COLOC experiments were those furnished in the IBM software manual. ^{13}C–^{1}H long-range couplings were set for maximum sensitivity at J = 4, 7, and 10 Hz.

Isolation. The dark brown sponge *Fascaplysinopsis* sp. was collected by SCUBA at Ndravuni, Fiji, and frozen. The sponge was then lyophilized (135.7 g, dry weight) and extracted with MeOH. The MeOH residue (42 g) was partitioned successively with 10% aqueous MeOH/hexanes, 20% aqueous MeOH/CCl_4, and 40% aqueous MeOH/$CHCl_3$. The majority of luffariellolide (0.45 g, 0.33% dry weight) was concentrated in the CCl_4 extract (2.64 g), while fascaplysin was located in the $CHCl_3$ extract (7.06 g). The $CHCl_3$ fraction was repeatedly chromatographed over Sephadex LH-20 in MeOH to give 4 as a brick red glass that crystallized from either MeOH or $CHCl_3$ (2.08 g, 2% dry weight).

Fascaplysin (4): mp 232–235 °C dec; FTIR (neat) 1712, 1618, 1594, 1502, 1462, 1450, 1080, 1061 cm^{-1}; UV (MeOH) λ_{max} 413 (ϵ 3100), 333 (3560), 301 (6800), 274 (5450), 262 (6400), 214 (7000) nm; (MeOH + OH$^-$, irreversible over time) 453 (ϵ 2700), 427 (2975), 398 (2295), 332 (5465), 274 (5801), 237 (6480), 210 (30,374) nm; ^{1}H NMR (TFA-*d*) δ 9.01 (1 H, d, J = 5.93 Hz), 8.69 (1 H, d, J = 5.93 Hz), 8.30 (1 H, d, J = 7.25 Hz), 8.09 (1 H, d, J = 7.91 Hz), 8.05 (1 H, d, J = 7.25 Hz), 7.95 (1 H, dd, J = 7.25, 7.91 Hz), 7.86 (1 H, dd, J = 7.25, 7.91 Hz), 7.76 (1 H, d, J = 7.91 Hz), 7.71 (1 H, dd, J = 7.25, 7.25 Hz), 7.52 (1 H, dd, J = 7.25, 7.25 Hz); ^{1}H NMR (DMSO-d_6) δ 13.5 (1 H, br s, N–H); ^{13}C (TFA-*d*) δ 186.4 (s), 149.9 (s), 149.8 (s), 145.4 (s), 141.0 (d), 138.8 (d), 135.0 (s), 134.8 (d), 129.5 (d), 128.5 (d), 127.2 (d), 126.4 (d), 126.1 (s), 123.5 (s) 122.4 (d), 122.2 (s), 117.2 (d), 116.1 (d); HRFABMS m/z 271.08606, $C_{18}H_{11}N_2O$ requires 271.08716; m/z 121 (100%); FABMS (matrix of glycerol + 18-crown-6 ether) MH$^+$ 535.

Acknowledgment. This work was supported in part by grants from the National Institutes of Health (Grants CA 36622 and CA 01179 (to C.M.I.); Grant CA24487 (to J.C.)) and the New York State Sea Grant (J.C.). We thank Dr. Uday Raj and the Institute of Marine Resources, University of the South Pacific, for use of their facilities. We also thank Dr. Miles Hacker, The University of Vermont, for supplying cytotoxicity data.

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Supplementary Material Available: Tables of fractional coordinates, thermal parameters, interatomic distances, interatomic angles, and torsional angles for 4 (6 pages). Ordering information is given on any current masthead page.

Photoisomerization of Some *N*-Aryl α,β-Unsaturated Iminium Salts[1]

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A series of *N*- and *C*-diaryl-substituted α,β-unsaturated iminium salts have been prepared in which a systematic change in the substituents on the aromatic rings was made. The photochemically induced isomerizations of these salts were examined in trifluoroacetic acid, a medium in which thermally induced isomerizations of these cations were generally slow. Photoisomerization about both the C═C and C═N partial double bonds of these iminium salts was observed, leading eventually to the formation of a photostationary state consisting of four isomers. Apart from cations containing a nitro substituent, the ratios of the quantum efficiencies for C═C vs C═N isomerization remained essentially constant as substituents on the two aryl rings were changed, suggesting that the perpendicular excited singlet states involved in these reactions have "biradical" character. The reduction potentials of the iminium salts were measured. Isomerization about the C═N bond of one of the salts was shown to occur by a photoinitiated electron transfer from tris(2,2′-bipyridine)ruthenium(II) dichloride.

Irradiation of α,β-unsaturated iminium ions in solution induces photoisomerization about both double bonds of the molecules, the C═N$^+$ and C═C bonds.[2,3] These reactions have application to the chemistry of vision, wherein the retinylidene iminium ion isomerizes about a specific C═C bond on light absorption.[4] The mechanism of this reaction of the visual pigments and the factors that determine the observed regioselectivity are of great interest.

In our previous work we have described the photoisomerizations of several *N*-alkyl-, C_3-aryl-, or C_3-alkyl-substituted α,β-unsaturated iminium salts.[2,3] The substituents present on these iminium salts seem to influence the regioselectivity of the photoisomerizations. It is possible that these effects are caused by a change in electron distribution in the excited states of these salts and that the substituent present can determine the preference for isomerization about either the C═N or C═C bond.[5]

In the present work we have carried out a detailed investigation of the isomerizations of a series of *N*- and *C*-diaryl-substituted α,β-unsaturated iminium salts in which a systematic change in the electron demand of the groups on the aryl rings is made. The purpose of these studies was to probe the effect of charge-stabilizing groups on the regioselectivity of the photoisomerizations about the C═N$^+$ and C═C bonds.[6]

Results

The iminium salts selected for this work were the *E,E* isomers **1a–i** in which the substituents on the two phenyl rings were varied. These cations were all isolated as crystalline, air-stable perchlorate salts by previously described procedures.[6] Their characterization by ^{1}H NMR

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[1] This work was supported by the Natural Science and Engineering Research Council of Canada.

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0022-3263/88/1953-3278$01.50/0

Table I. ^{13}C NMR Chemical Shift Data[a]

iminium salt	C_1	C_2	C_3	C_4	$C_{5,9}$	$C_{6,8}$	C_7	$C_{1'}$	$C_{2',6'}$	$C_{3',5'}$	$C_{4'}$	CH_3	other
1a	169.9	120.0	161.4	139.3	131.3	124.5	150.4	144.3	122.0	130.6	132.0	42.4	
1b	169.6	116.4	164.8	131.9	132.0	130.1	142.6	144.5	122.1	130.6	131.5	41.8	
1c	169.8	115.9	167.1	133.4	131.1	129.8	135.6	144.6	122.2	130.7	131.5	41.6	
1d	169.3	114.7	167.2	131	131.4	130.6	148.9	144.6	122.1	130.6	131.3	41.4	20.6
1e	168.6	113.4	166.3	127.3	134.2	115.7	166.1	144.7	122.1	130.6	131.1	41.1	55.4
1f	171.4	115.9	170.3	133.5	131.8	129.9	136.6	148.8	124.3	126.2	149.3	41.6	
1g	169.9	115.8	167.8	133.4	131.2	129.8	135.9	142.8	123.6	130.9	138.4	41.7	
1h	168.9	115.7	166.2	133.2	130.9	129.5	135.3	143.0	121.5	130.7	142.0	41.3	19.3
1i	168.8	115.9	166.3	133.5	130.9	129.7	135.4	138.3	123.9	116.1	161.3	41.7	55.6

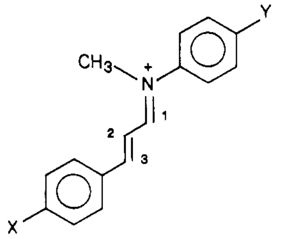
[a] In ppm, referenced to CF_3CO_2H at 114.7 ppm, in trifluoroacetic acid or deuteriated trifluoroacetic acid.

Table II. UV Absorption Data[a]

iminium salt	λ_{max}, nm	$\log \epsilon$	$\Delta\nu_{1/2}$, 10^{-5} cm^{-1}
1a	348	4.51	1.4
1b	368	4.60	1.6
1c	361	4.60	1.6
1d	378	4.58	1.7
1e	408	4.63	1.4
1f	370	4.56	1.6
1g	361	4.53	1.6
1h	360	4.49	1.5
1i	372	4.46	1.1
6	346		

[a] 10^{-5} M in trifluoroacetic acid.

spectroscopy has been given in an earlier publication,[6] and their ^{13}C NMR spectra are summarized in Table I.



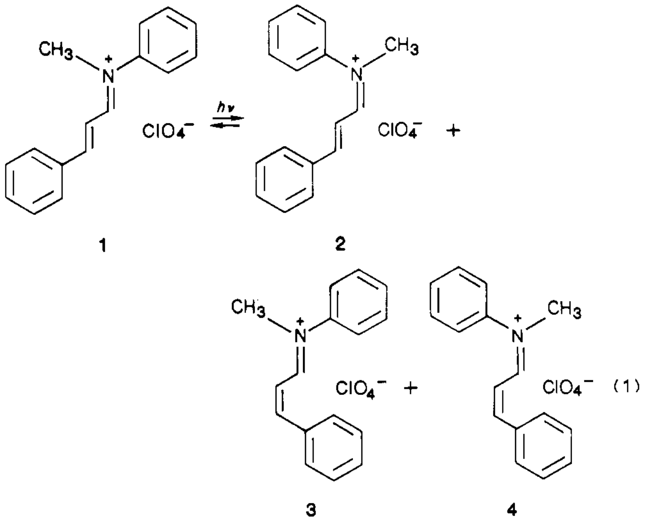
1a–c

	X	Y
1a	NO_2	H
b	Cl	H
c	H	H
d	CH_3	H
e	OCH_3	H
f	H	NO_2
g	H	Cl
h	H	CH_3
i	H	OCH_3

Absorption and Emission Spectra. Absorption spectra of trifluoroacetic acid solutions of iminium salts **1a–i** were obtained. The position of the long-wavelength absorption band varies with the substituent on the C_3-phenyl ring (Table II). The iminium salt **1e**, with an electron-donating methoxy group on the C_3-phenyl ring, exhibited the longest wavelength absorption maximum and the nitro-substituted compound **1a**, the shortest. Substituents on the *N*-phenyl ring do not have a large effect on the absorption maximum.

Attempts were made to measure luminescence from acetonitrile solutions of the iminium salts at room temperature and from a sulfuric acid/trifluoroacetic acid/acetic acid glass at 77 K. No luminescence could be detected with the equipment we have available. The estimated upper limit to the fluorescence quantum yield is 10^{-4}.

Photoisomerizations of iminium salts **1a–i** in trifluoroacetic acid solution were followed by ^1H NMR spectroscopy. The strong-acid medium was deliberately selected for this work as thermal isomerizations are inhibited in this solvent.[6] Solutions of iminium ions **1a–i** were irradiated at 350 nm to produce in each case a mixture of four species, three products in addition to starting material. The solutions were examined by ^1H NMR spectroscopy, and the products were identified as geometric isomers, shown in eq 1 (Table III).[7]



One of the products was found to have spectra identical with those of the *Z,E* isomer **2**, obtained previously by thermal isomerization of **1**.[6] Upon heating of the photomixture, products **3** and **4** revert to **1** and **2**. Products **3** and **4** were shown to have *Z* stereochemistry about the C=C bonds on the basis of the magnitude of their coupling constants across the C=C bonds. In all cases $J_{2,3}$ was found to be 11–12 Hz, a value that is characteristic of a *Z* configuration. The corresponding coupling constant for the *E* conformers typically has a value of 15–16 Hz.[2,3] In order to distinguish between the *E,Z* and *Z,Z* isomers, **3** and **4**, respectively, the isomerizations were followed as a function of time. At short irradiation times (<10% conversion) only one of the *Z* C=C isomers was detected in each mixture. It was assumed that this isomer is the *E,Z* isomer **3**, the product of a one-bond isomerization. After longer irradiation times, the secondary product, the *Z,Z* isomer **4**, was observed.

An exception was observed in the reaction of salt **1f**. This apparently isomerizes about both the C=C and C=N bonds in the primary reaction. The spectra of the *E,Z* and *Z,Z* isomers of **1f** were assigned by comparison with the data for the other iminium salts (Table III).

Separation of the isomers for further identification was not successful, as *E,Z* isomerization takes place under the conditions used for chromatography, in aprotic solvents in which the salts are soluble, and on crystallization.[6]

Quantum yields of degassed trifluoroacetic acid solutions of salts **1a–i** were measured with the use of an optical bench. Relative isomer concentrations were determined

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(7) ^1H NMR data for 1 and 2 are given in ref 6.

Table III. ^{1}H NMR Spectra[a]

iminium salt	H_1	H_2	H_3	aryl H	CH_3	other	$J_{1,2}$, Hz	$J_{2,3}$, Hz
3a	8.45 d	7.08 dd	*b*	*b*	4.05[b]		11	11
4a	8.52 d	6.30 dd	*b*	*b*	3.98[b]		11	11
3b	8.42[b]	6.83 dd	8.11 d	*b*	3.97 s		11	11
4b	8.61 d	6.11 dd	7.77 d	*b*	3.93 s		11	11
3c	8.45 d	6.82 dd	8.21 d	*b*	3.97 s		11	11
4c	8.61 d	6.12 dd	7.87 d	*b*	3.92 s		11	11
3d	8.44 d	6.73 dd	8.15 d	*b*	3.93 s	2.22 s	11	11
4d	8.61 d	6.03 dd	7.80 d	*b*	3.90[b]	2.29[b]	11	11
3e	8.40 d	6.67 dd	8.08 d	*b*	3.91 s	3.79 s	11	11
4e	8.59 d	5.98 dd	7.8[b]	*b*	*b*	*b*	10	10
3f	8.52 d	6.90 dd	*b*	*b*	4.02 s		11	11
4f	8.73 d	6.10 dd	7.98 d	*b*	3.98 s		11	11
3g	8.43 d	6.82 dd	8.22 d	*b*	3.95 s		11	11
4g	8.62 d	6.11 dd	7.89 d	*b*	3.92 s		11	11
3h	8.43 d	6.80 dd	8.17 d	*b*	3.95 s	2.27 s	11	11
4h	8.58 d	6.15 dd	7.84 d	*b*	3.90 s	2.32 s	11	11
3i	8.39 d	6.80 dd	8.14 d	*b*	3.95 s	3.79 s	11	11
4i	8.57 d	6.17 dd	7.85 d	*b*	3.89 s	3.84 s	11	11

[a] In ppm, referenced to $N(CH_3)_4{}^+BF_4{}^-$ at 3.10 ppm, in trifluoroacetic acid; s = singlet, d = doublet, dd = doublet of doublets. [b] Peaks hidden.

Table IV. Quantum Yields of Photoisomerization[a]

iminium salt	ϕ_{CN}	ϕ_{CC}	ϕ_{CC+CN}	ϕ_{CN}/ϕ_{CC}
1a	0.31 ± 0.04	<0.05		
1b	0.19 ± 0.02	0.18 ± 0.01		1.1
1c	0.20 ± 0.01	0.26 ± 0.03		0.8
1d	0.14 ± 0.02	0.17 ± 0.01		0.8
1e	0.25 ± 0.03[b]	0.11 ± 0.01		
1f	0.19 ± 0.01	0.22 ± 0.03	0.13 ± 0.05	
1g	0.15 ± 0.02	0.16 ± 0.02		0.9
1h	0.23 ± 0.05	0.18 ± 0.03		1.3
1i	0.17 ± 0.01	0.12 ± 0.02		1.5
7[c]	<0.05	0.58 ± 0.06		

[a] 0.04–0.09 M iminium salt in trifluoroacetic acid. Measured relative to the photodecomposition of potassium ferrioxalate at 366 nm. Errors are standard deviations of at least three runs. [b] Includes some thermal isomerization. [c] Reference 3.

by ^{1}H NMR analyses of the irradiated solutions. Other methods of analysis require either change of solvent or separation of the products. These procedures lead to thermal isomerization and were therefore avoided.[6] The results given in Table IV are corrected for small quantities of isomers **2** and **3** present before the irradiation.

Control experiments were run in order to ensure that the isomerizations observed were photochemically and not thermally induced. In one case, **1e**, a thermal isomerization was found to take place during the course of the photochemical experiment. The data given in Table IV are not corrected for this reaction. However, it was shown that this competing thermal reaction was absent when a weaker acid, prepared by adding sodium trifluoroacetate to the trifluoroacetic acid, was used as the solvent for the reaction; see below.[6] The quantum yield determined in this medium is given in Table V.

The quantum yields were measured over a 0.04–0.09 M concentration range for each salt. Within the error limits of the experiment (±10%), the quantum yields were not affected by changes in the concentration of the samples.

In preliminary experiments it was found that dissolved oxygen did not affect the quantum yields measured. Since the concentration of reactant is high relative to the expected concentration of oxygen in trifluoroacetic acid (about 10^{-3} M), it is unlikely that quenching of the excited state would be observed if it occurred.

Medium effects on the photoisomerization reaction were explored for salts **1a** and **1e**. The quantum yields were measured for the reaction of **1a** in the weaker acid media 0.01 M sodium trifluoroacetate in trifluoroacetic acid and 0.1 M sodium trifluoroacetate in trifluoroacetic acid as well as the more nucleophilic medium 0.1 M tetramethylammonium chloride in trifluoroacetic acid. The isomerization quantum yields of **1e** were measured in 0.01 M sodium trifluoroacetate in trifluoroacetic acid solution as well as the less nucleophilic solvent which contained 0.03 M sulfuric acid in trifluoroacetic acid solution. The quantum yield values given in Table V are corrected where necessary for thermal isomerization that occurred during the irradiation. Within the error limits of these determinations, it would appear that the quantum yields of the photoisomerization are not affected by the medium.

The quantum yields measured for C=C and C=N isomerization vary with substituent to some extent, but the ratio ϕ_{CC}/ϕ_{CN} is relatively insensitive to substituent for salts **1b–e,g–i**. The ratios of quantum yields measured for the nitro-substituted salts **1a** and **1f** differ significantly from those of the other salts.

The photostationary states of salts **1a–i** were produced by irradiating trifluoroacetic acid solutions of each salt in a Rayonet photoreactor for 36 h or longer. The mixtures

Table V. Medium Effects on Quantum Yields[a]

iminium salts	solvent	ϕ_{CN}	ϕ_{CC}
1a	0.01 M sodium trifluoroacetate in TFA	0.30 ± 0.05	
1a	0.1 M sodium trifluoroacetate in TFA	0.34	
1a	0.1 M $(CH_3)_4NCl$ in TFA	0.28	
1e	0.01 M sodium trifluoroacetate in TFA	0.13	0.13
1e	0.03 M H_2SO_4 in TFA	0.15	0.12

[a] Relative to the photodecomposition of potassium ferrioxalate, measured at 366 nm. Estimated error ±10%.

Table VI. Photostationary-State Compositions[a]

iminium salt	% *E,E*	% *Z,E*	% *E,Z*	% *Z,Z*
1a	25	56	9	10
1b	40	25	23	12
1c	37	26	24	13
1d	42	20	27	11
1e	54	16	22	8
1f	37	24	27	12
1g	38	26	24	12
1h	43	26	21	12
1i	48	25	19	8

[a] Determined by ^{1}H NMR. Solutions in TFA, irradiated at 350 nm for 36 h. Estimated errors ±10%.

Table VII. Reduction Potentials[a]

iminium salt	E_p, V	iminium salt	E_p, V
1a	−0.380	**1f**	−0.425
1b	−0.585	**1g**	−0.575
1c	−0.610	**1h**	−0.640
1d	−0.650	**1i**	−0.680
1e	−0.735		

[a] Measured by cyclic voltammetry, at 0.5 V/s, vs. SCE using 0.003 M iminium salt in 0.1 M tetrabutylammonium perchlorate in acetonitrile.

Table VIII. Isomerization of Iminium Salt 1f on Irradiation of Tris(2,2′-bipyridine)ruthenium(II) Dichloride (5)[a]

time, min	% *E,E*[b]	% *Z,E*[b]
0	>95	<5
30	73	27
60	63	37
83	62	38
120	60	40
150	58	42
24 h	54	46

[a] Concentrations: **1f**, 5×10^{-2} M; **5**, 2.5×10^{-2} M in trifluoroacetic acid. λ_{ex} >425 nm. [b] Measured by ^{1}H NMR; the peak height of the NCH_3 signal relative to the sum of the heights of the two CH_3 peaks.

were then analyzed by ^{1}H NMR spectroscopy. The compositions of the photostationary states are given in Table VI. Repeated attempts to isolate pure samples of the isomers **2**–**4** so that the photostationary states could be reached starting from these isomers were uniformly unsuccessful.[6]

Cyclic Voltammetry and Electron-Transfer Studies. Iminium salts **1a**–**i** in acetonitrile solutions, 0.1 M tetrabutylammonium perchlorate, were reduced by cyclic voltammetry. The reductions were irreversible at a scan rate of 0.5 V/s, and as a result the peak of the reduction wave, E_p, is reported (Table VII). The reduction waves are substituent dependent, with electron-withdrawing substituents facilitating reduction.

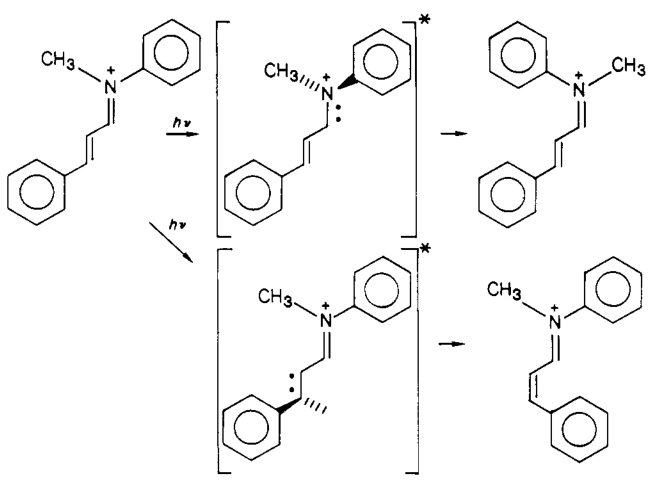
The electron donor tris(2,2′-bipyridine)ruthenium(II) dichloride (**5**) is known to luminesce when irradiated.[8] The addition of a small amount of iminium salt **1f** to a solution of **5** in acetonitrile quenched this luminescence.

Irradiation of **1f** in the presence of **5** under conditions where the donor absorbed all the incident light led to isomerization of the iminium salt. The reaction was monitored by ^{1}H NMR spectroscopy at regular intervals. Under these conditions isomerization about the C=N bond of the iminium salt was observed to give a mixture of *E,E* and *Z,E* isomers in a ratio similar to that of the thermal equilibrium (Table VIII).[6]

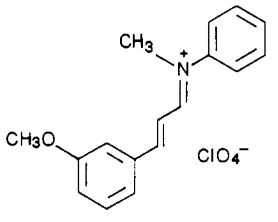
Discussion

In the currently accepted view of a photochemical *E*/*Z* isomerization, the excited molecule twists about the isomerizing double bond to reach an energy minimum where the molecule is twisted by 90° (the perpendicular state).[9] The energy surface can contain an energy barrier that separates the planar, fluorescing excited state from the perpendicular state. Such a barrier has been detected in the photoisomerizations of some alkenes.[10] In a two-bond isomerizing system such as **1**, either one of two twisted configurations can be achieved (Scheme I). If energy barriers exist to twisting about one or both of these bonds, then their relative heights should determine the product distribution, as in a ground-state reaction. In the absence of energy barriers, the relative depths of the energy wells corresponding to the two twisted configurations should determine the product distribution.[11] These energy wells act as funnels to the ground-state surface, on which further twisting occurs to give either the *E* or *Z* isomer with equal probability.[12]

Scheme I



Information about the initially formed excited state is provided by the electronic absorption data. The absorption bands shift to lower energy as the positive charge stabilizing ability of the C_3-aryl group increases, suggesting that the positive charge of the molecule is delocalized into the carbon frame relative to the ground state. For example, the *p*-methoxy-substituted molecule **1e** has a λ_{max} of 408 nm, suggesting a stabilized excited state relative to the *p*-nitro compound, λ_{max} 348 nm. In the *m*-methoxy iminium salt **6** and the *N*-*p*-methoxyphenyliminium salt **1i**, the methoxy substituent cannot stabilize the positive charge by resonance, and these salts have absorption maxima of higher energy than **1e** (λ_{max} 346 and 372 nm, respectively).



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Various processes can deactivate this planar excited species, including fluorescence, isomerization, or intersystem crossing from the singlet to the triplet state. Since luminescence was not observed in our experiments, definite conclusions about the multiplicity of the reaction could not be made.[13] However, in a related system, the sty-

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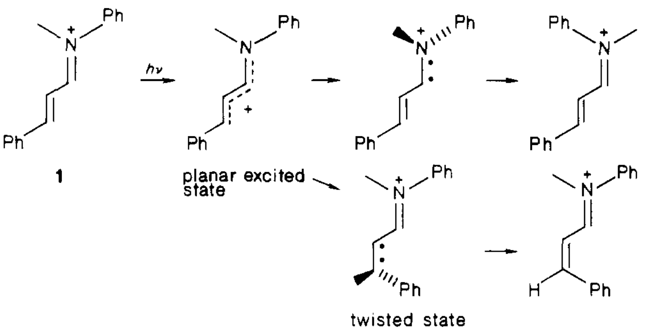
(13) Triplet sensitization or quenching experiments could aid in defining the multiplicity of the reaction, but the requirements are difficult to meet. Sensitizer or quencher molecules must be poor electron donors, must dissolve in trifluoroacetic acid without reacting to allow product analyses, and must not interfere with NMR analyses. We were not able to design suitable experiments.

Scheme II

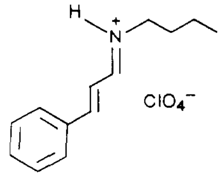


rylpyridinium salts, photoisomerization was observed from the excited singlet state unless a nitro substituent was present on the phenyl ring. In the latter case intersystem crossing to the triplet state preceded isomerization.[14] The quantum yield data given in Table IV indicate that the nitro-substituted salts **1a** and **1f** behave anomalously in the photoreaction, suggesting that a change in multiplicity is important in these systems. It would seem likely that the reactions of salts **1b–e,g–i** take place in the excited singlet state, and that of the nitro-substituted salts **1a** and **1f** in the triplet state.

The absence of luminescence also indicates that the planar excited state is very short-lived, suggesting that there is no significant energy barrier for the isomerization process.

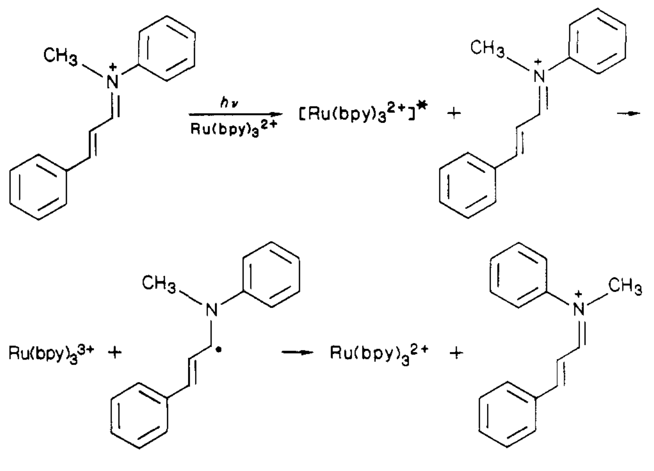
The reaction path that leads to isomerization has been studied theoretically. It was predicted that the delocalized charge distribution of the planar excited state of an iminium salt is maintained as the molecule twists about a double bond.[5] If this is so, then we surmised that charge-stabilizing substituents placed at either of the two extremes of the iminium ion 1 could influence the course of the reaction. By measuring the ratio ϕ_{CN}/ϕ_{CC} we could detect any influences that favor the isomerization of one bond relative to the other. It was concluded above that energy barriers are insignificant in these systems; therefore any information obtained from the data relates to the perpendicular state.

The most symmetrical salt, the unsubstituted salt **1c** isomerizes with approximately equal efficiency about both the C=C and C=N bonds. For the substituted systems **1b–e,g–i**, it can be seen from the data in Table IV that the quantum yields measured for C=C and C=N isomerization vary with substituent to some extent, but the ratio $\phi_{C=N}/\phi_{C=C}$ is largely unaffected. Thus positive charge stabilization is not important in the isomerization reaction. However, the reaction is not insensitive to substituents. In contrast to the salts studied here, the unsymmetrical iminium salt **7** isomerizes much more efficiently about the C=C bond than about the C=N bond.[3] In order for the isomerization to be affected by phenyl versus *n*-butyl substitution, but not by *p*-methoxyphenyl versus *p*-chlorophenyl, we suggest that the perpendicular states have "biradical" character, as shown in Scheme II. This conclusion is consistent with the recent report of calculations on a protonated Schiff base of pentadienal.[15]



7

Scheme III



Electron Transfer. The iminium salts **1a–i** are easily reduced, as measured by the E_p values given in Table VII. A similar reduction is possible with a chemical donor in solution, using the energy available from the excited state. The electron donor **5** has previously been shown to transfer electrons to cations[9] and to cause isomerization in stilbene.[16] That a similar reaction, involving electron transfer from **5** to the iminium salt, is possible is indicated by the quenching of the luminescence of **5** by **1f**. Although the energy of the excited state of **1f** if not exactly known, it can be seen from the absorption maximum (370 nm) that its first excited state is probably of higher energy than that of the donor (λ_{max} 448 nm), making direct energy transfer unlikely. The NMR-scale reaction provides further evidence of an electron-transfer reaction. The proposed mechanism, Scheme III, involves an intermediate species where free rotation about either bond can occur. The only observed isomerization in this case is about the C=N bond, as in the thermal isomerization reaction, to yield a product mixture of composition as in the thermal reaction. It is unlikely that an excited-state reaction would coincidentally yield the same product mixture.

Electron-transfer processes involving iminium salts have been observed previously;[17] however, this is the first reported example of C=N isomerization of an iminium salt by photoinitiated electron transfer.

Experimental Section

^1H NMR spectra were recorded on Bruker WM250 and AM500 spectrometers. The solvent used was trifluoroacetic acid, and the spectra are referenced to an internal standard, tetramethylammonium tetrafluoroborate, $(CH_3)_4NBF_4$, at 3.10 ppm. ^{13}C NMR spectra were recorded on either a Bruker WM250 spectrometer at 62.9 MHz or a Bruker WP80 spectrometer at 20.1 MHz. The latter spectra were obtained with TFA-*d* or D_2SO_4 in the solvent as lock compounds. All spectra are referenced to the CF_3 quartet of the solvent, CF_3COOH, at 114.7 ppm. Trifluoroacetic acid (TFA) was distilled from concentrated H_2SO_4. The iminium salts were synthesized and purified as described previously.[6]

Absorption spectra were recorded on a Pye Unicam SP8-100, a Hewlett-Packard 8451A, or a Perkin-Elmer Lambda 9 spectrophotometer.

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Fluoresence spectra were recorded on a Perkin-Elmer LS-5 fluorescence spectrophotometer. Deoxygenated solutions of iminium salts in acetonitrile (about 10^{-4} M) in 1-cm quartz fluorescence cells were used in attempts to observe room temperature fluorescence. Low-temperature attempts were made on a solution of **1c** (about 10^{-3} M) in H_2SO_4/TFA/acetic acid (2:2:1), which forms a glass at 77 K. The sample, in a quartz cell (3-mm o.d.), was cooled quickly in liquid N_2 and transferred to the sample compartment of the spectrophotometer, which was also cooled by liquid N_2. Luminescence was not observed in these experiments.

Quantum Yield Measurements. The optical bench consisted of a 150-W high-pressure xenon lamp, an IR filter, and a Jobin Yvon H.10 monochromator with a 16-nm band-pass isolating a 366-nm wavelength. The beam was collimated, filtered to remove higher order wavelengths of light, and then split with a glass plate set at 45° to the beam. A fraction of light was directed to a UV-enhanced silicon photodiode (EG&G Instruments UV 040 BQ) at 90° to the main beam (the comparison detector), the remainder being passed to the sample. A second photodiode placed behind the sample was the main detector. The diode signals were converted to digital output by a two-channel digital current integrator. The entire optical bench was housed in a light-tight box.

The comparison detector was calibrated by using ferrioxalate actinometry (0.06 M solution).[18] The solution absorbed all the incident light of the main beam. The calibrations were performed in duplicate for each series of experiments, ranging over a period of not more than 5 days, and were reproducible within 1%. The stability of the system was checked frequently during this period by measuring the ratio of light reaching the two detectors in the absence of a sample.

The sample cell used for the quantum yield measurements consisted of a cylindrical quartz cell, volume 0.5 mL, attached to a glass arm used for sample degassing. The iminium salt was weighed into the cell, dissolved in 0.5 mL of trifluoroacetic acid, and degassed with three freeze–pump–thaw cycles. After the third evacuation, dry N_2 was added to the cell, which was then closed by means of a Teflon stopcock. The samples were irradiated for periods of time corresponding to about 10% reaction, usually about 2 h. The sample compartment remained at room temperature during this time. After irradiation, about 0.3 mL of the sample was transferred to an NMR tube for analysis. During all manipulations, the samples were protected from room light. The irradiated solutions were stored in the refrigerator to avoid thermal reactions.

The quantum yields were measured for solutions of concentrations 0.04, 0.07, and 0.09 M. Salt **1f** was not soluble enough in TFA to allow a measurement at the highest concentration.

The quantum yield values were corrected for small amounts of isomers other than the *E,E* isomer present before irradiation. The quantum yields of salt **1d** are corrected for an impurity present in the salt, whose ^{1}H NMR spectrum contains a resonance that overlaps the resonance of H_1 of the *Z,E* isomer. The values are not corrected for back-reactions of the isomers produced during the irradiation. For the isomerization of **1f** the product composition observed at low conversion (<10%) remained essentially unchanged with frequent stirring of the solution during irradiation.

Other solvents used to measure quantum yields of isomerization of **1a** were 0.01 M sodium trifluoroacetate in TFA, 0.1 M sodium trifluoroacetate in TFA, and 0.1 M tetramethylammonium chloride in TFA. Quantum yields of isomerization of salt **1e** were measured in 0.01 M sodium trifluoroacetate in TFA and 0.03 M H_2SO_4 in TFA. Corrections for thermal isomerization that may have occurred during the sample manipulation were performed on these values.

The NMR method used to determine the quantities of each isomer present in the irradiated mixture was as follows. ^{1}H NMR spectra were obtained at room temperature and consisted of an average of at least 1200 scans. The detection limit is estimated at 0.5% under these conditions. The relative isomer amounts were measured as peak areas of the H_1 and H_3 doublets by cut and weigh. Insufficient resolution made it necessary to use the H_2 signals as well in some cases. The total peak areas were assumed to equal the quantity of *E,E* isomer initially used in the experiment; the amounts of each isomer were then determined from the relative areas of their respective peaks. The results were generally reproducible within 10%.

Photostationary States. Solutions of the iminium salts in TFA in NMR tubes were irradiated for 36 h or more in a Rayonet photoreactor containing 350-nm lamps (50-nm bandwidth). Isomer concentrations were determined from the H_1, H_2, and H_3 signals as outlined for the quantum yield measurements.

Cyclic Voltammetry. Spectra were recorded relative to a saturated calomel electrode (SCE) using an X–Y recorder.

All glassware and reagents were carefully dried prior to use. A solution of tetrabutylammonium perchlorate (150 mg, 0.1 M) in acetonitrile (3 mL) was degassed with a stream of argon, previously saturated with acetonitrile. After a background spectrum was recorded, the iminium salt (3 mg, 3×10^{-3} M) was added to the solution, which was again degassed. The reduction wave was recorded over the range +0.3 to −1.5 V at a scan rate of 0.5 V/s.

Electron-Transfer Experiment. A solution of tris(2,2′-bipyridine)ruthenium(II) dichloride[19] (**5**), in acetonitrile (10^{-5} M) was degassed by bubbling acetonitrile-saturated nitrogen through the solution. Luminescence of the solution was observed by irradiating at 480 nm; λ_{max} of the emission was 600 nm. Addition of 10^{-3} M iminium salt **1f** resulted in partial quenching of this luminescence peak.

At higher concentrations, the isomerization reaction of **1f** in the presence of the electron donor was followed by ^{1}H NMR. In the absence of light, **5** did not decompose in TFA; neither was the rate of thermal isomerization of **1f** enhanced by **5**. A light-induced decomposition of **5** was observed, although much slower than the isomerization reaction.[20] Iminium salt **1f** (5 mg, 4.5×10^{-2} M) and **5** (5 mg, 2.6×10^{-2} M) were dissolved in 0.3 mL of TFA in an NMR tube and irradiated with light of wavelength >425 nm. This was achieved by using a high-pressure 150-W xenon lamp and two cutoff filters. The peak height of the *N*-methyl signal of the *E,E* isomer of **1f** relative to the sum of the peak heights of the *N*-methyl signals of the *E,E* and *Z,E* isomers was used to determine percent composition of the mixture.

Registry No. **1a**, 98587-62-3; **1b**, 98587-64-5; **1c**, 98587-66-7; **1d**, 98587-68-9; **1e**, 98587-70-3; **1f**, 98587-72-5; **1g**, 98587-74-7; **1h**, 98587-76-9; **1i**, 98587-78-1; **2a**, 98587-80-5; **2b**, 98587-82-7; **2c**, 98587-84-9; **2d**, 98587-86-1; **2e**, 98587-88-3; **2f**, 98587-90-7; **2g**, 98587-92-9; **2h**, 98587-94-1; **2i**, 98587-96-3; **3a**, 114582-10-4; **3b**, 114582-12-6; **3c**, 114582-14-8; **3d**, 114582-16-0; **3e**, 114582-18-2; **3f**, 114582-20-6; **3g**, 114582-22-8; **3h**, 114582-24-0; **3i**, 114582-26-2; **4a**, 114582-28-4; **4b**, 114582-30-8; **4c**, 114582-32-0; **4d**, 114582-34-2; **4e**, 114582-36-4; **4f**, 114582-38-6; **4g**, 114582-40-0; **4h**, 114582-42-2; **4i**, 114582-44-4; **5**, 14323-06-9; **6**, 114582-46-6.

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