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Structure and Isomerization Phenomena of Olefin Radical Ions. The 1,2-Bis(*N*-methyl-4-pyridyl)ethylene Tetrafluoroborate Radical Cation

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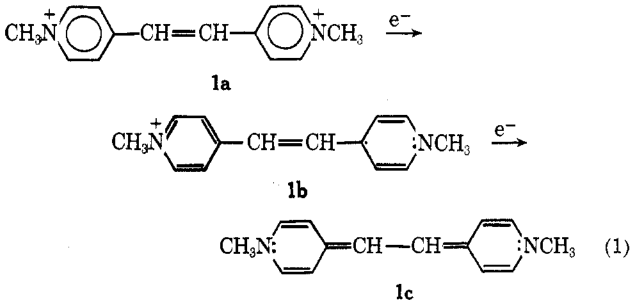
Preparation and structural studies of the radical cation of 1,2-bis(*N*-methyl-4-pyridyl)ethylene tetrafluoroborate by one-electron reduction of the parent diquaternary salt are reported. Both cis and trans isomers of the parent diquaternary are readily reduced to the radical cation by electrolytic reduction at −0.60 V (*vs.* SSCE), by reduction with zinc, or by photolysis in the presence of amines or ethers. The radical is quite stable and structurally similar to the stable methyl viologen radical cation. Cyclic voltammetry experiments indicate that reduction to the radical and neutral species are both reversible; disproportionation of the radical is evidently unimportant. A planar trans structure is indicated for the single form of the radical cation by results of esr and chemical quenching studies. Conversion of cis to trans is very rapid with the lifetime of the cis form evidently being less than 10 μsec at room temperature.

In previous papers[2-5] we have reported on the photochemical isomerization of electron-deficient olefin in various types of molecular complexes. Although in certain cases[3,4] photoisomerization has been found to proceed *via* excited states of the olefin, in other instances[2,4,5] there is strong evidence that electron transfer to the olefin within the excited complex occurs to form a transient radical ion which is the active species in isomerization. Although it has been established that radical anions of stilbene and related olefins can undergo facile geometric isomerization, there has been some uncertainty regarding the structures of these species and the mechanisms and rates for the isomerization. There is good evidence[6] that dianions of stilbene prefer a twisted conformation. The same twisted geometry has been proposed[7,8] for the electronically similar "phantom" excited singlet and triplet states of stilbene on the basis of experimental evidence as well as theoretical considerations. Because of similarities in their electronic structures, the dianion and triplet state of stilbene are predicted by molecular orbital theory to have similar geometric structures.[6] For stilbene radical anion, there is evidence that cis and trans isomers can exist. A difference of 0.03 V has been observed between the half-wave reduction potentials of *cis*- and *trans*-stilbene. In dimethylformamide (DMF), the lifetime of the cis anion is estimated to be in excess of 1 min at room temperature.[9] Furthermore, when *cis*- or *trans*-stilbene is reduced electrolytically in the presence of carbon dioxide in DMF, DL- and *meso*-diphenylsuccinic acid are isolated. Stereochemical analysis of the products indicates that *trans*-stilbene forms a larger proportion of DL acid in relation to meso acid than that formed from *cis*-stilbene.[9] These results are consistent with carboxylation of separate cis and trans radical anions.

Electron spin resonance (esr) experiments[10] have given additional information regarding cis–trans isomerism of stilbene radical anion. The same esr spectrum with roughly uniform line widths is obtained with either *cis*- or *trans*-stilbene over a wide range of temperatures. These results are interpreted in terms of a moderately rapid interconversion of cis–trans isomers which may well occur before esr spectra can be recorded. An interesting result of this work is the finding that rotation about the exocyclic bond joining the ethylenic carbon to the phenyl ring is rather slow and results in an unsymmetrical spin distribution in the phenyl rings. Thus, the bond has a considerable amount of double bond character as predicted by Huckel molecular orbital calculations. Similar hindered rotation is observed for the radical anions of *trans*-1,2-bis(4-pyridyl)ethylene, *trans*-azobenzene, and tolan.[10] Like the stilbene radical anion, only one radical species is observed for each of the above anions.

In the present paper we report an investigation of the structure and isomerization of the radical cation **1b** which is formed by one-electron reduction of 1,2-bis(*N*-methyl-4-pyridyl)ethylene tetrafluoroborate (**1a**) (eq 1). Recently we have found that **1a** undergoes very inefficient cis–trans isomerization upon direct or sensitized irradiation in inert solvents such as acetonitrile.[5,11] However, we find that formation of **1b** by one-electron reduction occurs on irradiation of **1a** in the presence of



1a

1b

1c

(1)

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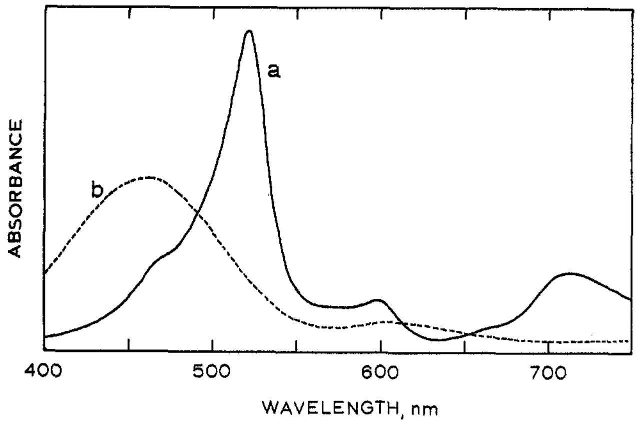
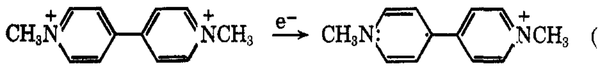


Figure 1.—(a) Visible absorption spectrum of 1,2-bis(*N*-methyl-4-pyridyl)ethylene tetrafluoroborate radical cation (**1b**) produced by electrolytic reduction of *trans*-**1a** in acetonitrile at −0.49 V *vs.* SSCE. (b) The spectrum of the neutral, doubly reduced form, **1c**.

certain electron donors.[5] **1b** can also be formed by electrolytic reduction of **1a** at a very low potential (−0.45 V *vs.* Ag/AgCl electrode in acetonitrile for the dimethiodide salt)[12] or *via* electron transfer between the doubly reduced species and **1a**.[13] Results from INDO and CNDO[14] molecular orbital calculations on **1a** and **1b**[15] suggest that the lowest antibonding π orbital has small coefficients on the ethylenic carbons. A lack of antibonding character in the ethylenic double bond could account for the reluctance of **1a** to undergo cis–trans isomerization from the excited singlet state. Similarly we anticipated that diminished antibonding character at the olefinic carbons might hinder isomerization in **1b** and permit the observation of cis and trans forms of the radical.

Radical **1b** is structurally similar to the stable methyl viologen radical cation (**2b**) produced by one-electron reduction of paraquat (**2a**). Paraquat has been used



(2)

2a **2b**

successfully as a redox indicator in chemical[16] and biological[17] electron-transfer systems, and has found wide commercial use as a herbicide.[18]

Our approach to the analysis of the structure of radical cation **1b** has included studies of its chemical and spectral properties and determination of the geometrical structure of the radical.

Results and Discussion

Methods of Production.—Electrolytic reduction of *trans*-**1a** in acetonitrile at −0.60 V *vs.* a standard saturated sodium chloride calomel electrode (SSCE) produces a red solution whose visible spectrum is shown in Figure 1a. At the same potential, the esr spectrum shown in Figure 2a is recorded, which we assign to radical **1b.** Upon reduction at the second half-wave potential, the solution turns yellow and gives the visible spectrum shown in Figure 1b which we assign to the neutral, doubly reduced form, **1c.**

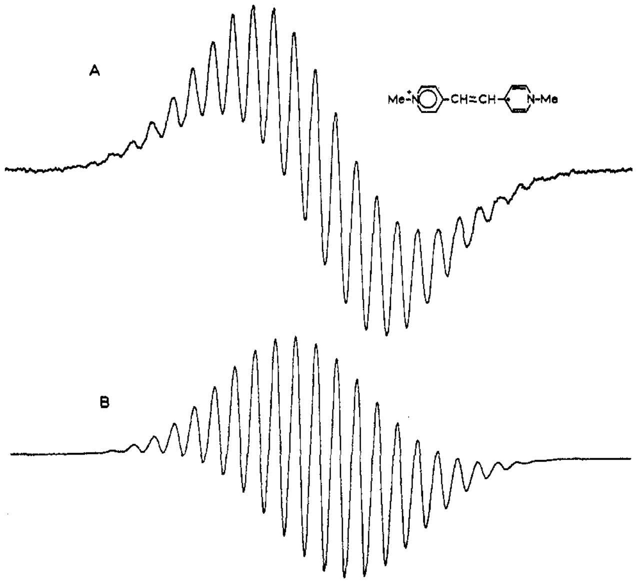


Figure 2.—(a) Esr spectrum of 1,2-bis(*N*-methyl-4-pyridyl)-ethylene tetrafluoroborate radical cation produced by electrolytic reduction of *trans*-**1a** in acetonitrile. (b) Computer-simulated spectrum using the coupling constants listed in Table I.

Reduction of *trans*-**1a** with powdered zinc or a distilled zinc mirror under nitrogen in acetonitrile initially produces the same visible spectrum shown in Figure 1a and the same esr spectrum shown in Figure 2a. Prolonged reduction on a zinc mirror in degassed solution produces the visible spectrum shown in Figure 1b.

In our earlier studies[5] of the photochemistry of **1a**, we observed formation of radical **1b** during the photolysis of **1a** in ethyl ether and in pyridine at 3130 Å. Although the radical lifetime in 1:1 ether–acetonitrile is fairly short (approximately 4 min as determined by visible spectra), the lifetime in 1:1 pyridine–acetonitrile is quite long (2 days). As we suggested earlier,[5] it may be possible that photochemical formation of radical **1b** involves electron transfer from ether or pyridine to an excited olefin singlet, or possibly electron transfer accompanying decay of an exciplex formed between **1a** and ether or pyridine. A similar photoreduction by electron transfer from ethanol or other alcohols to paraquat (**2a**) to produce the methyl viologen radical cation (**2b**) has been observed.[19,20]

In contrast to ethyl ether and pyridine, more reactive electron donors such as 2,6-lutidine, piperidine, *n*-butylamine, and di- and triethylamine react with the ground state of **1a** in acetonitrile under nitrogen to produce esr-detectable quantities of radical **1b**. Visible spectra of these solutions appear similar to that shown in Figure 1a. However, additional absorption appears between 350 and 400 nm which appears to be due to complex formation. The concentration of the radical cation is not sufficient to account for all of the starting

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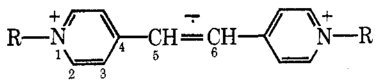
TABLE I

OBSERVED AND CALCULATED HYPERFINE COUPLING CONSTANTS



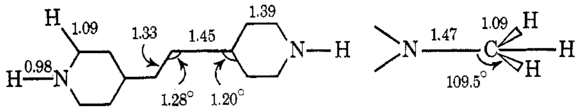
	Experimental[a]		Theoretical[b]			
			trans		cis,	twisted,
	R = CH₃	R = CH₂CH₃	R = H	R = CH₃	R = H	R = H
A_1^{N}	3.1	3.3	3.8	4.1	3.5	3.3
A_2^{H}	1.6	1.3	−1.8, −2.0	−1.6, −1.7	−2.1, −2.4	0.0, 0.2
A_3^{H}	<0.5	<0.5	−0.1, −0.2	−0.3, −0.4	0.2, 0.4	−1.6, −1.9
A_5^{H}	1.6	2.0	−1.3	−1.3	4.7	15.3
$A_{\mathrm{NH}}^{\mathrm{H}}$			−5.2		−4.9	−4.2
$A_{\mathrm{NCH_3}}^{\mathrm{H}}$	3.1			4.0, 5.2		
$A_{\mathrm{NCH_2Me}}^{\mathrm{H}}$		3.3				

[a] Hyperfine coupling constants extracted from spectra obtained experimentally. [b] Coupling constants predicted from INDO molecular orbital calculations; see text.

olefin. Therefore, the radicals have likely escaped from a nonparamagnetic (ground state) donor–acceptor complex in a manner analogous to radical formation from amine complexes of tetracyanoethylene.[21] In a typical experiment, 0.002 *M* **1a** and 0.2 *M* *n*-butylamine in acetonitrile produce a radical concentration of **1b** which is 16% that of starting olefin **1a** as determined by comparison of spins with a paramagnetic standard. A mixture of 0.001 *M* 1,2-bis(4-pyridyl)ethylene diethiodide and 0.2 *M* *n*-butylamine in acetonitrile produces a concentration of the *N*-ethyl substituted radical cation that is 56% that of starting olefin.

Analysis of Esr Spectra.—Hyperfine coupling constants from analysis of esr spectra obtained in this study are shown in Table I. Coupling constants from this Table were used to simulate the computer spectrum shown in Figure 2b. Methyl hydrogen coupling constants were assigned with the aid of *N*-deuteromethyl and *N*-ethyl substitution. Figure 3 shows the esr spectrum observed from zinc reduction of 1,2-bis(*N*-ethyl-4-pyridyl)ethylene iodide in acetonitrile; below it is the computer-simulated spectrum based on coupling constants in Table I. The ratio of methylene to methyl hydrogen coupling constants in Table I ($A^{\mathrm{H}}_{\mathrm{CH_2Me}}/A^{\mathrm{H}}_{\mathrm{CH_3}} = 1.06$) is very similar to the ratio of the methylene to methyl coupling constants for benzyl and methyl viologen ($^{\mathrm{H}}_{\mathrm{CH_2Ph}}/A^{\mathrm{H}}_{\mathrm{CH_3}} = 1.04$).[19] Based on the known ratio, $A^{\mathrm{H}}/A^{\mathrm{D}} = 6.5$,[22] the predicted spectral length of the *N*-deuteriomethyl substituted radical **1b** is 28 G. The experimentally observed spectrum has a length of 29 G. For methyl viologen the ratio of nitrogen to methyl hydrogen coupling constants is 1.06,[19] while for radical **1b** the ratio is near unity.

Other coupling constants were assigned on the basis of molecular orbital calculations using the INDO method. In using this method, reasonably good agreement has been previously obtained[23–25] between experimental and calculated hyperfine coupling constants for a large number of free radicals. One of the major approximations of INDO calculations involves the choice of appropriate geometries. As is the usual case, the precise geometry of the radical in question is unknown. In theory, the appropriate geometry could be obtained by adjusting the internal coordinates so as to minimize the molecular energy. Bond angles and lengths were varied to ascertain trends in molecular energies and coupling constants. Standard bond lengths and bond angles[26–28] for the trans geometry of the radical are shown below.



For the cis geometry, coordinates for the trans isomer were rotated 180° about the ethylenic double bond. Coordinates for the pyridyl rings were then rotated 34° about the C_4–C_5 bond axis in propeller fashion.[29] A twisted geometry was achieved by rotating coordinates for the trans isomer 90° about the ethylenic double bond. The energy of the twisted form was further minimized by changing exocyclic bond lengths to C_4–C_5 = 1.45 Å and C_5–C_6 = 1.33 Å.

Coupling constants predicted by INDO calculations for *trans*-**1b** (Table I) agree fairly well with those observed experimentally. The calculated methyl hydrogen coupling constants are expectedly in error since a rigid geometry was assumed for the methyl groups. Nevertheless, substituting a *N*-methyl group for a *N*-hydrogen is predicted to have only a small effect on the spin distribution of the trans radical. Except for differences in coupling constants for the ethylenic hydrogens, coupling constants predicted for the trans, cis, and twisted conformations of the radical show only small variations.

Isomerization of the Radical.—Both cis and trans isomers of **1a** can be prepared and are stable at room temperature. To determine whether cis and trans forms of radical **1b** could be detected, both isomers of **1a** were reduced by several methods under various conditions. Cyclic voltammetric measurements (at 200 mV/sec sweep rates) on solutions of *cis*-**1a** in acetonitrile at a platinum bead electrode yielded the

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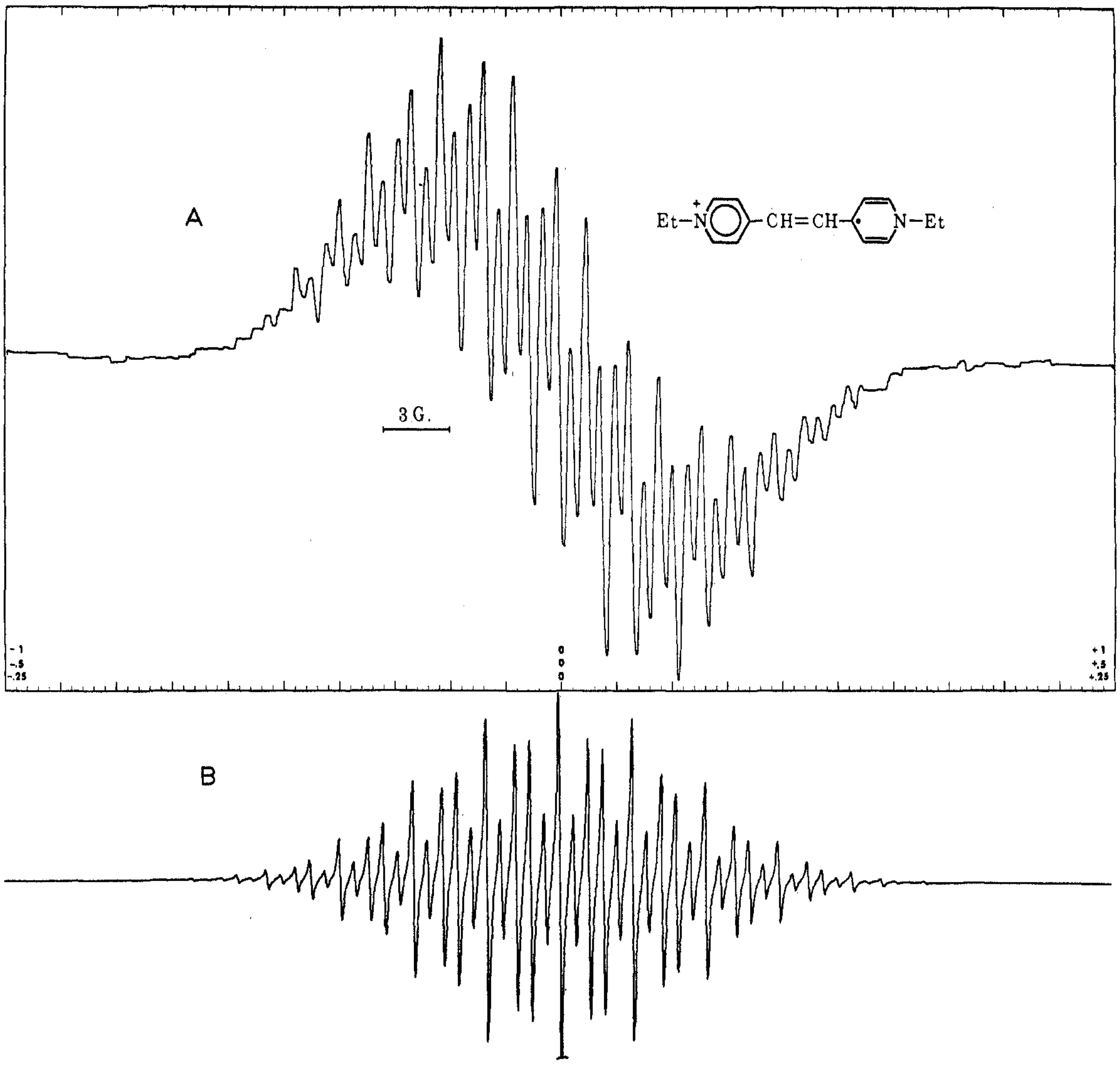

Figure 3.—(a) Esr spectrum of 1,2-bis(*N*-ethyl-4-pyridyl)ethylene iodide radical cation produced by zinc reduction of 1,2-bis(*N*-ethyl-4-pyridyl)ethylene iodide in acetonitrile. (b) Computer-simulated spectrum using the coupling constants listed in Table I.

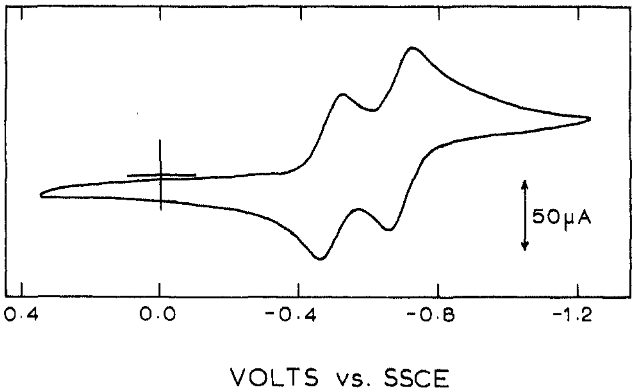

Figure 4.—Cyclic voltammogram of *trans*-1,2-bis(*N*-methyl-4-pyridyl)ethylene tetrafluoroborate in acetonitrile containing 0.1 *M* TBAH. Rate of scan was 200 mV/sec using a platinum bead electrode and a SSCE cell as reference.

same cyclic voltammogram as that obtained for the trans isomer (Figure 4). Peaks corresponding to two one-electron reversible reductions were identical within the accuracy of measurement for both isomers. Within the time scale of the cyclic experiments no disproportionation or other side reactions could be detected. Reduction potentials for *cis*- and *trans*-**1b** were also determined by single sweep voltammetry under conditions that would yield more precise results than those from cyclic measurements. For the cis and trans isomers, reduction potentials were −0.488 and −0.492 V (±0.003 V at 28 ± 0.5° *vs.* SSCE), respectively. Radical formation is accompanied by isomerization. An exhaustive electrolysis of *cis*-**1a** to **1b** at −0.60 V *vs.* SSCE at a platinum electrode followed by a reoxidation at 0.00 *vs.* SSCE resulted in complete cis to trans isomerization of **1a**. In fact, when only small portions of *cis*-**1a** were reduced to **1b**, total cis to trans isomerization of the solution occurred in less than 1 hr.

Esr spectra from zinc or electrolytic reduction of either *cis*- or *trans*-**1a** at room temperature were identical with that in Figure 2. At −60°, spectra obtained for the electrolytic reduction of *trans*-**1a** in butyronitrile under vacuum showed essentially the same linewidth broadening as that observed at room temperature. Electrochemical reduction of *cis*-**1a** at −0.60 V *vs.* SSCE under vacuum in butyronitrile at −30° produced spectra that were essentially the same as those produced from *trans*-**1a** at low temperatures. The spectra showed slight differences in peak intensities during the initial period of radical production, which could have resulted from nonhomogeneous solution currents. However, after several minutes, electrolytic reduction of *cis*-**1a** produced spectra that were identical with those from *trans*-**1a**. Line widths from spectra produced by electrolytic reduction of *cis*-**1a** showed very little temperature dependence and were the same as those produced from reduction of *trans*-**1a**.

As previously mentioned, photolysis of *trans*-**1a** in 1:1 ether–acetonitrile solutions produced visible spectra which are the same as those produced by either chemical or electrochemical reductions of *cis*- or *trans*-**1a**. Experiments were performed to determine whether new visible absorption could be detected on a microsecond time scale when *cis*-**1a** was irradiated by flash photolysis. Acetonitrile solutions of *cis*-**1a** were mixed with ether *via* a break-seal joint just prior to flashing, and solutions were flashed no more than twice within 10 min of mixing. Flash photolysis at approximately 325 nm produced no new transient absorption in the region of 400–630 nm having a lifetime of 10 μsec or longer.

Flash photolysis at 500–600 nm of an acetonitrile solution of **1b** produced by electrochemical reduction also failed to show changes in absorption in the regions of 400–490 and 610–630 nm having a duration of 10 μsec or longer.

One possibility suggested by these results from the esr and flash photolysis experiments is that the energy barrier to rotation about the ethylenic double bond of radical **1b** is too small to permit easy detection of unique cis and trans isomers. Theoretical predictions of the energy change as a function of rotation about the ethylenic double bond were obtained from INDO calculations. Results from these calculations for **1a** and **1b** are shown in Figure 5. The energy change between *trans*-**1a** and *trans*-**1b** is theoretically proportional to the reduction potential of *trans*-**1a**. Since voltammetric measurements yielded the same reduction potential for *cis*-**1a** as for *trans*-**1a**, the enthalpy change between *cis*- and *trans*-**1a** should be very similar to that between *cis*- and *trans*-**1b**. The voltammetric measurements are thus in accord with the relative enthalpy changes predicted by INDO calculations. The actual magnitude of the cis–trans enthalpy change is considerably overestimated by the INDO calculations, since the cis–trans enthalpy change for stilbene has been estimated experimentally to be about 3–4 kcal/mol.[30] Also, the energy maxima at 90° for the twisted forms of **1a** and **1b** are likely to be overestimated owing to the restricted choice of molecular coordinates. For stilbene, the energy of activation for conversion of cis to trans forms is found by experiment to be approximately 37 kcal/mol.[31] Although the calculations have their limitations in predicting actual energies, it is evident that the relative energy of activation for cis–trans isomerization for radical **1b** is predicted to be considerably less than that for **1a**.

The above experiments suggest strongly that the single radical observed in this study is *trans*-**1b**. The observed and calculated hyperfine coupling constants (Table I) also support a planar trans or cis form for **1b** but argue against a twisted structure. Computer-simulated esr spectra for planar cis and trans radical cations (compared in Figure 6) appear different enough so that a long-lived *cis*-**1b** could be detected under the experimental conditions. Therefore it seems safe to conclude that the only radical surviving long enough to detect in these experiments is *trans*-**1b**. It is perhaps a little surprising that *cis*-**1b** does not survive long enough to be detected in flash photolysis experiments or in the low-temperature reduction of *cis*-**1a**. Although the barriers to the radical estimated by INDO calculations are considerably lower than those for the unreduced olefin, reaction with free energies of activation in the range 14–16 kcal/mol (reasonable estimates based on predicted relative barriers for **1a** and **1b** and assuming that the barrier for **1a** is ~37 kcal/mol)[31] should be detectable under the flash photolysis conditions employed. However, a free energy of activation barrier as low as 12 kcal/mol would be nearly impossible to detect; so fast rotation can not be excluded as the mechanism for isomerization.

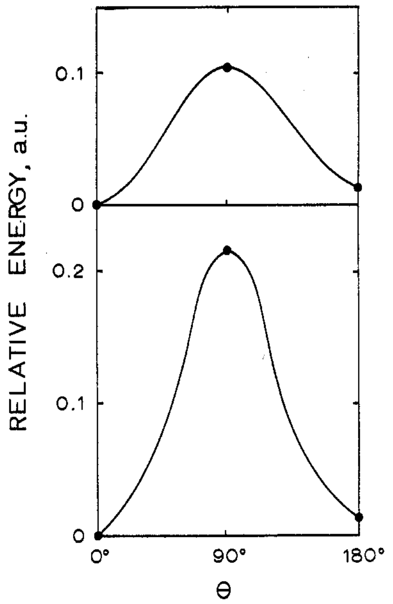

Figure 5.—Energies predicted by INDO molecular orbital calculations as a function of rotational angle about the ethylene bond: upper trace, radical cation **1b**; lower trace, starting dication **1a**.

Although disproportionation of the cis cation to **1a** and **1b** with subsequent generation of *trans*-**1b** (eq 3, 4)

$$2\ cis\text{-}\mathbf{1b} \overset{k_{eq}}{\rightleftarrows} \mathbf{1c} + cis\text{-}\mathbf{1a} \tag{3}$$

$$cis\text{-}\mathbf{1a} + \mathbf{1c} \xrightarrow{k_r} cis\text{-}\mathbf{1b} + trans\text{-}\mathbf{1b} \tag{4}$$

can certainly occur, it is unlikely that this provides the dominant route for isomerization at the concentrations employed in the flash experiments. The calculated rate expression for reaction from eq 3 and 4 is eq 5.

$$\frac{\mathrm{d}\,[trans\text{-}\mathbf{1b}]}{\mathrm{d}t} = k_r K_{eq}\,[cis\text{-}\mathbf{1b}]^2 = k_d\,[cis\text{-}\mathbf{1b}]^2 \tag{5}$$

Assuming $k_r = k_{diff} = 10^{10}\ M^{-1}\ \mathrm{sec}^{-1}$ [32] in acetonitrile and $K_{eq} = 2.5 \times 10^{-4}$ [12] and that all of the *cis*-**1a** is converted to *cis*-**1b** on flashing we estimate that even at the highest concentrations employed (0.001 *M*) no more than 5% isomerization by the above-outlined disproportionation path could occur. If less *cis*-**1b** is produced or if $k_r < k_{diff}$ the reacted fraction would be much lower. The equal wave heights of the cyclic

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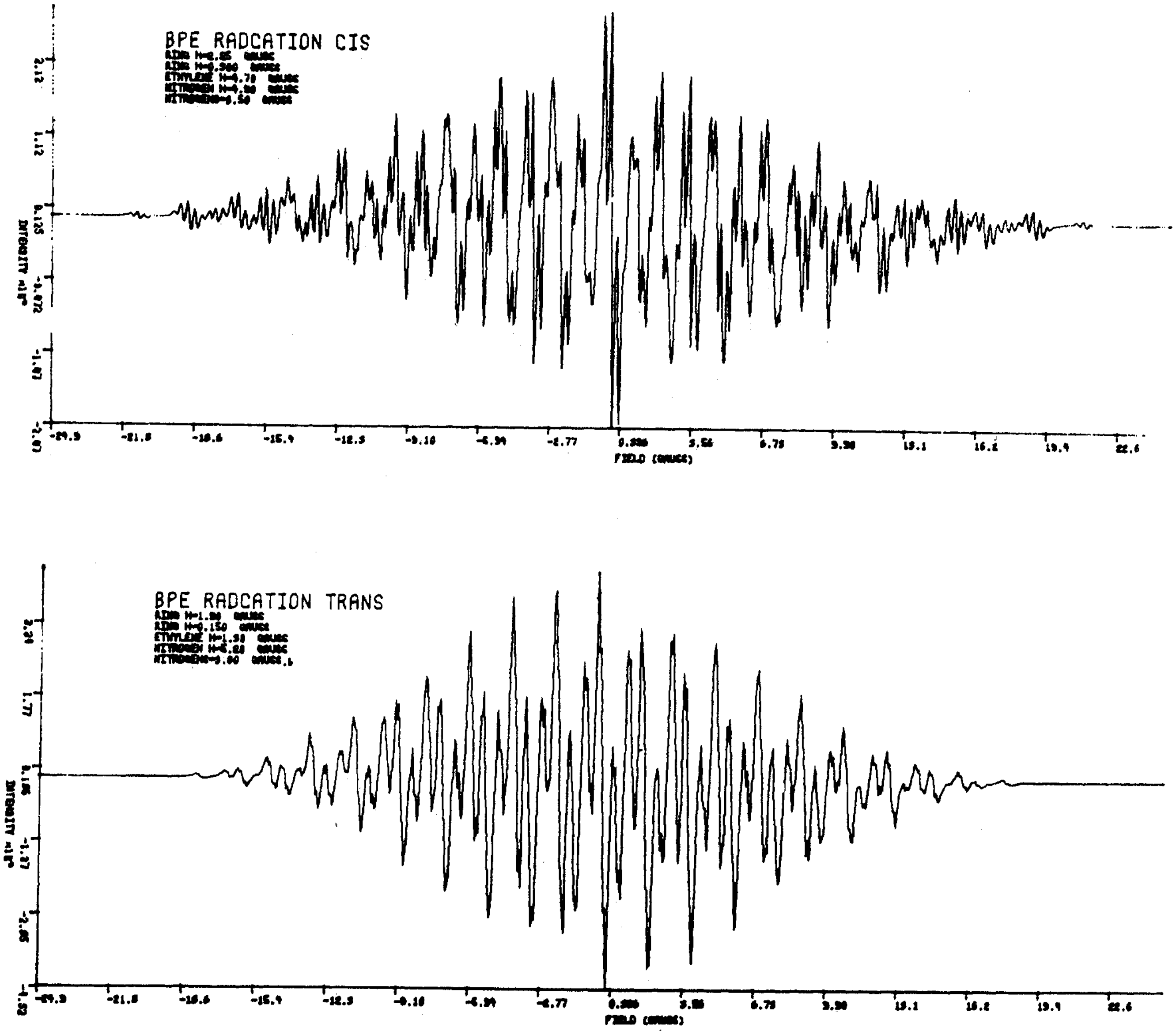

Figure 6.—Computer-simulated (using data in Table I) esr spectra for cis and trans olefin radical cations.

voltammograms (Figure 4) also rule out the occurrence of substantial disproportionation.

The presence of what is evidently such a low barrier to rotation in radical cation **1b** presents a striking contrast to the relatively large barriers indicated for other substituted ethylenic cation radicals.[33,34] However, as indicated earlier, the present system is really a reduced ethylene while the earlier cation radicals are oxidized ethylenes, so that perhaps the behavior of **1b** is best compared to that of radical anions.

It is frequently tempting to draw correlations between the behavior of excited states and one-electron reduced species. However, on a quantitative basis these comparisons are often less than satisfactory. In the present case radical **1b** apparently isomerizes *via* rotation much more readily than does the stilbene radical anion; in contrast, excited states of **1a** have some preference for planar cis and trans forms while stilbene excited states readily attain a twisted geometry. The observed rapid rate of isomerization of **1b** indicates that isomerization *via* formation of transient radical ions *via* electron transfer within excited molecular complexes is a viable mechanism for photoisomerization. Such a mechanism could conceivably be important in photobiological processes related to vision.

Experimental Section

Materials.—The preparation and purification of *cis*- and *trans*-1,2-bis(*N*-methyl-4-pyridyl)ethylene tetrafluoborate (**1a**) has been described in a previous publication.[5] The diethyl iodide salt of 1,2-bis(4-pyridyl)ethylene was prepared and purified by the same general procedure.[5] Butyronitrile was distilled from potassium permanganate and anhydrous sodium carbonate, and then dried by distillation from P_2O_5. Other solvents were of spectral quality and were distilled before use. The supporting electrolyte, tetra-*n*-butylammonium hexafluorophosphate (TBAH), was prepared by the general procedure of Lange and Muller[35] and Ferguson,[36,37] recrystallized three times from ethanol-water, and dried at 100° under vacuum for 10 hr. The paramagnetic standard, diphenylpicrylhydrazyl, was purchased from Aldrich Chemical Co., and was used without further purification.

Methods.—Visible spectra were recorded on either a Cary Model 14 or Unicam SP800B spectrophotometer. A Varian E-3 spectrometer, equipped with X-band frequencies and an E-3

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variable-temperature accessory, was used to record esr spectra. Computer-simulated spectra were obtained using a computer program written by Griffin.[38] Esr spectra recorded at room temperature were produced from solutions electrolyzed in a Varian E-3 electrochemical cell under oxygen-free nitrogen. At low temperatures, radicals were electrolytically generated in an esr vacuum cell designed by Holz[39] and modified by Rieke and Rich.[40] The cell was degassed by five freeze-pump-thaw cycles before sealing and could maintain a vacuum of at least 10^{-8} Torr for the duration of the experiment. A silver bead reference electrode was used in the cell.

Standard three-electrode operational amplifier circuitry was used. All electrical measurements are *vs.* the saturated sodium chloride colomel reference electrode (SSCE) and are uncorrected for junction potentials. The cell design and instrumentation have been described previously.[37] In a typical experiment, solutions containing 1×10^{-3} *M* **1a** and 0.1 *M* TBAH were studied electrochemically at a platinum electrode in any oxygen-free nitrogen atmosphere.

The apparatus for flash spectroscopic studies has been described[2] previously. Samples for flash photolysis were 1×10^{-4} *M* and were degassed by five freeze-pump-thaw cycles.

Zinc reductions were carried out under vacuum by exposing a 1×10^{-3} *M* solution of **1a** to a freshly distilled zinc mirror.

Registry No.—*trans*-**1b** (tetrafluoroborate), 34247-36-4; 1,2-bis(4-pyridyl)ethylene diethyl iodide radical cation, 34195-73-8.

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The Mechanism of Nucleophilic Substitution of *N*-Methyl-4-Substituted Pyridinium Salts[1]

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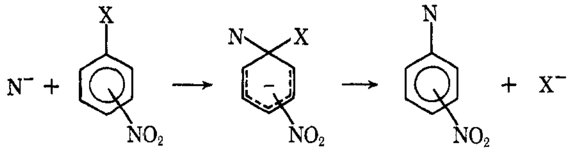
Rates and activation parameters have been determined for the reaction of sodium hydroxide in aqueous solution with *N*-methyl-4-halopyridinium salts and *N*-methyl-4-methoxypyridinium fluoroborate. The results obtained indicate that the mechanism is similar to the mechanism of nucleophilic displacement which occurs with halogenated nitrobenzenes.

Nucleophilic aromatic substitution of halogenated nitrobenzenes is a well-understood process.[2-9] The reaction occurs by a two-step mechanism (eq 1) and is significantly different from nucleophilic substitution at saturated centers in a number of respects. (1) The transition state is characterized by little or no carbon-halogen bond breaking. (2) The reactivity of various halogens is related to their inductive effects, rather than to their bond strengths. (3) The reaction proceeds *via* a Meisenheimer complex intermediate (**1**).[10]



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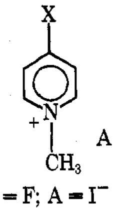
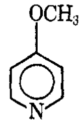
(1)

Nucleophilic displacements in heteroaromatic systems have been studied much less thoroughly than those in the benzene system. *N*-alkyl pyridinium salts undergo nucleophilic displacement much more readily than do the corresponding *N*-oxides, which in turn react more readily than do the corresponding unsubstituted compounds.[11] Meisenheimer-type complexes have been isolated from the reactions of a number of pyridine compounds.[12] However, it is not clear to what extent the mechanism in the pyridine series is like that of the benzene series.

The purpose of the present study was to obtain kinetic data for nucleophilic displacement reactions of compounds **2**–**7** in order to make comparisons with the corresponding nitro and dinitrobenzene compounds. From these data we hope to determine the extent to which the reaction mechanism in the pyridine series is similar to that in the benzene series.



2, X = F; A = I^-
3, X = Cl; A = I^-
4, X = Br; A = BF_4^-
5, X = I; A = BF_4^-
6, X = OCH_3; A = BF_4^-



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Results

Rates of reaction of compounds **2**–**6** with hydroxide ion in aqueous solution at several temperatures are summarized in Table I. All measurements were carried out spectrophotometrically under pseudo-first-

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[1] This research was supported by Grant NS 07657 from the National Institutes of Health.

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