bp 75–82 °C (0.001 torr)); imine **6** had bp 49–51 °C (0.01 torr) (the compound has been reported without a bp, but the ^{1}H NMR spectrum reported[22] was the same as that of our sample), imine **8** had bp 54–55 °C (0.01 torr) (lit.[21] bp 90–96 °C (0.1 torr)), and imine **11** had bp 75–76 °C (0.15 torr) (lit.[21] bp 75–80 °C (0.2 torr)).

Samples of 2-methyl-3-pentanone *N*-benzylimine (**5**) and *N*-phenylethylimine (**12**) for GC analysis were prepared by deprotonation and subsequent methylation of the corresponding 3-pentanone imines **1** and **4**. The preparation of **12** is representative. Imine **4**, 0.47 g (2.5 mmol), was added dropwise to a solution of 3 mmol of LDA in 10 mL of THF at 0 °C. After 1.5 h, the reaction mixture was cooled to −78 °C and 3.2 mmol of iodomethane was added dropwise. After 0.5 h, the solution was quenched with brine, and 10 mL of ether was added to the reaction mixture. After phase separation, the organic phase was washed with brine and then dried over $MgSO_4$. Analytical GC indicated a 96% conversion of **4** to **12**. The solvent was removed in vacuo, and the residue was purified by preparative GC (SE-30 on 80/100 Chromosorb G). The major isomer of imine **12** had the following ^{1}H NMR spectrum: ($CDCl_3$) δ 7.1–7.5 (m, 5 H), 4.6–4.9 (q, 1 H), 2.7–3.3 (m, 1 H), 2.25 (q, 2 H), 1.4 (d, 3 H), 1.0 (d, 6 H), 0.9 (t, 3 H). The major isomer of imine **5** had the following ^{1}H NMR spectrum: ($CDCl_3$) δ 7.2–7.3 (s, 5 H), 4.56 (s, 2 H), 2.3–2.4 (m, 1 H), 2.3 (q, 2 H), 1.1 (d, 6 H), 1.05 (t, 3 H).

Acetone-d_6 Benzylimine (10-d_6). Benzylamine (10 g) in CH_2Cl_2 was washed thrice with 10-mL portions of D_2O. The solution containing the deuterated amine was distilled (bp 180 °C) after drying over K_2CO_3. The ^{1}H NMR spectrum indicated >93% deuterium incorporation at nitrogen. A dry 100-mL flask, fitted with a universal water separator with a reflux condenser and a magnetic stirring bar, was charged with 50 mL of CH_2Cl_2, 5.5 g of benzylamine-*N*-d_2 (0.05 mol), and 8 g of acetone-d_6 (0.11 mol). The solution was heated at reflux until 1.0 mL of water was removed azeotropically. The solvent was removed at reduced pressure, and the resulting oil was flash distilled (oil bath temperature at 120 °C) under a 0.01 torr vacuum to yield 4 g (52%) of **10**-d_6; bp 70–74 °C (0.15 torr). An ^{1}H NMR spectrum indicated >93% deuterium content at the α positions by comparison of the α signals' integral with that of the benzylic position. Use of *N*-protiobenzylamine in this synthesis led to lower deuterium levels in the final product.

^{13}C NMR studies were performed in a manner similar to that previously reported.[3a] A "clean" LDA solution was prepared (1 M), and 2 mL of the solution was added to a dry, Ar-flushed 10-mm NMR tube fitted with a serum cap. After cooling the base solution to −78 °C, 260 mg of **1** (1.5 mmol) was added dropwise with shaking. The NMR tube was placed into the temperature equilibrated probe of the spectrometer. Spectra were obtained at 1, 11, 21, and 31 min and 1, 2, 4, and 8 h.

^{1}H NMR studies were performed in a manner similar to the ^{13}NMR studies. "Clean" LDA solution (0.5 mL, 1 M) was added to a dry, Ar-flushed 5-mm NMR tube. The base solution was cooled to −78 °C, and 70 mg (0.4 mmol) of **1** was added. The sample was inserted in the cooled probe of the spectrometer. Spectra were obtained as the probe temperature was raised.

^{2}H NMR studies were performed in a manner similar to the ^{13}C NMR studies. A solution of LDA (0.2 mol) in THF was prepared, and 2 mL of this solution was transferred by syringe into an Ar-flushed, 10-mm NMR tube fitted with a serum cap. Benzene-d_6 (20 μL) was added as an internal standard. The solution was cooled to −78 °C, and a solution of **10**-d_6 in THF (0.23 M, 1.0 mL) was added. The tube was placed in the −80 °C probe of the spectrometer. Spectra obtained within 5 min and after 1.5 h showed no benzyl-*d* signal. After several h at 25 °C, the ^{2}H NMR spectrum contained a signal for the benzylic position.

Regioselectivity and kinetic studies were performed in a manner similar to that previously reported.[3a] Thus, LDA solutions (10 mL) of the desired concentration were prepared in a 40-mL flask. After cooling the solutions to the desired temperatures (−78 °C or 0 °C), the appropriate amount of imine was added dropwise with stirring. At various times, 0.5 mL aliquots of the reaction mixtures were removed by syringe and added to tubes containing excess iodomethane in THF which had been cooled to −78 °C. Product ratios were determined by analytical GC.

Acknowledgment. This work was supported by grants from the National Institutes of Health (GM 26268) and the Robert A. Welch Foundation.

Registry No. **1**, 31776-82-6; **2**, 98611-97-3; **3**, 88101-29-5; **4**, 18805-17-9; **5**, 98611-95-1; **6**, 27845-52-9; (*E*)-**7**, 72037-48-0; (*Z*)-**7**, 77390-49-9; **8**, 77449-24-2; **9**, 98611-98-4; **10**, 1197-48-4; **10**-d_6, 98611-96-2; **11**, 18805-14-6; **12**, 98611-94-0; $PhCH_2NH_2$, 100-46-9; $PhCH_2ND_2$, 45579-94-0; $CD_3C(O)CD_3$, 666-52-4.

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Mechanisms of the Thermal Isomerization about the C=N$^+$ Bond of Some Iminium Salts[1]

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The thermal stereomutations of a series of *N*-aryl 3-arylpropenylidene iminium perchlorate salts have been examined. These salts crystallize as *E,E* isomers but isomerize thermally about the C=N bond in solution. The rates of isomerization (**8** → **9**) were measured at 100 °C in trifluoroacetic acid. A Hammett correlation of the rate constants indicated that two mechanisms operate in the system. The iminium salts with electron-withdrawing substituents react by a nucleophile-catalyzed mechanism, while those with electron-donating substituents isomerize by a protonation mechanism. This latter process was shown to involve protonation on nitrogen.

Iminium ions are implicated in several important natural processes. For example, it has been proposed that chlorophyll, the light-absorbing pigment of the photosynthesis process, forms an iminium ion in the natural system.[2] Another important iminium linkage is that between the light-absorbing retinal molecule and the protein opsin in rhodopsin, the visual pigment.[3]

A key feature of the chemistry of the visual pigments is the stereomutations which can occur about the multiple bonds in the retinal-derived chromophore. Photochemically and thermally induced isomerizations about several of the C=C bonds have been reported. In addition, recent

(1) This work was supported by a grant from the Natural Science and Engineering Research Council of Canada.
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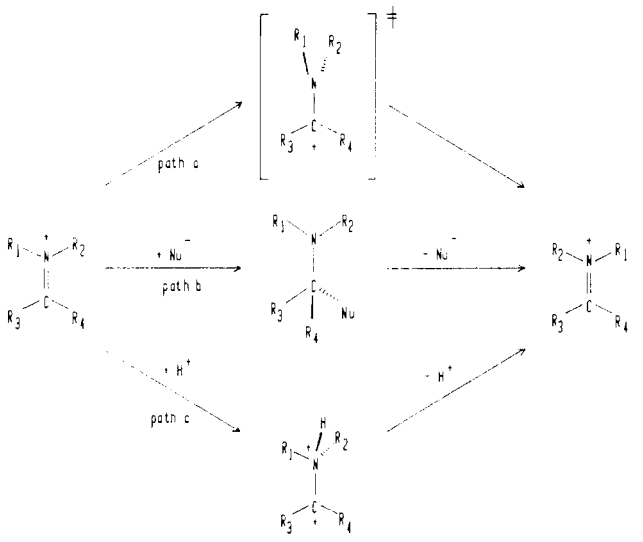
0022-3263/85/1950-4553$01.50/0

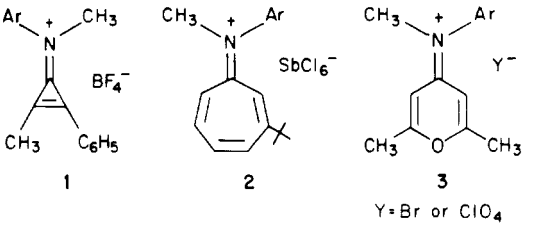
Scheme I



solid-state NMR investigations on bacteriorhodopsin, a related pigment involved in proton pumping in certain bacteria, have suggested that thermal C=N isomerization occurs in vivo.[4] The protein environment of the natural pigment causes many experimental difficulties, so most mechanistic studies involve model compounds, such as *N*-*n*-butyl retinylidene salts. Facile thermal C=N isomerization has been observed in addition to C=C isomerization in these systems.[5]

The basic routes whereby an iminium salt can undergo *E*/*Z* isomerization are shown in Scheme I. These are easy to depict, but relatively few studies of these isomerizations have been carried out with sufficient detail to allow the factors affecting the mechanism of the stereomutation to be clearly defined.[6-12]

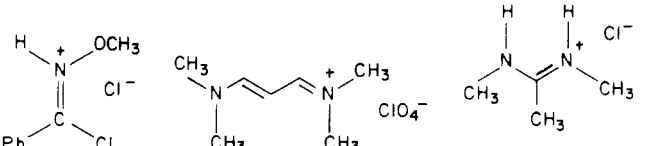
Theoretical calculations[13] show that the barrier to rotation of the parent cation, $CH_2{=}NH_2^+$, in the gas phase is 70 kcal/mol. In the transition state for rotation the positive charge becomes largely localized on the carbon atom, and consequently, charge-stabilizing groups on the carbon should lower the barrier to isomerization. Salts **1**–**3** have been reported to undergo a facile stereomutation about the C=N bond, and it has been suggested that this isomerization proceeds by a rotation mechanism.[7,8] In each



1 2 3 (Y = Br or ClO_4)

of these ions the carbon atom is part of a cyclic system in which a very stable aromatic cation can be formed in the transition state, thus lowering the barrier to stereomutation by rotation to a sufficiently low value to permit its observation.

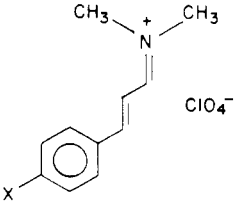
Stereomutations of iminium salts have been observed in several cases where there is not much stabilization of the rotational transition state. In one instance nucleophilic catalysis has been observed. Cation **4** has been shown to isomerize by addition of the counterion, Cl^-, to the iminium carbon, followed by rotation about the now single bond and loss of Cl^-.[9] Acid catalysed isomerizations have also been found, but the evidence presented does not establish the site of protonation involved in the reaction. In the case of **5**, deuterium incorporation at C_2 was observed when



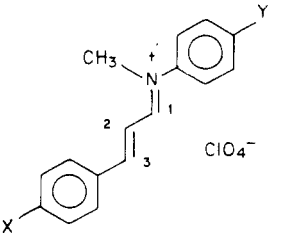
4 5 6

deuterated acid was used as solvent, and the authors suggested that the C=N isomerization involves protonation at this site.[10] However, the data given could also support an isomerization mechanism involving protonation at nitrogen. A strong analogy for this type of nitrogen protonation can be found in the C=C isomerization of some α,β-unsaturated iminium salts.[11] The salt **6** was also found to isomerize by an acid catalysed mechanism. In this case protonation was thought to occur on one nitrogen of the amidinium system.

It is clear from the limited amount of work reported in this area that the factors determining the mechanisms of iminium salt stereomutation about the C=N bond are not well defined and in view of the involvement of these processes in the visual pigments, further mechanistic studies are needed. Our approach is to study simpler, better defined systems. An earlier paper presented results on thermal and photochemical isomerization mechanisms about the C=C bond of α,β-unsaturated iminium salt **7**.[11] We now extend this with studies of thermal isomerizations about the C=N bond in related iminium salts, **8**.



7 X = NO_2, Cl, H, CH_3, OCH_3



8

8a: X = NO_2; Y = H
b: X = Cl; Y = H
c: X = H; Y = H
d: X = CH_3; Y = H
e: X = OCH_3; Y = H
f: X = H; Y = NO_2
g: X = H; Y = Cl
h: X = H; Y = CH_3
i: X = H; Y = OCH_3

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Table I. ^{1}H NMR Chemical Shift Data[a,b]

	H1	H2	H3	aryl H	CH_3	other	$J_{1,2}$, Hz	$J_{2,3}$, Hz
8a	8.59 d	7.55 dd	8.08 d	8.17 d, 7.89 d, 7.4 m	4.05 s		10	15
9a	8.75 d	6.74 dd	8.01 d	8.11 d, 7.62–7.31 m	3.98 s		10	16
8b	8.42 d	7.31 dd	7.95 d	7.62 d, 7.47–7.33 m	3.94 s		11	15
9b	8.59 d	6.55 dd	7.88 d	7.53 m, 7.37–7.21 m	3.90 s		10	15
8c	8.42 d	7.4[c]	8.01 d	7.70 d, 7.45–7.30 m	3.94 s		11	15
9c	8.58 d	6.60 dd	7.92 d	7.53 m, 7.47–7.22 m	3.90 s		10	15
8d	8.35 d	7.3[c]	7.95 d	7.58 d, 7.46–7.31 m, 7.22 d	3.90 s	2.29 s	11	15
9d	8.50 d	6.53 dd	7.87 d	7.52 m, 7.35–7.27 m, 7.09 d	3.86 s	2.26 s	11	15
8e	8.30 d	7.16 dd	7.92 d	7.71 d, 7.44–7.30 m, 6.96 d	3.87 s	3.83 s	11	15
9e	8.45 d	6.45 dd	7.84 d	7.53–7.24 m, 6.84 d	3.83 s	3.77 s	11	15
8f	8.60 d	*c*	8.17 d	8.30 d, 7.74–7.36 m	3.99 s		11	15
9f	8.69 d	6.57 dd	8.05 d	8.43 d, 7.64 d, 7.45–7.25 m	3.94 s		11	16
8g	8.42 d	7.33 dd	8.03 d	7.69 d, 7.53–7.28 m	3.92 s		11	15
9g	8.59 d	6.59 dd	7.95 d	7.53–7.23 m	3.88 s		11	15
8h	8.39 d	7.4[c]	7.98 d	7.68 d, 7.50–7.26 m	3.92 s	2.29 s	11	15
9h	8.54 d	6.64 dd	7.90 d	7.50–7.15 m	3.87 s	2.33 s	11	15
8i	8.38 d	7.31 dd	7.98 d	7.68 d, 7.50–7.33 m, 7.03 d	3.92 s	3.83 s	11	15
9i	8.54 d	6.65 dd	7.91 d	7.47–7.23 m, 7.10 d	3.87 s	3.85 s	10	16

[a] In ppm, referenced to $N(CH_3)_4^+BF_4^-$ at 3.10 ppm. [b] s = singlet, d = doublet, dd = doublet of doublets, m = multiplet(s). [c] Peaks hidden.

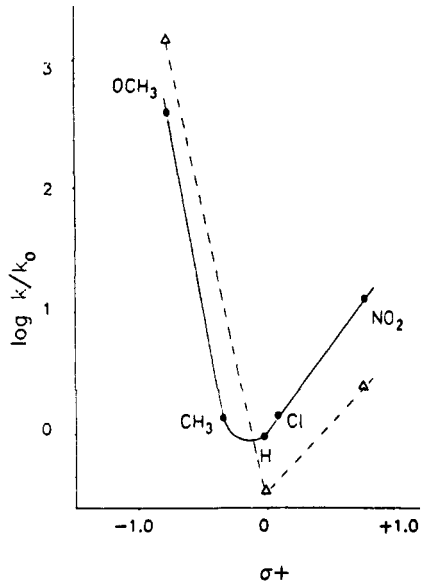


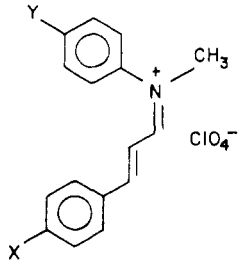
Figure 1. Hammett correlations for the rate constants for stereomutation of iminium salts with substituents on the C_3 aryl ring (**8a–e**), determined in TFA (—) and H_2SO_4/TFA (- - -). (The latter values are plotted by using log $k(H)$ in TFA as the reference point to show the effect of increased acidity on the rate constants.)

Results and Discussion

The iminium salts **8a–i** were selected for study. These ions, which are structurally similar to a related series used to define the mechanism of stereomutation about the C=C bond,[11] permit the electronic properties of the system to be altered in a controlled manner by changing the substituents on either or both of the aryl rings.

The salts were prepared as crystalline perchlorates from the appropriate aniline, a suitable cinnamaldehyde, and perchloric acid. The ^{1}H NMR spectra of solutions of the various salts in trifluoroacetic acid (TFA) (Table I) clearly indicated that only one stereoisomer was present in each case. The configuration about the C=C bond was evident from the large coupling constant between H_2 and H_3, $J_{2,3}$ ca. 15 Hz, which corresponds to an *E* double bond. A smaller coupling constant would have been expected if the double bond had a *Z* configuration.[14] As the configuration about the C=N bond cannot be determined readily by NMR techniques, the structure of a representative ion, **8b**, was established by X-ray crystallography. The salt was found to have the *E,E* configuration as is shown for **8**.[15]

On dissolution of any of the salts **8** in aprotic solvents such as acetonitrile or nitromethane, examination of the ^{1}H NMR spectra indicated that two isomers were present in an approximately 2:3 ratio. One of these, the minor isomer, was still **8** and the other was shown to be the corresponding C=N isomer **9**. The spectrum of the isomer **9** displayed the characteristically large coupling constant between H_2 and H_3 indicating an *E* configuration about this bond. Indeed mixtures containing the two possible C=C *Z* isomers **10** and **11**, in addition to **8** and **9**, could be obtained on irradiation of **8**. It was clear that the isomer **9** produced thermally from **8** was neither of these C=C *Z* isomers. Precipitation of the salts from CH_3CN solutions and redissolving the sample in TFA gave solutions containing only a single isomer, namely **8**, within the detection limits of NMR.



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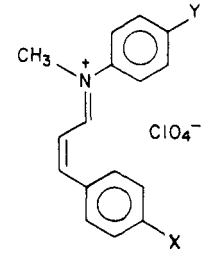

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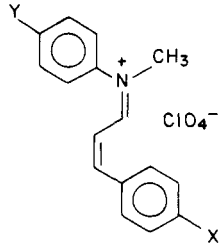

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Several points emerge from these results. First, mixtures of iminium salts **8** and **9** crystallize from solvents such as acetonitrile or nitromethane to give only one isomer. Similar observations have been made previously for aryl

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Table II. Isomerization Rate Constants at 100 ± 1 °C[a,b]

	TFA		TFA/H_2SO_4		
reaction	10^7k_f, s^{-1}	10^7k_r, s^{-1}	10^7k_f, s^{-1}	10^7k_r, s^{-1}	K[c]
8a → 9a	110	79	22	16	1.4
8b → 9b	12	9.6			1.3
8c → 9c	8.9	7.1	3.2	2.5	1.3
8d → 9d	12	11			1.1
8e → 9e	3400	2850	13 000	11 000	1.2
8f → 9f	370	430	170	190	0.86
8g → 9g	22	20	4.6	4.2	1.1
8h → 9h	7.3	6.1	6.4	5.4	1.2
8i → 9i	140[d]	110[d]	350	290	1.2

[a] Error ± 10%. [b] k_f,k_r = rate constants for the forward and reverse reactions, respectively. [c] K = equilibrium constant [**9**]/[**8**] at 100 °C. [d] Estimated from half-reaction time.

imines.[16] Second, thermodynamically the two C=N isomers are very similar in energy, and interconversion is reasonably rapid in the two aprotic solvents used here, although slow on the NMR time scale. However, in TFA the interconversion is sufficiently slow ($k \leq 10^{-6}$ s^{-1}) so as to allow observation of only the one isomer at ambient temperatures.

At elevated temperatures the isomerization of **8** to **9** was faster. The kinetics of this C=N isomerization could be conveniently measured at 100 °C by following changes in the NMR spectra of the samples. The data fit first-order kinetics in all cases but **8i**, and the rate constants are given in Table II. For **8i**, the rate constant was estimated from the half reaction time. Where prolonged heating was necessary, a product that was not a geometric isomer was formed in an apparently irreversible process. This product was not identified.

From the data given in Table II it is quite clear that the measured rate constants are very dependent on the nature of the substituents on either aryl ring. Both electron-donating and -withdrawing substituents facilitate isomerization. In the equilibrium geometry of these iminium salts the positive charge is formally delocalized onto the C_3 aryl ring and all the mechanisms shown in Scheme I for stereomutation about the C=N bond would be expected to change the extent of this charge delocalization. Hence the rates of isomerization of the salts with various substituents on the C_3 aryl ring should correlate with σ^+.[17] On the other hand, isomerization by the various mechanisms shown in Scheme I leads to a change in electron density at nitrogen, which can be delocalized onto the aryl ring attached to N. In the case of substituent changes on this ring, a correlation of the rate constants with σ^- is expected.[17] Figure 1 shows the two correlations found for the isomerizations of **8a–i**. In each case, two lines of opposite slope are needed to fit the data. Although the number of points is too small to place much significance on the magnitudes of the slopes of these lines, it is evident from both correlations that at least two different mechanisms are operative.

In order to gain further insight into the types of mechanisms involved, the effect of medium was investigated. The acidity of TFA was increased without substantially affecting overall solvent properties by adding a small amount of 100% H_2SO_4. This decreased H_0 to −5.4 from −4.3. The rates of isomerization of **8a,c,e–i** were measured in this more acidic medium. All data fitted first order kinetics and the rate constants are given in Table II.

A distinct difference in the behavior of the cations with donating and withdrawing substituents was observed in the stronger acid, substantiating the proposal that two mechanisms are operative, Figures 1 and 2.

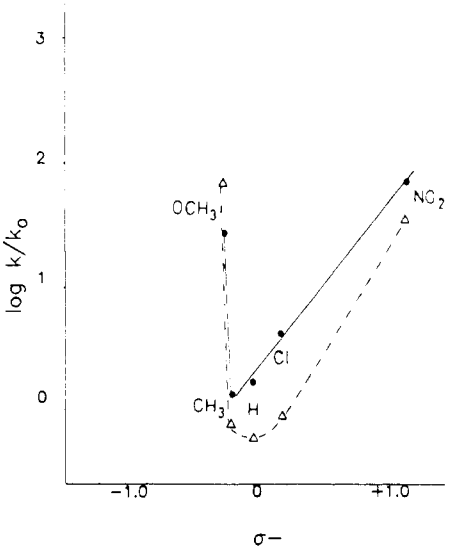


Figure 2. Hammett correlations for the rate constants for stereomutation of iminium salts with substituents on the N aryl ring (**8c, f–i**), determined in TFA (—) and H_2SO_4 (---). (The latter values are plotted by using log $k(H)$ in TFA as the reference point to show the effect of increased acidity on the rate constants.)

Proposed Mechanisms. Electron donating substituents on the C_3 aryl ring increase the rate of isomerization relative to that of the unsubstituted ion. While the rotation mechanism could account for this, the observation that in stronger acid media this reaction rate is increased indicates that the solvent acid participates in the reaction. These observations are consistent with a protonation mechanism in which a proton is added to the iminium ion in such a position that in the transition state positive charge on the C_3 aryl ring is enhanced.

To investigate the nature of the protonated intermediate, the isomerizations were followed in TFA-*d*. In each case, the isomerization proceeded without deuterium incorporation. At longer reaction times, exchange at C_2, C_6, and C_8 was detected for **8e**; however, as the exchange reactions were much slower than the stereomutation process, protonation at these carbon atoms cannot be involved in C=N isomerization. The only reasonable alternative is that protonation occurs on the nitrogen, path c, Scheme I. Our earlier work with the C=C stereomutations in related iminium salts showed that protonation on nitrogen was important in some cases.[11]

In principle it should be possible to detect the presence of the proposed dication intermediate in a very strongly acidic medium. One of the strongest acid media available is $HF/SbF_5/SO_2$; however, while C=N isomerization was very fast at −60 °C in this super acid, no dication could be detected by ^1H NMR in the solution.

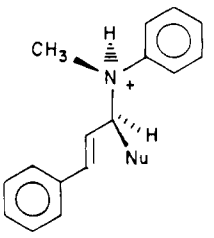
Electron-withdrawing substituents on the C_3 aryl ring also increase the rate of isomerization relative to that of the unsubstituted ion. In this case, the rate decreases when a more acidic medium is used. The rate of isomerization of the unsubstituted ion **8c** also decreases in the stronger acid. This can be understood in terms of a nucleophile addition mechanism (see path b, Scheme I). Such a mechanism would be expected to correlate with σ^+ with a positive ρ, and the rate would be retarded in the stronger acid where fewer nucleophiles exist in solution. In support of these conclusions, electron-withdrawing substituents on the *N*-aryl ring affect the isomerization rate in the same way as do the C_3 aryl ring electron-withdrawing substituents. **8f** and **8g** isomerize faster than **8c**, and these rates

(16) Carlson, E.; Jones, R. B. Jr.; Raban, M. *J. Chem. Soc., Chem. Commun.* **1969**, 1235–1237.
(17) Hammett, L. P. "Physical Organic Chemistry", McGraw-Hill: New York, 1970; p 360.

are decreased when measured in the TFA/H_2SO_4 mixture. Rates of nucleophile addition to an iminium bond, from hydrolysis experiments, show that this is indeed a very fast process. Hydroxide ion adds to the ferrocenyl iminium ion with a second-order rate constant of 3.3×10^3 L mol^{-1} s^{-1}.[18] Addition of H_2O, a weaker nucleophile, to an iminium system has a rate constant of 1.5×10^{-3} s^{-1} when H_2O is the solvent in the reaction.[19]

Electron-donating substituents on the *N*-aryl ring induce acid catalysed isomerization mechanisms, although **8h** isomerizes more slowly than the unsubstituted ion **8c** in TFA. In more acidic media **8h** and **8i** isomerize faster than **8c**. Acid catalysis was somewhat unexpected since the substituent cannot provide resonance stabilization to any protonated intermediate that can lead to isomerization. In deuterated media (TFA-*d*/D_2SO_4), no deuterium incorporation was found in a time corresponding to 30 half-lives of the isomerization. Again, it would seem that the nitrogen is protonated in the rate-determining step of these isomerizations.

The proposed mechanisms for C=N isomerization are thus an acid catalysed mechanism and a nucleophile addition mechanism. It should be noted that the intermediacy of species such as **12** in the reaction pathway cannot



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be ruled out. It has not been possible to detect an isomerization process which occurs by a simple rotation mechanism.

As this study shows, the mechanisms of stereomutation in iminium ions are finely balanced, keeping in mind that the medium used is relatively acidic. In less acidic media, or indeed in solvents where larger concentrations of nucleophiles exist, the nucleophile catalysed isomerization is expected to predominate. Presumably this is occurring when the salts studied here were dissolved in CH_3CN or CH_3NO_2. In addition, the substituents on the carbon atom of an iminium salt will have to be exceptionally effective at stabilizing a positive charge in order for the rotation mechanism to compete with the nucleophilic addition process in conventional media.

From these results, we suggest that the isomerization of highly conjugated molecules such as the retinylidene iminium ions should proceed by a nucleophile catalyzed mechanism. This should hold for C=N isomerization and also for isomerization about a C=C bond that is conjugated to the iminium group. Lukton and Rando[20] have measured rates of isomerizations about the 11, 13, and 9 C=C bonds of retinylidene iminium ions as a function of counterion and conclude that a more nucleophilic counterion increases the rate of isomerization. The nature of the analyses did not permit observation of C=N isomerization. Sheves and Baasov[5] have published similar work on the isomerization of 13-*cis*-retinylidene ions, using ^{1}H NMR analysis. Although C=N isomerization can be detected by this technique, rates of C=N isomerization were not reported. The rates of C=C isomerization as a function of counterion were measured; however the trends observed did not agree with the former report. Further studies are clearly needed in this area to resolve the controversy and assess the generality of our mechanistic conclusions.

Table III. Some Physical Data

compd	mp, °C	λ_{max}, nm	log ϵ
8a	186–187	348	4.51
8b	151–152	368	4.60
8c	185–185.5	361	4.60
8d	142.5–144	378	4.58
8e	165–166	408	4.63
8f	218–219.5	370	4.56
8g	193–194.5	361	4.53
8h	170.5–171.5	360	4.49
8i	173.5–174.5	372	4.46

Experimental Section

^{1}H NMR spectra were recorded on a Bruker WM250 spectrometer. A Varian EM 390 NMR spectrometer was used for kinetic measurements. Trifluoroacetic Acid (TFA) was distilled from concentrated H_2SO_4 and stored in a dry N_2 atmosphere. TFA-*d* was used as purchased from Aldrich. An approximately 0.01 M solution of H_2SO_4 in TFA was made by diluting 0.04 mL of 100% H_2SO_4 to 50.00 mL with TFA. H_0 values were determined by the Hammett indicator method using 2,4-dinitroaniline. The H_0 of TFA was −4.3 (lit. value −4.4 to −2.77[21]); TFA-*d*, −4.0; TFA/H_2SO_4, −5.4.

Syntheses. The iminium ions were all prepared by the same procedure. To a solution of 1.26 mL (.012 mol) freshly distilled *N*-methylaniline in 20 mL of ether in an ice bath was added dropwise a slight excess of perchloric acid (1.2 mL of 70% $HClO_4$, 0.014 mol). An ether solution (10 mL) of cinnamaldehyde (1.9 mL, 0.015 mol) was added and the mixture swirled and allowed to stand for about 15 min. The product precipitated from solution, was filtered, washed with ether, recrystallized from acetonitrile/ether, and dried in vacuo overnight. Melting points and UV maxima are given in Table III. ^{1}H NMR data are in Table I. All salts gave satisfactory elemental analyses.

Kinetic Measurements. Approximately 25 mg of iminium salt was dissolved in 0.3 mL of TFA in a medium-walled NMR tube. An internal standard, $(CH_3)_4NBF_4$ (3 mg), was added and the tube sealed. The relative concentration of iminium salt was measured by obtaining its ^{1}H NMR spectrum at 34 °C and comparing the peak height of the N-CH_3 proton peak to the peak height of the proton signal of the internal standard. The widths at half height of the peaks being compared were similar. The NMR tube was then placed in a constant temperature bath (100 ± 1 °C), and at regular intervals the isomerization reaction was stopped by cooling the tube rapidly. The change in composition was measured by ^{1}H NMR by monitoring the decrease in the NCH_3 peak of the starting isomer (for **8e** the height of the OCH_3 peak of the isomer being formed was measured). The rates of isomerization were determined by using the relationship $\ln (A_o - A_e/A - A_e) = (k_f + k_r)t$.[22] The slope of the graph gave the sum of the rate constants for the forward and reverse isomerizations. The rate constants were then determined from the equilibrium constant for the reaction, $A_e/B_e = k_r/k_f$. For the **8e** the equation used was $\ln (B_e/B_e - B) = (k_f + k_r)t$. Each rate reported is an average of at least two kinetic experiments. For the isomerization of **8i** in TFA the rate constant was estimated from the half reaction time.

Equilibrium Concentrations. The concentrations of the *EE* and *EZ* iminium salt isomers were determined by heating the samples to constant *EE*/*EZ* ratio, and measuring the relative peak heights of the two isomers as before. Where the equilibrium concentrations could not be easily measured from the NCH_3

(18) Bunton, C. A.; Davoudzadeh, F.; Jagdale, M. H.; Watts, W. E. *J. Chem. Soc., Perkin Trans. 2* **1984**, 395–399.
(19) Sayer, J. M.; Conlon, P. *J. Am. Chem. Soc.* **1980**, *102*, 3592–3600.
(20) Lukton, D.; Rando, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 4525–4531.
(21) Milne, J. B. in "The Chemistry of Non-Aqueous Solvents"; Lagowski, J. J., Ed., Academic Press: New York, **1978**; Vol. VB, pp 1–52.
(22) Moore, J. W.; Pearson, R. G. "Kinetics and Mechanism", 3rd ed.; Wiley: New York, 1981; p 304.

signals (8e,8i) other peaks in the spectrum were used.

Deuterium Incorporation. Samples were prepared as above, using TFA-*d* as solvent. The samples were heated at 100 °C, and the reaction monitored by ^1H NMR. **8h** was heated in TFA-d/D_2SO_4 (0.3 mL/1 μL) to an equilibrium mixture (about 3 h). The sample was analyzed by 250 MHz ^1H, ^{13}C, and ^2H NMR.

Registry No. **8a**, 98587-62-3; **8b**, 98587-64-5; **8c**, 98587-66-7; **8d**, 98587-68-9; **8e**, 98587-70-3; **8f**, 98587-72-5; **8g**, 98587-74-7; **8h**, 98587-76-9; **8i**, 98587-78-1; **9a**, 98587-80-5; **9b**, 98587-82-7; **9c**, 98587-84-9; **9d**, 98587-86-1; **9e**, 98587-88-3; **9f**, 98587-90-7; **9g**, 98587-92-9; **9h**, 98587-94-1; **9i**, 98587-96-3; PhNHMe, 100-61-8; O_2N-*p*-C_6H_4NHMe, 100-15-2; Cl-*p*-C_6H_4NHMe, 932-96-7; Me-*p*-C_6H_4NHMe, 623-08-5; MeO-*p*-C_6H_4NHMe, 5961-59-1; O_2N-*p*-C_6H_4CH=CHCHO-(*E*), 49678-08-2; Cl-*p*-C_6-H_4CH=CHCHO-(*E*), 49678-02-6; PhCH=CHCHO-(*E*), 14371-10-9; Me-*p*-C_6H_4CH=CHCHO-(*E*), 56578-35-9; MeO-*p*-C_6H_4CH=CHCHO-(*E*), 24680-50-0.

Photochemical Transformations. 40. Syn and Anti Migration in Photo-Wagner-Meerwein Rearrangements[1,2]

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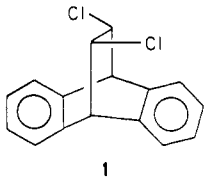
The photochemistry of the trans and cis isomers of 7,8-dichloro-2,3:5,6-dibenzobicyclo[2.2.2]octa-2,5-diene (**1** and **3**) has been explored. The singlet excited states of these compounds are photoactive. In acetonitrile, mixtures of *exo*- and *endo*-4,*anti*-8-dichloro-2,3:6,7-dibenzobicyclo[3.2.1]octa-2,6-diene (**2**-Cl), the *syn*-8-chloro epimers *exo*- and *endo*-**4**-Cl, *N*-(*anti*-8-chloro-2,3:6,7-dibenzobicyclo[3.2.1]octa-2,6-dien-*exo*-4-yl)acetamide (**2**-NHAc) and its *syn*-8-chloro epimer *exo*-**4**-NHAc were produced. In acetic acid, the dichloro compounds and a mixture of the *anti*- and *syn*-8-chloro-2,3:6,7-dibenzobicyclo[3.2.1]octa-2,6-dien-*exo*-4-yl acetates (**2**-OAc and **4**-OAc) were produced. In cyclohexane, irradiation of **2** gave the dichlorides epimeric at C-4 and C-8. All of the photoreactions proceeded with a preponderance of migration with retention at the migration terminus (syn migrations), in contrast to the ground-state reactions which proceed with clean inversion at the migration terminus (anti migration). Failure to see stereospecificity was shown not to be due to C-8 bridge migration. Quantum yields for the various reactions are reported. The results are discussed in terms of several reaction channels following excitation and electron transfer. Radical reductive monodechlorinations of **1** and **3** lead to stereoconvergent radical rearrangements. The syntheses of **2**-NHAc and **4**-NHAc by Ritter reactions from **2**-OAc and **4**-OAc respectively are described.

In the past few years, it has become apparent that the stereochemistry of photo-Wagner-Meerwein rearrangements is quite different from that of ground-state analogues. Ground-state rearrangements proceed, in general, with clean migration of groups anti to the nucleofuge. In the photochemical analogues, except in special cases,[3] syn (suprafacial) migrations are preferred over anti (antarafacial). Thus, for example, treatment of **1** with silver acetate in acetic acid leads cleanly, via anti migration, to **2**-OAc and that of the cis epimer **3** leads cleanly to **4**-OAc.[4]



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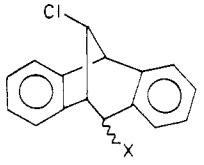

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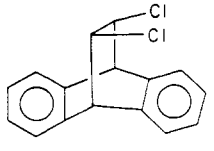

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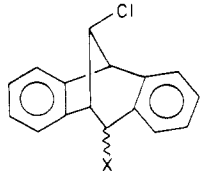

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On the other hand, as described in the preliminary communication[2] and as reported in detail here, direct irradiation of **1** with 254-nm light leads to a mixture containing approximately 75% of **4**-Cl and **4**-OAc (syn migration) products and 25% of the anti migration products **2**-Cl and **2**-OAc. (A simultaneous photolysis of **1** and *endo*-**4**-Cl showed that the solvolysis rearrangement of the nonbenzylic species **1** occurs more rapidly.) Similarly, irradiation of **3** gives about 75% of the syn migration products **2**-Cl and **2**-OAc and 25% of the anti migration products **4**-Cl and **4**-OAc. Data of a similar nature have been reported for cis and trans dichlorides[5] where one of the rings is substituted, that is the 2,3-naphtho-benzo and 2,3-veratro-benzo systems, with systems with nucleofugal groups other than chlorine[1] and for a monobenzobicyclooctadienyl system.[6]

Evidence has been adduced that these reactions proceed via an excited intramolecular electron-transfer state such as **5** or **6**, whose decay may follow either or both of two speculated modes. In the first of these, loss of chloride ion (or other nucleofuge) prior to migration gives the biradical cation **7**, for which stereospecific migration is not demanded (but can be allowed) and which therefore allows for migration of either the electron-deficient ring (denoted by Y) or the "normal" ring. A second process[5] assumes a suprafacial (syn) migration concerted with fragmentation

(1) Previous paper in series: Cristol, S. J.; Aeling, E. O. *J. Org. Chem.* **1985**, *50*, 2698. A portion of this work was described in a preliminary communication.[2]

(2) Cristol, S. J.; Opitz, R. J.; Bindel, T. H.; Dickenson, W. A. *J. Am. Chem. Soc.* **1980**, *102*, 7977.

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