The Photoisomerizations of Protonated Schiff Base Derivatives of Some Enals

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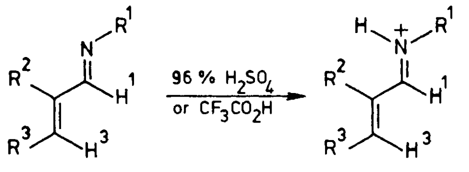
Summary Protonated n- and t-butyl Schiff base derivatives of some enals have been characterized and shown to undergo efficient *cis–trans* isomerization about both the C=N and C=C double bonds in strong acid media (H_2SO_4 and CF_3CO_2H).

THE chromophore of the visual pigment rhodopsin consists of 11-*cis*-retinal which is bound by a Schiff base linkage to the apoprotein opsin.[1] It is generally accepted that the Schiff base nitrogen atom is protonated[2] and that the primary photochemical event involves the *cis*- to *trans*-isomerization of the 11,12-double bond of the chromophore.[3] Despite the considerable current interest in this type of system, very little attention has been paid to the photochemistry of simpler protonated imines. We have examined the photoisomerizations of some protonated unsaturated imines and have found that efficient isomerizations occur about both the C=C and C=N double bonds.

The n-butyl and t-butyl imines (**1**) and (**2**), synthesized by a similar procedure to that described by Schlessinger,[4]† were readily protonated in the acids used to give stable solutions of (**3**) and (**4**), respectively. The 400 MHz ^{1}H n.m.r. spectra of these cations were consistent with the assigned structures. Each of these protonated imines exhibited an intense u.v. absorption in the region of 250 nm.

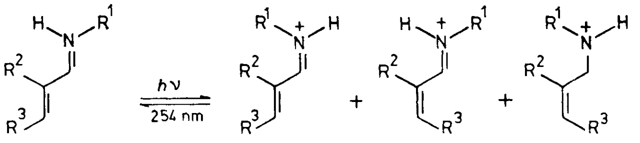


(1) $R^1 = Bu^n, R^2 = Me, R^3 = H$ (3)[λ_{max} 245 nm (4·2)]

(2) $R^1 = Bu^t, R^2 = H, R^3 = Me$ (4)[λ_{max} 250 nm (5·6)]

Irradiation of (**3**) in CF_3CO_2H (TFA) or H_2SO_4 led to the formation of a single new product which has a ^{1}H n.m.r. spectrum consistent with the C=N *Z* isomer (**5**). The cation (**3**) has a coupling constant across the C=N double bond, $J_{C,NH}$, of 18 Hz, indicative of the *E*-configuration[5] while (**5**) has $J_{C,NH} = 12$ Hz. A photostationary state consisting of 65% (**3**) and 35% (**5**) was established. This isomerization about the C=N double bond of a protonated enimine, which to our knowledge is unprecedented, was found to be a relatively efficient process. The quantum efficiency of the conversion of (**3**) into (**5**) in H_2SO_4 and TFA was measured using a relative method‡ and found to be 0·12 ± 0·02 in H_2SO_4 and 0·16 ± 0·02 in TFA.

Likewise irradiation of (**4**) led to the formation of (**6**) (12%), (**7**) (28%), (**8**) (10%), and residual (**4**) (50%). These cations were all identified from their 400 MHz ^{1}H n.m.r. spectra using various selective decoupling experiments. The quantum efficiency for the photoisomerization about the C=C double bond [(**4**) to (**7**)] was found to be 0·17 ± 0·02 in H_2SO_4 and 0·32 ± 0·04 in TFA. The iminium ions obtained on irradiation of (**3**) and (**4**) were stable in the acid media used and no thermal isomerization could be detected at temperatures up to 60 °C.



(3) (4) (5) (6) (7) (8)

At this point direct evidence about the multiplicity of the excited states involved in these isomerizaions is lacking. The absence of any detectable effect of dissolved oxygen suggests that the isomerizations are proceeding *via* excited singlet states just as has been found for the visual pigments.[1] The results outlined above however, clearly indicate that isomerization about the C=N bond of these protonated imines is one of the major relaxation pathways of their excited states. This raises the question as to whether a similar process is occurring with the visual pigments themselves.

A further point worth noting is the large solvent dependence of the quantum efficiency of C=C bond isomerization. The quantum efficiency is smallest in the more viscous solvent, H_2SO_4, suggesting that this effect is related to solvent viscosity. A similar large solvent dependence has been observed in the photoinduced *cis*–*trans*-isomerization of protonated α,β-unsaturated ketones.[6]

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† All new compounds have satisfactory elemental analyses.

‡ Quantum efficiencies were measured relative to the photodecomposition of potassium ferrioxalate. All reactions were carried out at 25 °C and monitored using a ^{1}H n.m.r. assay technique. Quantum efficiencies have been corrected for back reaction.

[1] B. Honig, *Annu. Rev. Phys. Chem.*, 1978, **29**, 31.
[2] T. G. Ebrey and B. Honig, *Q. Rev. Biophys.*, 1975, **8**, 129; G. Eyring and R. Mathies, *Proc. Natl. Acad. Sci. USA*, 1979, **76**, 33.
[3] T. Rosenfeld, B. Honig, and M. Ottolenghe, *Pure Appl. Chem.* 1977, **49**, 341.
[4] G. R. Kiezykowski, R. H. Schlessinger, and R. B. Sulsky, *Tetrahedron Lett.*, 1976, **8**, 597.
[5] G. A. Olah and P. Kreienbuhl, *J. Am. Chem. Soc.*, 1967, **89**, 4756; G. A. Olah and D. J. Donovan, *J. Org. Chem.*, 1978, **43**, 860.
[6] R. F. Childs and A. W. Cochrane, *J. Org. Chem.*, 1981, **46**, 1086.