75 °C. This second oxidation proceeded rapidly and was complete in 36 min. After washing and rinsing the resin with cyclohexane and water as above, a third oxidation of another 1.7 mmol of cinnamyl alcohol was carried out. The reaction required 2 h to reach completion. The resin was again filtered and washed as above, then used in a fourth oxidation using another 1.7 mmol of cinnamyl alcohol. This fourth oxidation reached completion in 7 h. After washing with cyclohexane, the resin was soaked in 2 N potassium hydroxide overnight, and the filtrate was titrated with standard ferrous ammonium sulfate in acidic medium. The titration showed that the resin still contained 1.9 mmol of chlorochromate after four successive oxidations of 1.7-mmol portions of cinnamyl alcohol (Table V).

Recycling of the Resin. The spent reagent, which was black after filtration of the desired product, was easily regenerated by washing with 2 N hydrochloric acid (or 2 N nitric acid) followed by 2 N aqueous sodium or potassium hydroxide and rinsing with water. This treatment effectively removed the chromium salts from the polymer and regenerated the PVP resin. The regenerated PVP was usually slightly darker than the original material, but was unaffected in its ability to produce a satisfactory PVPCC reagent (Table VI). After regeneration with CrO_3 and HCl, the recycled PVPCC, which was dark red, had an activity comparable to that of the fresh reagent, and its activity remained essentially constant through repeated oxidation–reduction cycles. The only losses which were observed were mechanical, due to the numerous transfers of wet polymers at the different stages of reaction or recycling. In a typical run these losses amounted to 1–2%.

Acknowledgment. Financial support of this work by the National Research Council of Canada in the form of a research grant and a graduate scholarship (to M.J.F.) is gratefully acknowledged.

Registry No.—Cinnamaldehyde, 104-55-2; 1-phenylethanone, 122-78-1; hexanal, 66-25-1; 4-methyl-4-penten-2-one, 3744-02-3; 3-hexanone, 589-38-8; cyclopentanone, 120-92-3; 2-octanone, 111-13-7; cyclohexanone, 108-94-1; butanol, 123-72-8; benzaldehyde, 100-52-7; PVPCC, 66212-21-3.

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(9) Cainelli et al. (ref 7) claim to observe an increase in rate for higher substrate to resin ratio; this is unlikely.

(10) The data shown on Table V suggest that the active sites may become coated with the oxidized material, thus slowing down the reaction. This is supported by the observation that, after washing with solvent, the partially spent resin can react again at a normal rate.

(11) An alternate regeneration procedure aimed at the selective removal of the spent chromium salt after reaction was not successful, as some CrO_3 leached from the polymer at the same time as the reduced chromium salt.

(12) Reference 7 shows that the recommended ratio of resin to alcohol for most reactions with the chromate ion exchange resin is of 3.5 g of resin per mmol of alcohol. However, such a high ratio is not well-suited for practical applications.

Effects of Structure on the Ease of Electron Removal from *o*-Phenylenediamines

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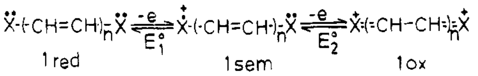
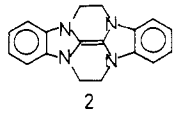
Received December 5, 1977

Cyclic voltammetric (CV) data are reported for 23 alkyl-substituted *o*-phenylenediamine derivatives, including examples with *N,N′*-alkyl bridging and bis bridging. The ^{13}C NMR shift at C_4,C_5 of the aromatic ring appears to be a good criterion for the average amount of lone pair, aromatic ring overlap in the neutral materials. For several examples, both $E°_1$ and $E°_2$ were measured by CV. $E°_1$ varies by over 1.1 V (25 kcal/mol) in the series investigated and is discussed in terms of electronic and steric effects. The dications are argued to be significantly nonplanar from the observed $E°$ values, and the 1,4,5,8-tetramethyl-1,2,3,4-tetrahydroquinoxaline dication was found to have nonequivalent CH_2 hydrogens at −88 °C by ^1H NMR.

Electrochemical studies allow measurement of the standard oxidation potential ($E°$) for electron-transfer reactions, providing that these reactions are electrochemically reversible, which requires both chemical reversibility and that electron transfer is rapid on the time scale of the experiment. $E°$ values are of particular interest because they are a measure (relative to the reference electrode used, or of one compound relative to another[1]) of the free energy difference between oxidized and reduced forms. More than 1 electron can be reversibly added to or removed from some compounds. Hünig[2] has suggested the term "violene" to designate radical cations of systems which have lone pair bearing heteroatoms flanking a π system (symbolized by **1red** below), so that the radical cation has $2n + 3$ electrons shared by $2n + 2$ atoms (**1sem**). For violenes, all three oxidation states are frequently long lived,[2] allowing both $E°_1$ and $E°_2$ to be measured electrochemically and other physical and chemical methods to be used to characterize these redox-related species. Hünig and co-workers[3] have carried out extensive studies of a variety of violenes. The difference in standard potentials for the two oxidations, $\Delta E° = E°_2 - E°_1$, is a measure of the disproportionation constant for the sem form, because $K_d = (\text{sem})^2/(\text{red})(\text{ox}) = \exp C\Delta E°$, where $C = (23.06 \times 10^3)/(1.987T)$, where $\Delta E°$ is in V, and T is in K. The K_d values observed for violenes vary tremendously with structure. An unusually large K_d was observed for **2**, $K_d = 2.6 \times 10^{14}$ ($\Delta E° = 0.85$ V), while at the other extreme, **3** has a negative $\Delta E°$,[4] the second electron being easier to remove than the first, in spite of the electrostatic problem in going to a dication. Fritsch and co-workers[4] pointed out that only the sem form of **3** has a strong requirement of planarity for the two



1red 1sem 1ox



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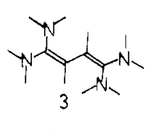

3

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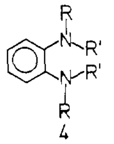
bulky olefins, so that $E°_1$ is increased because of this strain, and $E°_2$ decreased because of strain relief.

Because of our interest in the energy requirements for oxidation of tetraalkylhydrazines,[5] where the sem form is flattened at nitrogen and increases $\mathbf{R}_1\mathrm{N}_1\mathrm{N}_2\mathbf{R}_2$ strain, we have studied a series of their benzologues, 1,2-diaminobenzene derivatives (many of which can be characterized by general formula **4**). Steric interactions between the alkyl groups of the

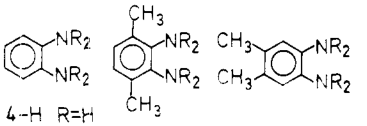


4

oxidized forms of **4** would be expected to be large and altered considerably when the R′ groups are linked to form a ring. We had originally hoped that by linking the R′ substituents of **4** a conformational dependence upon electron transfer rate such as has proven useful in six-membered ring cyclic hydrazines[6] would be observed electrochemically. This hope was not realized, presumably because of rapid conformational equilibration of conformations in the red forms. Nevertheless, our results show that geometry changes upon electron removal do strongly influence the standard potentials $E°_1$ and $E°_2$ in **4** and reveal that $\mathbf{4}^{2+}$ is decidely nonplanar, in contrast to $\mathbf{4}^{+\cdot}$.

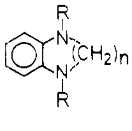
Results

A. Compounds Examined. To compare standard potentials in *o*-phenylenediamines with and without linking of the nitrogen substituents, several compounds were employed. In an attempt to have the formula numbering convey some structural information, we shall use the following system. **4**

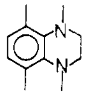


4-H R=H
4-Me R=Me 4A-Me 4B-Me R=Me
4-Et R=Et R=Me

will be used for systems where the nitrogen substituents are not linked, followed by abbreviations for these substituents. We also employed 3,6-dimethyl and 4,5-dimethyl ring-substituted compounds in some instances to examine the interplay of the electron-releasing and steric effects of the 3,6-dimethyl compounds. Suffixes A and B are used to designate the aryl ring methyl substitution pattern. The heterocyclic ring size is indicated by the number employed for the polymethylene-bridged compounds **5–9**, with suffix A or B for ring methyls and H or Me for the nitrogen substituents, as in the the example illustrated, **6A-Me.**

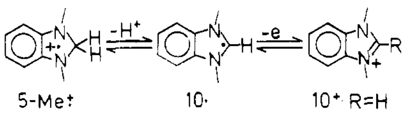


5 n=1
6 n=2
7 n=3
8 n=4
9 n=5



6A-Me

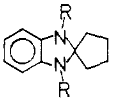
Unfortunately, **5-Me** showed a completely irreversible oxidation peak under all conditions employed ($E_p{}^{ox} = +0.31$, 23 °C, 100 mV/s; $E_p{}^{ox} = +0.3$, −78 °C, 100 mV/s). We believe that this problem is caused by the aromaticity of the deprotonated 2-electron oxidation product, dimethylbenzimidizolium cation $\mathbf{10}^+$. As illustrated in eq 1, formal loss of a proton



(1)

5-Me$^{+\cdot}$ 10· 10$^+$ R=H
11$^+$ R=Me

would give **10·**, which is very unstable relative to **10**·. The iodide of the 1,2,3-trimethylbenzimidazolium salt $\mathbf{11}^+$ is only reduced irreversibly at −1.76 V (23 °C, 100 mV/s). This indicates that loss of an electron and a proton from $\mathbf{5\text{-}Me}^{+\cdot}$ would give the product $\mathbf{10}^+$, which is approximately 2 V (46 kcal/mol) stabler toward oxidation. Although our data do not indicate what pathway is employed, $\mathbf{5\text{-}Me}^{+\cdot}$ decomposes extremely rapidly. In contrast, the four 2,2-dialkyl analogues of **5** studied (**12** and **13**) give cations which are long enough lived



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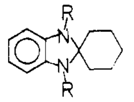
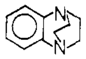


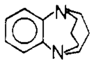
13

to measure $E°$, although all have noticably shorter lifetimes, especially for the dications, than corresponding derivatives of **6.**

To have examples of **4** in which the nitrogen lone pairs were precluded geometrically from overlap with the aryl ring, bisbridged systems **14** and **15** were prepared. In an attempt to



14



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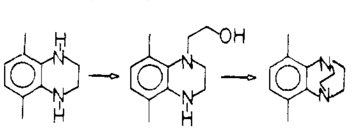
improve the yield for ring closure in the preparation of 3,6-dimethylbenzodabco, **14A**, the route shown in eq 2 was em-



(2)

6A-H 16 14A

ployed. Attempted isolation of *O*-tosyl-**16** led to apparent O to N rearrangement in concentrated solution, so this intermediate was cyclized directly by addition of *n*-butyllithium to form the *N*-lithio salt without concentration. Unfortunately the yield for **16** → **14A** was low (11%) and we found it more convenient to simply use ethylene bromide and the appropriate tetrahydroquinoxaline to obtain **14** and **14B** and propylene bromide and *o*-phenylenediamine to obtain **15,** all in very low yield. Because the products are easily sublimed from the tarry reaction products, chromatography did not need to be employed for isolation.

B. Lone Pair, Aryl Interactions. The geometry of the neutral *o*-phenylenediamine derivatives is clearly of interest in considering their oxidation potentials. We had hoped to be able to use low-temperature ^{13}C NMR to get conformational information, but even for **6A-Me,** no conformational broadening could be observed. Because low rotational and nitrogen inversion barriers are expected, perhaps this is not surprising. For *N,N*-dimethylaniline, a rotational barrier of 5.1 kcal/mol has been estimated[7] (although the barrier to nitrogen inversion these authors estimate seems likely to be far too high). *N,N*-Dimethylaniline is thought to have the nitrogen lone pair aligned for maximum overlap with the aryl π system, although the degree of bending at nitrogen seems quite uncertain.[7] One would expect changes in both the NMR and UV spectra upon rotation about the aryl carbon–nitrogen bond to decrease conjugation of the nitrogen lone pairs with the ring. Because deconjugation of the lone pairs should result in less π electron density at C_4,C_5 of the aryl ring, one should expect a downfield shift for $C_{4,5}$ in the ^{13}C NMR. Aromatic ^{13}C-NMR shifts are well known to be sensitive to π electron density.[8] In fact, the C_4,C_5 shifts of the full deconjugated **14** and **15** are rather close to the δ 128.5 of benzene itself, C_4,C_5 of the five-ring compound **12-Me,** which is constrained to have maximum conjugation δ 103.2, and the other compounds are intermediate (see Table I). In UV spectra, decreases in extinction coefficient

Table I. ^{13}C-NMR Chemical Shifts for Some *o*-Phenylenediamine Derivatives (δ from Internal Me_4Si)

Compd	Solvent	C_{12}	C_{36}	C_{45}	NCH_3	CCH_3	NCH_2	Other
4-Me	$CDCl_3$	144.73	121.20	117.44	41.22			
4A-Me	$CDCl_3$	144.45	135.40	126.70	43.26	18.60		
4B-Me	$(CD_3)_2CO$	143.75	120.04	129.38	41.99	19.11		
12-Me	$(CD_3)_2CO$	141.77	118.13	103.22	32.03		98.36	26.56, 28.66
6-Me	$CDCl_3$	136.25	117.73	110.28	39.08		49.80	
6A-Me	$CDCl_3$	139.69	128.43	123.98	43.90	18.81	45.40	
	$(CD_3)_2CO$	140.89	128.91	124.66	44.00	18.94	46.84	
6B-Me	$(CD_3)_2CO$	135.74	113.51	125.21	39.53	19.10	50.79	
7-Me	$CDCl_3$	143.17	121.29	117.10	42.30		53.60	26.56
8-Me	$(CD_3)_2CO$	142.68	119.73	45.69	38.59		51.26	26.22
9-Me	$(CD_3)_2CO$	145.47	121.39	117.25	37.50		53.90	28.50, 27.17
14	$(CD_3)_2CO$	153.50	123.97	127.39			51.49	
14A	$(CD_3)_2CO$	150.14	130.04	127.45		16.02	50.71	
14B	$(CD_3)_2CO$	150.54	124.82	134.98		19.96	56.67	
15	$(CD_3)_3CO$	152.47	129.05	128.05			51.38	29.06

Table II. Ultraviolet Spectra of Some *o*-Phenylenediamine Derivatives in Hexane

Compd	λ_{max}, nm (ϵ)		
5-Me	312 (5200)	264 (5400)	217 (29000)
12-Me	315 (7400)		224 (37000)
6-Me	311 (6100)	263 (3200)	229 (34000)
7-Me	ca. 303 (br) (3900)	266 (9400)	236 (26000)
8-Me	308 (5000)	270 (7500)	234 (29000)
9-Me	301 (4200)	273 (9800)	234 (24000)
6A-Me	ca. 300 (br) (1400)	264 (sh)	234 (24000)
4-Me	294 (2800)	268 (8500)	233 (21000)
4A-Me		269 (3200), 253 (5200)	215 (11000)
14	313 (150)		
14A	320 (21), 307 (24)		
14B	320 (50), 314 (44)	274 (1800), 265 (1500)	

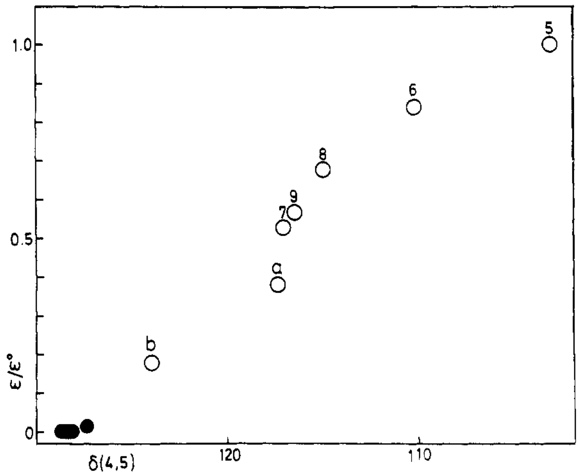


Figure 1. A plot of ϵ/ϵ^0 for the long wavelength UV absorption band vs. the ^{13}C-NMR chemical shift for the C_4,C_5 carbons for some tetraalkyl *o*-phenylenediamine derivatives. **5** is the five-ring compound **12-Me** (which has the largest extinction coefficient, ϵ^0) and **6–9** are **6-Me** to **9-Me**; (a) the tetramethyl compound **4-Me**; (b) **6A-Me**. The filled figures are for the bicyclic compounds **14** and **15**.

are observed for intramolecular charge-transfer bands when conjugative interaction is decreased, as has been studied for substituted nitroanilines,[9] benzocyclamines,[10] and benzocycloalkylanones.[11] We observe this effect for the longest wavelength band (near 310 nm) for *o*-phenylenediamines, ϵ being highest for **12-Me** and dropping substantially for some of the other compounds (see Table II). Because the bands are rather broad for many of the compounds they overlap, making ϵ (λ_{max}) for the ca. 310 nm band not easily measurable. Especially for the weak bands, the observed ϵ (λ_{max}) is a composite figure. Both **14** and **15** had observed long wavelength maxima, although conjugative lone pair, aryl ring interaction is geometrically precluded. We presume that the weak maxima observed near 310 nm have a completely different origin than those for ordinary *o*-phenylenediamines (and can only hope that impurities having intense absorptions in this region are entirely absent). For systems with only one conjugated group attached, analyses to extract twist angle from UV spectra have used a θ = arcos (ϵ/ϵ°) relationship,[9] where ϵ° is for a compound assumed to have zero twist. It is not obvious to us what relationship with θ should actually be followed in *o*-phenylenediamines, where there are two twist angles (which in principle could be different). Nevertheless, a plot of ϵ (λ_{max})/ϵ° vs. δ (C_4,C_5) (see Figure 1) gives a significant correlation (we have no reason to expect a linear correlation), and we suggest that both spectral measurements are reflecting the same thing, the amount of conjugation of the lone pairs with the aryl ring. We note that although **6-Me** has by both techniques larger lone pair, aryl ring conjugation, as expected for the diequatorial *N*-methyl compound, addition of 3,6-methyls in **6A-Me** greatly reduces conjugation, suggesting a change to the diaxial conformation (which, if it were the only conformation occupied, would not give NMR line broadening even if slow nitrogen inversion were achieved). Because of the ease of measurement and the lack of the overlap difficulties encountered in UV spectra of these compounds, we believe that the NMR method is the most reliable indicator of the average amount of conjugation of the long pair nitrogen orbitals with the aromatic ring π system.

C. Electrochemical Studies. Several of the compounds employed do not show reversible cyclic voltammograms at room temperature, and since a principal interest was comparison of E° values, we took our CV data in butyronitrile, a superior low-temperature electrochemical solvent.[12] Other experiences in our laboratories indicate that E° values in butyronitrile are found to be approximately 0.14 V positive of those run in acetonitrile. For conversion of our E° values (all referenced to SCE) to the silver, silver chloride reference electrode employed by Hünig's group, +0.046 V should be added.[13] For most compounds, CV data were determined near 23, 0, −25, and −50 °C. Only −50 °C and room temperature data are quoted in Table III. The values in parentheses are extrapolated from lower temperature results when reversibility was not achieved at room temperature. In a few cases, we could not determine E° at any temperature because of rapid ion decomposition. The results for systems **4–13**, where in at least some example of each system two electrochemically

Table III. Electrochemical Data for some *o*-Phenylenediamine Derivatives in Butyronitrile (0.1 M Tetrabutylammonium Perchlorate) vs. SCE

		Room temp data				Low temp data			
Compd	Registry no.	Temp, °C	E°_1	E°_2	ΔE°	Temp, °C	E°_1	E°_2	ΔE°
4-H	95-54-5	22	Irrev., $E_p^{ox} = 0.56$ (200 mV/s)			−48	Irrev., $E_p^{ox} = 0.50$ (200 mV/s)		
4-Me	704-01-8	23	0.60	0.84	0.24	−50	0.55	0.76	0.21
4-Et	57422-67-0	23	(0.61)	(0.85)	(0.24)	−50	0.50	0.78	0.19
4A-Me	66102-30-5	24	(0.68)	(0.72)	(0.04)	−46	0.61	0.65	0.04
4B-Me	54929-05-4	24	0.49	0.71	0.22	−48	0.43	0.61	0.18
6B-H	10579-68-7	24	0.24	Irrev.		−50	0.19	Irrev.	
6-Me	2427-06-7	23	0.36	0.98	0.61	−50	0.33	0.92	0.59
6A-Me	66102-31-6	24	0.53	0.80	0.27	−47	0.53	0.74	0.22
6B-Me	66102-32-7	24	0.22	0.83	0.62	−49	0.17	0.75	0.58
7-H	6516-89-8	23	0.43	Irrev.		−50	0.40	Irrev.	
7-Me	19560-66-8	23	0.39	0.94	0.55	−50	0.35	0.88	0.53
8-H	39161-58-5	24	Irrev.	Irrev.		−56	0.40	Irrev.	
8-Me	39161-60-9	23	0.42	0.88	0.46	−50	0.38	0.81	0.43
9-H	49809-51-0	22	Irrev.	Irrev.		−57	Irrev.	Irrev.	
9-Me	66102-33-8	23	0.59	0.88	0.29	−50	0.56	0.82	0.26
12-Me	66102-34-9	23	0.21	0.91	0.70	−50	0.18	0.85	0.67
12-Et	66102-35-0	23	(0.19)	(0.92)	(9.73)	−50	0.14	0.85	0.70
13-H	3190-03-2	21	0.23	Irrev.		−51	0.24	Irrev.	
13-Me	66102-36-1	23	0.22	0.94	0.72	−50	0.19	0.87	0.69

Table IV. Electrochemical Data for Derivatives of Benzodabco (14) and 9,10-Benzo-1,5-diazabicyclo[3.3.2]dec-9-ene (15)

Compd	Registry No.	Temp °C	Electrochemical behavior
14	7140-45-6	24	Irrev., $E_p^{ox} = 1.33$ (0.2 V/s)
		−45	Quasirev., $E^\circ \simeq 1.25 \pm 0.03$ (2–10 V/s)
14A	66102-37-2	23	Irrev., $E_p^{ox} = 1.27$ (0.2 V/s)
		−45	Quasirev., $E^\circ \cong 1.18 \pm 0.04$ (0.5–10 V/s)
14B	66102-38-3	24	Irrev., $E_p^{ox} = 1.26$ (0.5 V/s)
		−48	Irrev., $E_p^{ox} = 1.40$ (2 V/s)
15	7140-45-6	21	Irrev., $E_p^{ox} = 1.10$ (0.2 V/s)

well behaved waves were observed, appear in Table I. We believe the potentials reported to be accurate to +0.01 V.

Only a single, 2-electron oxidation peak was observed experimentally for **4A-Me.** ΔE° was determined by the procedure of Myers and Shain,[14] using the working curve presented in their paper. They emphasize that the curve is only applicable to reversible systems. We found that the ratio of observed anodic (i_p^a) cathodic peak currents was near one (observed 1.16, 1.02, 1.00, 0.85 at 20, 50, 100, and 200 mV/s scan rates), and that $i_p^a/v^{1/2}$ (v is the voltage scan rate) was nearly constant (3.80, 4.04, 3.75, 3.50 at the same scan rates), both criteria for reversibility. The quoted ΔE° value of 0.04 V was based on the 20 mV/s scan rate CV curve; we found that the difference in anodic and cathodic peak potentials increased slightly with scan rate, either indicating slight irreversibility or more likely incomplete iR compensation; we believe the ΔE° figure of 0.04 quoted in Table III is a maximum value, especially since one should begin to see resolution of the two oxidation waves at $\Delta E^\circ > 0.06$.

Several NH-substituted compounds were also examined and some showed reversible behavior for the first electron removal, but none gave long-lived enough dications to detect a reduction wave, so E°_2 could not be determined.

Our data for the benzobicyclic systems 14 and 15 are less accurate and are included in Table IV. Reduction waves for both $14^{+\cdot}$ and $14A^{+\cdot}$ could be observed at low temperatures, allowing estimation of E°, but the decomposition products appear to affect the electrode, because our reproducibility on different days was not as good as with other compounds. Although different workers on different days obtained values for E° of 14 and 14A varying by ±30–40 mV, data gathered on the same day for these compounds always gave the result that 14A has about a 50–70 mV lower standard potential than 14.

Van Duyne and Reilly[12] have discussed the drift to lower potential observed for E° when the temperature is lowered. The observed change was linear and they found dE°/dT values ranging from 0.31 to 0.45 mV/deg for reductions (nitrobenzene, ferrocene, and phenazine) and an oxidation (9,10-diphenylanthracene). Ammar and Saveant[15] studied the two reversible reduction potentials for a series of dinitroaromatic compounds and reported that ΔE° increases linearly with temperature, although they did not disclose dE°/dT for either step. They separate ΔE° (and hence K_d) into entropy and enthalpy terms, using $\Delta E^\circ = \Delta E_H - T\Delta\epsilon_s$. Larger dE°/dT values must have been observed for the second electron transfer than the first, because $\Delta\epsilon_s$ is $dE^\circ_1/dT - dE^\circ_2/dT$. This is reasonable considering that a diion should cause more solvent ordering than a monoion. The temperature behavior of some *o*-phenylenediamine E° values is summarized in Table V.

Discussion

A. Steric Interactions in the Radical Cations. The series of compounds studied has the same basic system in which to distribute positive charge, two dialkylamino groups substituted ortho on a benzene ring. The E° values observed will reflect both steric and electronic differences between the various compounds in solution, since E° is a measure of the free-energy difference between reduced and oxidized forms. We shall use the ca. −50° E° values, which have the advantage of not being extrapolated, in the discussion which follows.

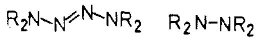
The tetramethyl compound **4-Me** shows a considerably higher E°_1 than the N,N′-bridged compounds **5-Me** and **6-Me,** clearly because of increased steric interaction in the electronically preferred completely planar form. As an extreme model, one might consider the possibility that one dimethylamino group of $(\mathbf{4\text{-}Me})^{+\cdot}$ would be completely planar with the ring and the other twisted 90° to minimize steric interaction. If this were the case, E°_1 of **4-Me** should be at least as high as that of *N,N*-dimethylaniline, since the twisted dimethylamino group should be electron withdrawing, because

Table V. Temperature Dependence of Oxidation Potentials for Some *o*-Phenylenediamine Derivatives

Compd	dE°_1/dT, mV/deg	dE°_2/dt, mV/deg	$-\Delta\epsilon_S$, mV/deg	ΔE_H, mV
4-Me	0.61	0.87	0.26	150
4B-Me	0.80	1.29	0.49	70
6-Me	0.46	0.81	0.35	510
6A-Me	0.35	0.86	0.51	120
6B-Me	0.60	1.11	0.51	460
7-Me	0.56	0.80	0.24	480
8-Me	0.56	0.95	0.41	350
9-Me	0.49	0.84	0.35	190
12-Me	0.40	0.85	0.44	570

of the greater electronegativity of nitrogen than carbon, rather than electron releasing. Although *N,N*-dimethylaniline shows an irreversible oxidation wave in acetonitrile,[16] its peak potential is near 0.83 V (converted to our solvent system), indicating a far higher E° value than that observed for **4-Me.** Both dialkylamino groups are clearly contributing to charge delocalization in (**4-Me**)$^{+\cdot}$, as well as for the other compounds considered here.

Studies on hydrazines[5] and 2-tetrazenes[17] have demonstrated that E° is decreased modestly when the alkyl group substituted on nitrogen is lengthened, as would be expected by consideration of Taft σ^* values.[17] Considering the 2-tetrazene systems, **17,** E° is 0.08 V lower for **17-Et** than for **17-Me.** In the corresponding hydrazine system, **18,** E° is only 0.04 V lower for **18-Et** than for **18-Me,** which we have argued[17] occurs principally because of $\mathbf{RN_1N_2R}$ steric strain in the radical cation, which has an olefin-like geometry, with nearly eclipsed $\mathbf{RN_1N_2R}$ groups and larger strain compared to the gauche netural **18.**[5] Electron removal from **17, 18,** and **4** should all cause flattening at nitrogen (or increased barrier for bending from planarity at nitrogen) and alignment of the spin-bearing orbitals at nitrogen with each other (in $\mathbf{18}^{+\cdot}$) or with the bridging π system (in $\mathbf{17}^{+\cdot}$ and $\mathbf{4}^{+\cdot}$). Such a geometrical preference causes little strain in $\mathbf{17}^{+\cdot}$, but the strain thus induced is easily detectable in E° values for **18**[17] and would be expected to cause an even greater effect in **4.** We suggest that this is the explanation for the 0.04 V observed *increase* in E°_1 for **4-Et** compared to **4-Me,** which is the opposite direction of that expected inductively. When this alkyl, alkyl steric interaction is eliminated (although an increase in alkyl, ring interaction is still present), as in the **12-Et** vs. **12-Me,** the ethyl compound is easier to oxidize than the methyl one (by 0.04 V), as expected.



$R_2N{-}N{=}N{-}NR_2$ $R_2N{-}NR_2$

17 18

Another "inductive" effect on E°_1 is clearly seen when the benzene ring C_4,C_5 hydrogens are replaced by methyls. See Figure 2 for a graphical presentation of the data. Here there is virtually no steric difference, but the methyls should stabilize the positive charge-bearing carbons on which they are substituted in the cations. The experimental result is an appreciable decrease in E°: ΔE°_1(**4B-Me-4-Me**) = −0.21 V (4.8 kcal/mol), ΔE°_1(**6B-Me-6-Me**) = −0.16 V (3.7 kcal/mol). The effects on E°_2 are noted to be surprisingly close to those on E°_1, −0.15 and −0.17 V, respectively. A rather larger effect upon E°_2 than upon E°_1 might have been predicted because of greater charge density presumed to be at C_4,C_5 in the dication. The effect of NMe for NH substitution on E°_1 was measured for four examples (**6B, 7, 8,** and **13**) and was found to be quite small, an E° decrease of 0.02 to 0.05 V. We presume the small effect reflects a significant steric strain increase in the flatter radical cation when the larger methyl is substituted for hydrogen (for we would expect the true inductive effect to be considerably larger), but solvation differences for replacement of NH by NCH_3 also will affect E° (as always) and we have no way of estimating this effect.

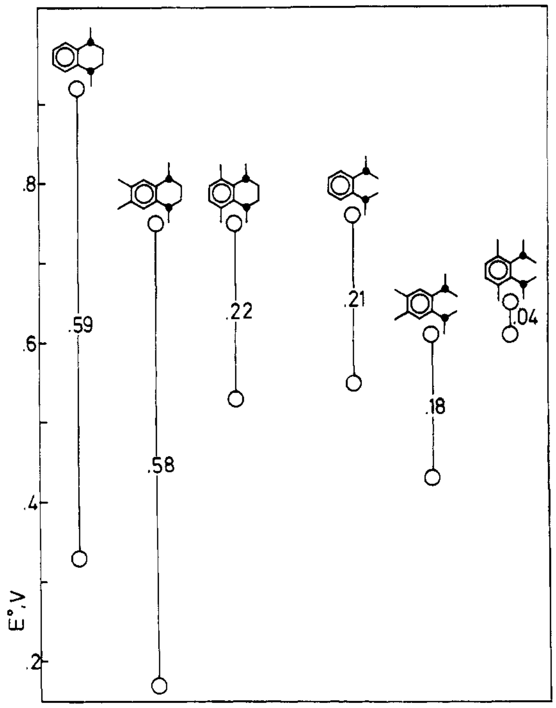
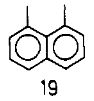


Figure 2. A graphical display of the effect of 3,6 and 4,5 methylation on E°_1 and E°_2 on **6-Me** and **4-Me.** The numbers given are ΔE°, V.

Increases in steric strain in the radical cation are quite obvious for the substitution of methyl for hydrogen at C_3 and C_6 of **6** and **4** (Figure 2). Despite an inductive effect working in the opposite direction, ΔE°(**4A-Me-4-Me**) is +0.06 V (1.4 kcal/mol) and ΔE°_1(**6A-Me-6-Me**) is +0.20 V (4.6 kcal/mol). The inductive effect of methyl substitution at C_3,C_6 will presumably be substantially smaller than that at C_4,C_5 because charge density should be smaller. The methyl, methyl interaction in 1,8-dimethylnaphthalene (**19**) has been estimated to be 7.6 kcal/mol,[18] so a significant fraction of the strain expected in a completely planar (**6A-Me**)$^{+\cdot}$ is being observed in E°_1 for this compound, making it clear that there is a significantly stronger preference for planarity at the nitrogen atoms in *o*-phenylenediamine radical cations than there is in the neutral species.



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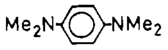


$Me_2N{-}C_6H_4{-}NMe_2$

20

In contrast to the other compounds, the geometry of **12-Me** presumably changes little upon electron removal, because the lone pairs are already well aligned for charge delocalization, and the nitrogens are apparently flatter than in the other

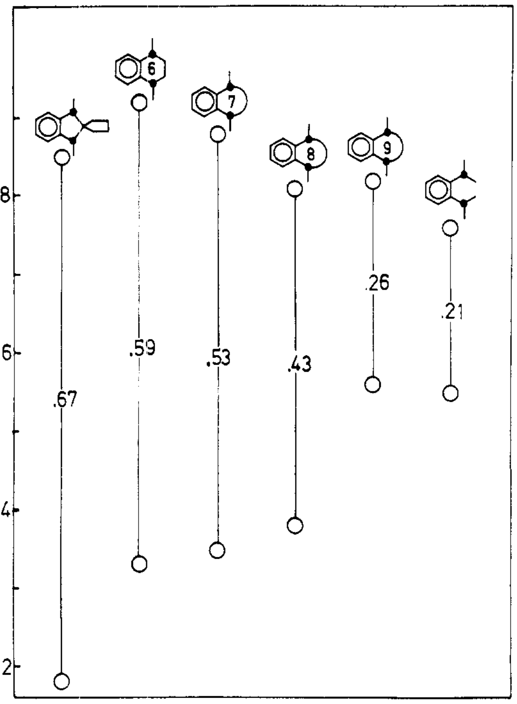
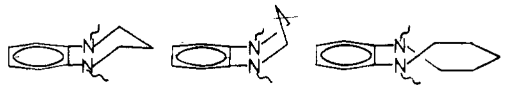


Figure 3. A graphical display of the effect of heterocyclic ring size on $E°_1$ and $E°_2$ for *o*-phenylenediamine derivatives.

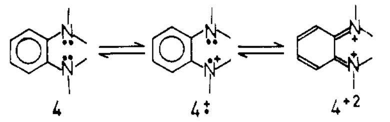
compounds, due to the dialkyl substitution α to the nitrogens. Here the $\Delta E°$ is the largest observed in the *o*-phenylenediamine series, 0.67 V (−50), 0.70 V (+23 °C), and $E°_1$ is +0.21 V at 23 °C. It is interesting to compare $E°_1$ and ΔE for **12-Me** with those of *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine, **20.** $E°_1$ (converted to our solvent) is 0.17 V, $\Delta E° = 0.58$ V.[19] The 0.05 V difference in $E°_1$ seems surprisingly small, considering that the positively charged nitrogens are closer in $(\textbf{12-Me})^{+\cdot}$ and there is a possibility for inductive destabilization through the single connecting carbon in this molecule. Some factors tending to make this difference smaller than it would otherwise be are an increase in strain in planar $(\textbf{20})^{+\cdot}$ compared to the neutral compound, a probable decrease in strain for $(\textbf{12-Me})^{+\cdot}$ compared to the neutral compound (the nitrogens appear to be forced to be one more planar than they would otherwise be by the dialkyl substitution α to the nitrogens), and the inductively greater releasing effect of the dialkyl bridging carbon of **12-Me** replacing two methyls of **20.**

The six- to nine-membered ring heterocyclic compounds have an interesting pattern of $E°_1$ values (Figure 3) in that the first three members of the series, **6-Me, 7-Me,** and **8-Me,** have rather similar $E°_1$ values at 0.33, 0.35, and 0.38 V, respectively. In contrast, $E°_1$ for **9-Me** at 0.56 V is 4.1 kcal/mol higher than for **8-Me** and is close to the value for the acyclic compound, **4-Me.** The interplay of torsional and cross-ring strain in both neutral and radical cationic forms which gives rise to this pattern is presumably quite complex. Unfortunately, we cannot interpret the observed pattern reasonably with the data in hand.

B. Dication Geometry. The most interesting, but initially surprising, aspect of the $E°_2$ values in Table II (see Figures 2 and 3) is the compensating effect of changes in $E°_1$ and $E°_2$. We have discussed $E°_1$ largely in terms of steric destabilizations which occur upon the flattening at nitrogen and aryl,N rotations which must result to enforce the aryl,NR_2 planarity which is energetically preferred for the radical cation. Writing valence bond structures, it is clear than in the dication 4^{2+}, which has each nitrogen sp^2 hybridized, there should be an even stronger requirement for planarity at nitrogen. The tendency for $E°_2$ to decrease when $E°_1$ increases is quite clear in our data. This can hardly be an inductive-dominated result when the similarity of $E°_1$ and $E°_2$ changes in **6B** and **4B** are considered and the seven- to nine-membered ring compounds

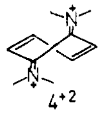


7-Me chair 7-Me boat 9-Me anti



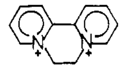
4 $4^{+\cdot}$ 4^{+2}

are included. Instead, our data seem to require that alkyl,alkyl interaction be smaller in the dication than in the monocation. The only reasonable way this could happen would be if there were significant twisting of $\mathbf{4}^{2+}$ from planarity (see the ex-



4^{+2}

aggerated view below), which models suggest is quite reasonable ($\mathbf{4}^{2+}$ is distinctly quinonoid and has greatly reduced aromaticity compared to either $\mathbf{4}^{+\cdot}$ or **4**). Twist at the "aryl" NC–CN bonds should be far easier and such a motion would not only decrease steric interactions but increase the N^+,N^+ distance. It is known that diquat dication **21** has a 20.4° aryl,aryl twist angle from an x-ray structure determination.[20]



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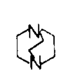
For our systems, we attempted to get evidence for such a twist, which seemed to us to be required by the $E°$ data, by NMR studies. Unfortunately, the dications, although long lived on the CV time scale in many cases, do decompose rather rapidly. Nevertheless, a 0.15 M solution of **6A-Me** at −88 °C gave ^{1}H-NMR singlets at δ 2.28, 2.56, 2.90, and 6.76, which we assign to the CCH_3, NCH_3, NCH_2, and CH protons, respectively. Addition of 2 equiv of $NO^+BF_4^-$ gave a spectrum showing singlets at δ 2.64, 2.56, and 7.53 and a complex multiplet between δ 3.94 and 4.95. We attribute this spectrum to the unstable $(\textbf{6A-Me})^{2+}$ species, which could only give a multiplet for the NCH_2 protons if it were nonplanar, and equilibration of the pseudoaxial and pseudoequatorial protons was slow on the NMR time scale. Unfortunately, the species giving this spectrum decomposes in a few minutes at −88 °C.

When lone pair,aryl ring interaction is geometrically precluded, as in **14** and **15,** $E°_1$ is greatly increased and the radical cation lifetime is decreased. We were able to see reduction waves and measure $E°_1$ at low temperature only for **14** and **14A** (Table IV). $E°$ for **14** is considerably higher than for dabco, **22**[21,22] ($E°_1 = 0.69$), which is not surprising because one



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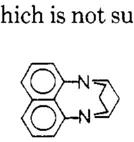

23

through-bond interaction is made far less important (σ_{CC} for an aryl C–C bond should be substantially lower in energy than for a single C–C bond) and the sp^2 carbons are inductively electron withdrawing. There is a distinct, though small, decrease in $E°_1$ for **14A** vs. **14**, which we presume is an inductive effect. Unfortunately, $(\textbf{14B})^{+\cdot}$ did not have a long enough lifetime for E° measurements. (**15**)$^{+\cdot}$ cannot have the through-bond stabilization of **22**$^{+\cdot}$ and **14**$^{+\cdot}$. It also quite obviously lacks the dramatic though-space stabilization of **23**$^{+\cdot}$ ($E^\circ = +0.11$ V in acetonitrile[23]), seeming to indicate that the great strain in **23**, which has essentially planar nitrogens in the neutral form,[23] is very important in lowering E°_1 for this compound.

Experimental Section

***N,N,N′,N′*-Tetramethyl-*o*-phenylenediamine (4-Me)** was prepared by methylation of the diamine with trimethyl phosphate[24] and purified by VPC.

***N,N,N′,N′*-Tetraethyl-*o*-phenylenediamine (4-Et)** was prepared by reductive ethylation. *N,N′*-Diethyl compound (0.82 g; 5 mmol), 20 mL of acetonitrile, 2.2 g (50 mmol) of acetaldehyde, and 1.0 g of sodium cyanoborohydride were stirred, while 25 drops of acetic acid were added in 5-drop batches over 7 h. After stirring 12 h, the mixture was basicified (4 mL, 15% NaOH) and extracted with pentane (3 × 25 mL). After drying with sodium sulfate and concentration, the mixture was distilled to give 0.81 g (bp 125 °C (21 min)) of a colorless oil, consisting of **4-Et** with the trimethyl compound as the major impurity; purification was by VPC.

***N,N,N′,N′*-Tetramethyl-3,6-dimethyl-*o*-phenylenediamine (4A-Me)** was prepared by heating the diamine,[25] mp 66–70 °C (lit.[25] mp 75 °C), with a twofold molar amount of trimethyl phosphate[24] in 70% yield; purification was by VPC: NMR ($CDCl_3$) δ 1.2 (s, 6 H), 2.79 (s, 2 H), 6.9 (s, 2 H).[26]

***N,N,N′,N′*-Tetramethyl-4,5-dimethyl-*o*-phenylenediamine (4B-Me)** was prepared by heating the commercial diamine with a twofold molar amount of trimethyl phosphate,[24] giving a 40% yield of crude **4B-Me** after Kügelrohr distillation; purification was by VPC: NMR ($(CD_3)_2CO$) δ 2.11 (s, 6 H), 2.66 (s, 12 H), 6.68 (s, 2 H).[26]

1,4-Dimethyltetrahydroquinoxaline (6-Me) was prepared by $LiAlH_4$ reduction of the bis formate using the method of König and Huisgen,[27] bp 110–120 °C (1 mm) (lit.[27] bp 180–190 (atm)), final purification by VPC.

5,8-Dimethylquinoxaline. To a solution of 9.5 g (7 mmol) of 2,3-diamino-*p*-xylene dissolved in 140 mL of water at 60 °C was added a solution of 10.56 g of 40% aqueous glyoxal (7.3 mmol), 16.6 g of sodium bisulfite, and 68 mL of water which had been heated to 70 °C. After stirring at 60 °C for 45 min, the mixture was cooled to room temperature in an ice bath, neutralized with 38.3 g of sodium carbonate, and extracted with ether (3 × 100 mL). After drying with $MgSO_4$ and removal of ether, sublimation gave 6.0 g (54%) of a light yellow solid: mp 68–70 °C; NMR ($CDCl_3$) δ 2.78 (s, 6 H), 7.50 (s, 2 H), 8.86 (s, 2 H).[26]

5,8-Dimethyl-1,2,3,4-Tetrahydroquinoxaline (6A-H). 5,8-Dimethylquinoxaline (6.0 g; 3.8 mmol) in 200 mL of benzene was stirred over 2.0 g of Alfa pelletized, nonpyrophoric Raney nickel for 15 min and hydrogenated at 40 psi H_2 in a Parr shaker. After filtration, concentration gave 5.1 g (83%): mp 68–69 °C; NMR ($CDCl_3$) σ 2.04 (s, 6 H), 3.44 (m, 6 H), 5.40 (s, 2 H); IR (CCl_4) 3410 cm^{-1} (m).[26]

1,4,5,8-Tetramethyl-1,2,3,4-tetrahydroquinoxaline (6A-Me) was prepared in 87% yield by reductive alkylation (using a procedure similar to that for **4-Et** but using formalin as the aldehyde), bp 105–107 °C (0.1 mm), and solidified after VPC: mp 56–60 °C; NMR ($CDCl_3$) δ 2.30 (s, 6 H), 2.69 (s, 6 H), 3.03 (s, 4 H), 6.72 (s, 2 H).[26]

6,7-Dimethylquinoxaline was prepared from 4,5-dimethyl-*o*-phenylenediamine using the procedure employed for 5,8-dimethylquinoxaline in 71% yield: mp 101–102 °C; NMR ($(CD_3)_2CO$) δ 2.4 (s, 6 H), 7.72 (s, 2 H), 8.66 (s, 2 H).[26]

6,7-Dimethyl-1,2,3,4-tetrahydroquinoxaline (6B-H) was prepared by the same procedure as the 5,8-dimethyl compound (except that the product was less soluble in benzene and the catalyst had to be filtered from a hot solution) in 74% yield: mp 152–153 °C; NMR ($CDCl_3$) δ 2.0 (s, 6 H), 3.24 (s, 4 H), 3.3 (s, 2 H), 6.2 (s, 2 H).[26]

1,4,6,7-Tetramethyl-1,2,3,4-tetrahydroquinoxaline (6B-Me) was prepared by reductive methylation (see **6A-Me**) in 92% yield and purified by Kügelohr distillation: mp 33–36 °C; NMR ($(CO_3)_2CO$) δ 2.0 (s, 6 H), 2.68 (s, 6 H), 3.1 (s, 4 H), 5.14 (s, 2 H).[26]

1,4-Dimethyl-2,3-dibenzo-4,5,6,7-tetrahydro-1,4-diazapine (7-Me) was prepared by reductive methylation (see **6A-Me**) of **7-H**[26] in 24% yield and purified by VPC: NMR ($CDCl_3$) δ 6.87 (s, 4 H), 3.02 (t, 4 H), 2.85 (s, 6 H), 1.76 (pentet, 2 H).[26]

1,4-Dimethyl-2,3-benzo-1,4-diazacyclooct-2-ene (8-Me) was *prepared by reductive methylation (see* **6A-Me**) *of* **8-H**[28] *in 33% yield* and purified by VPC: NMR ($CDCl_3$) δ 6.75 (s, 4 H), 3.21 (m, 4 H), 2.80 (s, 6 H), 1.73 (m, 4 H).[26]

1,4-Dimethyl-2,3-benzo-1,4-diazacyclonon-2-ene (9-Me) was prepared by reductive methylation of **9-H**[28] in 27% crude yield and purified by VPC: NMR ($CDCl_3$) δ 6.71 (s, 4 H), 3.03 (m, 4 H), 2.67 (s, 6 H), 1.65 (m, 6 H).[26]

1,3-Dimethyl-2,2-tetramethylenebenzimidazoline (12-Me) was prepared by refluxing 2.1 g (15.4 mmol) of *N,N′*-dimethyl-*o*-phenylenediamine and 1.3 g (15.5 mmol) of cyclopentanone in 25 mL of benzene over a water separator for 20 h. Distillation gave 1.55 g (50%) of an oil, bp 120–125 °C (1.5 mm), which solidified (mp 79–81 °C) after sublimation: NMR ($CDCl_3$) δ 6.35 (m, 4 H), 2.76 (s, 6 H), 1.54–2.09 (8 H).[26]

1,3-Diethyl-2,2-spirotetramethylenebenzimidazoline (12-Et) was prepared as **12-Et**: bp 125–123 °C (0.3 mm); 71% yield; NMR ($CDCl_3$) δ 6.36 (m, 4 H), 3.15 (quartet, 4 H), 1.58–2.25 (m, 8 H), 1.27 (t, 6 H).[26]

1,3-Dimethyl-2,2-pentamethylenebenzimidazoline (13-Me) was prepared as **12-Me**: bp 135–140 °C (1.5 mm), 60% yield; mp 55–56 °C (after sublimation); NMR ($CDCl_3$) δ 6.36 (m, 4 H), 2.81 (s, 6 H), 1.28–1.88 (m, 10 H).[26]

5,8-Dimethyl-1-(2-hydroxyethyl)-1,2,3,4-tetrahydroquinoxaline (16). A solution of 5.05 g (3.1 mmol) of **6A-H** in 50 mL of methanol was cooled to −78 °C while 1.37 g (3.1 mmol) of ethylene oxide was added. After warming to room temperature, the mixture was stirred for 10 days and concentrated by rotary evaporation. Kügelrohr distillation gave a light yellow oil which solidified upon trituation with ether: 3.32 g (52%); mp 93–95 °C; NMR ($CDCl_3$) δ 2.08 (s, 3 H), 2.29 (s, 3 H), 3.0 (m, 5 H), 3.4 (t, $J = 4$, 2 H), 3.80 (t, $J = 4$ Hz, 2 H), 6.74 (d, $J = 8$ Hz, 1 H).[26]

3′,6′-Dimethyl-2,3-benzo-1,4-diazabicyclo[2.2.2]oct-2-ene (14B). *16 (1.03 g; 5 mmol) in 25 mL of dry tetrahydrofuran was cooled* in a dry ice–ethanol slush while 0.12 g (5 mmol) of sodium hydride was added. After stirring at −78 °C for 5 min, 0.95 g (5 mmol) of tosyl chloride was added. After 15 min of stirring, the mixture was warmed slowly to room temperature and 4.5 mL of 1.16 M butyllithium was added dropwise. The THF was distilled off after the solution was stirred for 2 h at room temperature and 25 mL of 1 M sodium bicarbonate was added. Ether extraction gave a dark oil, from which 0.107 g (11%) of **14A** was sublimed during attempted Kügelrohr distillation: mp 85–89 °C; NMR ($(CD_3)_2CO$) δ 2.24 (s, 6 H), 2.4–3.2 (m, 8 H), 6.95 (s, 2 H).[26]

2,3-Benzo-1,4-diazabicyclo[2.2.2]oct-2-ene (15). A mixture of 5.36 g (40 mmol) of **6-H**, 100 mL of dimethylformamide, 6 g of sodium carbonate, and 7.52 g (40 mmol) of ethylene bromide was heated at 120 °C for 2 days and the DMF was distilled off at reduced pressure. Water (80 mL) and sodium hydroxide were added. The strongly basic solution was extracted with ether giving a dark oil from which 160 mg (2.5%) of **14** was sublimed in a Kugelrohr apparatus: mp 140–141 °C (acetone); NMR ($(CD_3)_2CO$) δ 2.51–3.4 (m, 8 H), 7.04–7.86 (m, 4 H).[26]

4′,5′-Dimethyl-2,3-dibenzo-1,4-diazabicyclo[2.2.2]oct-2-ene (14A) was prepared from **6B-H** using the same method as for **14** and giving **14b** in 4.2% yield: mp 119–123 °C (after sublimation); NMR ($CDCl_3$) δ 2.20 (s, 6 H), 2.72 (m, 8 H), 6.82 (s, 2 H).[26]

9,10-Benzo-1,5-diazabicyclo[3.3.2]dec-9-ene (14). A mixture of 5.4 g (50 mmol) of **4-H,** 100 mL of DMF, 5 g of sodium carbonate, and 20.2 g (100 mmol) of 1,3-dibromopropane was treated in the same way as in the preparation of **14,** giving 350 mg (3.7%) of **15:** mp 75–76 °C; NMR ($(CD_3)_2CO$) δ 1.1–1.5 (m, 2 H), 1.9–2.3 (m, 2 H), 2.8–3.4 (m, 8 H), 7.12 (s, 4 H).[26]

Apparatus. The same electrochemical apparatus was used as previously.[6b] All data reported are in butyronitrile[6b] containing 0.1 M tetrabutylammonium perchlorate, are referenced to SCE, and were recorded at planar gold electrode. ^{13}C-NMR spectra were taken on a Varian FX-60 instrument (off-resonance decoupled spectra were used in making assignments) and UV spectra on a Cary 118. An A.E.I. MS.9 was used for high-resolution mass-spectroscopy measurements.

Acknowledgment. We thank the National Science Foundation for partial financial support of this work, both through research grants and the Major Instrument Program, as well as the Graduate School of the University of Wisconsin.

Registry No.—4A-H, 35975-12-3; **4B-H,** 3171-45-7; **5-Me,** 3204-31-7; **6A-H,** 66102-39-4; **16,** 66102-40-7; *N,N′*-diethyl-*o*-phenylenediamine, 24340-87-2; 5,8-dimethylqiunoxaline, 64931-22-2; 6,7-dimethylquinoxaline, 7153-23-3; *N,N′*-dimethyl-*o*-phenylenediamine, 3213-79-4; cyclopentanone, 120-92-3.

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(1) All E^0 values mentioned in this paper are formal potentials corresponding to the supporting electrolyte concentration employed, 0.1 M tetrabutylammonium perchlorate.

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Stereospecific Vicinal Oxyamination of Olefins by Alkylimidoosmium Compounds

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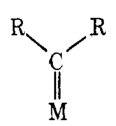
Received January 10, 1978

The reaction of trioxo(*tert*-alkylimido)osmium(VIII) complexes with a variety of olefins (30 different cases) affords, after reduction of the intermediate osmate esters, vicinal amino alcohols in fair to excellent yields. The synthetic utility of this new reaction was evaluated by examining the effects of solvent, temperature, olefin substitution patterns, and functional groups. Where possible the imidoosmium(VIII) reagents were compared to osmium tetroxide. Stereospecific preparations of both (*E*)-1-deuterio-1-decene and (*Z*)-1-deuterio-1-decene are described.

During our studies on oxygen atom transfer chemistry of transition metal oxo compounds (1) with olefins, it occurred to us that similar reactions might take place with the nitrogen (2) and carbon (3) analogues of the oxo species. The transition metal oxo compounds which react with olefins are typically d^0 substances having from two to four oxo groups. Cis dihydroxylation of olefins to form vicinal diols is a unique reaction of these oxidants (eq 1). We report here further examples of an aza analogue of this transformation (eq 2).[1]

1

2



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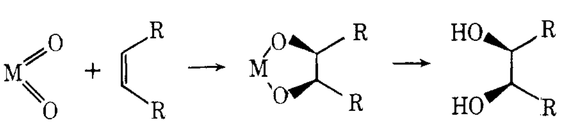
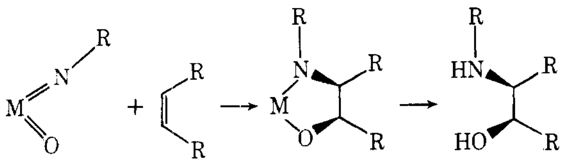
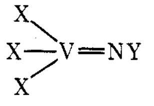


(1)



(2)

The only known d^0 alkylimido transition metal species are compounds of vanadium[2] and osmium.[3] In the case of vanadium the compounds have the general structure **5**, and in the case of osmium only two substances (**6a**[3a,b] and the related monoimido species derived from *tert*-octylamine[3b]) have been described. In addition to the known *tert*-butylimido compound **6a**, we have prepared the new adamantyl derivative **6b** and the *tert*-amyl derivative **6c**. All three were synthesized in about 90% yield by treating the amine with OsO_4 in olefin-free pentane or CH_2Cl_2. We were pleased to find that the imido reagents all reacted with a variety of olefins to afford, after reductive cleavage of the osmate esters, vicinal tertiary alkylamino alcohols in fair to excellent yields. The mode of addition of reagents **6** has been shown to be stereospecific and in most cases highly regioselective.



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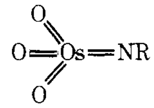

6a, R = *tert*-butyl
b, R = 1-adamantyl
c, R = *tert*-amyl

A number of methods are available for synthesis of β-amino alcohols.[4] Each method varies with respect to starting material, overall yield, regiospecificity, and stereochemistry, However, only this new procedure allows direct cis addition of the oxygen and nitrogen moieties to the olefinic bond.

Results and Discussion

Stereochemistry. The mode of the addition of alkylimidoosmium compounds to olefins in CH_2Cl_2 was established

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