A Quantitative Examination of the Photoisomerization of Retinal Iminium Salts by High-Field ¹H NMR Spectroscopy[1]

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Abstract: High-field ¹H NMR spectroscopy has been used to examine quantitatively the photoisomerizations of the *N-tert*-butyl, *N-n*-butyl, and *N,N*-dimethyl all-trans iminium salts of retinal, **1**, **2**, and **3**, respectively. The NMR analytical method developed, which was shown to be more reliable than previously used hydrolysis/HPLC techniques, allowed for the composition of the starting mixtures to be assayed. Under the conditions chosen, CD_2Cl_2 as solvent and ClO_4^- as counterion at 22 °C, the various isomers of the retinylidene iminium salts were shown to be stable thermally. Irradiation of either **1**, **2**, or **3**, using incident light of wavelengths 350, 436, or 468 nm, led in each case to the formation of only the 11-cis isomers as initial photoproducts. The quantum efficiencies, corrected for back-reaction by extrapolation to zero conversion, of the isomerizations of **1**, **2**, and **3** to the corresponding 11-cis isomers are 0.25, 0.17, and 0.18, respectively. Estimates of the quantum yields for the reverse isomerizations are given.

Light-adapted bacteriorhodopsin contains an all-trans retinal chromophore linked to a protein bacterioopsin via a protonated Schiff base.[2] On absorption of light this chromophore photoisomerizes about the $C_{13,14}$ double bond to form the intermediate K_{625} with a quantum efficiency of 0.30.[3,4] The reverse reaction also occurs photochemically and proceeds with a much higher efficiency ($\phi = 0.69$).[3,4] In a related reaction the visual pigment rhodopsin, which contains an 11-cis retinal chromophore, efficiently photoisomerizes about the $C_{11,12}$ bond to form the all-trans isomer.[5]

In an effort to understand these reactions, there have been several studies on the photochemistry of the parent retinals,[6-9] their Schiff base derivatives,[10-14] and the protonated Schiff bases.[11-15] In general these photoisomerizations have been reported to proceed both with significantly lower efficiencies and with reduced selectivity as compared to the natural pigments. Product formation in the case of all trans Schiff bases[12,13] and protonated Schiff bases[13,15] has been found to be both wavelength and solvent dependent.

In the case of the photolysis of the all-trans retinylidene iminium salts there are some significant practical difficulties associated with these measurements, and some uncertainty remains as to the accuracy of previously reported results. In the first place it has been shown that thermal cis/trans isomerizations can take place in conjugated iminium salts in a variety of solvents.[16-19] Recently,

Rando and co-workers[18,19] have shown that cis retinylidene iminium salts are extremely susceptible to rapid nucleophilic catalyzed isomerizations. These reactions have been shown to occur in the presence of chloride and acetate ions[19] as well as in methanol.[20] Unfortunately, these nucleophiles have been present in excess amounts in several previously reported photochemical studies which lead to dark reactions which complicate the analysis of the photoinduced reactions.[12,13,15] A second difficulty arises in the analysis of the mixtures produced on irradiation. One approach used involves the hydrolysis of the salts and analysis of the recovered mixture of retinals.[13,15] Potentially, isomerization can occur during the hydrolytic step itself and the resulting analysis may not accurately reflect the composition of the irradiated solutions. Alternatively, analyses have been performed using multicomponent UV methods.[13,14] This second method is direct and obviates the necessity of the troublesome hydrolytic step, but lacks precision, particularly when more than one photoisomer is produced.

In this paper we wish to report the use of high-field ¹H NMR spectroscopy as a method to identify and quantitatively measure *directly* the primary photoproducts arising from the irradiation of all-trans retinylidene iminium salts. Using this technique it has been shown that the reactions are highly regioselective and wavelength independent, and can proceed with relatively high efficiencies.

Results and Discussion

The iminium salts **1–3** were prepared as solids using modified
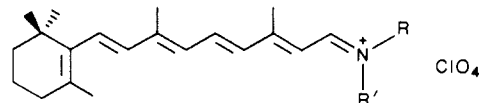
1: R = *t*-Bu; R' = H
2: R = *n*-Bu, R' = H
3: R = R' = Me

methods of Blatz[21] and Leonard.[22] The purity of the salts was assessed by high-field ¹H NMR spectroscopy, and it was noted in each case that in addition to major amounts of the all-trans isomer, minor amounts of an isomeric iminium salt were present. The ¹H NMR spectra of the major isomers were quite consistent with their formulation as the all-trans iminium salts **1–3** (Table

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Table I. ^{1}H NMR Chemical Shift^a Data for Retinylidene Iminium Salts

| position	1	2	3	6	7	8	9
C(2)H	1.50 t	1.53 t	1.51 t	1.50 t	1.50 t	1.53 t	1.51 t
C(3)H	1.61 m	1.65 m	1.61 m	1.61 m	1.61 m	1.65 m	1.61 m
C(4)H	2.06 t	2.09 t	2.09 t	2.06 t	2.06 t	2.09 t	2.09 t
C(7)H	6.47 d	6.56 d	6.59 d	6.59 d	6.47 d	6.56 d	6.59 d
C(8)H	6.21 d	6.27 d	6.31 d	6.31 d	6.21 d	6.27 d	6.36 d
C(10)H	6.29 d	6.33 d	6.36 d	6.33 d	6.74 d	6.75 d	6.75 d
C(11)H	7.43 dd	7.51 dd	7.59 dd	7.48 dd	7.03 t	7.04 dd	7.08 t
C(12)H	6.58 t	6.56 d	6.64 d	7.22 d	6.23 d	6.18 d	6.23 d
C(14)H	6.65 d	6.72 d	6.62 d	6.13 d	6.73 d	6.30 d	6.41 d
C(15)H	8.19 dd	8.34 dd	8.56 d	8.76 d	8.20 dd	8.25 dd	8.58 d
C(16)H							
	1.05 s	1.08 s	1.08 s	1.07 s	1.05 s	1.08 s	1.08 s
C(17)H							
C(18)H	1.74 s	1.77 s	1.78 s	1.78 s	1.77 s	1.77 s	1.78 s
C(19)H	2.10 s	2.13 s	2.16 s	2.14 s	2.07 s	2.10 s	2.09 s
C(20)H	2.32 s	2.36 s	2.46 s	2.43 s	2.46 s	2.45 s	2.56 s
C(1')H		3.74 dt	3.74 s	3.75 s		3.74 dt	3.76 s
C(1'')H			3.47 s	3.47 s			3.47 s
C(2')H	1.51 m	1.81 m			1.51 s	1.81 m	
C(3')H		1.43 m				1.43 m	
C(4')H		0.99 t				0.96 t	
$J_{10,11}$	11.89	11.81	11.77	11.77	12.43	12.96	11.59
$J_{11,12}$	14.90	14.70	14.68	14.60	11.80	11.77	11.65

^{a} s = singlet, d = doublet, t = triplet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet. Values in ppm; numbering of carbons as in text; referenced to CD_2Cl_2, 5.32 ppm; measured at 21 °C.

Table II. Composition of Starting Retinylidene Iminium Salts

	relative percentage of isomers^a			
compd	all-trans	13-cis	11-cis	9-cis
1	96.5	3.5	nd	nd
2	90.5	9.5	nd	nd
3	87.3	12.7	nd	nd

^{a} nd isomer not detected.

Table III. Absorption Spectra of Retinylidene Iminium Salts^a

compd	λ_{max} (nm)	ϵ_{max} ($\times 10^{-4}$)
1	472	4.26
2	476	4.06
3	498	4.05

^{a} In CH_2Cl_2 at 22 °C.

I). The amounts of the minor isomers varied from 3.5% in the case of **1** to 12.7% with **3** (Table II). These minor isomers were shown to be the 13-cis isomers **4–6** on the basis of their ^{1}H NMR

4: R = *t*-Bu, R' = H
5: R = *n*-Bu, R' = H
6: R = R' = Me
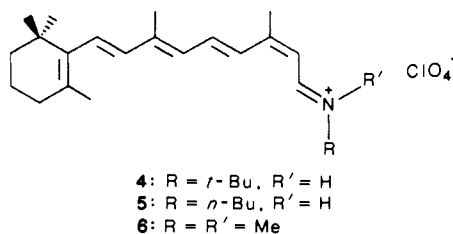
spectra and comparison of these with published data.[23] These assignments were confirmed by the independent synthesis of **6** by treatment of 13-*cis*-retinal with dimethylammonium perchlorate at 0 °C to give a mixture of **3** (60%) and **6** (40%). This mixture was sufficiently enriched in **6** to allow its spectrum to be completely assigned (Table I).

The choice of solvent and counterion used in these studies was critical. In order to prevent thermally induced cis/trans isomerizations, it was necessary to use a nonnucleophilic solvent and counterion. Retinylidene iminium salts have limited solubility in nonpolar solvents. Eventually, CD_2Cl_2 was shown to be a suitable solvent: dissolving appreciable amounts of the iminium salts and being ideal for ^{1}H NMR purposes since the residual ^{1}H resonance at 5.32 ppm does not interfere with any of the retinylidene iminium salt resonances. Perchlorate counterions were used in order to reduce the possibility of nucleophile catalyzed thermal isomerizations of the photochemically generated iminium salts.[19] With this combination of solvent and counterion the salts were shown to be thermally stable with no change in composition of the solutions of **1–3** being observed when kept at 22 °C in the

absence of light for the duration of a typical photochemical experiment (ca. 60 min).

Photoisomerizations: Product Identification. The UV spectral data of **1–3** in CD_2Cl_2 are given in Table III. The absorption maxima and band intensities are similar to those previously reported for retinylidene iminium salts.[12,15] The photoisomerizations of dilute solutions of salts **1–3** in CD_2Cl_2 at 22 °C were monitored by high-field ^{1}H NMR spectroscopy both as a function of time and wavelength of irradiation. It was clear, irrespective of the wavelength used (350, 436, and 468 nm), that in each case a single photoisomer was being produced in the initial stages of the photoreactions (Figure 1). The minor amounts of the 13-cis isomers present in the solutions of **1–3** did not appear to interfere with the photoreactions at the early stages of the reaction. With continued irradiation, a complex mixture of several isomers was produced.

In each case the identity of the initial photoproduct was established by examination of the ^{1}H NMR spectra of the mixtures after irradiation. The peaks associated with the photoproduct could be identified by comparing spectra obtained at different irradiation times. As the resonances associated with the photoproducts were different from those associated with the 13-cis isomers **4–6**, it was clear that these isomers were not being produced in the initial stages of the photoreaction. The primary photoproducts were identified as the 11-cis isomers **7–9**. For
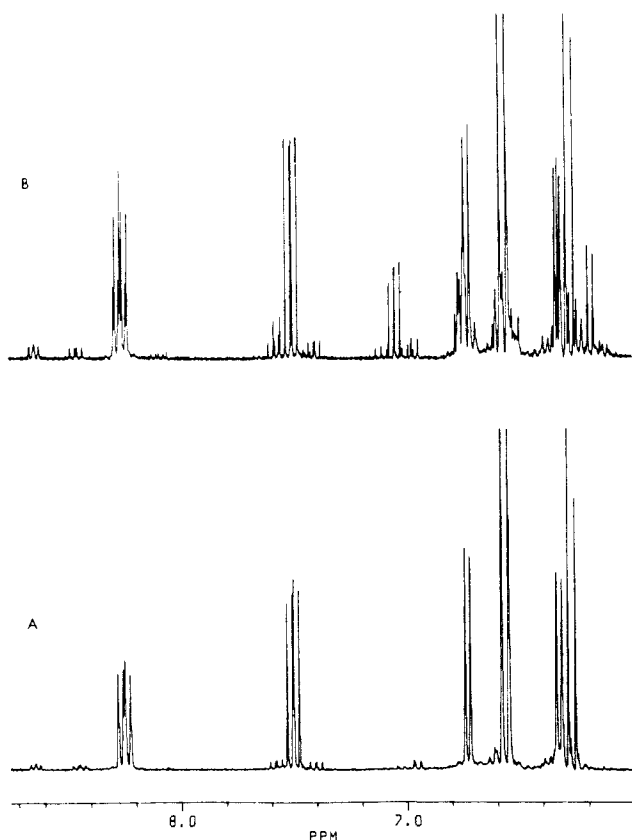

7: R = *t*-Bu; R' = H
8: R = *n*-Bu; R' = H
9: R = R' = Me

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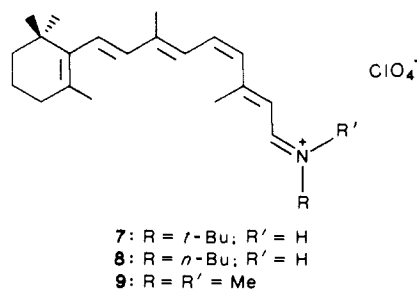
Figure 1. Photoisomerization of *n*-butylretinylidene iminium perchlorate (2) as followed by 500-MHz ^{1}H NMR spectroscopy: (A) vinylic region, before irradiation; (B) after irradiation at 350 nm.

example, in the case of the photoisomerization of **1** the photoproduct exhibited a resonance at 7.1 ppm which could be attributed to H_{11}. This resonance appeared as a triplet with coupling constants of 11.8 Hz for both $J_{11,12}$ and $J_{11,10}$, clearly indicating a cis configuration about the $C_{11,12}$ bond of the photoproduct. The coupling constants found here are very comparable to those reported by Shriver and co-workers.[24] While the chemical shifts of H_{11} and the other protons in the spectrum of the photoproducts cannot be compared directly to those reported by Shriver et al., as different solvents and temperatures were used in each case, the overall pattern and magnitudes of the chemical shifts of the 11-cis isomers produced in this work (Table I) are very similar to those previously reported.

An additional photoproduct was observed in each case on continued irradiation of **1–3**. These products were identified as the 9-cis isomer **10–12** on the basis of their ^{1}H NMR spectra and

10: R = *t*-Bu, R′ = H
11: R = *n*-Bu, R′ = H
12: R = R′ = Me
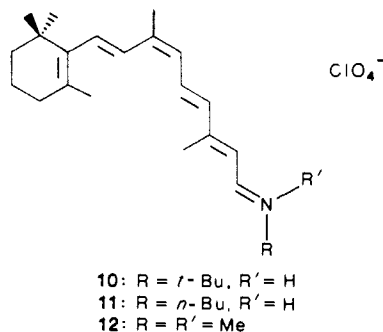
recovery of the corresponding retinal isomers; see below. Unlike the 11-cis isomers **7–9**, the 9-cis compounds **10–12** could not be identified from coupling constants across the $C_{9,10}$ bond because of the methyl group at C_9. However, a comparison of the chemical

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Table IV. Composition of Retinylidene Iminium Salt Mixtures As Determined by ^{1}H NMR and HPLC[a]

compound irradiated	product	composition after irradiation,[b] %	
		^{1}H NMR	HPLC
1	**1** (all-trans)	44.6	37.3
	4 (13-cis)	5.9	12.0
	7 (11-cis)	20.3	19.5
	10 (9-cis)	29.2	31.3
3	**3** (all-trans)	37.6	40.8
	6 (13-cis)	6.0	11.6
	9 (11-cis)	27.1	21.7
	12 (9-cis)	29.3	25.8

[a] Each value is the average of two experiments. ^{1}H NMR data are obtained from the integration of the C(20)H resonance for each isomer; irradiations carried out at 468 nm. [b] The same irradiated sample of **1** or **3** was used for both the ^{1}H NMR and HPLC analyses.

shifts of the C_{18} and C_{19} methyl group resonances with those reported for retinal isomers suggested that these isomers must be 9-cis.[25] However, at this stage the ^{1}H NMR spectra became exceedingly complex and the complete assignment of resonances for the 9-cis isomers was impossible. The compositions reached on more extended irradiations of **1** and **3** are given in Table IV.

Further confirmation of the identity of the photoproducts was obtained by hydrolysis of the iminium salts and examination of the mixture of retinals produced by HPLC. The compositions of the iminium salt solutions derived by the irradiation of **1** and **3** as determined both by high-field ^{1}H NMR spectroscopy and HPLC analysis of the corresponding retinals obtained after hydrolysis are given in Table IV. It can be seen that the HPLC analysis confirms the presence of the all-trans, 13-cis, 11-cis, and 9-cis retinal isomers. However, in each case there are some significant differences in composition as measured by ^{1}H NMR spectroscopy as compared to HPLC. In particular it should be noted that there is considerably more of the 13-cis isomer present after hydrolysis than is present in the original CD_2Cl_2 mixtures of the iminium salts, or upon irradiation.

The results shown in Table IV clearly indicate that C=C bond isomerizations are occurring during the hydrolysis of the iminium salts and recovery of the retinals. This would particularly seem to be the case about the $C_{13,14}$ bond, and it is interesting that the amount of 13-cis retinal present in the hydrolyzed mixtures by HPLC resembles that found in the thermodynamic equilibrium of all-trans retinal itself.[26] It is clear that there is need for considerable caution in using the hydrolysis/HPLC method of analysis as a quantitative technique for these systems.

One further type of photoproduct which potentially could be formed on irradiation of **1** or **2** involves isomerization about the C=N bond. It should be noted that this particular isomerization cannot be determined using the hydrolysis technique, as stereochemistry about the C=N bond is eliminated during hydrolysis. The thermal stability of these isomers would be expected to be less than that of the other cis isomers described here, and potentially these isomers might not survive the conditions used for the irradiations. Indeed, previous studies have shown that thermally induced C=N syn/anti isomerizations are rapid at room temperature.[23,27] In order to check for the formation of these isomers CD_2Cl_2 solutions of **1** were irradiated at −60 °C and the NMR assays run at this temperature. While photoisomerizations of **1** proceeded at this temperature to form the 11-cis isomer **7**, there was no evidence to suggest that **13** was being formed.

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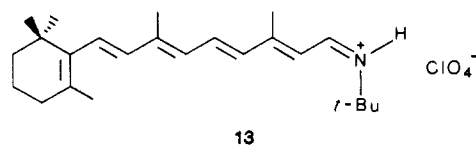
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(26) Rando, R. R.; Chang, A. *J. Am. Chem. Soc.* **1983**, *105*, 2879.
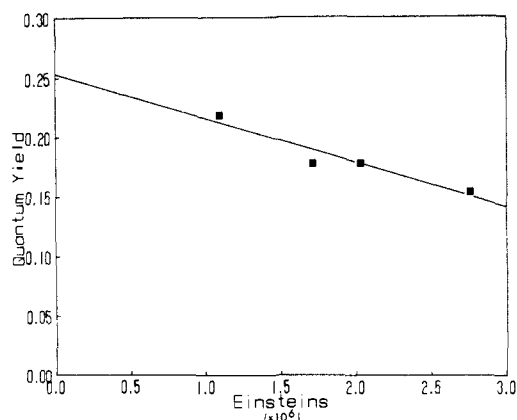(27) Sharma, G. M.; Roels, O. E. *J. Org. Chem.* **1973**, *38*, 3648.

Figure 2. Determination of quantum yield for **1 → 7** at 468 nm. Plot of einsteins of light absorbed at different irradiation times vs. measured quantum yield.

Table V. Quantum Yield Data

reaction	$\lambda_{excitation}$	ϕ
1 → 7	468	0.25 ∓ 0.03
2 → 8	468	0.17 ∓ 0.02
3 → 9	468	0.18 ∓ 0.02

a In CH_2Cl_2 at 22 °C.

Quantitative Measurements. In order to carry out quantitative studies on the photoisomerizations of these retinylidene iminium salts, it is necessary to know that the products of the irradiations are thermally stable under the photochemical conditions. The duration of a typical irradiation to yield up to a 5% conversion of salts **1-3** to the 11-cis isomers **7-9** was less than 60 min. Control experiments run with mixtures of the iminium salts showed that all the isomers identified above were stable for at least a 2-h period, a time which well exceeds that necessary for the irradiations and subsequent ¹H NMR analyses.

Using these techniques it was possible to detect isomers present at relative concentrations greater than 0.5%. Quantitative measurements were constructed on solutions containing greater than 1% of the minor isomers. The error in these quantitative measurements was ∓5%.

Quantum yields for the conversion of **1** and **2** to **7** and **8**, respectively, were determined using 468-nm light and ferrioxalate actinometry. Care was taken to avoid exposure of the samples to room light before or after the analyses. The samples were not degassed, since it has been previously shown that dissolved oxygen does not quench the photoreaction of retinylidene iminium salts.[12,13] Assays were carried out by comparing the areas of the ¹H NMR signals due to the methyl groups at C_{13}. These signals were well separated from other resonances, and they provided a sensitive measure of composition as they were singlets of relative intensity 3. All photochemical conversions were kept below 5% as the products of the photoisomerizations absorb light at the wavelengths used and can photochemically revert to the starting salts. In order to correct for the back-photoisomerization the apparent quantum yields were measured at various degrees of conversion and plotted against the amount of light absorbed.[8] These plots were extrapolated back to zero conversion to give a corrected quantum yield (Figures 2 and 3). The reproducibility and precision of the NMR assay method was excellent as can be seen from these typical plots.

The quantum yields obtained for the conversion of **1** and **2** to **7** and **8**, respectively, are given in Table V. The value quoted for the conversion of **2** to **8** has been corrected for the presence of the 13-cis isomers in the starting solutions by assuming that fraction of light absorbed by the 13-cis isomer was proportional to its concentration and that the efficiency of isomerization of the 13-cis isomer to the all-trans isomer was low. The quantum efficiency of the conversion of **3** to **9** was measured relative to the conversion of **2** to **8**. This quantum yield was corrected for the presence of the 13-cis isomer **6** in solutions of **3**.
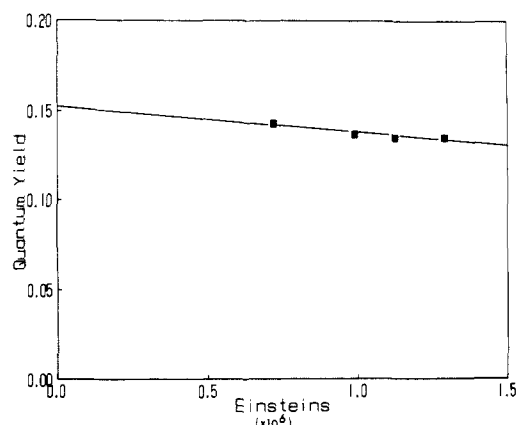

Figure 3. Determination of quantum yield for **2 → 8** at 468 nm.

Discussion

It is clear from the results presented above that high-field ¹H NMR techniques provide a convenient and powerful method to directly analyze mixtures of retinylidene iminium salts. By using this techique it is evident that C=C bond isomerization occurs both during the preparation and hydrolysis of the retinylidene iminium salts. The occurrence of isomerization on the formation of the iminium salts indicates that great caution should be exercised in using these salts for quantitative studies without a direct assay being made of the composition of the starting mixture. The ease of isomerization about the $C_{13,14}$ bond during hydrolysis of the retinylidene iminium salts suggests that such a procedure is not a good quantitative method for analyzing these systems.

Not only does ¹H NMR spectroscopy provide a good analytical tool for these systems but the judicious selection of solvent and counterion made in this work has ensured that the retinylidene iminium salts are thermally stable. In contrast to previous studies,[13,15] these retinylidene iminium salts were isolated and recrystallized to ensure a one-to-one cation-to-anion relationship. These factors were particulary important in that they allowed for a quantitative approach to the examination of the photoisomerizations of retinylidene iminium salts.

The results presented here show that the primary photoisomers obtained on irradiation of the all-trans salts **1-3** are the 11-cis isomers **7-9**, irrespective of the wavelength of the light used. Waddell and Donahue[15] have reported that the 11-cis isomer was the primary photoproduct on irradiation of all-trans retinylidene iminium salts at 436 nm, whereas at 468 nm the 13-cis isomer was dominant and the 11-cis isomer not formed. Becker et al.[13] have shown that the 11-cis isomer is the primary photoproduct at 355 nm. The results reported here verify the work of these groups at 355 and 436 nm and raises considerable doubt about the validity of the previous result of 468 nm, particularly in view of the analytical procedure used by these authors. This wavelength independence of the product formed on irradiation of the all-trans isomers is consistent with the photoreactions occurring only from the first excited singlet state, S_1. Previous investigations, which corroborate this finding, have shown that singlet–triplet intersystem crossing for these iminium salts is very inefficient ($\phi < 0.001$).[28]

In terms of the quantitative results it should be stressed that the quantum yields determined in this work are for the specific conversion of the all-trans retinylidene iminium salts to their 11-cis isomers. The previous approaches used only allowed the determination of a total quantum yield for the isomerization of the starting retinal to a mixture of several photoproducts. The photoisomerization of **1** is significantly more efficient than that of **2** (Table V). This variation of quantum yield with substituent on nitrogen has been noted previously for the cis–trans photoisomerizations of poly(ethylene glycol) retinylidene iminium salts.[14] It should be noted that the quantum yield for isomerization of **2** is essentially the same as that of the dimethyl-substituted im-

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inium salt **3**. This implies that hydrogen bonding of the counterion to the nitrogen proton in **2** does not alter either the selectivity or efficiency of the photoisomerization. This has been previously observed by Childs and Dickie[17] in studies of some 3-aryl-2-propenylidene iminium salts.

The quantum yield for the isomerization of **1** to **7** is the highest reported for the trans to cis conversion of a retinylidene iminium salt. The efficiency of this reaction is virtually identical with that reported for the primary photoisomerization of light-adapted bacteriorhodopsin.[3] It should be pointed out that a key difference in the in vitro systems studied here is the different regioselectivity of their reactions as compared to the natural pigments. The photoisomerization of **1** occurs selectively about the $C_{11,12}$ bond, whereas the natural system forms the 13-cis isomer. It would seem clear that the binding site in the natural pigment is directing the position of isomerization. Corroboration of this is found in the binding studies of the various retinal isomers with bacterioopsin in which it was shown that the 11-cis isomer does not bind to the protein.[29] The restrictions imposed on the chromophore by the binding site are absent in CD_2Cl_2 solutions and the molecule follows the energetically most favored path in the excited state which is to form **7**.

The visual pigment, rhodopsin, contains an 11-cis retinal chromophore which is photochemically converted to the all-trans form with a quantum efficiency of 0.67.[30] The reactions studied in this work involve the reverse photoisomerization. It is interesting to use the data obtained here to estimate a value for the photoisomerization of the 11-cis to all-trans retinylidene iminium salts. These retinylidene systems are complex in that isomerizations eventually occur about several of the C=C double bonds. However, it is clear that the all-trans isomers primarily photoisomerize to the 11-cis isomers and that the latter species preferentially reverts to the former isomer rather than to a di-cis isomer.[12,14] While a complete photostationary state for all the isomers was not reached for either **1**, **2** or **3**, in each case after a 2-h irradiation the ratio of the 11-cis isomers to all other isomers had reached a limiting value consisting of about 24% of the 11-cis isomer and 40% of the all-trans. Using this value as a approximation for the true photostationary state with extinction coefficients for the all-trans and 11-cis isomers at 468 nm, the irradiating wavelength, it is possible to estimate the magnitude of the quantum efficiency for the conversion of the 11-cis to all-trans isomers by using the standard relationship expressing the photostationary state.[31]

Using this approach a value of the quantum yield for the photoisomerization of **8** to **2** of 0.4 is obtained, a value similar to those previously reported values for this isomerization, 0.05–0.37.[31] A quantum yield of 0.59 was estimated for the photoisomerization of the N-tert-butyl systems **7** to **1**. This latter value is comparable in magnitude to the reported value of 0.67 for the quantum yield of the similar reaction of rhodopsin.[30] It is particularly gratifying that these simple retinylidene iminium salts can exhibit the same high degree of regioselectivity and efficiency in their photoreactions as the natural pigments. In rhodopsin the site of isomerization is identical with that noted in

these studies, namely the $C_{11,12}$ bond. However, as is shown by a comparison of the results obtained here with bacteriorhodopsin, the protein would clearly seem to be altering the regiochemistry of its photoreaction.

Experimental Section

General. all-trans-Retinal and 13-cis-retinal were obtained commercially (Aldrich, Fluka) and used as obtained. all-trans-Retinal was analyzed by HPLC and found to be >99% pure. Ethyl ether was distilled over $LiAlH_4$ and stored under nitrogen. Methylene chloride was distilled over P_2O_5 and stored under nitrogen. Deuterated methylene chloride (MSD Isotopes) was used as received. All experiments were carried out under a nitrogen atmosphere in a darkroom. ^{1}H NMR spectra were obtained at either 250 MHz on a Bruker WM250 spectrometer or at 500 MHz on a Bruker AM500 spectrometer.

Preparation of Salts 1–3. The salts **1** and **2** were prepared using methods similar to Blatz[21] or Leonard,[22] by stirring all-trans-retinal (2.8 mmol) with the appropriate amine (28.2 mmol) in 50 mL of anhydrous ether, over molecular sieves for 24 h. The solution was filtered and evaporated. The resulting yellow solid was redissolved in ether and evaporated twice more to ensure complete removal of excess amine. Protonation of each imine was achieved by adding a dilute ethereal solution of $HClO_4$ to the imine dissolved in ether at −40 °C until precipitation was complete. The red solid iminium salt was filtered, recrystallized from methylene chloride/ether at −20 °C twice, and dried under vacuum. The iminium salt **3** was prepared by stirring all-trans-retinal (0.7 mmol) and freshly prepared dimethylammonium perchlorate (0.35 mmol) in absolute ethanol for 3 h. A small quantity of anhydrous ether was added to induce crystallization. The salt was purified in a fashion similar to that for **1** and **2**.

Absorption Spectra. The absorption spectra of iminium salts **1–3** were measured on an Hewlett-Packard HP8451 diode array spectrophotometer using 10^{-5} M solutions of the salts in methylene chloride.

Photoisomerizations. These were carried out by irradiating solutions of the iminium salts in methylene chloride contained in thin-walled ^{1}H NMR tubes. The irradiation wavelengths were 350, 436, and 468 nm at a temperature of 22 °C. The source of light was either a Rayonet photoreactor with the appropriate lamps or an Osram XBO 150W/S high-intensity xenon lamp and monochromator. The course of isomerization was followed by ^{1}H NMR spectroscopy directly on the irradiated solutions.

Quantum Yield Determinations. The light source used for the irradiation of the iminium salts **1–3** was an Osram XBO 150W/S high-pressure xenon lamp placed in a PRA ALH215 arc lamp housing, and operated with a PRA M303X lamp power supply. The light was passed through a PRA ALH1 jacketed infrared filter. A PRA B102 monochromater with 16-mm bandwidth entrance and exit slits was used, followed by a 425-nm cut-off filter (Corning No. 3389). Collimated light was passed through a beam splitter to the samples.

In both cases a UV enhanced silicon chip diode detector placed behind each of the sample and comparison channels was used to assess the amount of light passing through each sample. These were connected to a "home-built" digital current integrator.

Samples of each iminium salt were carefully weighed (3–10 mg) and dissolved in CD_2Cl_2 (0.5 mL) in 22-mm o.d. × 2-mm quartz "lollipop" cells. Quantum yields for **1** and **2** were determined using ferrioxalate actinometry at 468 nm. Photon flux was determined before and after each series of four irradiations and was found not to vary by more than 5%. The quantum yield for **3** to **9** was determined relative to the conversion of **2** to **8** at 350 nm. After each irradiation the entire sample was pipetted into a 5-mm o.d., thin-walled NMR tube for 250- or 500-MHz ^{1}H NMR analysis. Assay of these compounds was accomplished using the relative areas of $C_{20}H$ (Table 1). The areas of these resonances were integrated by a cut and weigh technique.[17] Using this technique the integrated areas of the resonances for C_{20} were reproducible to 5%. The data were used in the determination of the actual quantum yields as illustrated in Figures 2 and 3.

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