogram of 1,1,4,4-tetrakis(dimethylamino)-2,3-dimethylbutadiene (I) at platinum.

Disproportionation constants (Table II) for the cation radicals of these aminoalkenes were calculated through eq 1 using values of $E_2^{o\prime} - E_1^{o\prime}$ from the cyclic polarograms. Coulometric half-oxidation of solutions of each compound gave high concentrations of cation radical (see esr results below).

Distortion of the Cyclic Polarograms of the Tetraaminobutadienes at Platinum. Figures 6 and 7 show the cyclic polarograms at platinum for compounds I and III, respectively. Compare these with those at mercury (Figures 1 and 2). Of all the compounds we studied only I and III showed a difference between mercury and platinum electrodes. At lower potential scan rates their cyclics at platinum approach those at mercury. The distortion was first thought to be primarily due to absorption of the dications, which is reasonable at the unusually cathodic oxidation potentials involved. However, closer analysis of voltage scan rate and concentration effects indicated incongruities with theoretical adsorption behavior,[14] *e.g.*, an anodic shift in E_{p_a} with increasing scan rate (*cf.* Figure 6 of ref 14, which is shown for a reduction). Our current hypothesis is that the rates of both electrode reactions (heterogeneous rates) are somewhat slow at platinum, with the rate of oxidation being even slower than the rate of reduction (*i.e.*, the transfer coefficient, α, being >0.7). The two reduction peaks for the 1,1,4,4-tetrakis(dimethylamino)-2,3-dimethylbutadiene cyclic polarogram at platinum (Figure 7) are also unexplained.

Nature of the Initial Oxidation Product. For those compounds which oxidize to chemically unstable products there is some question as to the number of electrons which are transferred in the initial step. Recent comprehensive studies have indicated that a one-electron oxidation to the monocation radical is a general feature for organics, with only a few singular exceptions.[3,5,7,15] Our results support this generalization.

For the aminoalkenes which oxidize to chemically stable monocations, the fact that this initial process is a one-electron[16] transfer was established in three ways. In exhaustive controlled-potential coulometry, a net one electron per molecule was removed. An esr study of the oxidized solutions confirmed the presence of radical cations (see below). Lastly, the cyclic polarograms satisfied the diagnostic criteria for a reversible one-electron oxidation.[3a]

For the moderately long-lived monocations, it could be ascertained that a one-electron process was involved from the fast scan cyclic polarograms. This conclusion of an initial one-electron step was extrapolated to the very reactive monocations on the basis of their closely related structure and similar cyclic polarograms.

Electron Spin Resonance Studies. The longer-lived monocation radicals (having a half-life of at least 1 min) were studied by esr. These results are summarized in Table III.

Most of these radicals were prepared by (1) coulometric oxidation to the monocation or (2) mixing equivalent quantities of the neutral compound and the dication. However, the lifetimes of the monocation radicals of V and XVII necessitated the use of a flow-mixing system to maintain an optimal concentration (*ca.* 0.1 m*M*) during long magnetic field scans (for maximum resolution). An apparatus based on a four-jet flow-mixing quartz esr flat cell[17] was constructed.

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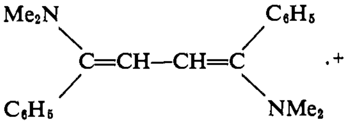
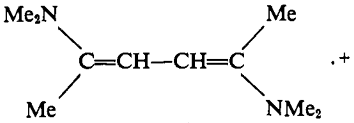
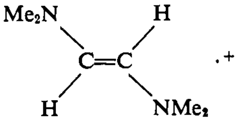
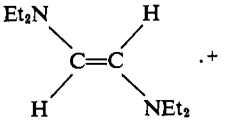
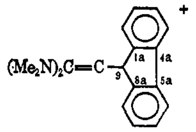
[14] R. H. Wopschall and I. Shain, *Anal. Chem.*, **39**, 1514 (1967).

[15] V. D. Parker, K. Nyberg, and L. Eberson, *J. Electroanal. Chem.*, 22, 150 (1969).

[16] Except for disproportionation of a few of the monocations, which has already been discussed in detail.

[17] This flow-mixing esr cell was obtained from Mr. Gunther Weiss, Master Glassblower, Research Instrument Service, University of Oregon Medical School, Portland, Ore. 97201.

Table III. Esr Results for the Stable Radical Cations

Radical cation	Hyperfine coupling constants, G[a]
$(Me_2N)_2C{=}CH{-}CH{=}C(NMe_2)_2\cdot^+$ III·+	a^H (2) ~ 13 (10–16)[b] a^N (4), a^H (12), a^H (12) ~1.2 or 2.4 (1.0–2.8)
 VI·+	a^H (2) = 9.82 a^H (12) = 5.64 a^N (2) = 4.31 $\Sigma a_{C_6H_5}{}^H$ (10) ≤ 0.6
 V·+	c
$(Me_2N)_2C{=}C(NMe_2)_2\cdot^+$ II·+	a^N (4) = 4.85[d] a^H (12) = 3.28[d] a^H (12) = 2.84[d]
$(Me_2N)_2C{=}CH(NMe_2)\cdot^+$ IV·+	e
	a^H (2) = 4.35[f] a^N (2) = 6.94[f] a^H (12) = 8.16[f]
	a^H (2) = 5.07[f] a^N (2) = 8.07[f] a^H (8) = 4.04[f]
$(Me_2N)_2C{=}CCl_2\ \cdot^+$ XXII·+	g
 XI·+	h

[a] In acetonitrile–0.1 M TEAP. [b] Approximate values and ranges for this partially resolved spectrum (see Figure 9). [c] Only slightly resolved (5100 theoretical absorption peaks). [d] From Table I, footnote g. [e] From S. S. Tseng and W. H. Urry, private communication, 1968. This spectrum was somewhat resolved, but has not been interpreted. There are 220,000 theoretical absorptions. [f] B. C. Gilbert, R. H. Schlossel, D. H. Geske, and W. M. Gulick, Jr., 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, Abstract PHYS-113, Division of Physical Chemistry. [g] This spectrum was somewhat resolved (Figure 10), but has not been interpreted (3400 theoretical absorptions). [h] This spectrum was totally unresolvable (20,000 theoretical absorptions). The spectral width was very small (6 G between the maximum and the minimum of the unresolved first-derivative absorption).

It employed gravity feed and was prepurged and blanketed with high-purity nitrogen. The oxidant utilized was a dilute acetonitrile solution of the tris-(p-bromophenyl)amine monocation radical[5a] (deep blue, prepared coulometrically). This oxidant has the excellent properties of being a strong oxidant ($E^{o\prime}$ = +1.08 V *vs.* sce) and remarkably stable (it is stable for months *in solution* if isolated from air and water). An acetonitrile solution of the substrate to be oxidized was of a concentration in slight excess of the oxidant concentration (to avoid oxidation beyond the monocation radical). A slow flow (0.1–1.0 ml/min) maintained a steady-state concentration of the desired cation radical (the desired redox reaction was complete.)

It is most unfortunate that many of the esr spectra were unresolvable or only partially resolvable, and hence uninterpretable by the usual means. This is in spite of the very narrow line widths obtainable with dilute radical solutions in acetonitrile. The problem is

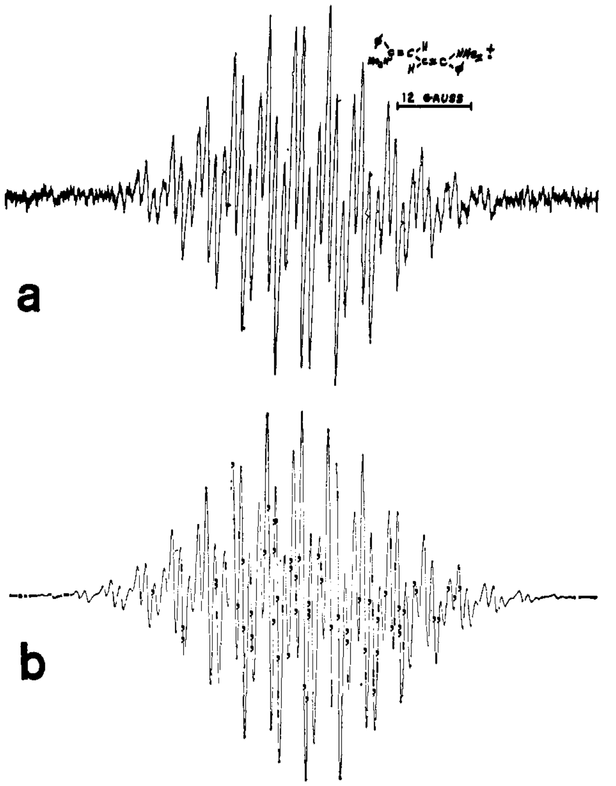


Figure 8. (a) Electron spin resonance spectrum of the 1,4-bis-(dimethylamino)-1,4-diphenylbutadiene (VI) monocation in acetonitrile. (b) Computed spectrum using a Lorentzian line shape and the coupling constants given in Table III.

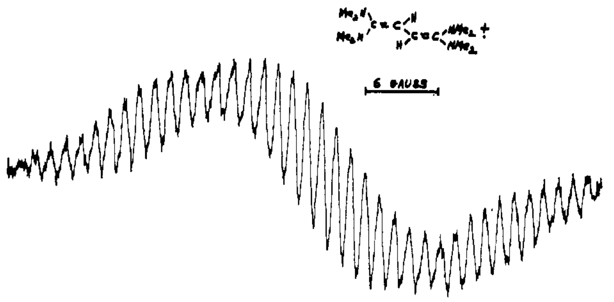


Figure 9. Esr spectrum of the 1,1,4,4-tetrakis(dimethylamino)-butadiene (III) monocation in acetonitrile.

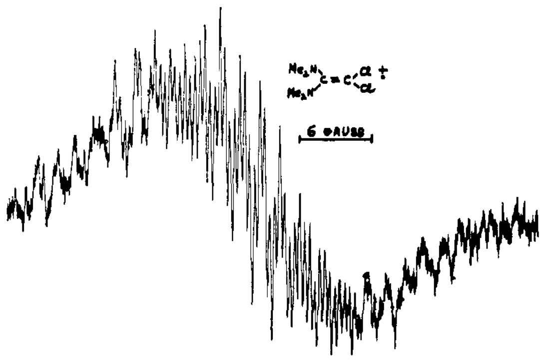


Figure 10. Esr spectrum of the 2,2-dichlorovinylidenebis(dimethylamine) (XVII) monocation in acetonitrile.

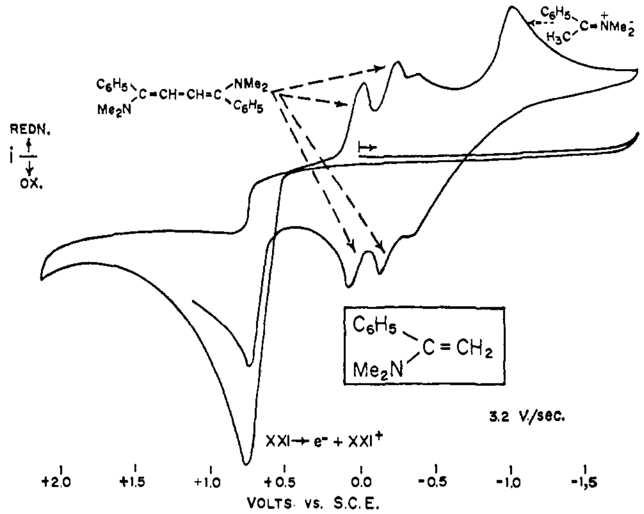
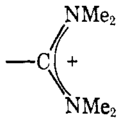


Figure 11. Cyclic polarogram of 1-(dimethylamino)styrene (XXI).

the very complex hyperfine patterns (3000–220,000 theoretical absorption peaks for the unresolved spectra).

The most significant observation from the esr studies is the polarization of the unpaired electron *away* from the dimethylamino substituents. This is especially obvious for III$^+$, but is also seen with VI$^+$ and in the narrow spectrum of XI$^+$. As discussed previously, the *opposite* is true of the positive charge in the monocations. The strong electron-donating character of the dimethylamine groups is reflected in their effect on the oxidation potentials. Indeed, the isolated segment



is shown to be very stable by the remarkable ease of forming dications of compounds I–VI.

The narrow spectrum of XI$^+$ is attributed to the unpaired electron spending most of its time on those carbons to which no magnetic nuclei are directly attached (those numbered 1a, 4a, 5a, 8a, and 9 in the diagram of Table III). The lack of sizable splittings from the ring hydrogens (such would markedly increase the observed spectral width) indicates that the unpaired electron is mostly on C-9.

Although the spectrum of XVII$^+$ (Figure 10) was not interpreted, it is quite clear that a sizable splitting is present for the chlorines. Unfortunately, this considerably complicates the spectrum, especially with the two common chlorine isotopes having different nuclear magnetic moments (although the spin quantum numbers are both $^3/_2$). Sizable splittings due to chlorines have been observed for other cation radicals, *e.g.*, the tris(*p*-chlorophenyl)amine monocation.[5a]

The esr of VI$^+$ (Figures 8a and 8b) shows surprisingly small splittings for the ten phenyl hydrogens (all are buried within the observed line width). This indicates that the phenyls are quite twisted from the plane of the butadiene backbone. Apparently the charge stabilization of the dimethylaminos is much more significant than any stabilization available with the phenyls.

The Fate of the Radical Cations. Lifetimes. The lifetimes for the monocation radicals have been measured using cyclic (controlled-potential) coulometry (for $t_{1/2} > 1$ min) or cyclic voltammetry with the method of Nicholson and Shain[18] (for $t_{1/2}$ of 10^{-3}–10 sec). The lifetimes were determined for 3 m*M* solutions of substrate in acetonitrile containing 0.1 *M* TEAP. These data are given in Table I.

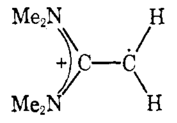
The lifetimes of the cation radicals formed by oxidation of aminoalkenes seem to depend on two factors: the number of atoms over which the electronic vacancy can be spread, and the extent to which the reactive site is hindered (in most of the compounds studied, this is the vinyl carbon *not* bearing nitrogen substituents). Of these, delocalization appears to be the more important; all the long-lived radicals (II–VI, XI, and XVII) can delocalize the hole over at least six atoms (including the two Cl atoms of XVII). The four ions of intermediate lifetime (IX, XII, XIII, and XXII) are presumably too hindered to undergo the rapid coupling reactions characteristic of the less highly substituted species[19] (see below and ref 1b) and must decompose by some alternate, slower pathway (indeed, IX is known to do so[8]). From structural considerations, it is likely that the oxidized forms of XII and XXII first lose protons from methyl groups, with the resulting radicals undergoing various subsequent reactions.

Coupling Reactions of the Cation Radicals. In a few cases we were able to observe by cyclic voltammetry some stable, electroactive products from the oxidation of certain aminoalkenes. In particular XV and XXI were observed to give products which exhibited reversible redox reactions at much more negative potentials than the parent compounds (Figure 11 and ref 1b). These were subsequently identified as the deprotonated dimers III and VI by comparison of their cyclic polarograms with those, respectively, of XV and XXI (*cf.* Figures 4 and 11). The formation of the dication of III from XV was confirmed by chemical oxidation of XV, isolation of the product, and comparison (nmr) with authentic III^{2+} obtained from chemical oxidation of III. A plausible mechanism for the formation of these products follows. Dimerization is a reasonable

$$\mathrm{XV} \xrightarrow{-e^-} (\mathrm{Me_2N})_2\overset{+}{\dot{C}}\mathrm{CH_2CH_2}\overset{+}{\dot{C}}(\mathrm{NMe_2})_2 + 2\mathrm{XV}$$

$$2\mathrm{CH_3C(NMe_2)_2}^+ + \mathrm{III} \underset{+2e^-}{\overset{-2e^-}{\rightleftharpoons}} \mathrm{III}^{2+}$$

reaction for a radical such as XV to undergo, and XV is known[20] to be a reasonably strong base. The esr results discussed above clearly indicate a strong dominance of this resonance structure for XV$^+$



A similar pathway can be written for the conversion of XXI, a *monoaminoethylene*, to VI. It is reasonable to suppose that other enamines and enediamines which possess unblocked reaction sites on the original double

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[18] R. S. Nicholson, *Anal. Chem.*, 38, 1406 (1966); see also Table I, footnote *a*.

[19] Evidence from chemical oxidation studies shows that most of the short-lived cation radicals undergo fast β-coupling reactions. None of the moderately long-lived radicals react this way.[8]

[20] J. D. Wilson, C. F. Hobbs, and H. Weingarten, *J. Org. Chem.*, 35, 1542 (1970).

bond react as XV and XXI do, by tail-to-tail dimerization of the cation radical formed on oxidation, and indeed X has been found to give the conjugate diacid of I on chemical and electrochemical oxidation.[1b,8] The structures of XV and XXI merely happen to be such that the products from their oxidations are identifiable by electrochemical techniques.

Effects of Protonation of Aminoalkenes. The cyclic polarogram for the oxidation of XXI (Figure 11) exhibits a broad, irreversible reduction wave at −1.0 V. This wave was found to be due to the conjugate acid of the starting material $CH_3(C_6H_5)C{=}N^+(CH_3)_2$. In general, enamines and enediamines protonate on carbon; in the medium we employed these conjugate acids are reduced at potentials in the range −0.7 to −1.7 V (*vs.* sce).

Figure 12 confirms that these reductions are due to the protonated species. The solid line shows the polarograms for 2,3-bis(dimethylamino)butadiene (XVIII). Initially, there are no species electroactive in the region of +0.4 to −1.7 V; then this aminoethylene undergoes two irreversible oxidations, following which a small reduction peak is seen at −0.3 V and a large broad reduction peak at −1.1 V. The dashed line shows the effect of protonating some of XVIII (1 part of H_2SO_4 was added to 2 parts of XVIII). Note the decrease in the aminoethylene oxidation peak heights. The small peak at −0.3 V is due to "free" protons in solution, *i.e.*, associated with acetonitrile and/or perchlorate. (This reduction peak is present with solutions of acids, sulfuric or perchloric, in acetonitrile–TEAP. It becomes dominant on addition of a large excess of acid to the aminoethylene solution and then increases in height linearly with acid concentration.) The large reduction peak at −1.1 V is now present before oxidation of any aminoethylene, and it is not observed for a solution of sulfuric acid in the medium. Hence, this peak is attributable to the reduction of the protonated aminoethylene. The other aminoethylenes which oxidize to reactive monocations also show subsequent irreversible reductions of the protonated forms. Several of these were confirmed as above by acid addition.

Surprisingly, we observed that the reductions of several of the protonated aminoethylenes become reversible one-electron processes with a large excess of acid present. Rapid protonation of the radical product may occur, stabilizing it electronically and sterically.

In support of this hypothesis, we have observed that the neutral radical formed on electroreduction of the N,N,N′,N′-tetramethylchloroformamidinium ion has a relatively long lifetime ($t_{1/2}$ = 1 sec).

$$[(CH_3)_2N]_2C^+{-}Cl + e^- \longrightarrow [(CH_3)_2N]_2\dot{C}Cl$$

Experimental Section

Cyclic voltammetry was performed using a Hewlett-Packard 3300A function generator including the 3302A triggering plug-in, a Wenking 66TS10 potentiostat, a Moseley 7030AM recorder for slow sweeps, and a Tektronix 502A oscilloscope with a Tektronix C-12 camera for fast sweeps. The electrochemical cell was cylindrical with about a 60 cm^3 volume. The working electrode was a Beckman 39273 platinum disk. A platinum wire served as the auxiliary electrode. The reference electrode was a saturated calomel separated by a fine glass frit and a Luggin capillary with saturated tetraethylammonium perchlorate (TEAP) in acetonitrile filling the capillary and the section with the calomel. The capillary was placed as close as practical to the platinum disk working electrode so as to minimize the uncompensated resistance.[21] The solutions were initially purged and constantly blanketed with high-purity tank nitrogen. Liquid samples were introduced from a drybox into a deaerated portion of solvent plus electrolyte *via* a microsyringe.

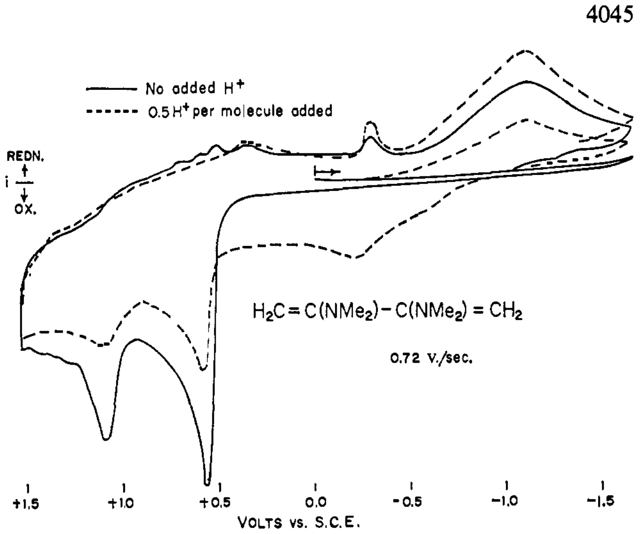

Figure 12. Cyclic polarograms of 2,3-bis(dimethylamino)butadiene (XVIII). Effects of protonation.

For coulometric studies the Wenking 66TS10 was used with a high-precision integrator, constructed from precision resistors, an Anadex DF-100 DC-to-frequency converter, and an Anadex CF-503R electronic counter.[22] The electrolysis cell was the same as that used for cyclic voltammetry except that the working electrode was a cylindrical platinum gauze and the platinum gauze auxiliary electrode was isolated by two large medium-porosity glass frits (saturated TEAP in acetonitrile between the frits and in the auxiliary compartment).

For the esr studies a Varian V4502-15 spectrometer with 100-kHz modulation was employed.

Acetonitrile was purified by triple distillation (retaining the center cuts).[23] Tetraethylammonium perchlorate (TEAP) was prepared by the double decomposition of lithium perchlorate with tetraethylammonium bromide and was twice recrystallized from water. All potentials are given in volts *vs.* sce.

Substrates. Samples of tris- and tetrakis(dimethylamino)ethylene (IV and II) were kindly provided by Drs. W. H. Urry and S. S. Tseng of the University of Chicago. II was also prepared by the pyrolysis of tris(dimethylamino)methane.[24]

The preparations of 1,1,4,4-tetrakis(dimethylamino)butadiene (III), 2-methylpropylidenebis(dimethylamine) (IX), propylidenebis(dimethylamine) (X), and 2,2-dichlorovinylidenebis(dimethylamine) (XVII) have been described.[25] So have the preparations of 9-[bis(dimethylamino)methylene]fluorene (XI), 9-(1-dimethylamino)ethylidenefluorene (XII), and 9-(dimethylamino)methylenefluorene (XVI),[26] as have those of 2,6-dimethylcyclohexenyl-1-dimethylamine (XIII),[27] 1-cyclohexenyldimethylamine (XIV),[28] and tetrakis(dimethylamino)methane (XIX).[29]

The following compounds were prepared by the $Ti(NMe_2)_4$ method of Weingarten and White:[25,30,31] 2,3-dimethyl-1,1,4,4-tetrakis(dimethylamino)butadiene (I) from N,N,N′,N′,2,6-hexamethylsuccinamide; 1,4-bis(dimethylamino)-1,4-diphenylbutadiene (VI) from 1,4-diphenyl-1,4-butanedione; 1,3-bis[bis(dimethylamino)methylene]cyclobutane (VII) from N,N,N′,N′-tetramethylcyclo-

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(21) S. P. Perone, *Anal. Chem.*, 38, 1158 (1966).

(22) Constructed by J. M. F. using the concept of A. J. Bard and E. Solon, *ibid.*, 34, 1181 (1962).

(23) G. A. Forcier and J. W. Olver, *ibid.*, 37, 1447 (1965).

(24) H. Weingarten and W. A. White, *J. Org. Chem.*, 31, 3427 (1966).

(25) H. Weingarten and W. A. White, *ibid.*, 31, 2874 (1966).

(26) H. Weingarten and N. K. Edelmann, *ibid.*, 32, 3293 (1967).

(27) W. A. White and H. Weingarten, *ibid.*, 32, 213 (1967).

(28) H. Weingarten and W. A. White, *ibid.*, 31, 4041 (1966).

(29) H. Weingarten and W. A. White, *J. Amer. Chem. Soc.*, 88, 2885 (1966).

(30) H. Weingarten and W. A. White, *ibid.*, 88, 850 (1966).

(31) Further details of the preparations of these compounds will be reported later.

butane-1,3-dicarboxamide; 1,1,5,5-tetrakis(dimethylamino)-1,4-pentadiene (VIII) from N,N,N′,N′-tetramethylglutaramide; and 2,2-difluorovinylidenebis(dimethylamine) (XX) from difluoroacetic acid.

2,5-Bis(dimethylamino)-2,4-hexadiene (V) was prepared by the $Ti(NMe_2)_4$ method from 2,5-hexanedione as a liquid, bp 79° (1.5 Torr) (it solidifies near 0°). It exhibits an nmr spectrum consisting of singlets at τ 4.8 (2 H), 7.4 (12 H), and 8.2 (6 H). Its mass spectrum includes a parent ion at *m/e* 168; an M + 1 peak equal to 12.1% of M^+ (expected for $C_{10}H_{20}N_2$: 11.9%); and fragment ions corresponding to $[M - (CH_3)_2NH]^+$ and $[M - (CH_3)_2NHCH_3]^+$, reasonable fragments for this structure.

2,3-Bis(dimethylamino)butadiene (XVIII) and 1-dimethylaminostyrene (XXI) were prepared by the $TiCl_4$–$HNMe_2$ method of White and Weingarten[27,31] from 2,3-butanedione and acetophenone, respectively. The preparation of 1-methyl-3-dimethylamino-2 butenylidenedimethylammonium fluoroborate (XXII) will be described elsewhere.[20]

Acknowledgments. We thank Professor W. H. Urry and Dr. S. S. Tseng of the University of Chicago for their gracious gifts of samples and Dr. Urry and the many others who have helped in discussions.

Thiazolothiazoles. II.[1a] The Parent Heterocycle and Its Carboxylic and Amino Derivatives[1b]

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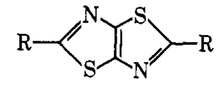
Received January 15, 1970

Abstract: Side chain oxidation of 2,5-bis-β-styryl and 2,5-bis-2-furylthiazolo[5,4-*d*]thiazole with permanganate furnished 2,5-thiazolothiazoledicarboxylic acid in good yields. The dicarboxylic acid has served as starting material for a variety of thiazolothiazole derivatives that are inaccessible by direct routes. Stepwise decarboxylation led to 2-thiazolothiazolecarboxylic acid and to the parent heterocycle. Thiazolothiazole is remarkably stable and does not undergo electrophilic substitution reactions. The nucleus is attacked by strong nucleophilic reagents and was converted by means of *n*-butyllithium to 2-thiazolothiazolyllithium. Experiments leading to 2,5-diamino and 2-aminothiazolothiazole and their derivatives are reported.

The reaction of dithiooxamide with aromatic aldehydes affords a general synthesis of 2,5-diarylthiazolo[5,4-*d*]thiazoles,[1a] but we have been unable to obtain directly the parent heterocycle or its alkyl derivatives by means of a similar condensation with formaldehyde or other simple aliphatic aldehydes.[2] The present paper describes the synthesis of a series of carboxylic and amino derivatives, and of the parent thiazolo[5,4-*d*]thiazole (**1**) by an indirect route from the readily available condensation products of dithiooxamide with cinnamaldehyde or furfural.

Owing to the high stability of the thiazolothiazole nucleus, 2,5-thiazolothiazoledicarboxylic acid (**2**) can be obtained in high yields by permanganate oxidation of either the 2,5-bis-β-styryl (**3**) or 2,5-bis-2-furyl (**4**) derivative of thiazolothiazole. The dicarboxylic acid (**2**) separated from aqueous media as a relatively stable dihydrate which can be converted to the anhydrous acid by prolonged drying over phosphorus pentoxide at low pressure. The strongly electrophilic character of the thiazolothiazole system is disclosed by the relatively high acidity of the dicarboxylic acid: pK_1 and pK_2, 2.52 and 3.05. The rather small diminution in acidity for the second acidic hydrogen, ΔpK 0.53, indicates that inductive electron release from the carboxylate anion is not effectively transmitted between the 2 and 5 positions of the bicyclic system (*cf.* terephthalic acid, ΔpK *ca.* 1.0; fumaric acid, ΔpK *ca.* 1.5).



1, R = R′ = H
2, R = R′ = COOH
3, R = R′ = $CH{=}CHC_6H_5$
4, R = R′ = C_4H_3O
5a, R = R′ = $COOCH_3$
b, R = R′ = $COOC_2H_5$
6a, R = COOH; R′ = $COOCH_3$
b, R = COOH;
R′ = $COOC_2H_5$
7a, R = H; R′ = $COOCH_3$
b, R = H; R′ = $COOC_2H_5$
8, R = H; R′ = COOH
9, R = COOH; R′ = $CONH_2$
10, R = COOH; R′ = CON_2H_3
11, R = H; R′ = $CONH_2$
12, R = H; R′ = CON_2H_3
13, R = R′ = $CONH_2$
14, R = R′ = CON_2H_3
15, R = R′ = CON_3
16, R = R′ = $NHCOOC_3H_7$
17, R = R′ = $N(CO)_2C_8H_4$
18, R = R′ = NH_2
19, R = H;
R′ = $NHCOOC_3H_7$
20, R = H; R′ = $N(CO)_2C_6H_4$
21, R = H; R′ = NH_2

The dibasic acid (**2**) was converted readily to the dimethyl ester (**5a**) by direct esterification with methanol in the presence of hydrogen chloride, or by diazomethane. The diethyl ester (**5b**) was prepared similarly from ethanol. Controlled saponification of the dimethyl and diethyl esters furnished the monoesters, *e.g.*, 5-carbomethoxy-2-thiazolothiazolecarboxylic acid (**6a**). Decarboxylation of these led to the corresponding esters of 2-thiazolothiazolecarboxylic acid (**7**) which upon hydrolysis gave 2-thiazolothiazolecarboxylic acid (**8**) in a pure state. Aminolysis and hydrazinolysis of the half-esters (**6**) afforded the monoamide (**9**) and the monohydrazide (**10**) of the dibasic acid which by decarboxylation afforded the amide (**11**) and the hydrazide (**12**) of the monocarboxylic acid

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(1) (a) Part I: *J. Amer. Chem. Soc.*, 82, 2719 (1960); (b) abstracted from the Ph.D. Theses of D.H.R. (1960) and R.K. (1956); (c) Todd Fellow in Chemistry, 1956–1959; to whom inquiries may be directed, Esso Research and Engineering Company, Linden, N. J. 07036; (d) to whom inquiries may be directed, School of Pharmacy, University of California, San Francisco, Calif. 94122.

(2) A previously reported Mannich-type condensation of dithiooxamide with aliphatic and aromatic aldehydes in the presence of secondary amines (O. Wallach and J. Froelich, *Chem. Zentr.*, II, 1024 (1899)) has been reinvestigated in this laboratory by Dr. Hector Belmares-Sarabia, Ph.D. Thesis, Cornell University, 1963.