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Photochemical and Thermal Stereomutations of 3-Aryl-2-propenylideniminium Salts[1]

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Abstract: The photochemical and thermal stereomutations of some 3-aryl propenylideniminium salts have been examined. Salts **1**–**7** in trifluoroacetic acid solution undergo efficient cis/trans isomerization about the C═C bonds on irradiation. These reactions involve singlet excited states of the iminium salts. Photoisomerization also occurs about the C═N bonds of **6** and **7**, although the quantum efficiencies of these isomerizations were very much less than those about the C═C bonds. The thermally induced isomerizations of **9**–**13** to **1**–**5**, respectively, were examined in trifluoroacetic acid and trifluoroacetic/sulfuric acid mixtures. A Hammett σ^+ correlation of the rate constants of these isomerizations as a function of the aryl substituent was markedly curved, indicating that at least two mechanisms were involved in these reactions. With variation of acid strength and the use of deuterated acids it was shown that the stereomutations take place by a Michael type nucleophilic addition when the aryl substituents are electron withdrawing and by protonation at nitrogen with electron-donating aryl substituents. This latter mechanism was confirmed by examination of deuterium exchange at nitrogen of some related *n*-butyliminium salts.

Unsaturated iminium salts are important compounds. They have commercial significance, for example in the cyanine dyes, and biological importance in the visual pigments. The chromophore of the visual pigment rhodopsin consists of 11-*cis*-retinal that is bound by a Schiff base linkage to the apoprotein opsin.[2] It is generally accepted that the Schiff base nitrogen is protonated[3] and that the primary photochemical event in the natural pigment involves the cis to trans isomerization of the $C_{11}C_{12}$ bond of the chromophore.[4]

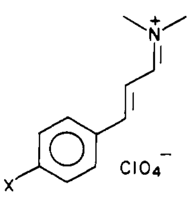
In contrast to the extensive work on the chemistry of the visual pigments, comparatively little work has been reported on the photochemistry of simpler unsaturated iminium salts. Cis/trans isomerizations about C═C bonds conjugated with the iminium function have been observed.[5,6] In addition we have recently shown that photoisomerization also takes place about the C═N bonds of these salts.[6] The photocyclization of protonated benzalaniline to protonated phenanthridine presumably also involves an initial isomerization about the C═N bond.[7] Mariano and co-workers have recently reported a series of photoreactions of iminium salts that involve electron transfer as a key step.[8]

The mechanisms of the thermally induced stereomutations about the C═C bonds of unsaturated iminium salts have also received little attention.[9] This is surprising in view of the importance of such reactions in iminium salts. For example, bacteriorhodopsin, the light-harvesting pigment of *Halobacterium halobium*, in the dark-adapted state contains the 13-cis and all-trans forms of the retinal iminium salt chromophore in thermal equilibrium.[10] Solution studies of this system have been reported, but the results are difficult to interpret.[11]

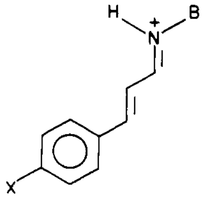
In this paper we report a quantitative study of the photochemically induced cis/trans isomerizations of some 3-arylpropenylideniminium salts. This photoisomerization allows the ready generation of solutions of the salts that contain substantial amounts of the less-stable cis isomers. Taking advantage of this simple preparative method, we have undertaken a study of the ground-state stereomutations of these unsaturated iminium salts. By combining substituent effects with solvent dependencies, it has been possible to define the mechanisms of these cis to trans isomerizations.[12]

Results and Discussion

The salts **1**–**5** were prepared by reacting the appropriately substituted cinnamaldehyde with dimethylammonium perchlorate.



1, X = H
2, X = OCH_3
3, X = CH_3
4, X = Cl
5, X = NO_2



6, X = H
7, X = NO_2
8, X = OCH_3

Solutions of **6**, **7**, and **8** were obtained by dissolution of the corresponding imines in trifluoroacetic or sulfuric acid. The ^{1}H NMR spectra of these iminium salts are given in Table I. The structures of **1** and **2** have been obtained by X-ray crystallography.[13] Both cations were shown to exist in s-trans conformations and with little delocalization of the positive charge from nitrogen onto the carbon framework. The s-trans conformation was also shown to be preferred for these cations in solution.

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Table I. ^{1}H NMR Data for Iminium Salts

	chemical shift,^{a,b} ppm							coupling constant, Hz		
compd	H_1	H_2	H_3	aryl H	NH	N group	other	$J_{1,2}$	$J_{2,3}$	$J_{N,1}$
1	8.20 d	7.08 dd	7.79 d	7.34 dd, 7.43 d, 7.60 d		3.50 s, 3.59 s		10.6	15.3	
9	8.26 d	6.26 t	7.97 d	7.27 dd, 7.35 d, 7.44 d		3.53 s, 3.61 s		10.4	11.1	
2	8.09 d	6.92 dd	7.71 d	6.92 d, 7.61 d		3.45 s, 3.54 s	3.82 s	10.8	14.8	
10	8.25 d	6.41 t	7.86 d	6.98 d, 7.13 d		3.48 s, 3.60 s	3.83 s	10.8	10.8	
3	8.13 d	7.01 dd	7.74 d	7.16 d, 7.44 d		3.47 s, 3.56 s	2.26 s	10.8	14.8	
11	8.26 d	6.47 t	7.92 d	7.18 s		3.50 s, 3.60 s	2.26 s	10.8	10.8	
4	8.20 d	7.05 dd	7.73 d	7.30 d, 7.52 d		3.50 s, 3.59 s		10.8	14.9	
12	8.25 d	6.56 t	7.89 d	7.31 d, 7.34 d		3.53 s, 3.62 s		10.5	11.0	
5	8.36 d	7.29 dd	7.86 d	7.81 d, 8.20 d		3.60 s, 3.67 s		10.2	15.5	
13	8.30 d	6.79 t	7.97 d	7.50 d, 8.21 d		3.60 s, 3.67 s		10.3	11.4	
6	8.25 dd	7.06 dd	7.75 d	7.32 dd, 7.42 d, 7.52 d	9.2 bd	3.70 q, 1.68 m, 1.32 m, 0.85 t		10.3	15.5	17.2
11	8.25	7.20 dd	7.88 d	7.32 dd, 7.42 d, 7.61 d	9.2 bd	3.75 q, 1.68 m, 1.32 m, 0.85 t		11.0	15.3	
16	8.42 dd	6.58 t	7.90 d	7.24 dd, 7.35 d, 7.42 d	9.2 bd	3.70 q, 1.68 m, 1.32 m, 0.85 t		10.3	10.3	17.2
7	8.43 dd	7.23 dd	7.83 d	7.73 d, 8.20 d	9.2 bd	3.77 q, 1.71 m, 1.33 m, 0.85 t		9.8	15.9	16.5
15	8.43 dd	7.39 dd	7.98 d	7.82 d, 8.23 d		3.84 t, 1.71 m, 1.33 m, 0.85 t		10	14.6	11
17	8.45 dd	6.80 t	7.92 d	7.48 d, 8.22 d		3.8 t, 1.71 m, 1.33 m, 0.85 t		11	11	
18	8.45 dd	6.93 t	8.12 d	7.5 d, 8.2 d		3.8 t, 1.71 m, 1.33 m, 0.85 t		11	11	
8	8.12 dd	6.92 dd	7.67 d	7.54 d, 6.92 d	9.2 bd	3.64 t, 1.66 m, 1.31 m, 0.85 t		9.8	14.7	15.9

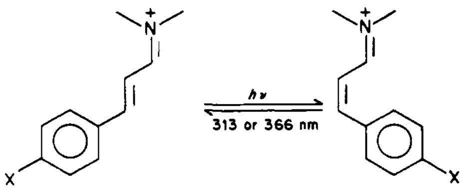
[a] bd = broad doublet, d = doublet, dd = doublet of doublets, q = quartet, dq = doublet of quartets, s = singlet, t = triplet, m = multiplet.
[b] In ppm from $(CH_3)_4N^+BF_4^-$ (3.10 ppm) in TFA solution.

Table II. UV Spectra of Iminium Salts

compd	solvent	λ_{max}, nm	log ε
1	TFA	341	4.4
2	TFA	384	4.6
3	TFA	359	4.6
4	TFA	350	4.5
5	TFA	323	4.4
6	H_2SO_4	340	4.9
7	H_2SO_4	335	4.4

The UV spectra of these salts are given in Table II. Absorption maxima are intense and range from 323 to 384 nm depending on the ring substituent. The high intensity of these bands suggest they are of π,π^* character. Attempts were made to observe fluorescence emission of **1** at room temperature in 98% H_2SO_4 and at 77 K in an acid glass (3:1, v/v, methanesulfonic/*n*-propanesulfonic acids[14]). No emission could be detected in either medium.

Photoisomerization: Qualitative Observations. Irradiation of salts **1–5** in TFA solutions at 313 and/or 366 nm led to the formation of a single photoproduct in each case. The reactions were monitored by ^{1}H NMR spectroscopy at 250 or 400 MHz, and the products were identified as the corresponding cis isomers **9–13**. This identification was based on the very close similarity of the ^{1}H NMR spectra of the photoproducts to those of the starting salts and the magnitudes of the coupling constant between H_2 and H_3, Table I. The products were shown to be thermally stable under the conditions used for the irradiations. A photostationary state was set up in each case after some 4–24 h irradiation, Table III.



9, X = H
10, X = OCH_3
11, X = CH_3
12, X = Cl
13, X = NO_2

Table III. Photostationary-State Compositions

starting salt	irradiation λ, nm	products, %
1	313	1 (43), 9 (57)
2	366	2 (48), 10 (52)
3	313	3 (53), 11 (47)
4	313	4 (38), 12 (62)
5	313	5 (59), 13 (41)
6	313	6 (53), 6 (47)^a
7	313	7 (35), 17 (40), 18 (10), 15 (15)

[a] This is not a true photostationary state; see text.

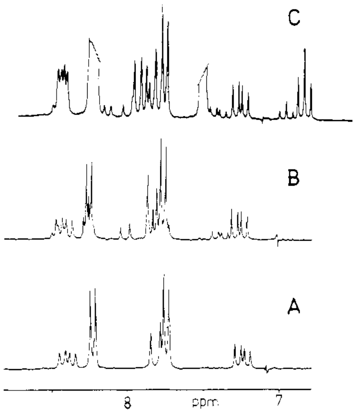


Figure 1. ^{1}H NMR spectra of (A) salt **7**, (B) salt **7** after heating, and (C) salt **7** after irradiation (note: spectrum C is obtained in TFA-*d*).

In the cases of **6** and **7** the photoisomerizations are potentially more complex as isomerism about both the C=C and C=N bonds could lead to mixtures containing up to four isomers. The corresponding C=N isomers of **6** and **7** could be produced by heating solutions of these cations in acid solution, Figure 1. In each case an equilibrium was established at 100 °C with some 20% of an additional isomer present in solution. Identification of these isomers as **14** and **15**, respectively, was made on the basis of their ^{1}H NMR spectra, which displayed a characteristic coupling constant of 11 Hz between H_1 and the NH protons, Table I. At room temperature the thermal interconversions of these C=N stereoisomers was slow and could be neglected in comparison with the rates of the photochemical reactions.

Irradiation of a solution of **6** in TFA appeared initially to lead to the production of a single photoisomer. This photoproduct had a different ^{1}H NMR spectrum to that of **14**. This new product

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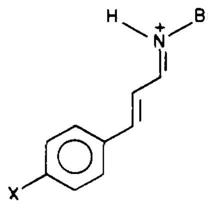
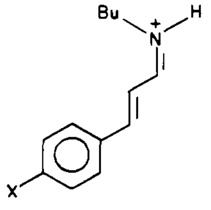
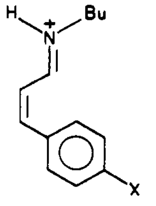


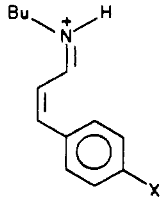
6, X = H
7, X = NO_2



14, X = H
15, X = NO_2



16, X = H
17, X = NO_2



18, X = NO_2

was identified as **16** on the basis of the coupling constant across the C=C bond, Table I. The situation with **7** was more complicated. As can be seen from Figure 1C, a complex ^1H NMR spectrum was obtained on irradiation. Two of the materials present could be identified readily as **7** and its C=N isomer **15**. Two additional cations also appeared to be present that were closely related to **7** and **15**. This is evident, for example, in the 6–7 ppm region of the ^1H NMR spectrum (Figure 1C), where two additional resonances associated with H_2 proton resonances can be seen. By systematic decoupling of the spectrum it was possible to identify all the vinyl proton resonances of these two additional products and obtain the various coupling constants. On the basis of coupling constants the additional products were identified as **17** and **18**, Table I. The results obtained with **7** prompted us to return and examine the irradiation of **6** for extended periods of time. On irradiation of **6** for periods exceeding 1 week it was possible to detect small amounts of the corresponding cis C=N isomers. A photostationary state did not seem to have been reached in this time.

Photoisomerization: Quantitative Aspects. The quantum yields for the photoisomerizations of **1–7** to **9–13**, **16**, and **17**, respectively, were measured. Quantitative analyses were carried out by ^1H NMR spectroscopy directly on the irradiated acid solutions. In all cases the reactions were carried out to less than 10% conversion, and the values obtained corrected for back reaction. The quantum yields obtained are summarized in Table IV. All the quantum yields reported are for aerated solutions. Degassing with a nitrogen purge had no effect on the efficiency of these reactions.

As it has not yet proved possible to synthesize the pure cis isomers **9–13**, no direct measurement of the quantum yield for the reverse cis to trans photoisomerizations could be made. Values for the quantum efficiency of the conversion of **9** → **1** and **13** → **5** were estimated from the composition of the photostationary state, Table III, the quantum yields for the forward reactions, and the extinction coefficients of the various isomers. The extinction coefficients of **9** and **13** at 313 nm were obtained by difference spectroscopy of solutions of **1** and **5** with photostationary state mixtures of **1** and **9** and **5** and **13**, respectively.

In the case of the photoisomerization of **7**, where both C=N and C=C bond isomerization is observed at the photostationary state, attempts were made to measure the quantum yields for isomerization about the C=N bond. Even after conversion of some 20% of **7** to **17**, it was not possible to detect any of the C=N isomers **15** and **18** in the solutions (detection limit by ^1H NMR spectroscopy 2%). This means that the quantum yield for the conversion of **7** to **15** must be <0.05.

The quantum yield for the conversion of **1** to **9** was measured at two wavelengths. No significant difference was observed on irradiation at 313 or 365 nm, Table III.

Discussion of Photochemical Results. Photoisomerization can in principle occur about both the C=C and C=N bonds of these iminium salts. Efficient isomerization about the C=C bonds was observed on irradiation of all the salts, and a photostationary state was reached in each case. The compositions of these photostationary states were quite different from the thermodynamic ratio of products. For most of these iminium salts photoisomerization about the C=N bond could not be detected because of the dimethyl substituents on the nitrogen atoms. Salts **6** and **7** are unsymmetrically substituted at nitrogen, and in both cases photoinduced isomerizations about the C=N bond were detected. However, it is clear that isomerization about the C=C bond occurs much more efficiently than about the C=N bond. Indirect evidence to suggest that a similar preference for photoisomerization about the C=C bonds of the *N,N*-dimethyl substituted salts comes from a consideration of the quantum yields for the trans to cis and cis to trans reactions of **1** and **9**, Table III. The sum of these two quantum yields is very close to 1 ($\phi_{1\to9} + \phi_{9\to1} = 1.05 \mp 0.08$), which leaves little room for the occurrence of photoisomerization about the C=N bond. The only system where there appears to be a sizeable quantum yield of C=N isomerization appears to be with the *p*-nitro-substituted salts **5** and **13**. In this case the quantum yields for the isomerizations about the C=C bonds only sum to 0.6 ($\phi_{5\to12} + \phi_{12\to5} = 0.60 \mp 0.05$), and in the absence of any emission it is suggestive that the remaining energy results in C=N isomerization.

Table IV. Quantum Yields for Isomerization of Iminium Salts

reaction	excitation λ, nm	quantum yield[a,b]
6 → 16	313	0.58 ± 0.06
1 → 9	313	0.60 ± 0.06
1 → 9	366	0.75 ± 0.08
9 → 1[c]	313	0.45 ± 0.05[c]
2 → 10	366	0.59 ± 0.04
3 → 11	313	0.52 ± 0.05
4 → 12	313	0.58 ± 0.09
5 → 13	313	0.27 ± 0.02
13 → 5[c]	313	0.33 ± 0.03[c]
7 → 17	313	0.47 ± 0.05

[a] Errors are standard deviation of 3–4 runs. [b] Measured relative to the photodecomposition of potassium ferrioxalate, reactions have been corrected for back reaction. [c] Calculated value, see text.

The excited states involved in these reactions are of π,π^* character and are likely singlet states. Oxygen was shown to have no discernable effect on the efficiencies of the photoisomerizations pointing to the involvement of either singlet or very short lived triplet states. The very large difference in the quantum yields for isomerization about the C=C and C=N bonds of **7** indicates that these reactions are not coupled as might be expected for triplet reactions.[15] Mariano and co-workers have also found that the electron-transfer reactions of related iminium salts involve singlet states.[8]

The most likely pathway for the photoisomerizations of these unsaturated iminium salts would seem to involve a photochemically induced rotation about either the C=N or C=C bond. Electron-transfer reactions are unlikely under the conditions used in these reactions, and it is difficult to account for the efficient formation of substantial amounts of the thermodynamically less-stable cis isomers with radical cation intermediates.

For singlet excited states, where isomerizations about the two double bonds are uncoupled, one can think of the two possible rotations as competing processes. The originally produced vertically excited singlet state can relax by either rotation about the C=N or C=C bonds to give two distinct twisted excited states. Relaxation of these to the ground-state energy surface would lead to stereomutation about either but not both bonds. The partitioning of the initially formed vertically excited iminium salt between these two possible paths will depend on the shape of the

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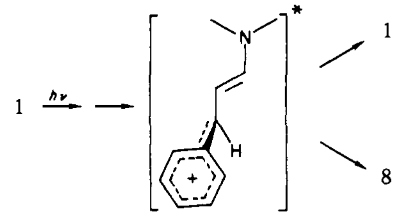
Table V. Isomerization Rate Constants at 100 ± 0.5 °C

reaction	substituent[a]	$k \times 10^6$, s^{-1} TFA	$k \times 10^6$, s^{-1} TFA/H_2SO_4
9 → 1	H	1.6[b]	0.94
10 → 2	OCH_3	2000	6200
11 → 3	CH_3	4.6	29
12 → 4	Cl	2.0	0.94
13 → 5	NO_2	19	3.1

[a] Substituent on phenyl ring. [b] Error ±10%.

excited-state energy surface and this presumably will reflect the relative energies of the two possible twisted excited states.

Salem and Bruckmann[16] have suggested that rotation about the C=C bond of an excited unsaturated iminium salt will lead to a large charge redistribution with the positive charge moving from nitrogen to the other end of the ion, eq 1. Evidence to suggest the correctness of this charge polarization in the twisted π,π^* excited states of the related protonated enones has recently been reported.[17] The relative energy of a twisted, charge-polarized excited state of these iminium salts would be expected to be dependent on the nature of the substituents on the phenyl ring. It is interesting in this regard that the *p*-nitro-substituted salts **5**/**13** are the only systems in which there could be an appreciable amount of C=N isomerization occurring in competition with C=C rotation. A twisted species such as is shown in eq 1 with charge localized on the phenyl end of the ion would be a relatively high-energy species when the ring is nitro substituted.



(1)

Thermal Isomerizations. The isomerizations of solutions of salts **9**–**13** to the corresponding trans isomers **1**–**5**, respectively, were examined in trifluoroacetic acid (TFA) and in a solution of 0.015 M H_2SO_4 in TFA. In each case a photostationary state was generated photochemically, the solutions were heated to 100 ∓ 0.5 °C to cause the isomerizations to proceed, and the reactions were monitored by ^1H NMR spectroscopy at 34 °C. Good first-order kinetics were observed in each case. The results are summarized in Table V.

The rate constants of these C=C bond isomerizations of these iminium salts are dependent on the nature of the substituent on the phenyl ring. The relationship is not a simple one, however, as both electron-donating and -withdrawing substituents increase the rate relative to the unsubstituted ion. This is clearly shown in a Hammett type correlation with σ^+, Figure 2.[18] The large change in slope of the Hammett plot as a function of substituent change is indicative of a change in mechanism in this series of salts.

The observed Hammett correlation can be broken down into two distinct regions. The data for the isomerization of **10** and **11** to **2** and **3**, respectively, lie on a steep, negatively sloping region ($\rho = -5.6$), implying that in the transition state for the rate-limiting step there is a large decrease in the electron density in the C_3-phenyl moiety. On the other hand, the data for **9**, **12**, and **13** lie in a region with a shallow positive slope ($\rho = 1.4$), indicating a modest increase in the electron density at the C_3-phenyl grouping in the transition state for stereomutation of these salts. It would seem that two completely different mechanisms must be operative in the cis to trans isomerizations of these closely related salts.

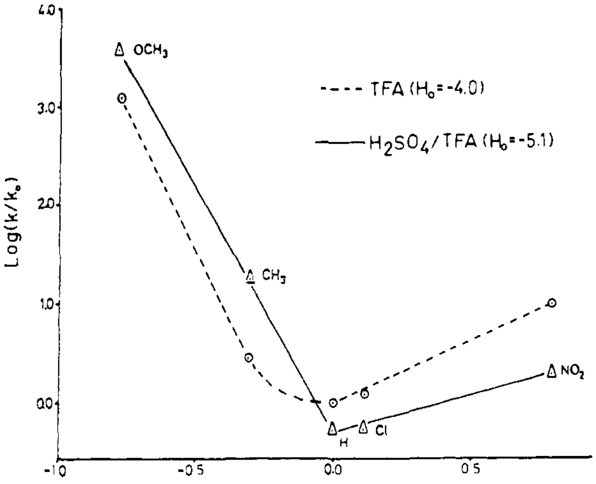
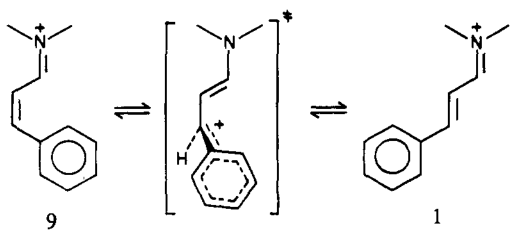
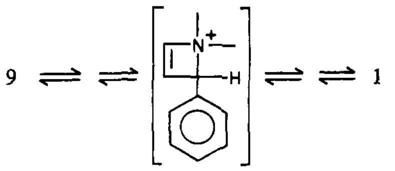


Figure 2. Hammett σ^+ plot for the rate constants determined in TFA (---) and H_2SO_4/TFA (—). (The latter values are plotted with log *k*(H) in TFA as the reference point so as to show the changes in rate constant on increase in acidity.)

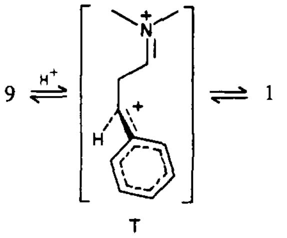
Possible Mechanisms. Several different broad types of reaction mechanism can be considered for these isomerizations. There are two intramolecular paths, bond rotation, eq 2, and azetinium formation, eq 3. Intermolecular possibilities involve protonation at either C_2 or at nitrogen, eq 4 and 5, respectively, and a Michael addition route, eq 6.[19]



(2)



(3)



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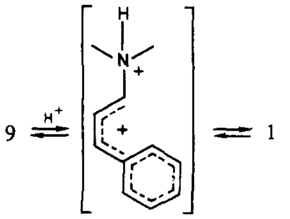

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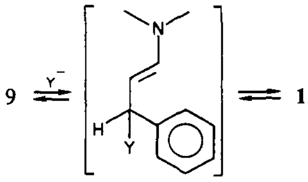

(6)

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[17] Childs, R. F.; DiClemente, T.; Lund-Lucas, E. F.; Richardson, T. J.; Rogerson, C. V. *Can. J. Chem.* **1983**, *61*, 856.

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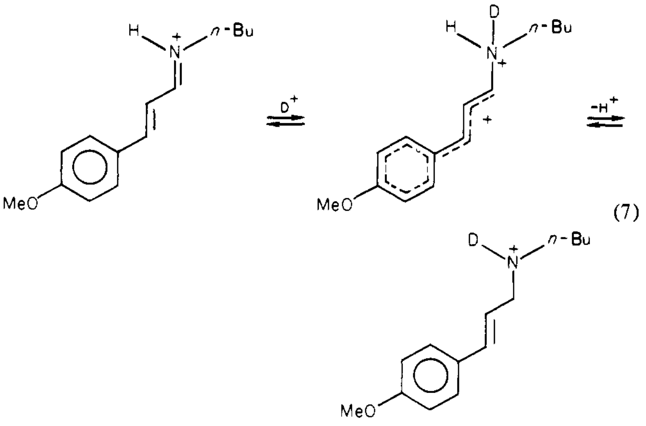
The charge distribution shown in the transition state for the rotation mechanism, eq 2, seems the most likely and is supported by MINDO/3 calculations.[12] The two mechanisms involving protonation at C_2 or N to give dications would also lead to a decrease in the electron density at the C_3-phenyl grouping. Cyanine dyes are known to protonate at C_2 in aqueous sulfuric acid,[20] and Hammond and Newman[21] have proposed a mechanism involving protonation at nitrogen to account for the isomerization of amidinium salts in acid media. All of these mechanisms would be expected to show a Hammett σ^+ correlation with a steeply negative slope. In contrast, the ring closure route, eq 3, and Michael addition pathway, eq 6, would both be expected to give a correlation with σ^+ with a positive slope. The data obtained for the isomerization of salts **10** and **11** are consistent with either the operation of the rotation or the two protonation mechanisms, whereas the data for salts **9**, **12**, and **13** are consistent with isomerization proceeding via the ring closure or Michael addition routes.

Two approaches were used to differentiate between these various possibilities. The first of these involved variation in the acidity of the acid medium. The addition of sulfuric acid to TFA enhances the acidity of the medium and should correspondingly reduce its basicity. The acid strengths of the TFA and 0.015 M H_2SO_4 in TFA used in these studies was measured on the H_0 scale at 25 °C with 2,4-dinitroaniline as an indicator. Values of −4.0 and −5.1 were found for TFA and H_2SO_4/TFA, respectively. The value obtained for 0.015 M H_2SO_4 in TFA agrees well with that previously found.[22] However, the value obtained for TFA itself is considerably lower than that reported.[23] The important point, however, is not the absolute magnitudes of H_0 of the acids used in this study but that the H_2SO_4/TFA medium is a stronger acid than TFA. The kinetic results were obtained at 100 °C, and while the relative acidities of the acids will be maintained, the absolute acidities will be different from those measured at 25 °C.[24]

Kinetic data obtained for the isomerizations of salts **9**–**13** in the TFA/H_2SO_4 mixture are summarized in Table V. Again in all cases good first-order kinetics were observed. The results are also plotted in Figure 2. As can be seen from these data, the rate constants for the isomerizations of **10** and **11** are increased in the more acidic medium. Such a result is inconsistent with a simple rotation mechanism where solvent acidity changes should have little effect and points to the involvement of a protonation mechanism. On the other hand, the rate constants for isomerization of salts **9**, **12**, and **13** are all decreased in the more acidic medium. Medium acidity would be expected to have little effect on the rate of isomerization if it proceeded by the ring closure route, eq 3. However, such a reduction would be expected for the Michael addition route, eq 6, and this medium dependence suggests that this mechanism is operative with these salts in TFA.[25]

To differentiate between the two protonation type mechanisms, the isomerizations of **10** and **11** were studied in deuterated TFA and TFA/D_2SO_4. The rates of deuterium exchange of both salts were found to be very much slower than those of the isomerization reactions. On prolonged heating some exchange of H_2 and the aryl protons in **2** were observed, but in neither case was exchange at C_2 found to occur during the course of the isomerizations. This result rules out the possibility that the pathway for the isomerization of **10** and **11** involves protonation at C_2 and by elimination suggests that nitrogen protonation is involved.

The possibility of protonation at nitrogen was examined with **8**. The nitrogen basicity of this salt would be expected to be similar to that of the *N,N*-dimethyl salts studied above. Dissolution of this salt in deuterated TFA or TFA/D_2SO_4 resulted in an exchange of the NH proton for deuterium. These reactions could be followed by ^1H NMR at 34 °C and complete exchange, 5 half-lives, occurred in 45 min in TFA and was complete by the time the NMR spectrum of **8** was obtained (<15 min) in TFA/D_2SO_4. The acceleration of this exchange process in the stronger acid indicates that exchange is occurring by a protonation rather than a deprotonation mechanism, eq 7. These exchange reactions took place at 34 °C whereas the isomerizations were run at 100 °C. Thus exchange at nitrogen of **8** is much faster than the rate of the isomerization of **10**. As **8** can be considered as a good model for **10**, this result strongly suggests that protonation at nitrogen is the mechanism of the isomerization of **10** and **11**.



(7)

In conclusion we have shown that the thermally induced cis to trans isomerization in the unsaturated iminium salts studied here occurs either by protonation at nitrogen or by addition of a nucleophile to C_3. The acid media used in this study are relatively strong, and it is likely in less acidic media that nucleophilic addition mechanisms predominate. A further point to note is that certain thermal isomerizations of protonated enones in superacid media have frequently been suggested to occur via a C_2 diprotonation mechanism.[26] The results of this study suggest that this postulate should be reexamined.

Experimental Section

General. TFA was distilled from concentrated H_2SO_4 and stored in a dried container in a drybox. TFA-*d* was obtained commercially and used as obtained. Methanesulfonic and *n*-propanesulfonic acids were distilled under vacuum twice and stored in reacti-flasks. ^1H NMR spectra were obtained at 250 MHz on a Bruker WM 250 spectrometer or at 400 MHz on a Bruker WH 400 spectrometer. This latter instrument is located at the Southwestern Ontario Regional NMR Centre at the University of Guelph, Guelph, Ontario. Tetramethylammonium tetrafluoroborate ($(CH_3)_4N^+BF_4^-$, δ 3.10) was used as an internal standard and sample concentrations ranged from 0.25 to 0.75 M.

Preparation of Salts 1–5. These were prepared by the same general method.[27] The appropriately substituted cinnamaldehyde (16 mmol) and dimethylammonium perchlorate (16 mmol) were dissolved in methanol (15 mL) and stirred overnight. The resulting yellow crystals were isolated by vacuum filtration and recrystallized from methanol to constant melting point. Yields, analyses, etc. are given in Table VI.

***trans,trans*-*N*-*n*-Butyl-3-phenyl-2-propenylidenimine (19)** was prepared[28] by adding cinnamaldehyde (16 mmol) dropwise to a stirred, cooled mixture of *n*-butylamine (38 mmol) and anhydrous K_2CO_3 in anhydrous ether (30 mL). After the addition was complete the mixture was warmed to room temperature and stirred for 4 h. The mixture was

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[19] A further mechanism that could be considered involves the formation of a cyclopropyl cation and subsequent ring opening. This process, which energetically seems unlikely, has been ruled out in the case of the analogous isomerizations of protonated enones (Childs, R. F.; Lund, E. F.; Marshall, A. G.; Morrisey, W. J.; Rogerson, C. V. *J. Am. Chem. Soc.* **1976**, *98*, 5924).

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[21] Hammond, G. S.; Newman, R. C., Jr., *J. Phys. Chem.* **1963**, *67*, 1655, 1659.

[22] Hyman, H. H.; Garber, R. A. *J. Am. Chem. Soc.* **1959**, *81*, 1847.

[23] Eaborn, C.; Jackson, P. M.; Taylor, R. *J. Chem. Soc.* **1966**, 613.

[24] Johnson, C. D.; Katritzky, A. R.; Shapiro, S. A. *J. Am. Chem. Soc.* **1969**, *91*, 6654.

[25] No deuterium incorporation was observed when the isomerizations of **9**, **12**, and **13** were carried out in TFA-*d*. Nitrogen protonation of the enamine intermediate proposed in the isomerization is likely very rapid. It would appear that C protonation and consequent exchange of the C_2 proton is slow compared to reionization of the enamine to form the iminium salts.

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Table VI. Some Physical Data and Elemental Analyses for the Imines and Iminium Salts

			str freq, cm^{-1}			calcd, %			found, %		
compd	mp, °C	% yield	$\nu_{C=N}$	$\nu_{C=C}$	mol form.	C	H	N	C	H	N
6	*a*	75	1635	1618	$C_{13}H_{17}N$	83.37	9.15	7.48	83.02	9.22	7.91
7	63-64	50	1640	1625	$C_{13}H_{16}N_2O$	67.22	6.94	12.06	67.54	7.00	12.39
1	132-133	95	1655	1611	$C_{11}H_{14}NClO_4$	50.88	5.43	5.39	50.88	5.52	5.28
2	155-156	50	1662	1581	$C_{12}H_{16}NClO_5$	49.75	5.57	4.83	49.73	5.72	4.60
3	150-151	75	1663	1615	$C_{12}H_{16}NClO_4$	52.66	5.89	5.12	52.32	6.05	4.97
4	144-145	69	1660	1618	$C_{11}H_{13}NCl_2O_4$	44.92	4.45	4.76	45.08	4.53	4.82
5	165-166	60	1670	1620	$C_{11}H_{13}N_2ClO_6$	43.36	4.30	9.19	43.51	4.37	8.96

[a] Liquid.

filtered, the ether removed from the filtrate, and the residue distilled to give **19** (bp 150 °C (2 mm)) in 75% yield.

***trans*,*trans*-*N*-*n*-Butyl-3-(*p*-nitrophenyl)-2-propenylidenimine (20)** was prepared as **6** above except instead of distilling the residue it was chromatographed on neutral alumina (eluting with 10% ether in petroleum ether). Yield 50%, physical properties are listed in Table VI.

Fluorescence Measurements. The emission spectrum of **1** was measured with an Aminco-Bowman spectrophotofluorometer (American Instrument Co. Inc.) equipped with an Aminco xenon lamp power supply (Part No. 422-829). The output from this instrument was fed into a Hewlett-Packard Model 7047A X-Y recorder. An excitation wavelength of 313 nm was employed, and the sample emission was monitored from 320 to 600 nm. Samples were prepared such that they had an absorbance of 1.0 at 313 nm. Room temperature fluorescence spectra were obtained in a 98% H_2SO_4 solution with a standard 10-mm quartz fluorescence cell. Spectra at 77 K were measured in a rigid acid glass (3:1 mixture by volume of methanesulfonic and *n*-propanesulfonic acids[14]) by using a thin quartz tube cooled in a partially silvered quartz Dewar filled with liquid nitrogen. There was no detectable emission at either of these temperatures.

Photoisomerizations were carried out by irradiating solutions of the iminium salts in thin-wall NMR tubes. Concentrations of the salts were typically 0.5 M and the volume of acid (TFA or H_2SO_4) was that normally used in an ^{1}H NMR experiment. Irradiations were carried out at 30 °C in a Rayonet Photoreactor equipped with either 300- or 350-nm lamps. The course of the reactions was followed by ^{1}H NMR spectra run directly on the acid solutions.

Quantum Yield Measurements. The light source used in these measurements was an Osram HBO 200-W high-pressure mercury lamp placed into a Bausch and Lomb SP-200 housing. This was coupled with a Bausch and Lomb monochromator (Catalog No. 33-86-07) with entrance and exit slits set for a 20-nm bandwidth. The collimated beam was passed through a beam splitter inside a light-tight box. Samples were contained in quartz cells. The samples were prepared by weighing the imine or iminium salt (25–40 mg) into the sample container and dissolving in TFA (0.5 mL).

The quantum yield for the conversion of **1** to **9** was measured at 313 nm with potassium ferrioxalate actinometry. The percent conversion, in all cases, was less than 10% and was corrected for back reaction. After irradiation an aliquot was pipetted from the sample holder and placed in a 5-mm NMR tube for 400-MHz ^{1}H NMR assay. This assay was determined by the measurement of the relative areas (a cut and weigh technique was used) of the signals due to the H_1 proton for **1** and **9** at δ 8.20 and 8.26, respectively. In this case and all those mentioned below at least three separate runs were performed, and the ratio for the beam splitter was measured after every other run. Quoted errors are standard deviations calculated from these values.

Quantum yields for the conversions of **3** to **11**, **4** to **12**, **5** to **13**, **6** to **15**, and **7** to **17** were determined at 313 nm, and the yields for the conversions of **1** to **9** and **2** to **10** were measured at 366 nm. These values were determined by an analogous procedure to that described above. Except for the conversions of **5** to **13** and **7** to **17**, the compositions were monitored by the same method as above (resonances at δ 8.09 and 8.25 of **2** and **10**, respectively, δ 8.13 and 8.26 of **3** and **11**, respectively, δ 8.20 and 8.25 of **4** and **12**, respectively, and δ 8.25 and 8.42 of **6** and **15**, respectively). In the cases of **5** and **13** and **7** and **17**, the composition was monitored by the measurement of the relative areas of the signals due to the $H_{6,8}$ protons of **13** and **17** (δ 7.50 and 7.48, respectively) and the resonances of the H_2 protons of **5** and **7** (δ 7.29 and 7.23, respectively). Correction was made for the relative number of protons involved for each resonance.

The quantum yields for the conversions of **9** to **1** and **13** to **5** were calculated with the equation

$$\phi_{t\to c}C_t\epsilon_t = \phi_{c\to t}C_c\epsilon_c$$

where $\phi_{t\to c}$ are the quantum yields for the conversion of the trans to cis isomer (**1** to **9** and **5** to **13**), $\phi_{c\to t}$ are the yields for the reverse reaction (**9** to **1** and **13** to **5**), C_t and C_c are the concentrations at the photostationary state of the trans and cis isomers, respectively, and ϵ_t and ϵ_c are the corresponding molar extinction coefficients at the appropriate wavelength.

The molar extinction coefficient of **1** at 313 nm (ϵ_t 5750 cm^{-1} M^{-1}) was determined from its absorption spectrum whereas the value for **9** (ϵ_c 6220 cm^{-1} M^{-1}) was estimated from the absorption spectrum of the photostationary-state mixture. The low-energy absorption bands for **1** and **9** were superimposed. It was assumed that the absorbance at 313 nm was due to the sum of the absorbances for the two isomers. The relative concentrations of **1** and **9** at the stationary state had been determined by ^{1}H NMR assay so that the extinction coefficient of **9** could be calculated and hence the quantum yield. This procedure was repeated and the two values averaged to give the quantity reported in Table IV. The error was estimated at ±10%. A value for the conversion of **13** to **5** was determined by an analogous procedure. The molar extinction coefficients of **5** and **13** determined at 313 nm were 28 200 cm^{-1} M^{-1} and 32 500 cm^{-1} M^{-1}, respectively.

***H_0* measurements** were made by using a conventional UV technique with 2,4-dinitroaniline (pK_a −4.3) as an indicator. The 2,4-dinitroaniline was recrystallized from CH_3OH to constant melting point (mp 177.5–8.5 °C).

Measurement of Rate Constants. The rate constant for the conversion of **9** to **1** at 100 °C was determined as follows: An appropriate amount of iminium salt **1** (25 mg) was dissolved in TFA (0.3 mL), and a small amount of $(CH_3)_4N^+BF_4^-$ was added as an internal standard. This mixture was placed into a medium-walled NMR tube that was then sealed. The sample was irradiated in a Rayonet Photochemical Reactor (Southern New England Ultraviolet Co., RPR-100) fitted with 16 RPR-3000 A lamps until a photostationary state was reached. A ^{1}H NMR spectrum of this mixture was recorded. The peak height of the center of the triplet at δ 6.26, which was due to the H_2 proton of the cis isomer **9**, was ratioed with the peak height of the singlet at δ 3.10 due to the internal standard (peak widths at half-height were the same). This ratio was used as a dimensionless concentration function.

The sample was heated in a constant temperature bath ($T = 100 \mp 0.5$ °C), and about once every 24 h the sample was cooled quickly to 25 °C and its ^{1}H NMR spectrum was obtained. The concentration of **9** was determined by the method described above. This procedure was continued for at least 2 half-lives and a plot of ln (ratio) vs. time gave a good linear correlation (correlation coefficient = 0.995). The slope of this line, which was determined by linear regression, was equal to the first-order rate constant. A second run was performed and the two values of the rate constant were averaged (see Table V). These two values did not differ by any more than 10%, which was the estimated error.

This procedure was repeated for the conversions **10** to **2**, **11** to **3**, **12** to **4**, and **13** to **5**. In all cases the triplet due to the H_2 proton of the cis isomer was used to monitor the kinetics (δ 6.41 for **10**, 6.47 for **11**, 6.56 for **12**, and 6.79 for **13**). The only alteration was that, in the case of **2**, the photochemical reactor was fitted with RPR-3500 A lamps.

The rate constants determined in the 0.015 M H_2SO_4/TFA solvent were measured by an analogous procedure.

Deuterium Exchange Experiments. The above isomerizations were repeated in both TFA-*d* and D_2SO_4/TFA-*d* solvents. In all cases there was no detectable exchange (^{1}H NMR) at any site during the time of the isomerizations. The NH proton in **8**, was found to exchange rapidly in both solvent media at 34 °C. At this temperature exchange was complete in 45 min in TFA-*d* and in 15 min in D_2SO_4/TFA-*d*.

Registry No. 1, 86119-07-5; **2**, 86119-09-7; **3**, 86119-11-1; **4**, 86119-13-3; **5**, 86119-15-5; **6**, 86119-16-6; **7**, 86119-17-7; **8**, 86119-18-8; **9**, 86119-20-2; **10**, 86119-22-4; **11**, 86119-24-6; **12**, 86119-26-8; **13**, 86119-28-0; **14**, 86119-29-1; **15**, 86119-30-4; **16**, 86119-31-5; **17**, 86119-32-6; **18**, 86119-33-7; **19**, 86119-34-8; **20**, 86119-35-9; cinnamaldehyde, 104-55-2; *n*-butylamine, 109-73-9.