Tetrahedron Vol. 37, No. 19, pp. 3385 to 3395, 1981
Printed in Great Britain

0040-4020/81/193385-11$02.00/0
Pergamon Press Ltd.

PHOTOCHEMISTRY OF IMINIUM SALTS

ELECTRON TRANSFER MECHANISMS FOR SINGLET QUENCHING AND PHOTOADDITION OF N-ELECTRON DONATING ALCOHOLS AND ETHERS[1]

PATRICK S. MARIANO,*[2a] JEROME STAVINOHA,[2b] and ELLIOTT BAY[2c]

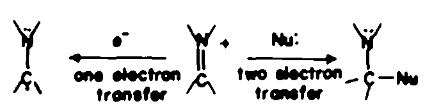
Department of Chemistry, University of Maryland, College Park, Maryland 20742 and Texas A&M University, College Station, TX 77843, U.S.A.

(*Received in USA April 1981*)

Abstract—Several aspects of past and current studies in the area of iminium salt photochemistry are discussed. Investigations of olefin–iminium salt photoaddition and photocyclization reactions are reviewed and conclusions about electron-transfer pathways for fluorescence quenching and reaction are discussed. The results of recent studies of alcohol and ether photoaddition to 2-phenyl-1-pyrrolinium salts are presented. These C–C bond forming processes occur in moderate yields to produce β-amino alcohol or ether products. In addition, alcohols and ethers serve as efficient quenchers of pyrrolinium salt fluorescence. Rate constants for quenching appear to be dependent upon both the oxidation potential of the alcohols and ethers and the availability of C–H bond α to oxygen. This data along with deuterium isotope effects on quenching combine to suggest a common mechanism for both fluorescence quenching and photoaddition. The nature of this mechanism is tested using the comparative quenching efficiencies of the tertiary alcohols *t*-butyl alcohol and 1,2,2-trimethyl-1-cyclopropanol. The latter alcohol having a weak C–C bond adjacent to the hydroxyl function quenches the fluorescence of 2-phenyl-1-pyrrolium salts at a rate two orders of magnitude greater than for t-butyl alcohol. The observations made are interpreted in terms of a sequential electron-proton transfer mechanism for quenching and photoaddition. Lastly, the relationship of iminium salt photochemical studies to other investigations of electron-transfer photochemistry is discussed.

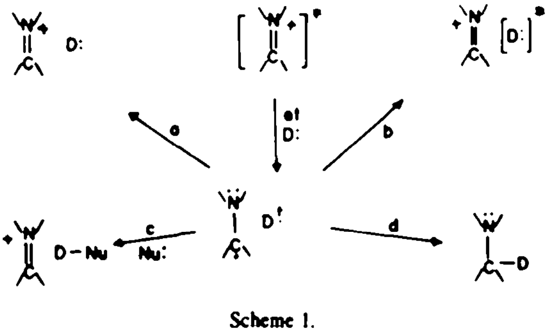
Several years ago we initiated exploratory studies of the excited state chemistry of systems containing the iminium salt $(>\overset{+}{N}=C<)$ grouping. Our interest in this area was stimulated by several factors. Firstly, although qualitative aspects of the photochemistry of nitrogen heteroaromatic salts had been investigated in reasonable detail,[3] comparable efforts probing the mechanistic and synthetic details of simple iminium salt excited state chemistry appeared more scarce. Secondly, we felt that the photochemistry of compounds having this chromophore might hold biochemical relevance.[4] Lastly, a simplified analysis of the electronic features of the iminium salt grouping suggested the possibility of predicting the reactive modes of excited state decay. These should resemble those available to olefins and include *EZ* isomerization[5] and 2 + 2 cycloaddition.[6] Importantly, iminium salts are lacking n-π^* excited states and, thus, should not be prone to follow H atom abstraction pathways as do their imine counterparts and carbonyl compounds.[7]

The principal feature of iminium salt excited states arises from the presence of the positive charge delocalized over nitrogen and adjacent carbon. The ground states of these systems serve as excellent acceptors in one[8] and two[9] electron transfer processes depicted in eqn (1). The excited states of these systems are expected to undergo one electron reduction even more readily than the corresponding ground states.[10] Accordingly, calculations[10] taking into account excited state energies and reduction potentials of various iminium salts suggest that one electron transfer to the excited species should occur rapidly from a number of unlikely one electron donors such as simple olefins,[6b,11] aromatic hydrocarbons,[12] alcohols and ethers.[1] Importantly, electron transfer in these cases could serve as initial steps in pathways leading to quenching (path a, Scheme 1),[11] photosensitization (path b, Scheme 1)[13] donor reaction (path c, Scheme 1),[14] and donor–iminium salt photoaddition (path d, Scheme 1).[15]



(1)

Iminium salt-olefin photoadditions. Our initial studies were designed to explore the photochemistry of olefin–iminium salt systems in order to determine the efficiency and chemical result of electron transfer for π-donors to the excited iminium salt chromophore. The free energies and rates of electron transfer to singlet excited states of C-phenyl conjugated iminium salts are predicted to be favorable when olefin donors with π-oxidation potentials lower than *ca.* 2.6 eV are used (Table 1). Consistent with this expectation is the observation that several olefins of this type serve as excellent quenchers of 2-phenyl-1-pyrrolinium perchlorate (1) fluorescence (Table 1). Rate constants for quenching (*kq*)



Scheme 1.

Table 1. Calculated free energies (ΔG°_{et}) and rate constants (k_{et}) for electron transfer and measured fluorescence quenching rate constants (kq) for olefin-2-phenyl-1-pyrrolinium salt systems

Olefin	Olefin[a] $E_{1/2}$ (+) (V vs. SCE)	ΔG°_{et}[b] (kcal/mol)	k_{et} ($M^{-1}\cdot sec^{-1}$)	kq (25°C)[c] ($M^{-1}\cdot sec^{-1}$)
$(CH_3)_2C=CH_2$	2.29	-13.4	1.3×10^{10}	-
cyclohexene	2.03	-19.4	1.4×10^{10}	6.0×10^9
butadiene	2.17	-16.1	1.4×10^{10}	-
$(CH_3)_2C=CHCO_2CH_3$[d]	2.70	-3.9	0.8×10^{10}	3.7×10^9
$CH_2=C(CH_3)CO_2CH_3$	3.37	+11.5	1.1×10^2	-
$CH_2=CHCO_2CH_3$	3.80	+21.5	8.5×10^{-6}	-
$CH_2=CHCN$	3.97	+25.4	1.4×10^{-8}	6.6×10^8

[a] $E_{1/2}$ (+) of olefins were calculated from known ionization potentials[8] (ref 23) using the realtionship of Miller.[16]

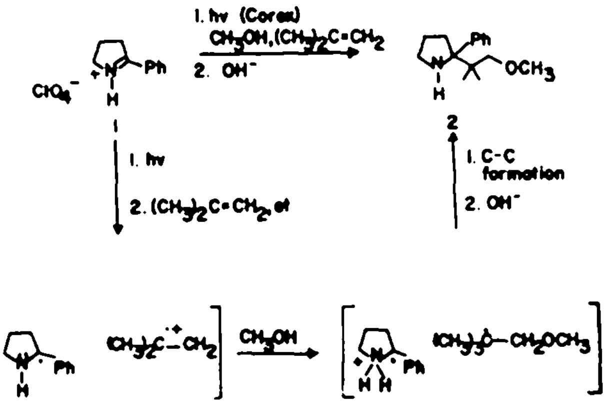
[b] Experimentally determined $E_{1/2}(-)$ of the pyrrolinium salt is ca. 0.99 V (CH_3CN) vs. SCE.

[c] Photophysical data for the pyrrolinium salt 1 in acetonitrile include $\phi_f = 0.16$, $\tau = 16$ nsec, $k_f = \phi_f/\tau = 9.7 \times 10^6\ sec^{-1}$, λmax emission = 375 nm, $k_d = 5.0 \times 10^7\ sec^{-1}$.

[d] Ionization potentials and thus, $E_{1/2}(+)$ estimated using a cumulative methyl substitutent effect.

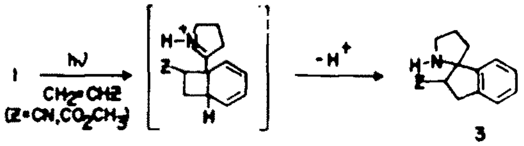
were found to be near the diffusion controlled limit in acetonitrile (*ca.* $1 \times 10^{10}\ M^{-1}\cdot sec^{-1}$). Importantly, quenching by an exchange energy transfer mechanism is not possible in these cases where olefin singlet energies lie *ca.* 10–20 kcal/mol higher than the iminium salts.

Photochemical observations we have made offer further support for the operation of electron transfer processes in olefin–iminium salt systems. For example, 2-phenyl-1-pyrrolinium perchlorate (1) undergoes addition of isobutylene in a high yielding, regiocontrolled fashion yielding the adduct 2. Similar pathways are followed in reaction of 1 with a number of other electron rich olefins, including cyclohexene, butadiene, methylcyclohexene, methyl β,β-dimethylacrylate and isopropenylcyclopropane. Importantly, the chemo- and regio selectivities displayed in conversion of 1 to 2 as well as in related photoadditions can be fully understood in terms of electron transfer mechanisms in which nucleophilic attack on the cation radical fragment occurs prior to C–C bond formation (Scheme 2). A qualitative test was employed to substantiate this rationale. As summarized above, the efficiency of electron transfer and, thus, photoadditions

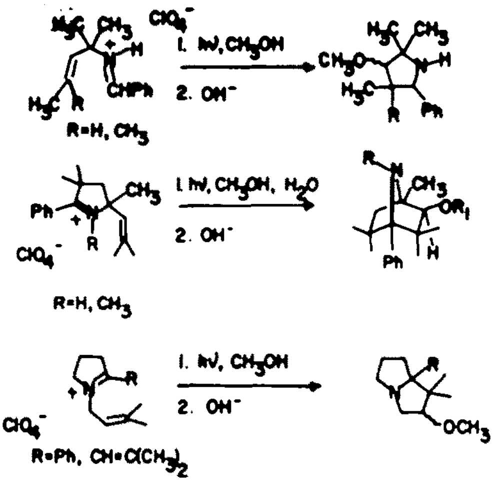


Scheme 2.

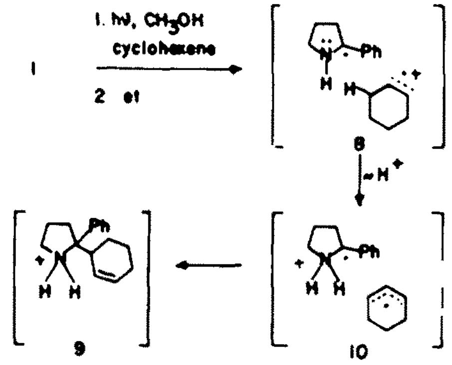
which ensue, should depend upon the oxidation potentials of olefinic donors. Indeed, rate constants for electron transfer from olefins known to photoadd to the singlet excited state of 1 are calculated to be near the diffusion controlled limit (Table 1). However, electron transfer from the electron poor olefins, acrylonitrile, methyl acrylate and methyl methacrylate should be inefficient. Significantly, the typical β-aminoether adducts are not produced upon irradiation of 1 in the presence of these olefins. Instead, the epimeric spirocyclic amines 3 are generated through alternate $\pi2+\pi2$ arene–olefin cycloaddition followed by ring expansion.[6b,11b]



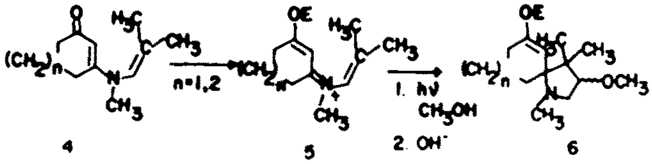
N-*Allyliminium Salt Photocyclizations*. Intramolecular counterparts of olefin-iminium salt photoadditions serve as useful methods for heterocyclic ring construction.[11a,11c] Results from investigations of N-allyliminium salts show that photocyclizations occur to generate 3-pyrrolidinyl ethers or alcohols in monocyclic, and bridged and fused bicyclic structural environments. Examples demonstrating this aspect are presented in Scheme 3. More recently,[18] we have found that O-substituted eniminium perchlorates 5, derived from β-enaminone precursors 4 undergo photocyclization producing mixtures of epimeric spirocyclic aminoethers 6 when irradiated in methanol. Together these observations illustrate the versatility of the process and suggest its potential in synthetic applications.



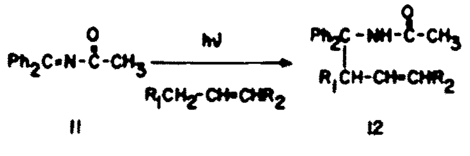
Scheme 3.



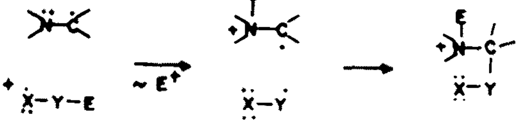
Scheme 4.



Electron–proton transfer processes. Observations made during the course of investigations of cyclohexene photoadditions to the pyrrolinium salt 1 demonstrate that alternate reaction pathways are available to cation radical pairs generated by electron transfer. Specifically, formation of the diastereomeric γ,δ-unsaturated amine adducts 9 could occur from the cation radical pair 8 via a stepwise process in which proton transfer to the amine radical nitrogen or solvent leads to the allyl radical pair 10 (Scheme 4). Analogous pathways, i.e. deprotonation, are commonly seen for cation radicals derived by electron impact in mass spectra fragmentations of olefins. Coupling in 10 leads to the addition product 9. Alternatively, a concerted, ene-type process ($\pi3s+\sigma2s+\pi1s$) could transform the cation radical pair directly to addition products. It should be mentioned that hydrogen atom abstraction pathways operating in additions of olefins to N-acylimines (e.g. 11 → 12),[19] could also be responsible for the analogous iminium salt reactions. Conversely, sequential electron–proton transfers could ensue when excited states of electron deficient imines interact with electron rich olefins. In any event, the possibility that sequential electron–proton transfers might be at work in olefin–iminium salt photochemistry has stimulated thoughts about the design of other systems with a similar potential. Specifically, these initial studies prompted an exploration for other photogenerated cation radical pairs



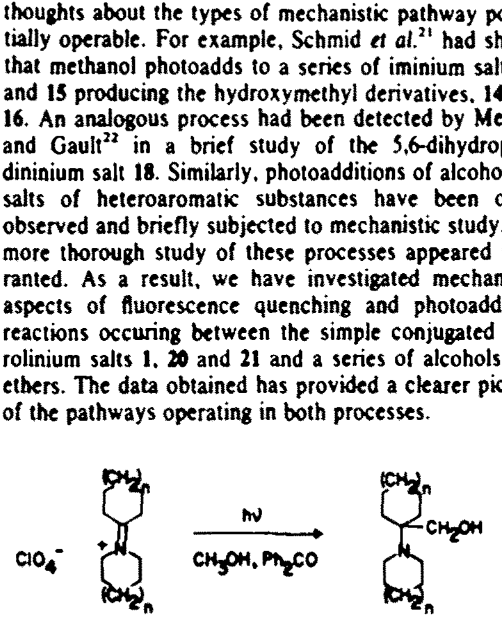
capable of further reaction by elimination of an electrophile β-disposed with respect to the positively charged center (eqn 2). The results of the first phase of that effort are the subject of the remaining studies described below.



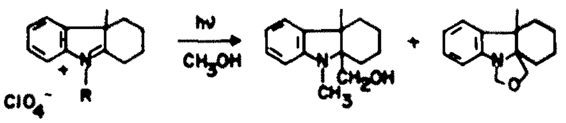
(2)

Alcohols and ethers as electron donors. Thus far we have surveyed our investigations of iminium salt photochemistry in which electron transfer from olefinic π-electron donors occurs and results in fluorescence quenching and photoaddition reactions. Simple theoretical treatments[10] permit the prediction that other types of substances should be capable of serving as one electron reducing agents of iminium salt excited states. These include materials with such common functionality as esters, carboxylic acid salts and aromatic systems. Indeed, electron transfer from these moieties to iminium salt excited states may be involved in decarboxylative addition[20] and benzylation processes[12] observed to occur in a number of systems. Moreover, this evaluation suggests that simple alcohols and ethers should act as one electron donors to singlet excited states of 2-phenyl-1-pyrrolinium perchlorates and related conjugated iminium salts. As a result, we directed the next phase of our efforts to an investigation of the photochemical behavior of iminium salt–alcohol and ether systems.

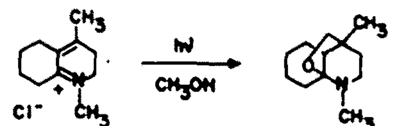
At the outset we were aware of prior work conducted by others which had uncovered a number of interesting observations that appeared to be consistent with our thoughts about the types of mechanistic pathway potentially operable. For example, Schmid *et al.*[21] had shown that methanol photoadds to a series of iminium salts **13** and **15** producing the hydroxymethyl derivatives, **14** and **16**. An analogous process had been detected by Meyers and Gault[22] in a brief study of the 5,6-dihydropyridininium salt **18**. Similarly, photoadditions of alcohols to salts of heteroaromatic substances have been often observed and briefly subjected to mechanistic study.[15] A more thorough study of these processes appeared warranted. As a result, we have investigated mechanistic aspects of fluorescence quenching and photoaddition reactions occuring between the simple conjugated pyrrolinium salts **1**, **20** and **21** and a series of alcohols and ethers. The data obtained has provided a clearer picture of the pathways operating in both processes.



13 14

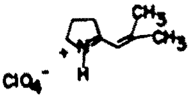


15 16 17



18 19

20



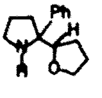
21

RESULTS

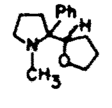
Fluorescence quenching. The fluorescence efficiencies and lifetimes of the 2-phenyl-1-pyrrolinium perchlorates, **1** and **20**, the latter material prepared by methylation of the parent pyrroline with methyl iodide followed by perchlorate ion exchange, have been measured in the presence and absence of the alcohols and ethers listed in Table 2. The data obtained was employed in deriving the fluorescence quenching rate constants shown in Table 2. All measurements were made on 10% aqueous acetonitrile solutions to minimize solvent effects. However, fluorescence efficiencies and quenching rate constants were found to be independent of water, perchloric acid and iminium salt concentrations. Furthermore, the addition of quenchers to the iminium salt solutions does not alter the UV spectroscopic properties of these substances. Thus, the quenching processes can not be attributed to trivial effects.

Kinetic isotope effects on fluorescence quenching were determined for both OD and OCD substitution by use of the alcohol and ether pairs listed in Table 3. When fluorescence measurements were made with OD labelled alcohols, 10% deuterium oxide-acetonitrile solutions were employed. Deuterium substitution on nitrogen of the NH-pyrrolinium salt **1** has no effect on its absorption or emission spectroscopic properties.

Photoaddition reactions. In order to determine if the observed fluorescence quenching by these simple alcohols and ethers is associated with excited state reaction processes, the photochemistry of the pyrrolinium salts **1**, **20** and **21** was explored. Irradiation of **1** in tetrahydrofuran solution leads to generation of the diastereomeric (1.2:1) 2-tetrahydrofuranylpyrrolidine adducts **22**. This substance is obtained in a 42% yield after basic work up of the mixture followed by molecular distillation. Analogous adducts **23** are formed (66%) when the corresponding 1-methylpyrrolinium salt **20** is photolyzed in THF. Importantly, benzophenone sensitized irradiation of **1** in THF solution causes efficient disappearance of the salt but does not result in production of the adducts **22** despite the high probability that triplet energy transfer is occurring under these conditions.[11b,c] More conclusive information about the nature of the state participating in these photoaddition processes arises by simple comparison of the quantum efficiencies for fluorescence quenching and reaction. In neat THF solution, the multiple k_{qT}[THF] equals 8×10^2. Thus, the efficiency for triplet formation can be maximumally 0.001. Accordingly, the measured quantum yield for formation of **22** from **1** in THF solution of 0.015 is consistent only with a reaction pathway initiated from the singlet excited state of **1**.



22



23

Irradiation of the pyrrolinium salts in methanol results in formation of interesting addition products which correspond to introduction of a 2-pyrrolidinyl moiety at the position α to oxygen. For example, the β-carbinolamine **24** is generated (43%, $\phi = 0.011$) from **20** by irradiation in methanol with Corex filtered-light followed by basic work-up and molecular distillation. When the methyl group is missing from nitrogen, the initially formed

Table 2. Rate constants for electron transfer (calcd) and fluorescence quenching of pyrrolinium salts 1 and 20 by alcohols and ethers

Quencher	$E_{1/2}(+)^a$ (V vs SCE)	ΔG_{et} [b] (kcal/mol)	k_{et} [b] ($M^{-1} \cdot sec^{-1}$)	kq [c] ($M^{-1} \cdot sec^{-1}$)
CH_3OH^d	3.8	+21	1.2×10^{-6}	$6.5 \pm 0.3 \times 10^7$
CH_3OH^e	-	-	-	$5.4 \pm 0.3 \times 10^8$
CH_3CH_2OH	3.5	+15	5.0×10^1	$2.0 \pm 0.1 \times 10^8$
$(CH_3)_2CHOH$	3.2	+8	1.0×10^5	$7.3 \pm 0.4 \times 10^8$
$(CH_3)_3COH$	2.5	-9	9.5×10^7	$1.9 \pm 0.1 \times 10^7$
p-dioxane	2.0	-20	1.4×10^{10}	$3.7 \pm 0.1 \times 10^9$
$(CH_3CH_2)_2O$	2.5	-9	9.5×10^7	$1.2 \pm 0.1 \times 10^9$
THF	1.9	-22	1.4×10^{10}	$4.1 \pm 0.2 \times 10^9$
28^d	2.5	-9	9.5×10^7	$5.1 \pm 0.3 \times 10^9$
28^e	-	-	-	$3.1 \pm 0.2 \times 10^9$

a) Oxidation potentials either taken from reference 23b or calculated according to Miller[16] using recorded ionization potentials.[23b]

b) Calculated by using the relationships suggested by Weller,[10] and the following data for **1**: $E_{0,0}$=89 kcal/mol and $E_{1/2}(-)$=0.99v (CH_3CN).

c) Pyrrolinium salt concentrations were 1×10^{-4}, singlet lifetime for **1** is 16 nsec and **20** is 1 nsec in 10% aqueous acetonitrile at 25°C.

d) Salt **1**

e) Salt **20**

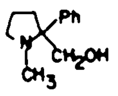
Table 3. Deuterium isotope effects on quenching rate constants by alcohols and ethers of pyrollinium salt 1 and 20 fluorescence

Pyrrolinium Salt	Quencher System	kqCH/kqCD [a]	kqOH/kqOD [a]
1	CH_3OH/CH_3OD	-	1.36 ± 0.06
1	CH_3OH/CD_3OH	1.5 ± 0.06	-
1	CH_3CH_2OH/CH_3CH_2OD	-	1.41
1	$(CH_3)_2CHOH/(CH_3)_2CHOD$	-	1.25
1	$(CH_3)_2CHOH/(CD_3)_2CDOH$	1.12	-
1	$(CH_3)_3COH/(CH_3)_3OD$	-	1.54
1	THF/d_8-THF	1.20	-
1	1,2,2-trimethylcyclopropanol	-	1.04
20	CH_3OH/CD_3OH	1.19 ± 0.18	-
20	1,2,2-trimethylcyclopropanol	-	1.04

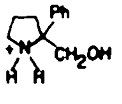
a) Rate constants determined at 25°C in 10% aqueous CH_3CN

hydroxymethyl adduct **25** is not detected but instead its formaldehyde condensation product, **26** is isolated (15%, $\phi = 0.0005$). It should be noted that a similar oxazolidine adduct **17** was obtained by Schmid by irradiation of an indolinium salt **15** in methanol.[21a] Finally, irradiation of methanol solutions of **21** brings about formation of the 2-hydroxypropyl-1-pyrroline **27** (43%). This product results from a conjugate addition pathway similar to that operating in transformation of the dihydropyridinium salt (**18** → **19**).[22]

Useful information about the nature of the fluorescence quenching and photoaddition reaction mechanisms for alcohol and ether-iminium salt systems has come from study of the interesting tertiary alcohol, 1,2,2-trimethylcyclopropanol (**28**). This material was prepared by the method of DePuy.[24] Irradiation of 2-phenyl-methyl-1-pyrrolinium perchlorate (**20**) in a solution containing **28** and methanol in a molar ratio of *ca.* 1:40 leads to formation of both the methanol adduct **24**, described above, and a material identified on the basis of spectroscopic data as the 4-pyrrolidinyl-2-pentanone **29**. The ratio of photoadducts **24** and **29** was found by glc analysis to be 1:2.7. Thus, based upon the relative quenching rate constants for cyclopropanol **28** and methanol (Table 2), the relative concentrations of each alcohol in the reaction mixture, and the product ratio, it is possible to estimate that the efficiency for production of **29** is *ca* 18 times greater for methanol adduct production. This gives an estimated quantum yield of 0.2 for formation of **29** from **20** if irradiations were conducted in neat **28**.

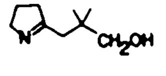


24

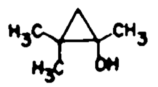


25

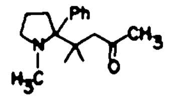
26



27



28



29

DISCUSSION

Pyrrolinium salt fluorescence quenching by alcohols and ethers. The results presented above demonstrate that simple alcohols and ethers serve as reasonably efficient quenchers of phenylpyrrolinium salt fluorescence. Based upon the outcome of control experiments designed to search for trivial sources of quenching, we can conclude that singlet state deactivation can not be attributed to effects associated with solvent-salt interactions. Specifically, decreases in the fluorescence efficiencies of **1** and **20** caused by simple alcohols and ethers are not due to alterations in absorption or emission properties induced by solvent viscosity, ion pairing, degree of hydrogen bonding, or solvent polarity. The experimental findings suggest that other mechanisms are involved in singlet quenching and reaction. A loose correlation exists between the estimated free energies (ΔG_{et}) and associated rate constants (k_{et}) for electron transfer and measured fluorescence quenching rate constants (k_q) for a number of alcohol and ether quenchers. It should be emphasized that the observed relationship between k_{et} and k_q is not precise since evaluations of the energetics for electron transfer in these systems are only qualitative due to assumptions inherent in the Weller treatment[10b] and lack of accurate electrochemical data for alcohols and ethers. One electron oxidation potentials ($E_{1/2}(+)$) for the quenchers are not available in the electrochemical literature and thus need to be estimated by use of correlations between ionization potentials and $E_{1/2}(+)$.[16] In addition, the uncertain relationship between singlet energies derived from 0,0-bands and enthalpy changes upon excitation, and the uncertainty in estimating the enthalpic component of ΔG_{et} attributable to changing solvent-salt interactions attending electron transfer in charged systems both contribute to inaccuracies in calculated ΔG_{et} and k_{et} values. However, it is reasonable to expect that the trends noted reflect a dependence of k_q upon oxidation potentials of the quenchers. The availability of hydrogens on carbons α to oxygen appears to also have a pronounced effect upon fluorescence quenching. This is illustrated by the large discrepancy between the observed rate constants for quenching by t-butyl alcohol and the predicted electron transfer rate. Furthermore, the values for k_q correlate with rate constants for H atom abstraction from alcohols and ethers by t-butylperoxy radicals or benzophenone triplets (Table 4).[25]

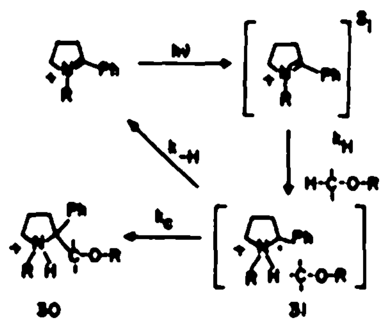
Based upon these trends, two limiting mechanisms can be proposed for both fluorescence quenching and photoaddition. Importantly, both processes occur from the same excited state and therefore can be considered together under a unified mechanism. The H atom abstraction mechanism presented in Scheme 5 is clearly the more simple one of the two in accounting for both quenching and reaction processes. Commitment of the system to quenching by this pathway occurs at the step in which the π–π^* singlet iminium salt abstracts a hydrogen α to the alcohol or ether oxygen. Importantly, the large difference between the efficiency of singlet quenching (e.g. $\phi_q = 0.99$ for neat THF solution) and photoaddition ($\phi = 0.015$ for **1** + THF) requires that partitioning of the radical pair **3** favors back H-transfer (k_{-H}) regenerating the ground state salt over coupling (k_c) to produce the adduct **30** by approximately two orders of magnitude.

Several factors argue against the operation of the H atom abstraction mechanism and in favor of the alternate electron–proton transfer sequence outlined in Scheme 6. Firstly, both t-butyl alcohol and 1,2,2-trimethylcyclopropanol serve as reasonably efficient quenchers of fluorescence despite the fact that neither have readily abstractable α-hydrogens. Secondly, quenching through abstraction of non α-hydrogens in the tertiary alcohols appear unlikely since 2,2,4-trimethylpentane does not quench the fluorescence of **20** in spite of the prediction that it should serve as an excellent donor in H-abstraction processes.[26] Furthermore, no photoadducts indicative of alternate H-abstraction modes are produced when **20** was irradiated in t-butyl alcohol as solvent. Lastly, the electronic structure of $\pi-\pi^*$ singlet states of iminium salts does not appear conducive to H atom abstraction.[27] On the other hand,

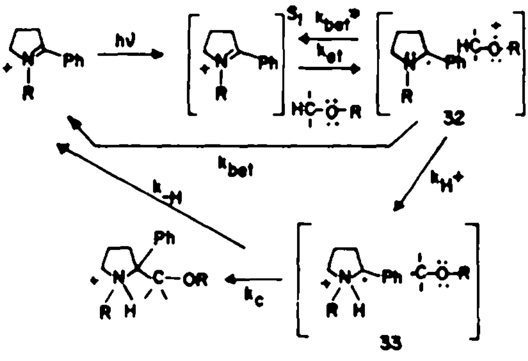
Table 4. Hydrogen atom abstraction rate constants[21]

H-Atom Donor	k_H [a] $(M^{-1}\cdot sec^{-1})$	k_H relative
CH_3OH	2.9×10^{-5}	1
CH_3CH_2OH	1.1×10^{-4}	3.8
$(CH_3)_2CHOH$	1.8×10^{-4}	6.2
THF	8.3×10^{-4}	29.6
$(CD_3)_2CDOH$	5.5×10^{-5}	1.9
d_8 - THF	3.0×10^{-4}	10.3

[a] Measured at 25°C in benzene by using $(CH_3)_3CO\cdot$ as abstracting agent.



Scheme 5.



Scheme 6.

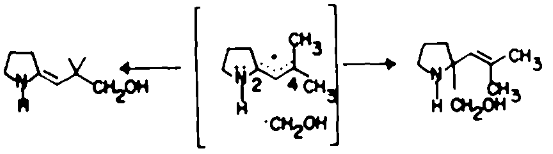
the sequential electron-proton transfer mechanism shown in Scheme 6 would be consistent with these observations. In this mechanism partitioning of the initially formed cation radical pair **32** can occur by back electron transfer (k_{bet}) to produce the ground state iminium salt[28] or by proton transfer ($k_H\cdot$) yielding the radical pair **33**, precursor of the adduct. The relative efficiencies for fluorescence quenching and product formation would be controlled at this stage as well as by the relative magnitudes of k_{-H} and k_c. Moreover the rate of proton transfer ($k_H\cdot$) should have a direct effect upon the efficiency of fluorescence quenching only if a pathway exists for regenerating the singlet iminium salt from **32**. A back electron transfer step ($k_{bet}\cdot$) of this type should be available in cases where electron transfer in the forward direction is endergonic or only slightly exergonic as appears to be the case for the alcohol-iminium salt systems. Thus, the relative magnitudes of $k_H\cdot$ and k_{bet} compared to $k_{bet}\cdot$ would directly effect quenching efficiencies. On the basis of these mechanistic postulates t-butyl alcohol is expected to serve as a quencher of the fluorescence of **1** but with a rate constant reflective of the unavailable proton transfer route.

Although distinction between the two fluorescence quenching mechanisms presented above cannot be simply made, it is possible to summon evidence which supports arguments in favor of the sequential electron–proton transfer pathway. Ground and excited state hydrogen atom abstractions involving alcohols and ethers display normal α–CH deuterium isotope effects ($k_H/k_D \sim 3$–4). Typical are the isotope effects of 3.94, 3.70 and 2.8–3.3 for hydrogen abstractions by triplet benzophenone,[29a] triplet acetone[29b] and t-butoxy radicals.[21] Thus, a normal primary deuterium isotope effect is expected for fluorescence quenching if the H atom abstraction mechanism were operable. On the otherhand, if cleavage of the C–H bond occurs in a step which follows electron transfer, a smaller C–D isotope effect is anticipated. Furthermore, OD exchange should cause an observable α-secondary isotope effect on quenching by the sequential mechanism. The observed OD and CD isotope effects on alcohol and ether quenching of pyrrolinium salt fluorescence are fully consistent with the electron–proton transfer mechanism. The CD isotopes effects observed in this system are similar to those reported for other electron quenching processes such as biacetyl fluorescence by amines, phenols and alcohols,[30] and the more directly related paraquat fluorescence quenching by alcohols.[31]

Photoaddition reactions. Photoadditions of alcohols with α-hydrogens to iminium salts represent a potentially interesting class of carbon–carbon bond forming reactions. These processes, proceeding most probably via the electron–proton transfer mechanism discussed above, result in the production of β-aminoalcohols through coupling of radical pair intermediates. Several features of these additions require further discussion. Firstly, formation of the fused bicyclic oxazolidine **26** from **1** requires that formaldehyde be generated under the photolytic conditions employed. This can occur by disproportionation of either the hydroxymethyl radical or methoxyl radical arising by oxygen deprotonation of the methanol radical cation. Likewise, protonated formaldehyde would arise by hydrogen atom loss from carbon of the methanol radical cation. All of these processes should occur with concomitant reduction of the pyrrolinium salt, a process which has remained undetected in our systems but which finds precedent in the work of Schmid.[21a] Moreover, methoxy radicals have been proposed and detected as intermediates in photoreduction of the paraquat dication.[32]

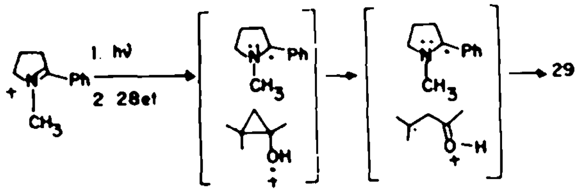
Photoaddition of ethers to the pyrrolinium salts resulting in formation of β-aminoethers follow analogous mechanisms. The only other reaction of this type that we have uncovered involves addition of tetrahydrofuran to styryl-pyridinium salts, a process proposed to follow an electron transfer mechanism.[33]

Lastly, the conjugate addition of methanol to the isobutenylpyrrolinium salt **21** is fully consistent with pathways having the radical pair **35** as the key intermediate leading to adduct **27**. The rates of the competitive modes of coupling yielding **34**, the tautomer of **27**, or the unsaturated amine **36** should be controlled by FMO interactions. Specifically, the coefficient at C-4 should be larger than at C-2 in the aminoallyl radical frontier molecular orbital (ψ_3). Thus, addition to the terminal carbon should predominate.



34 **35** **36**

Cyclopropanol quenching and photoaddition. One of the intriguing aspects of the mechanisms for quenching and reaction of iminium salts with alcohols and ethers concerns the potential link that exists between proton and back electron transfer and quenching efficiencies. Accordingly, in the sequential mechanism presented in Scheme 6, the cation radical pair can undergo back electron transfer to reform the iminium salt excited singlet state in competition with decay to ground state and proton transfer. Thus, the availability of low energy reaction pathways to the cation radical such as proton transfer would cause more efficient quenching. One such process could be rupture of weak C–C bonds as are found in the cation radical **37** generated by electron transfer from the tertiary cyclopropanol **28**. The validity of this hypothesis is corroborated by the observation that **28** serves as a very efficient quencher of pyrrolinium salt fluorescence (Table 2) despite the lack of α-hydrogens and in comparison to t-butyl alcohol. The small OD deuterium isotope effect (1.04 ± 0.06 for **1** and 1.06 ± 0.06 for **20**) indicates that a H atom abstraction mechanism similar to that involved in reaction of **28** with benzophenone triplets ($\theta_H/\theta_D \sim 5$)[34] is not operating here. Consistent with the rationale that rapid C–C bond cleavage in the cation radical **37** caused efficient quenching is the observation that the addition product **29** is formed efficiently by irradiation of **20** in methanolic solutions containing the cyclopropanol **28**. Taken together, the results presented above appear to support the sequential electron–proton transfer mechanism for alcohol and ether fluorescence quenching and reaction with iminium salts.



37 **38**

EXPERIMENTAL

General. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee. NMR spectra were recorded on Varian HA-100, XL-100, EM-360 or T-60 (proton) and Jeol PS-100 (carbon) spectrometers with TMS as an internal standard. IR spectra were taken by using Beckman IR-8 or Perkin Elmer 298 spectrometers with polystyrene as reference. Solution-phase UV absorption spectra were measured using either a Beckman Acta-III or a GCA McPherson EV-700-56 spectrophotomer. Gas chromatographic analyses were performed on a Varian-940 chromatograph with flame ionization detection. Preparative gas chromatographic work was done on a Varian-2700 chromatograph. Fluorescence emission and excitation spectra were recorded on a Perkin Elmer MPF-44B spectrometer equipped with a Perkin Elmer DCSU-1 differential corrected spectra unit. The singlet lifetime of 2-phenyl-1-pyrrolinium perchlorate was determined with a single photon counting, nanosecond spectrofluorometer built from ORTEC components. The singlet lifetime of 1-methyl-2-phenyl-1-pyrrolinium perchlorate was estimated by the procedure reported by Turro.[15] Mass spectrometric data were recorded at 70eV on a Dupont 21-390 mass spectrometer. High resolution mass spectra were taken on CEC-21-110 double focusing, mass spectrometer. All preparative irradiations were performed with a Hanovia, 450 W, medium pressure, mercury lamp in a quartz immersion well with glass filtered-light on solutions purged with N_2 before and during irradiations. Molecular distillations were conducted by using a Kugelrohr apparatus at reduced pressure. All organic solns were dried with Na_2SO_4.

1-*Methyl-2-phenyl-1-pyrrolinium perchlorate* (**20**). A mixture of 2-phenyl-1-pyrroline (4.28 g, 0.029 mol), MeI (41.9 g, 0.29 mol) and diethyl ether (20 mL) was heated at reflux for 24 hr. Concentration *in vacuo* gave a residue which was eluted through a perchlorate anion exchange column (Dowex-1) with MeOH. The eluant was concentrated *in vacuo* and the residue crystallized from EtOH yielding 3.67 g of **20** (48%). ^1H NMR (d_6-acetone) δ 1.8 (m, 2H), 3.1 (m, 2H), 3.9 (m, 2H), 3.13 (s, 3H), 7.1 (m, 5H); UV (MeOH) max (ε) 258nm (11,200). (Found: C, 50.88; H, 5.61 N, 5.28; Cl, 13.38. Calc. for $C_{11}H_{14}NClO_4$: C, 50.88; H, 5.43; N, 5.39, Cl, 13.65).

Fluorescence quantum yields and quenching. Fluorescence quenching rate constants (kq) were determined by using the Stern–Volmer method from slopes (kq τ) of Φ_{f_0}/Φ_{f_q} vs [Q] plots and measured or calculated singlet radiative lifetimes (τ). Fluorescence measurements for alcohol quenching were made by using 10% water acetonitrile solns. Quenching by O-deuterated alcohols was determined by using 10% D_2O acetonitrile solns. Quenching rate constants were found to be independent of water, acid and iminium salt concentrations in the ranges comparable to those used in the quenching studies. No dueterium isotope effect on the absorption or emission spectra of 2-phenyl-1-pyrrolinium perchlorate was detected. The quenchers do not absorb light in the excitation region of the iminium salts. Addition of quencher does not change the UV spectra of the iminium salts. The fluorescence spectra were corrected for both the spectral distribution of the lamp and the wavelength dependence of the optics and light detectors. Fluorescence quantum yields were determined by using the method of Parker and Reese[36] with napthalene as a standard[37] and were found to be $\Phi = 0.16$ for 2-phenyl-1-pyrrolinium perchlorate and $\Phi = 0.07$ for 1-methyl-2-phenyl-1-pyrrolinium perchlorate.

Irradiation of 2-phenyl-1-pyrrolinium perchlorate in THF

Preparation of 2-phenyl-2-(tetrahydrofuran-2-yl)pyrrolidine (**22**). 2-Phenyl-1-pyrrolinium perchlorate was prepared by adding 70% (w/w) $HClO_4$ (530 mg, 3.69 mmol) to 2-phenyl-1-pyrroline (400 mg, 2.93 mmol) in 3 mL of MeOH. Portions (3 mL) of benzene were added and successively removed *in vacuo* to azeotrope off the H_2O present. This was repeated until the salt crystallized. A soln of the salt in 200 mL anhyd THF was irradiated (Corex) for 1 hr. K_2CO_3 was added and the mixture was stirred. The photolysate was filtered and concentrated *in vacuo*. The crude mixture was dissolved in $CHCl_3$, washed with satd $NaHCO_3$ aq and brine, dried and concentrated *in vacuo*. Molecular distillation (50–55°, 0.05 torr) gave a clear oil (251 mg, 42%) consisting of a 1.2 : 1 mixture of the diastereomeric THF adducts **22**. IR (neat) 3035, 2995, 2945, 2910, 2855, 1595, 1485, 1445, 1065, 770 and 710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.0–2.4 (m, 9H, NH, methylenes not α to O or N), 2.4–3.2 (m, 2H, CH_2 α to N), 3.4–4.4 (m, 3H, CH_2 α to O, CH α to O), 7.1–7.7 (m, 5H, aromatic H); mass spectrum (70 eV) *m/e* (rel intensity) 147 (11), 146 (100), 145 (4), 143 (3), 117 (5), 104 (5), 103 (3), 91 (3), 77(4), 43 (3) 41 (3); UV (EtOH) λ max 251nm (ϵ, 417), 257nm (365), 263nm (241); ^{13}C NMR ($CDCl_3$) major isomer) δ 145.1 (s, C-1 aromatic), 127.8 (d, meta aromatic), 127.3 (d, ortho aromatic), 126.4 (d, para aromatic), 84.3 (d, CH α to O), 70.9 (s, C-2 of pyrrolidine ring), 69.0 (t, CH_2 α to O), 45.6 (t, CH_2 α to N), 36.9 (t, C-3 of pyrrolidine ring), 26.0, 25.9, 25.4 (t, C-4 of pyrrolidine ring, other methylenes of the THF ring). (Found: C, 77.51; H, 8.90; N, 6.43. Calc. for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45).

Benzophenone-sensitized irradiation of 1 in tetrahydrofuran

A soln containing 2-phenyl-1-pyrroline (400 mg, 2.76 mmol) 70% (w/w) perchloric acid (530 mg, 3.69 mmol) and benzophenone (6.00 g, 33.0 mmol) in 200 mL THF was irradiated for 2.0 hr through a Uranium-glass filter. K_2CO_3 was then added, the mixture was filtered and the filtrate concentrated *in vacuo*. The residue was dissolved in $CHCl_3$ and washed with 10% HCl. The acid portion was neutralized and extracted with $CHCl_3$. This $CHCl_3$ extract was washed with brine, dried and concentrated *in vacuo*. Molecular distillation gave the following results: 2-phenyl-1-pyrroline (80 mg, 20%) (< 50°, 0.05 torr) and a mixture (130 mg) of mainly one product (*ca* 85% by glc) (50–110°, 0.06 torr) and small amounts of three others. The major product (R_f 0.27, silica gel, ether) was not fully characterized, but was determined not to be **23** (R_f 0.47, silica gel, ether) as shown by glc, tlc and ^{1}H NMR analyses. A trace (< 2%) of the tetrahydrofuranyl adduct **22** was suggested by glc and tlc analysis.

Irradiation of 1-methyl-2-phenyl-1-pyrrolinium perchlorate in THF

Preparation of 1-methyl-2-phenyl-2-(tetrahydrofuran-2-yl) pyrrolidine (**23**). A soln of 1-methyl-2-phenyl-1-pyrrolinium perchlorate (440 mg, 1.70 mmol) in anhyd THF (110 mL) was irradiated (Corex) for 4 hr. The photolysate was concentrated *in vacuo* giving a residue which was dissolved in $CHCl_3$. The $CHCl_3$ soln was washed with $NaHCO_3$aq, dried and concentrated *in vacuo* giving a light yellow oil which was purified by molecular distillation (60°C, 0.01 Torr) yielding 209 mg (66%) of **23**, as a colorless oil. ^{1}H-NMR ($CDCl_3$) δ 7.3 (m, 5H, aromatic), 3.6–4.1 (m, 3H, CH_2O-CH), 0.8–2.8 (m, 10H), 1.45 (s, 3H, N-CH_3); high resoln mass spectrum (70eV) calcd. for $C_{15}H_{21}NO$: *m/e* 231.16234, found *m/e* 231.16230.

Irradiation of 2-phenyl-1-pyrrolinium perchlorate in methanol

Preparation of 5 - phenyl - 1 - aza - 3 - oxabicyclo[3.3.0]*octane* (**26**). A soln of 2-phenyl-1-pyrroline (400 mg, 2.76 mmol) and 70% (w/w) perchloric acid (530 mg, 3.69 mmol) in 200 mL MeOH was irradiated (Corex) for 11 hr. K_2CO_3 was added and the mixture filtered. The filtrate was concentrated *in vacuo*. The crude residue was dissolved in $CHCl_3$, washed with sat $NaHCO_3$aq and brine, dried, and concentrated *in vacuo*. This material was subjected to molecular distillation (45–55°, 0.02 torr) giving 80 mg (15%) of **26**. A large quantity of polymeric material remaining in the distillation pot. IR ($CHCl_3$) 3035, 2985, 2950, 2925, 2850, 1490, 1445, 1275, 1100, 1025, and 920 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.6–2.3 (m, 4H, methylenes at C-3 and C-4 of pyrrolidine ring), 2.8–3.1 (m, 2H, CH_2 α to N), 3.59 (d, J = 9 Hz, 1H, H α to O), 4.02 (d, J = 9Hz, 1H, other H α to O), 4.24 (d, J = 6.5 Hz, 1H, H of CH_2 α to N and O), 4.58 (d, J = 6.5 Hz, other H α to N and O), 7.1–7.5 (m, 5H, aromatic H); mass spectrum (70 eV) *m/e* (rel intensity) 189 (7, M$^+$), 172 (8), 160 (14), 159 (58), 158 (100), 133 (11), 131 (15), 103 (35), 91 (35), 77 (26); UV (EtOH) λ_{max} 252 (ϵ, 552), 257nm (465), 261nm (408), 264nm (328), 268nm (275); ^{13}C NMR (d$_6$-acetone) δ 148.9 (s, C-1 aromatic), 128.9 (d, meta aromatic), 127.0 (d, para aromatic), 126.3 (d, ortho aromatic), 89.3 (t, C-3), 78.4 (t, C-4), 77.3 (s, C-5), 57.1 (t, C-8), 42.1 (t, C-6), 26.3 (t, C-7); high-resolution mass spectrum (70eV) calc. for $C_{12}H_{15}NO$: *m/e* 189.115355, found: *m/e* 189.114598.

Irradiation of 1-methyl-2-phenyl-1-pyrrolinium perchlorate in methanol. Preparation of 1 - methyl - 2 - hydroxymethyl - 2 - phenylpyrrolidine (**24**). A soln of 1 - methyl - 2 - phenyl - 1 - pyrrolinium perchlorate (445 mg, 1.75 mmol) in MeOH (440 mL) was irradiated (Corex) for 6 hr. Concentration of the crude photolysate gave a residue which was dissolved in $CHCl_3$. The $CHCl_3$ soln was washed with sat. $NaCHO_3$ aq and brine, dried and concentrated *in vacuo* giving a residue which was subjected to molecular distillation (95°, 0.4 torr) yielding 140 mg of **24** (42%). ^{1}H NMR (CCl_4) α 2.02 (s, 3H), 1.75–3.2 (m, 7H), 2.65 (s, 1H), 3.73 (dd, 2H, J = 6 Hz and 11 Hz), 7.13 (s, 5H), IR (liq film) 3390, 2940, 1670, 1450, 1060, 760, 700 cm^{-1}; *m/e* (rel intensities) 191 (< 0.5), 174 (24), 160 (100), 91 (10), 77 (11), 51 (5): high resolution mass spec of M-17 *m/e* 174.1281 ($C_{12}H_{16}N$ requires 174.1283).

Irradiation of 2-isobutenyl-1-pyrrolinium perchlorate in methanol

Preparation of 2-(2,2-dimethyl-3-hydroxyprop-1-yl)-1-pyrroline (**27**). A soln of 2-isobutenyl-1-pyrroline[11c] (0.200 g, 8.0 mmol), perchloric acid (3 mL of 70% $HClO_4$) and 200 mL of MeOH was irradiated (Corex) for 10 hr. The crude photolysate was neutralized with K_2CO_3, filtered through Celite, and concentrated *in vacuo*. The residue was dissolved in CH_2Cl_2 and washed with water. Concentration of the CH_2Cl_2 soln gave an oil which was purified by molecular distillation yielding 107 mg (43%) of adduct **27**. ^{1}H-NMR ($CDCl_3$) δ (br.s., 1H, hydroxyl), 3.80 (br.s., 1H, α to N), 3.35 (s, 2H, α to hydroxyl), 2.30 (br.s., 2H, allylic *endo* to ring), 1.90 (br.s., 2H, allylic exo to ring), 1.15 (br.s., 2H, methylene) and 1.00 (s, 6H, methyl), ^{13}C-NMR ($CDCl_3$) δ 178.3 (s, imine), 71.5 (t, α to hydroxyl), 65.0 (s, gem dimethyl), 60.4 (t, allylic to ring), 44.3 (t, allylic *endo* to ring), 40.2 (t, α to N), 35.9 (t, methylene) and 25.7 (q, methyl); IR (lig film) 3300, 2980, 1660, 1450, 1395, 1050 cm^{-1}; high resolution mass spec, *m/e* 155.041621 ($C_9H_{17}NO$ requires 155.042784).

Irradiation of 1-methyl-2-phenyl-1-pyrrolinium perchlorate in the presence of 1,2,2-trimethylcyclopronan-1-ol

Preparation of 4-methyl-4-(1-methyl-2-phenylpyrrolidin-2-yl)pentan-2-one (**29**). A soln of 1-methyl-2-phenyl-1-pyrrolinium perchlorate (200 mg, 0.77 mmol), 1,1,2-trimethylcyclopropanol[34] (5 g, 5.0 mmol) and MeOH (80 mL) was irradiated (Corex) for 35 min. Solvent and excess cyclopropanol were removed by molecular distillation (25°, 5 torr). The reside was treated with sat $NaHCO_3$aq and extracted with ether. The ethereal extracts were dried and concentrated *in vacuo* giving a material which was purified by preparative glc (160°, 30 mL flow rate, 1 ft × 1/8 in, 5% OV-101 on Chromosorb GHP) yielding **29** (5%). The ratio of **29** to adduct **24** obtained from this reaction is 2.7 : 1 as determined by glc analysis. The spectral characteristics of adduct **29** are as follows: ^{1}H NMR ($CDCl_3$) δ 1.38 (s, 6H), 2.17 (s, 6H), 0.9–1.75 (m, 4H), 2.0–3.2 (m, 4H), 7.4 (s, 5H); IR (CCl_4) 2960, 1710, 1450, 1360 cm^{-1}; *m/e* (rel intensities) 259 (1.1), 172 (1.5), 161 (13), 160 (100), 158 (7), 118 (4), 91 (4), 77 (6), 65 (1.5), 55 (2); high resolution mass spec *m/e* 259.192692 ($C_{17}H_{25}NO$ requires 259.193605).

Quantum yield measurements. Quantum yields were measured with a "linear optical bench" system equipped with a high pressure, 450 W mercury lamp (Illumination Industries Model CA-200-8003), the output of which was focused with a quartz collimator and passed through a quartz-faced, water-cooled, three 1 cm compartment filter solution cell containing separately, 1.0 M (262.86 g/L) nickel sulfate hexahydrate in 5% H_2SO_4, 0.8 M (224.88 g/L) cobalt sulfate heptahydrate in 5% H_2SO_4, and 0.0001 M (0.0315 g/L) bismuth chloride in 10% HCl. The UV transmission of this filter was 250–310nm, with a maximum at 280nm. The filtered light passed through a beam splitter which diverted light 90°. The light not diverted passed through two quartz-faced, water-cooled cells aligned in series. During actinometer calibration runs, both the front and back cells were filled with 0.006 M potassium ferrioxalate. During photolysis runs, the front cell contained iminium salt solutions. The back cell contained potassium ferrioxalate in order to monitor light not absorbed by the substrate. The diverted light was received by a silicon solar cell in order to monitor the light output. The signal received by the solar cell was amplified and fed through a Raytheon RC-4151 voltage/frequency converter. Integration of this signal was performed by counting the frequency transmitted by the converter.

The amount of light not diverted was determined by calibration of the solar cell against ferrioxalate actinometry. The light absorbed by the front cell containing the potassium ferrioxalate was determined at several different percent conversions ranging from 0.3 to 1.2% (0.1 mE to 0.4 mE). A plot of mE *versus* the number of counts obtained from the electronic counter for each run gave the following equation as determined by a least-squares analysis: $mE = 2.91 \times 10^{-8} \times$ no. of counts $+ 0.01$. The confidence factor (r^2) was 0.998. The light output for each photolysis was obtained using this equation.

The quantum yield for formation of the tetrahydrofuran adduct 22 was measured by use of a 1×10^{-5} M soln of 2-phenyl-1-pyrrolinium perchlorate in anhyd THF. Product analysis was by glc (5′ × 1/8″, 1.5% 00101 on Anasorb G, 160°, 9 mL/min) by using triphenylmethanol as internal standard. $\phi = 0.015$ at 0.85% conversion to product.

The quantum yield for formation of the methanol adduct 24 was measured by use of a 3×10^{-5} M solution of 1-methyl-2-phenyl-1-pyrrolinium perchlorate in anhydrous methanol. Product analysis was by glc (5′ × 1/8″, 5% OV101 on 100–120 Chromosorb GHP, 126° mL/min) by using trans-stilbene as internal standard, $\phi = 0.01$ at 8% conversion to product.

Acknowledgements—Financial support for these studies derived from grants from the National Institutes of Health (GM 27251) and the National Science Foundation (CHE 09813). We thank Dr. Richard Mayer for the use of his spectrofluorimetric equipment in the early phases of the work. Dr. Andrea Leone-Bay is acknowledged for contributing experimental work related to the preparation of one of the photoadducts. Contributions to the studies of iminium salt photochemistry have also been made by Tammy Tiner-Harding, Dr. Ung Chan Yoon, Suzanne Quillen, D. Kazuya Ohga, Alexander Lan.

REFERENCES

[1] A preliminary report of these studies has appeared in J. Stavinoha, E. Bay, A. Leone and P. S. Mariano, *Tetrahedron Lett.* 3455 (1980).

[2a] Author to whom correspondence should be addressed at the University of Maryland; [b] current address, Texas Eastman Inc., Longview, Texas; [c] current address, Department of Chemistry, The Ohio State University.

[3] See A. Lablache-Combier, *Photochemistry of Heterocyclic Compounds* (Edited by O. Buchardt, pp. 207–287, Wiley, New York (1976).

[4a] The photochemistry of iminium salts should find significance in relationship to the excited state processes of the visual pigment, protonated rhodopsin;[4b,4c] [b] Reviews of this topic are found in *Acc. Chem. Res.* **8**, 81 (1975); [c] B. Honig, U. Dinur, K. Nakanishi, V. Balogh-Nair, M. A. Gaivinowicz, M. Arnaboldi and M. G. Motto, *J. Am. Chem. Soc.* **101**, 7084 (1979); M. A. Gaivinowicz, M. Arnaboldi and M. G. Motto., *ibid.* **101**, 7086 (1979).

[5] B. D. Dickie and R. F. Childs, *Abstracts, 63rd Canadian Chemical Conference.* OR-91, Ottawa (1980).

[6a] P. S. Mariano and A. Leone-Bay, *Tetrahedron Lett.* 4581 (1980); [b] P. S. Mariano, J. Stavinoha, J. Pepe and G. Meyer, *J. Am. Chem. Soc.* **100**, 7714 (1978).

[7a] A. Padwa, *Chem. Rev.* 77, 17 (1977); [b] A. C. Pratt, *Chem. Soc. Rev.* **6**, 63 (1977).

[8] C. P. Andrieux and J. M. Saveant, *J. Electroanal. Chem.* **26**, 223 (1970).

[9] See H. Bohme and H. G. Viehe, *Iminium Salts in Organic Chemistry* Wiley, New York (1976).

[10a] In general electronic states of organic systems are both more easily reduced and oxidized than the corresponding ground states, [b] semi-empirical approaches to calculating rates of one electron transfer in excited states are found in D. Rehm and A. Weller, *Is. J. Chem.* **8**, 259 (1970); [c] a recent theoretical treatment of electron transfer is found in F. S. Scandola and V. Balzani, *J. Am. Chem. Soc.* **101**, 6140 (1979).

[11a] P. S. Mariano, J. L. Stavinoha and R. Swanson, *Ibid.* **99**, 6781 (1977); [b] J. L. Stavinoha and P. S. Mariano; *Ibid.* **103**, 3136 (1981); [c] J. L. Stavinoha, P. S. Mariano, A. Leone-Bay, R. Swanson and C. Bracken, *Ibid.* **103**, 3148 (1981).

[12] Preliminary results of photoaddition of toluenes to iminium salts have been presented in L. Klingler and P. S. Mariano, *Abstracts of 15th Middle Atlantic Regional Meeting*, OR 275, Washington (1981).

[13] Excellent reviews of electron transfer quenching are found in *The Exciplex*, Edited by M. Gordon and W. R. Ware, Academic Press New York (1975).

[14] A. J. Maroulis, Y. Shigemitsu and D. R. Arnold, *J. Am. Chem. Soc.* **100**, 535 (1978) and Refs. cited.

[15a] Literature examples of electron transfer processes in heteroaromatic systems have been reviewed[15b]; [b] D. G. Whitten, *The Photochemistry of Heterocyclic Compounds*, Edited by O. Buchard, pp. 524–573. Wiley, New York (1976).

[16] L. L. Miller, G. D. Nordblom and E. A. Mayeda, *J. Org. Chem.* **37**, 916 (1972).

[17] T. S. Cantrell, *J. Org. Chem.* **42**, 4238 (1977) and Refs. cited.

[18] Unpublished results of P. S. Mariano and T. Tiner-Harding, Texas A&M University.

[19] N. Toshima, S. Asao and H. Hivai, *Bull. Soc. Chem. Jap.* **51**, 578 (1978), A. Padwa and W. P. Koehn, *J. Org. Chem.* **40**, 1896 (1975).

[20a] H. Nozaki, M. Kato and R. Noyori, *Tetrahedron Lett.* 4259 (1967); [b] R. Noyori, M. Kato, M. Kawanisi and H. Nozaki, *Tetrahedron* **25**, 1125 (1969); [c] J. R. Barnett, A. S. Hopkins and A. Ledwith, *J. Chem. Soc.* Perkin Trans. II; **11**, **80** (1973).

[21a] H. Goth, P. Cerrutti and H. Schmid, *Helv. Chim. Acta* (1967), **50**, 1759; [b] P. Cerrutti and H. Schmid; *Ibid* **47**, 203 (1964), **45**, 1992 (1962).

[22] R. Gault and A. I. Meyers, *J. Chem. Soc. Chem. Commun.* 778 (1971).

[23a] C. K. Mann and K. K. Barnes, *Electrochemical Reactions in Non Aqueous Systems.* Marcel–Dekker, New York (1970); [b] K. N. Houk and L. L. Munchausen, *J. Am. Chem. Soc.* **98**, 937 (1976); K. Watanabe, *J. Chem. Phys.* **26**, 542 (1957).

[24] C. H. DePuy, W. C. Arnex and D. H. Gibson, *J. Am. Chem. Soc.* **90**, 1830 (1968).

[25] H. Paul, R. D. Small and J. C. Sciano, *J. Am. Chem. Soc.* **100**, 4520 (1978).

[26] Based upon Sciano's data,[25] the rate constant for H-atom abstraction should be $8 \times 10^{-5}\ M^{-1} \cdot sec^{-1}$ or nearly as large as with EtOH.

[27] A. Weller, *Z. Electrochem.* **61**, 956 (1957); G. Jackson and G. Porter, *Proc. Roy. Soc. Ser. A.*, **260**, 13 (1961).

[28] Back electron transfer can occur from the cation radical to generate the iminium salt triplet state, thus, serving as part of an induced mechanism for intersystem crossing. The efficiency of this process as compared to reformation of the excited singlet if both are exergonic should depend upon whether the radical fragments are weakly or strongly interacting in the radical cation pair.

[29a] W. M. Moore, G. S. Hammond and R. P. Foss, *J. Am. Chem. Soc.* **83**, 2789 (1961); G. S. Hammond, W. P. Baker and W. M. Moore, *Ibid.* **83**, 2795 (1961); W. M. Moore and M. Ketchum, *Ibid.* **84**, 1369 (1962); [b] G. Porter, S. K. Dogra, R. O. Loutfy, S. E. Sugamori and R. W. Yip, *J. Chem. Soc.* Farad. Trans. I., **69**, 1462 (1973).

[30] N. J. Turro and R. Engel, *J. Am. Chem. Soc.* **91**, 7113 (1969).

[31] A. Ledwith, *Acc. Chem. Res.* 5, 133 (1972); A. S. Hopkins, A. Ledwith and M. F. Stom, *J. Chem. Soc.* Chem. Commun. 494 (1970).

[32] A. Ledwith, P. J. Russell and L. H. Sutcliffe, *Proc. Roy. Soc. A* **332**, 151 (1973).

[33] M. T. McCall and D. G. Whitten, *J. Am. Chem. Soc.* **91**, 5681 (1969); J. W. Hopp, M. T. McCall and D. G. Whitten, *Ibid.* **93**, 5496 (1971).

[34] C. H. De Puy, H. L. Jones and W. B. Moore, *Ibid.* **95**, 477 (1973); C. H. De Puy, H. L. Jones and D. H. Gibson, *Ibid.* **94**, 3924 (1972).

[35] N. J. Turro, *Modern Molecular Photochemistry*, **88**, Benjamin, New York (1978).

[36] C. A. Parker and W. T. Reese, *Analyst* **85**, 587 (1960).

[37] W. R. Dawson and M. W. Windsor, *J. Phys. Chem.* **72**, 3251 (1968).