The material could not be sufficiently purified for elemental analysis. The highest *m/e* peak in the high-resolution mass spectrum corresponded to $M^+ - N(CH_3)_2$; calcd for $C_{16}H_{26}N_5O_2$ 320.2077, found 320.2082.

1,4-Bis[*N*-[[(dimethylamido)amino]cyclopropyl]phenylamino]-2-butyne (14). A 10-mL quartz test tube was charged with 49.8 mg (0.125 mmol) of 1,4-bis[(5-oxopyrrolin-2-yl)-phenylamino]-2-butyne (**8**) in 10 mL of reagent-grade acetonitrile. The test tube was equipped with a cold finger and nitrogen inlet and outlet. The solution was degassed for 10 min prior to and during irridation in a Rayonet reactor equipped with 2537-Å lamps. After 1 h of irradiation the starting material had disappeared as indicated by IR spectroscopy. Dimethylamine was then bubbled through the solution for 10 min. Rotary evaporation of the solvent yielded 56.1 mg of **14** (92%) as a slightly yellow solid, mp 180–181 °C dec, which was pure by ^1H NMR spectroscopy. An analytical sample of **14** prepared by alumina TLC, eluting with ethyl acetate, had the following physical properties: mp 179–181 °C dec, IR (CH_2Cl_2) 2.91, 3.40, 6.05, 6.66 μm; ^1H NMR ($CDCl_3$) δ 1.20 (s, 8 H), 2.77 (s, 12 H), 4.42 (s, 4 H), 5.48 (br, 1 H), 6.6–7.40 (m, 10 H); mass spectrum, *m/e* (relative intensity) 488 (3.5), 372 (13), 270 (25), 269 (13), 225 (30), 220 (20), 218 (12), 198 (12), 197 (20), 183 (14), 143 (11), 132 (14), 130 (16), 72 (base). The material could not be sufficiently purified for elemental analysis. The highest *m/e* peak in the high-resolution mass spectrum corresponded to the molecular ion; calcd for $C_{28}H_{36}N_6O_2$ 488.2900, found 488.2893.

Acknowledgment. Support of this research by Grants GM-18349 and GM-24965 from the National Institute of General Medical Sciences is gratefully acknowledged. Acknowledgment is also made to The University of Nebraska Regional Mass Spectrometry Center, funded by NSF, for technical assistance. We also thank Professor Mitchell Winnik for a helpful discussion.

Registry No. **1**, 29473-56-1; **3**, 68321-93-7; **4**, 75812-67-8; **5**, 75812-68-9; **6**, 75812-69-0; **7**, 14130-04-2; **8**, 75812-70-3; **9**, 45812-71-4; **10**, 75812-72-5; **13**, 75812-73-6; **14**, 75812-74-7; dimethylamine, 124-40-3; *N*-methylaniline, 100-61-8.

Quantum Efficiencies of the Cis/Trans Photoisomerization of Protonated α,β-Unsaturated Carbonyl Compounds

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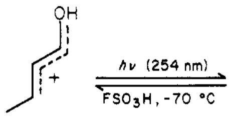
Received November 4, 1980

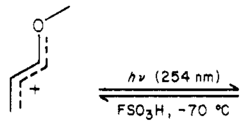
The quantum efficiencies of the photoinduced interconversion of protonated *trans*- and *cis*-pent-3-en-2-ones (**1** and **2**, respectively) have been measured. In FSO_3H at 25 °C with 254-nm light $\Phi_{1\to2}$ was found to be 0.64 and $\Phi_{2\to1}$ to be 0.65. These isomerizations are more efficient than the interconversions of the corresponding neutral ketones. Change of the acid medium from FSO_3H to FSO_3H/SbF_5 (1:1) or reduction in the temperature at which the irradiations were carried out substantially reduced the quantum efficiency of the conversion of **1** to **2**. In both cases, this effect was attributed largely to an increase in viscosity. The quantum efficiencies of the cis/trans photisomerizations about the carbon–carbon double bonds of several other α,β-unsaturated carbonyl compounds were determined. Photoisomerism about the carbon–oxygen bond of 1-methoxyallyl cation was also found to be a relatively efficient process.

A considerable number of different types of carbocation have been found to be photoreactive.[1] These range in complexity from the protonated imines associated with the chemistry of vision[2] to the comparatively simple protonated enals.[3] Despite the variety of photoreactions which have been observed, very little quantitative work has been reported hitherto.[4]

Protonated, conjugated enals and acyclic enones have been shown to undergo cis/trans isomerization about the carbon–carbon "double" bond on irradiation in superacid media (eq 1).[3] Eventually a photostationary state is established between the two conformers, and, unlike the case with the corresponding neutral carbonyl compounds,[5-9] no other products have been detected even on prolonged irradiations. The related *O*-methyl derivatives undergo both carbon–carbon and carbon–oxygen bond isomerizations on irradiation (eq 2).[10] It would seem likely that a similar carbon–oxygen bond isomerization occurs with the protonated enals and enones; however, exchange of the proton on oxygen with the acid pool precludes the detection of such a reaction.



(1)



(2)

These protonated α,β-unsaturated carbonyl compounds represent one of the basic chromophores present in many of the carbocations that have been shown to photoisom-

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(1) For reviews see: Cabell-Whiting, P. W.; Hogeveen, H. *Adv. Phys. Org. Chem.* **1973**, *10*, 129; Childs, R. F. *Rev. Chem. Intermed.* **1980**, *3*, 285.

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0022-3263/81/1946-1086$01.25/0

Table I. UV Spectral Data of Cations

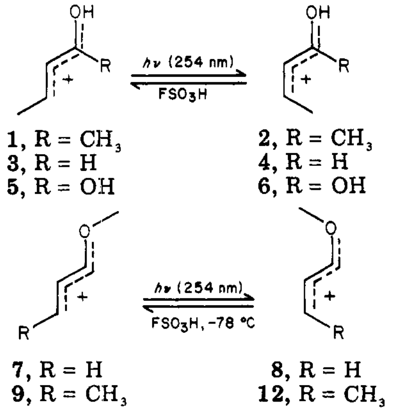
cation	λ_{max}, nm	log ϵ	log ϵ_{254}
1[a]	261	4.27	4.20
2[a]	273	4.13	3.80
3[b]	258	4.64	
5[b]	236	4.61	
6[c]	238	4.61	
7[d]	234	3.97	
9[d]	256	4.28	

[a] This work. [b] Zalewski, R. I.; Dunn, G. E. *Can. J. Chem.* 1968, *46*, 2469. [c] Reference 3. [d] Reference 10.

erize. We report here the quantum efficiencies of their photoinduced cis/trans isomerizations.

Results

The cations **1**–**3**, **5**, and **6** were prepared by dissolving the corresponding carbonyl compounds in FSO_3H or FSO_3H/SbF_5 media at −78 °C. All of these ions have been reported before and have been shown to undergo cis/trans isomerization about the carbon–carbon "double" bond on irradiation at 254 nm.[3,11] The methoxy cations **7** and **9** were prepared from the acetals as described in an earlier paper.[10] The UV spectral data of these ions are given in Table I.



Rearrangement of the thermodynamically less stable cis isomers to the trans isomers of the aldehyde and ketone precursors of these ions occurred on neutralization of the superacid media. Consequently, it was necessary to assay the cation composition directly in the acid solutions. The UV spectra of the cis/trans cation pairs were, in general, too similar to permit quantitative analysis, and hence ^{1}H NMR spectroscopy was employed. This meant that relatively high concentrations of the cations had to be used (ca. 0.2 M) and substantial degrees of photochemical conversion had to be achieved (5–10%) to get reasonable composition measurements. The optical densities of the solutions at 254 nm were very high as a result of these high concentrations.

The quantum efficiencies were measured in a relative manner by using low-pressure mercury lamps as a light source. Samples were contained in quartz tubes and irradiated by using a "merry-go-around" which could be inserted in a partially silvered quartz Dewar.

Table II. Quantum Efficiences[a]

starting matl	product	solvent	temp, °C	Φ
1	2	FSO_3H	25	0.64 ∓ 0.05[b]
1	2	FSO_3H/SbF_5	25	0.43 ∓ 0.04
1	2	FSO_3H	−68	0.38 ∓ 0.05
2	1	FSO_3H	25	0.65 ∓ 0.07
3	4	FSO_3H	−68	0.26 ∓ 0.04
5	6	FSO_3H	−68	0.23 ∓ 0.03
6	5	FSO_3H	−68	0.39 ∓ 0.04
7	8	FSO_3H	−68	0.15 ∓ 0.03
9	12	FSO_3H	−68	0.29 ∓ 0.06
10	11	hexane	25	0.33 ∓ 0.05[c]

[a] All isomerizations are corrected for back reaction.
[b] Same value for aerated or argon degassed solution.
[c] This work.

Table III. Photostationary State Compositions[a]

cation (%)	temp, °C	cation (%)	temp, °C
1 (38), **2** (68)	25	**5** (58), **6** (42)	−68
1 (37), **2** (63)	−68	**7** (73), **8** (27)	0
3 (46), **4** (54)	−68	**9** (31), **12** (49)[b]	−68

[a] Irradiations at 254 nm; ∓2%; all samples in FSO_3H.
[b] The C_1O *Z* isomers of **9** and **12** are also present.

The thermal isomerization of **2** to **1** in FSO_3H is sufficiently slow at 25 °C to allow measurement of the quantum yield for the photochemical interconversion at this temperature.[3] Potassium ferrioxalate actinometry was used, and the results obtained are given in Table II.[12] With the high optical densities of the solutions it seemed possible that a layering effect might occur. However, there was no detectable change in the measured quantum efficiencies whether or not the solution was agitated by an argon stream during the irradiation.

The quantum efficiency for the conversion of **1** to **2** was found to drop when FSO_3H/SbF_5 (1:1) was used as the acid medium as compared to that obtained in FSO_3H.

For measurement of the quantum efficiencies for the photoisomerizations of the other cation pairs it was necessary to work at low temperatures to minimize thermally induced stereomutations. The quantum efficiency for the conversion of **1** to **2** in FSO_3H was obtained at −68 °C by comparing the degree of reaction observed at this temperature and at 25 °C using identical irradiation times and conditions. Alternatively, ferrioxalate actinometry was used before the low-temperature reaction. These experiments were repeated several times, and consistent results were obtained. Agitation of the solutions with an argon stream during the irradiation did not alter the observed quantum efficiencies within the experimental errors.

By use of the value for the conversion of **1** to **2** established at −68 °C, the relative efficiencies of the photoisomerizations of **3** to **4**, **5** to **6**, **6** to **5**, **7** to **8**, and **9** to **12** were obtained at −68 °C in FSO_3H (Table II). Other photoisomerizations of **9** occur,[10] but it was not possible to assay the complex mixtures obtained sufficiently accurately to obtain meaningful values of the quantum efficiencies of these processes.

The photostationary states reached in each of the cation pairs are given in Table III. In the case of interconversion of **1** and **2**, the photostationary state composition was the same at both 25 and −68 °C. No deuterium incorporation was observed when the photoisomerizations were carried out in FSO_3D.

In view of the conflicting quantum efficiencies reported for the conversion **10** to **11** in hydrocarbon solvents,[7,9] we repeated this determination in hexane and obtained a value of 0.33 ∓ 0.05. This value compares favorably with

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(11) Brouwer, D. M. *Tetrahedron Lett.* **1968**, 453. Olah, G. A.; Halpern, Y.; Mo, Y. K.; Liang, G. *J. Am. Chem. Soc.* **1972**, *94*, 3554. Deno, N. C.; Pittman, C. U., Jr.; Wisotsky, M. J. *Ibid.* **1964**, *86*, 4370.

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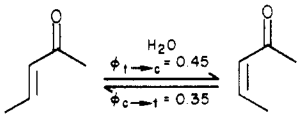
that measured by Graf and Lillya.

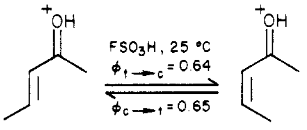
Discussion

The cis/trans phosoisomerizations of acyclic α,β-unsaturated carbonyl compounds on direct irradiation appear to proceed via singlet states.[5-9] While direct evidence is lacking with these protonated enones, it would seem likely that singlet states are again involved. Oxygen has no detectable effect on the quantum yield for the photoisomerizations of 1 → 2 in acid, and intersystem crossing is expected to be less efficient when the enones are O-protonated.

One common feature observed with the photoinduced stereomutations of unsaturated carbonyl compounds is that the sum of the quantum efficiencies of the trans to cis and cis to trans reactions do not sum to unity, e.g., eq 3.[7] The cis isomers also undergo a relatively inefficient photoenolization; however, the quantum efficiency of this process ($\Phi = 0.05$ in the case of *cis*-pentenone) is generally too small to restore the sum to unity. In the absence of any fluorescence, some nonradiative decay process which does not involve the formation of a common twisted intermediate is required.[13]



10 11 (3)



1 2 (4)

In this regard it is of interest that the quantum efficiencies of the photoisomerization of the protonated pentenones 1 and 2 in FSO_3H at room temperature would seem to sum to somewhat more than unity ($\Phi_{t\rightarrow c} + \Phi_{c\rightarrow t} = 1.29 \pm 0.12$; eq 4). Protonation of a carbonyl compound raises the energy of the n,π^* state, and the results we have obtained here support the suggestion that the failure to obtain a common/twisted intermediate in the neutral systems is associated with proximity of their n,π^* and π,π^* states.[6]

Twisting about the carbon–carbon double bonds of 1 and 2 is not the only relaxation path open to the excited states of these cations, for unlike the neutral enones, isomerization can also occur about the carbon–oxygen bonds.[14] The *O*-methyl cation 7 was found to convert to 8 with a quantum efficiency of 0.15 (FSO_3H, −68 °C, Table II), and if rotation about the carbon–oxygen bond of the protonated species 1 and 2 occurs with comparable efficiency, then the quantum yield sum will be considerably in excess of unity. This could mean that the carbon–oxygen and carbon–carbon bond isomerizations are linked together and both isomerizations can result from the absorption of a single photon or that the probability of a twisted intermediate relaxing to one or the other of the stereoisomers differs depending on its genesis.[15]

From the results given in Table II, it would seem that there is little structural dependence on the quantum efficiencies for the photoinduced cis/trans isomerization of a variety of protonated unsaturated carbonyl systems. In all of the cases studied in FSO_3H at −68 °C, the quantum efficiencies for photoisomerizations about the carbon–carbon bonds are similar. Even the replacement of the proton on oxygen with an *O*-methyl group does not alter the efficiency of the reaction significantly (compare $\Phi_{3\rightarrow 4}$ with $\Phi_{9\rightarrow 12}$).

The quantum efficiency of the photochemical cis/trans isomerization of 1 to 2 is both medium and temperature dependent. Thus, as can be seen from the data in Table II, $\Phi_{1\rightarrow 2}$ changes from 0.64 in FSO_3H to 0.44 in FSO_3H/SbF_5. A comparable drop was found on lowering of the temperature. No photoisomerization of 1 could be detected when it was irradiated in a 1:1 FSO_3/SbF_5 mixture at −68 °C.

When the acid is changed from FSO_3H to FSO_3H/SbF_5, two effects are operative, namely, an increase in the acidity of the medium[16] and also an increase in viscosity. Apart from FSO_3H at 25 °C,[16] the viscosities of these acid media have not been reported. Qualitatively it was noted that the addition of SbF_5 to FSO_3H at room temperature somewhat increased the viscosity of the acid. This enhancement in viscosity was particularly noticeable at −68 °C, where the mixed acid had a thick treacle-like consistency, whereas FSO_3H was still a mobile liquid. The similar reduction in quantum efficiency observed either on lowering the temperature or on addition of SbF_5 to the FSO_3H suggests that the viscosity of the medium is an important factor in these reactions.

The viscosity dependence of the quantum efficiencies of certain cis/trans photoisomerizations has been reported before.[17] The magnitude of the effect found here seems to be fairly large as compared to some of the other systems studied and may be associated with the much more specific solute/solvent interactions expected with these cationic systems.[18] Twisting about the carbon–carbon double bond in an excited state of a cation such as 1 would be expected to alter its charge distribution. A good model for the ion when this bond is twisted by 90° would be a structure with essentially a full positive charge on C_3. Unlike the sudden polarization associated with the twisting of an excited-state olefin diradical,[19] substantial changes in charge distribution of a cation such as 1 would be expected to occur over a considerable range of twist angles. Calculations on the related protonated retinylidene Schiff bases by Salem and Bruckmann indicate that significant charge redistribution occurs at twist angles as low as 60°.[20] This being the case, some degree of solvent reorganization would then be required when 1 undergoes an excited-state twisting of the carbon–carbon double bond, and this could be the origin of the large solvent-viscosity dependence.

The lack of a temperature dependence of the photostationary state set up between 1 and 2 strongly suggests

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(14) An alternative but less likely mode of photoreaction of these protonated enones would involve the formation of a protonated oxete as an intermediate. The isomerization of protonated oxetes to protonated enones is a very rapid reaction[8] and could lead to stereomutation about the carbon–carbon double bond. Friedrich and Schuster[8] have shown that highly substituted enones can be photochemically converted to oxetes in what appears to be a relatively inefficient reaction as compared to cis/trans isomerization.

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(17) Gegiou, D.; Muszkat, K. A.; Fischer, E. *J. Am. Chem. Soc.* **1968**, *90*, 12. Görner, H.; Schulte-Frohlinde, D. *Ibid.* **1979**, *101*, 4388. For a review see: Saltiel, J.; D'Agostino, J.; Megarity, E. D.; Metts, L.; Neuberger, K. R.; Wrighton, M.; Zafiriou, O. C. *Org. Photochem.* **1973**, *3*, 1.

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(19) Bonacić-Koutecký, V.; Bruckmann, P.; Hiberty, P.; Koutecký, J.; Leforestier, C.; Salem, L. *Agnew Chem., Int. Ed. Engl.* **1975**, *14*, 575.

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that the quantum efficiency for the conversion of **2** to **1** exhibits a similar temperature/viscosity behavior to that found for conversion of **1** to **2**.

The implications of the large solvent effect on the quantum efficiencies for these photoisomerizations of these protonated enones extend further than to just the immediately related cations. We have observed a similar dependence in the photochemical conversion of a series of protonated imines.[21] In this regard it is of considerable interest to note that a similar marked quantum yield temperature dependence has been observed with the protonated *n*-butylamine Schiff bases of retinal,[22] a phenomenon which is in contrast to the behavior of the visual pigments themselves.[2] It is clear that a better understanding of these effects will be of importance in fully determining the chemical processes occurring in the visual pigments.

Experimental Section

General Methods. ^{1}H NMR spectra were measured on a Varian EM 390 spectrometer, the probe temperature being measured with a methanol sample. UV spectra were obtained by using a Cary 14 instrument. Analytical gas chromatography was carried out with a Varian 3700 gas chromatograph coupled with a Varian CDS 111 data system. A 6 ft × $^1/_8$ in. copper column packed with 15% Carbowax on Chromosorb W was used. FSO_3H was purified by distillation, purging the distillate with nitrogen, and a subsequent redistillation.

The cations **1**–**3**, **5**, and **6** were prepared by weighing the carbonyl compound precursor (10–20 mg) into a quartz tube, cooling the tube to −78 °C, and adding cooled FSO_3H or FSO_3H/SbF_5 (~0.5 mL). Solution was achieved by mixing with a thin glass rod at low temperature. After all the samples for a particular run were made up, more acid was added so that each tube had an equal volume. The total volume of acid used in a tube for a typical run was 0.75 mL. Cations **7** and **9** were obtained as described previously,[10] and the sample volumes were adjusted as above.

Photochemical Apparatus. The light source used in these experiments consisted of five low-pressure mercury lamps (Southern New England Ultraviolet Co., RPR 2537 Å) arranged in a circle around a partially silvered quartz Dewar. The Dewar could be cooled with an FTS system Flexicool FC 2084P1 refrigerator unit, the probe of which was mounted axially in the center of the Dewar. This probe served as an axle for a "merry-go-round" which was constructed from Teflon. The merry-go-round was arranged to rotate in the Dewar and contain up to six tubes. Methanol was used as a heat-transfer medium. Without the cooling unit on, the inside of the Dewar remained at 25 °C during the course of an irradiation. After the cooling unit was switched on, a temperature of −68 °C was reached after some 20–25 min of cooling, and this temperature was maintained during the subsequent irradiations. Samples were contained either in 5-mm-i.d. quartz tubes or 5-mm-o.d. quartz NMR tubes. Sample stirring was carried out with a stream of argon.

The quantum efficiency of the conversion of **1** to **2** in FSO_3H was measured relative to potassium ferrioxalate.[12] The composition of the acid solutions was determined by measurement of the relative intensities of the methyl group resonances of **1** and **2** at δ 2.48 and 2.62, respectively.[3] Each spectrum was recorded some five or six times, and relative peak heights were used to obtain the composition of the solutions (the peak half-widths of the two signals were the same). In this and every case mentioned below, duplicate samples were used in each run, and at least two separate runs were performed. Stirring the samples with an argon stream did not have any detectable effect on the measured quantum efficiencies.

The quantum efficiency of the conversion of **2** to **1** in FSO_3H was measured relative to the conversion of **1** to **2** in the same acid.

The quantum efficiency of the conversion of **1** to **2** at low temperatures was obtained by preparing four samples of **1**. Two were irradiated at 25 °C and removed from the merry-go-round. Without turning off the lamps, the Dewar was cooled, and the remaining two tubes were irradiated for the same length of time. The degree of conversion in each tube was assayed as above. The experiment was repeated, and consistent results were obtained. This experiment was also carried out by using potassium ferrioxalate to measure the initial light intensity, and the same results were obtained.

The quantum efficiencies of the conversion of **3** → **4**, **5** → **6**, **6** → **5**, **7** → **8**, and **9** → **12** were all measured at −68 °C relative to the conversion of **1** → **2**. Assays were carried out by monitoring at −50 °C the resonances at δ 9.59 and 9.08 of **3** and **4**, respectively, at δ 2.19 and 2.43 of **5** and **6**, respectively, at δ 5.01 and 4.87 of **7** and **8**, respectively, and at δ 8.96 and 9.50 of **9** and **12**, respectively.

The quantum efficiency for the conversion of **10** to **11** in hexane was measured at 254 nm by using a relative method and a potassium ferrioxalate actinometer. The degree of conversion of **10** to **11** was measured by gas chromatography using a column temperature of 75 °C when the retention time of **10** was 2.8 min and that of **11** was 1.5 min.

Acknowledgment. The financial support of the Natural Science and Engineering Research Council of Canada is gratefully acknowledged.

Registry No. **1**, 58113-66-9; **2**, 58113-70-5; **3**, 61082-06-2; **4**, 61082-10-8; **5**, 61082-07-3; **6**, 61082-11-9; **7**/**8**, 69858-66-8; **9**, 69858-67-9; **10**, 3102-33-8; **11**, 3102-32-7; **12**, 69858-68-0.

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(21) Dickie, B. D.; Childs, R. F., unpublished results.

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