In this equation, ΔB is the number of moles of benzophenone consumed and t is the time interval of irradiation.

General Procedure for Quantum Yield Analyses. To ensure that the sample and actinometer solutions absorbed equal amounts of the 313-nm radiation, solutions of ketone (1.75 ml) were made up such that the optical densities of the solutions at 313 nm were >2.0 (>99% of the light at 313 nm absorbed). In some instances, these optical densities were <2.0 at 313 nm, and, as a result, the final quantum yields were corrected to 100% absorption. All samples were irradiated to low conversion (<10%).

The quantum yield for product formation (Φ_P) was determined from eq 5 where ΔP is the number of moles of product formed, and t

$$\Phi_P = (\Delta P)(6.02 \times 10^{23})/(t)(I) \qquad (5)$$

and I are irradiation time and source intensity (vide supra). The quantity ΔP was determined by uv, nmr, or glpc, and the limits of error on quantum yield calculations are estimated at ±10–20%.

General Procedure for Sensitization Reactions. Solutions of sensitizer and ketone were prepared such that the sensitizer absorbed >90–100% of the incident radiation at 313 nm. In most cases, a second solution was prepared containing ketone but with

no sensitizer. For each solution the total optical density was >2.0.

For most experiments, samples were transferred to 10 × 75 mm Pyrex test tubes and thoroughly degassed by three freeze–pump–thaw cycles and sealed. Samples were then irradiated in parallel at 313 nm and analyzed for product formation by glpc, uv, or nmr. For the sensitized irradiation of ketone **34** with m-xylene, irradiation was carried out at 254 nm with low-pressure mercury lamps.

General Procedure for Quenching Experiments. Solutions of ketone in an appropriate solvent were prepared as described above for quantum yield determinations except that varying amounts of 1,3-pentadiene (purified by bulb-to-bulb distillation on a vacuum line) were added to the solutions. Four to six solutions containing different concentrations of quencher were usually prepared, in addition to blanks containing no quencher. Equal aliquots of each solution were transferred to 10 × 75 mm Pyrex test tubes which were stoppered and irradiated in parallel. Product formation was measured by glpc and the Stern–Volmer analyses were repeated at least once to afford averaged values of $k_q\tau_t$. The limits of error for $k_q\tau_t$ are estimated at ±10%. Fluorescence quenching experiments were carried out in similar fashion except that fluorescence intensities were measured with a Hitachi Perkin-Elmer MPF-2A spectrofluorimeter.

Photochemical Reactivity of Keto Imino Ethers. IV.[1] Type I and Type II Reactions

T. H. Koch,* R. J. Sluski, and R. H. Moseley

Contribution from the Department of Chemistry, University of Colorado, Boulder, Colorado 80302. Received December 9, 1972

Abstract: The photochemical reactivity of 2-ethoxypyrrolin-5-one (**1**), 6-ethoxy-4,5-dihydro-2(3H)-pyridone (**2a**), and 6-propoxy-4,5-dihydro-2(3H)-pyridone (**2b**) is described. Irradiation of **1** in tert-butyl alcohol solvent gave 2-methyl-2-propyl N-(ethoxycyclopropyl)carbamate (**3**). When the irradiation was conducted in tetrahydrofuran solvent, a precursor, ethoxycyclopropyl isocyanate, was isolated. A mixture of glutarimide (**7**) and (Z)-2-methyl-2-propyl N-(ethoxyethylidene)carbamate (**5a**) was obtained from the irradiation of **2a** in tert-butyl alcohol solvent. With **2b**, glutarimide, (Z)-2-methyl-2-propyl N-(propoxyethylidene)carbamate (**5b**), and (E)-2-methyl-2-propyl N-(propoxyethylidene)carbamate (**6b**) were formed. Neither **2a** nor **2b** reacted with dimethoxyethene or cyclohexene in the 2 + 2 cycloaddition reaction. Formation of carbamates **3**, **5a**, **5b**, and **6b** is discussed in terms of the Norrish type I mechanism, and formation of glutarimide, in terms of the Norrish type II mechanism. Evidence is presented which suggests that **1** and **2a** react from the n,π* singlet state.

The Norrish type I reaction[2] or α cleavage is a common photochemical reaction of saturated ketones. Cleavage of medium ring alkanones gives enals and/or ketenes via intermediate biradicals. The reaction occurs predominantly from the triplet excited state, although the first excited singlet has also been implicated.[3] For cyclic α,β-unsaturated ketones, photocycloaddition is generally so competitive that α cleavage is not observed.[4] 2-Cyclopentenones substituted in the 5 position, however, have recently been shown to preferentially α-cleave in dilute solution giving cyclopropyl ketenes among other products.[5]

These reactions have been shown to occur under sensitized conditions; however, the details of the mechanism are still unknown. In this report we will describe

$$X = Y = Ph$$
$$X = Y = CH_3$$
$$X = C_2H_5; \quad Y = H$$
$$X = n\text{-}C_3H_7; \quad Y = H$$
$$X = OC_2H_5; \quad Y = H$$
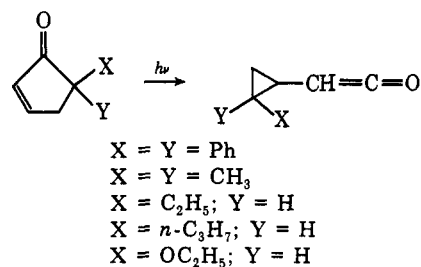
the photochemical type I cleavage of cyclic keto imino ethers which structurally resemble 2-cyclopentenone and 2-cyclohexenone. In these examples, α cleavage occurs to the complete exclusion of photodimerization or cycloaddition to olefins.

While Norrish type II photoreactions[2] have been reported for aliphatic,[6] aromatic,[6] and α,β-unsaturated

(1) Paper III: T. H. Koch and R. M. Rodehorst, *Tetrahedron Lett.*, 4039 (1972).

(2) C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, 1504 (1945).

(3) J. C. Dalton, K. Dawes, N. J. Turro, D. W. Weiss, J. A. Barltrop, and J. D. Coyle, *J. Amer. Chem. Soc.*, **93**, 7213 (1971), and references therein.

(4) P. E. Eaton and W. S. Hurt, *ibid.*, **88**, 5038 (1966); J. L. Ruhlen and P. A. Leermakers, *ibid.*, **88**, 5671 (1966); E. Y. Y. Lam, D. Valentine, and G. S. Hammond, *ibid.*, **89**, 3482 (1967).

(5) W. C. Agosta, A. B. Smith, III, A. S. Kende, R. G. Eilerman, and J. Benham, *Tetrahedron Lett.*, 4517 (1969); W. C. Agosta and A. B. Smith, III, *J. Amer. Chem. Soc.*, **93**, 5513 (1971).

(6) P. J. Wagner, *Accounts Chem. Res.*, **4**, 168 (1971).

ketones[7] with γ hydrogens in accessible locations, similar reactivity for structurally related imines is unknown. Padwa[8] and others[9] have shown that imines in general have little tendency to abstract hydrogen atoms. Photoreduction of imines presumed to involve hydrogen atom abstraction by the nitrogen of an excited carbon–nitrogen double bond in fact occurs by chemical sensitization. In chemical sensitization, a ketyl radical derived from a carbonyl compound present in the reaction mixture as an impurity, an added sensitizer, or as a photogenerated species donates a hydrogen atom to the imine. We will describe a photoelimination reaction of keto imino ethers which resembles the type II photoelimination reaction of ketones and might involve γ-hydrogen abstraction by the nitrogen of a carbon–nitrogen double bond.
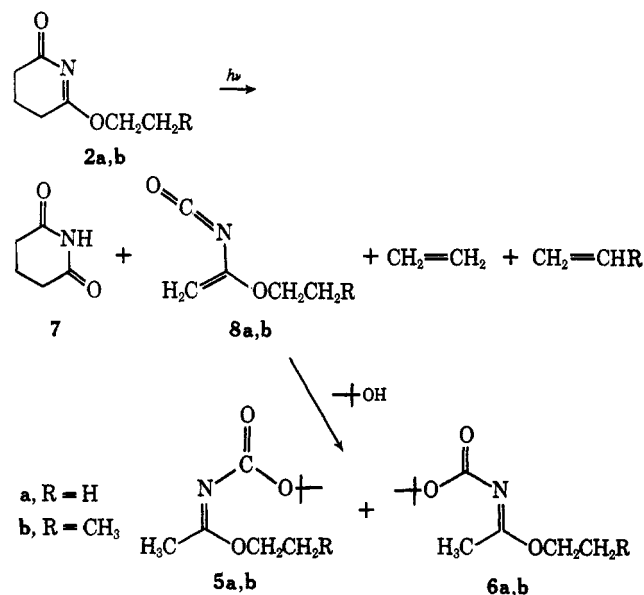
Results

Synthesis of Reactants. The ethyl keto imino ether, 2-ethoxypyrrolin-5-one (**1**), was prepared by the O-alkylation of the silver salt of succinimide with iodoethane.[10] Similarly, 6-ethoxy-4,5-dihydro-2(3H)-pyridone (**2a**) and 6-propoxy-4,5-dihydro-2(3H)-pyridone (**2b**) were synthesized by the O-alkylation of the silver salt of glutarimide with iodoethane and iodopropane, respectively. The occurrence of alkylation on oxygen in all the reactions was established by the appearance of intense carbon–nitrogen double bond stretching bands in the ir spectra of **1**, **2a**, and **2b** in the region of 6.3–6.4 μ. In the nmr spectra of **1**, **2a**, and **2b** the methylene protons adjacent to oxygen absorb in the region δ 4.3–4.4 ppm, also consistent with O-alkylation.

Photochemical Reactions. Irradiation of a *tert*-butyl alcohol solution of **1** with Vycor filtered light from a

1   **4**   **3**
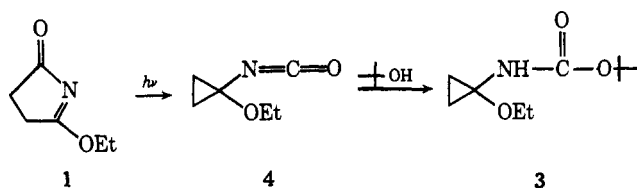
450-W mercury lamp resulted in formation of 2-methyl-2-propyl N-(ethoxycyclopropyl)carbamate (**3**) in 70% isolated yield.[11] When the irradiation was conducted in the nonhydroxylic solvent, tetrahydrofuran, ethoxycyclopropyl isocyanate (**4**) was isolated in 78% yield. The ir spectrum of **4** showed a characteristic isocyanate stretching band at 4.40 μ. In the nmr the cyclopropyl protons appeared as an AA'BB' pattern from δ 0.8 to 1.4 ppm and the ethoxy group as a triplet at δ 1.2 and a quartet at δ 3.7 ppm.

Irradiation of a *tert*-butyl alcohol solution of **2a** under similar conditions resulted in the formation of two products, 2-methyl-2-propyl N-(ethoxyethylidene)carbamate (**5a**) in 15% yield and glutarimide

(7) W. L. Schreiber and W. C. Agosta, *J. Amer. Chem. Soc.*, **93**, 6292 (1971).

(8) A. Padwa, W. Bergmark, and D. Pashayan, *ibid.*, **91**, 2653 (1969); A. Padwa and M. Dharan, *Tetrahedron Lett.*, 1053 (1972).

(9) M. Fischer, *Chem. Ber.*, **100**, 3599 (1967); W. F. Smith, Jr., and B. W. Rossiter, *J. Amer. Chem. Soc.*, **89**, 717 (1967); E. V. Donckt and G. Porter, *J. Chem. Phys.*, **46**, 1173 (1967).

(10) W. J. Comstock and H. L. Wheeler, *Amer. Chem. J.*, **13**, 522 (1891).

(11) The interpretation of the spectroscopic data establishing the structural assignment is given in our earlier communication: T. H. Koch and R. J. Sluski, *Tetrahedron Lett.*, 2391 (1970).

2a,b

7   **8a,b**   + CH₂=CH₂ + CH₂=CHR

a, R = H
b, R = CH₃

5a,b   **6a,b**

(**7**) in 23% yield. The identity of glutarimide was established by comparison with an authentic sample, and the structure of **5a** was established from the spectroscopic evidence. In the ir of **5a**, carbon–oxygen and carbon–nitrogen double bond stretching bands appear at 5.80 and 6.00 μ, respectively. The nmr spectrum contains an ethoxy pattern at δ 1.25 (triplet) and 4.10 ppm (quartet), a *tert*-butyl singlet at 1.00 ppm, and an allylic methyl singlet at 2.10 ppm. The photoproduct was assigned the Z stereochemistry as shown in structure **5a** from the nmr spectrum of **5a** compared with the nmr spectrum of the carbamate photoproducts of 6-propoxy-4,5-dihydro-2(3H)-pyridone (**2b**) (*vide infra*).

Irradiation of **2b** in *tert*-butyl alcohol solvent gave two carbamate products assigned structures **5b** and **6b** in the ratio 12:1 by nmr integration as well as glutarimide. The isomeric carbamates were not separable by glpc but were characterized as a mixture by nmr spectroscopy. The nmr absorptions assigned to the major carbamate photoproduct include a methyl triplet at δ 0.94 ppm, a *tert*-butyl singlet at 1.52 ppm overlapping with a methylene sextet at 1.60 ppm, an allylic methyl singlet at 2.07 ppm, and a methylene triplet at 4.02 ppm. The minor carbamate photoproduct has a distinguishable *tert*-butyl singlet at δ 1.50 ppm, an allylic methyl at 2.40 ppm, and a methylene triplet at 3.62 ppm. The methyl triplet and methylene sextet of the minor and major carbamate photoproducts overlap. The ir spectrum is also consistent with the assigned structures with carbon–oxygen and carbon–nitrogen double bond stretching bands at 5.85 and 6.0 μ, respectively.

When **2a** or **2b** was irradiated with CS-056 filtered light from a 200-W mercury lamp in the aprotic solvent glyme in an ir solution cell at room temperature and the progress of the reaction monitored by ir spectroscopy, the appearance of an isocyanate stretching band at 4.45 μ and a glutarimide carbonyl stretching band at 5.85 μ was observed. The isocyanate photoproducts from **2a** and **2b** were assigned the structures ethoxyvinyl isocyanate (**8a**) and propoxyvinyl isocyanate (**8b**), respectively, consistent with the ir evidence and the structures of the carbamates.

The stereochemistry assigned to the carbamates can

Table I. Quantum Yield and Uv Absorption Data for **1** and **2a**

Compd	Uv absorption, nm	ϕ Carbamate	ϕ Imide	Stern–Volmer slope[a]	ϕ_{isc}	$k_q\tau_T{}^b$	$\tau_T{}^c$
1	265 (ϵ 45)	0.31		1.4 ± 0.5	0.19 ± 0.01	60 ± 5	3 × 10⁻⁸
2a	275 (ϵ 60)	0.067	0.025	1.2 ± 0.5	0.10 ± 0.02	49 ± 5	2.5 × 10⁻⁸

[a] Stern–Volmer plots are for quenching by cis-piperylene over the concentration range 0.01–0.10 M quencher. All quantum yield measurements are with 0.20 M keto imino ethers in tert-butyl alcohol at 30°. [b] The $k_q\tau_T$ values were calculated from plots of reciprocal of cis-piperylene isomerization quantum yield vs. reciprocal of cis-piperylene concentration. [c] Triplet lifetimes were calculated assuming the rate of quenching was equal to the rate of diffusion, 2 × 10⁹ l./(mol sec) in tert-butyl alcohol at 30° [the rate of diffusion in tert-butyl alcohol at 30° was calculated from data in the "International Critical Tables of Numerical Data, Physics, Chemistry, and Technology," Vol. 7, McGraw-Hill, New York, N. Y., 1930, p 211].

now be established. One can reasonably assume that the carbamate formed in the irradiation of **2a** results from the addition of tert-butyl alcohol to the vinyl isocyanate **8a** in such a way as to give the sterically least hindered product. If the least hindered carbamate is actually **6a**, then increasing the size of the alkoxy substituent of the vinyl isocyanate should have no effect on the stereochemistry of the addition of tert-butyl alcohol; however, this is not the case. When the alkoxy substituent is changed from ethoxy to propoxy two stereoisomeric carbamates are formed. We conclude then that the carbamate product from the addition of tert-butyl alcohol to **8a** is in fact **5a**. The major product from the addition of tert-butyl alcohol to **8b** is also assigned the Z stereochemistry (**5b**) since the nmr chemical shifts of the allylic methyl and O-methylene protons of the major carbamate product are similar to those of **5a** and different from those of the minor carbamate product.[12]

The irradiation of **2b** in tert-butyl alcohol was also conducted on a vacuum line and the gaseous products were collected in a liquid nitrogen cooled trap. Mass spectral analysis of the trapped products indicated that ethene and propene were present with ethene as the major constituent. The identity of the gaseous products was established by comparison of the mass spectral fragmentation patterns with those reported in the literature.[13]

When either **1** or **2a** was irradiated in the presence of the electron rich olefin, dimethoxyethene, or the electron neutral olefin, cyclohexene, no photocycloaddition to the carbon–oxygen or carbon–nitrogen double bonds occurred. Only the rearrangement and elimination reactions described for irradiations in the absence of olefins were observed. This result is in contrast to the reported 2 + 2 cycloadditions of olefins to the carbon–nitrogen double bonds of the structurally related molecules, 3-ethoxyisoindolone[14] and 2-phenyl-2-oxazolin-4-one.[15]

Spectroscopic and Quantum Yield Measurements. Ultraviolet absorption data for **1** and **2a** are given in Table I. For both keto imino ethers the longest wavelength absorption is of the n–π* configuration and the maximum of the π–π* band appears in the vacuum uv. It is interesting to note that for both molecules the positions of the n–π* and π–π* bands appear at much shorter wavelength than the corresponding ab-

sorptions of structurally related α,β-unsaturated ketones. For example, the π–π* bands of 3-ethoxy-2-cyclohexenone and 3-butoxy-2-cyclopentenone appear at 238 nm.[16]

The quantum yields of formation of **3**, **5a**, and **7** also appear in Table I. Quantum yields were measured at 30° at 2537 Å with a rotating cell holder in a Rayonet photochemical reactor. The light intensity was measured with potassium ferrioxalate actinometry[17] and analyses were obtained by gas chromatography.

cis-Piperylene was employed as a photochemical quencher. Over the concentration range 0.01–0.10 M cis-piperylene, the quantum efficiencies of the reactions of **1** and **2a** were not appreciably effected. This result is indicated by the slopes of the respective Stern–Volmer plots (average slope 1.3 l./mol). Energy transfer to cis-piperylene, however, did occur since the isomer, trans-piperylene, was observed in the reaction mixture.[18] Plots of the reciprocal of cis–trans isomerization quantum yield vs. reciprocal of cis-piperylene concentration were linear with slopes and intercepts as follows: quenching of **1**, intercept = 9.4 ± 0.6, slope 0.155 ± 0.014 l./mol; quenching of **2a**, intercept = 17.1 ± 2.8, slope = 0.36 ± 0.04 l./mol.

Acetone (triplet energy approximately 78 kcal/mol)[19] was investigated as a possible photosensitizer for the rearrangement of **1**. Over the concentration range 0.1–1.0 M acetone, no sensitization occurred. As shown in Table II, when the quantum yield data were corrected for light absorption by acetone, a slight quenching effect was observed. Plotting the data in

Table II. Quenching of Rearrangement of **1** by Acetone

[1]	[Acetone]	$\phi_0/\phi_q{}^a$	% light in acetone	Corr ϕ_0/ϕ_q
0.20	0.10	1.08	9	1.00
0.20	0.20	1.29	16	1.08
0.20	0.40	1.58	28	1.14
0.20	0.61	1.91	37	1.19
0.20	0.81	2.22	43	1.22
0.20	1.01	2.45	49	1.25

[a] ϕ_0/ϕ_q represents the ratio of the quantum yield of rearrangement of **1** in the absence of acetone to the quantum yield in the presence of acetone.

(12) The assignment of the stereochemistry of the major isomers, **5a** and **6a**, is in agreement with the assignment for simple aryl and alkyl imino ethers: R. M. Moriarty, C. Yeh, K. C. Ramey, and P. W. Whitehurst, J. Amer. Chem. Soc., 92, 6360 (1970).

(13) A. Cornu and R. Massot, "Compilation of Mass Spectral Data," Heyden and Sons, Ltd., London, 1966, pp 6C and 10C.

(14) T. H. Koch and K. H. Howard, Tetrahedron Lett., 4035 (1972).

(15) T. H. Koch and R. M. Rodehorst, ibid., 4039 (1972).

(16) H. N. A. Al-Jallo and E. S. Waight, J. Chem. Soc. B, 73 (1966).

(17) C. G. Hatchard and C. A. Parker, Proc. Roy. Soc., Ser. A., 235, 518 (1956).

(18) A referee has suggested that cis–trans isomerization of piperylene could occur via an addition–elimination reaction with the proposed biradical intermediates (vide infra), as an alternative to triplet energy transfer. This mechanism seems less likely since the piperylene concentration was never more than 0.10 M and since products of piperylene–biradical cycloaddition were not observed.

(19) A. A. Lamola and N. J. Turro, "Energy Transfer and Organic Photochemistry," Wiley, New York, N. Y., 1969, p 94.

the Stern–Volmer fashion gave a slope of 0.26 ± 0.02 l./mol.

Discussion

The photoreactions ultimately yielding carbamate products (**3**, **5a**, **5b**, **6b**) most likely occur by the Norrish type I mechanism. The rearrangement of electronically excited **1** via this mechanism would occur by initial homolytic cleavage α to the carbonyl giving a 1,5 diradical. Subsequent rearrangement to a 1,3 diradical followed by ring closure would yield the isocyanate **4** which was isolated and trapped with *tert*-butyl alcohol as the carbamate **3**. Type I cleavage of the homologous systems **2a** and **2b** followed by rearrangement would give 1,4 diradicals. Elimination of ethene would then yield vinyl isocyanates **8a** and **8b** observed by ir spectroscopy. Subsequent 1,4 addition of *tert*-butyl alcohol to the isocyanates would produce the isolated carbamates **5a**, **5b**, and **6b** (Scheme I).

Scheme I
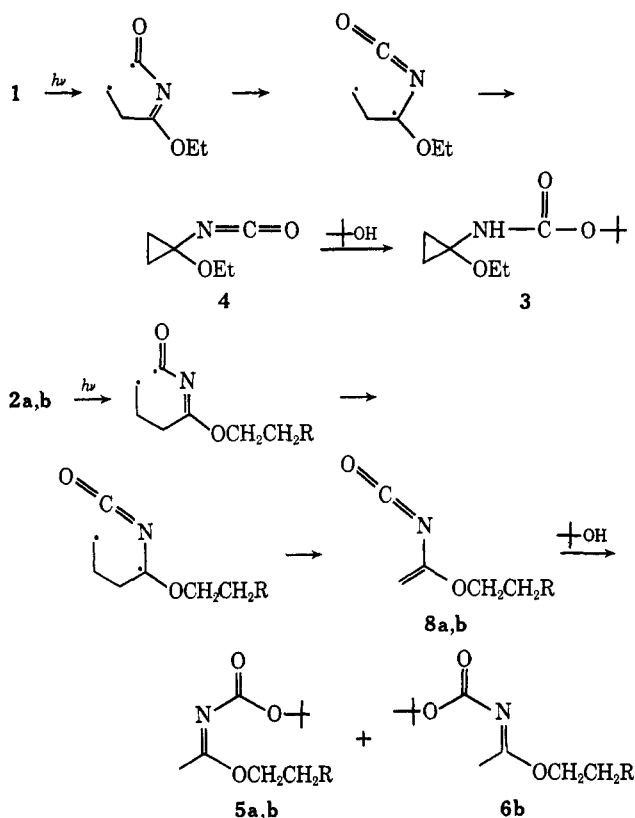
Alternatively, the carbamates might arise from 1,2 addition of *tert*-butyl alcohol to the isocyanates followed by a 1,3-proton shift. Consistent with this mechanism, ethene was observed by mass spectroscopy as a product from the irradiation of **2b**. Products of cyclization of the 1,4 diradicals, cyclobutane type products, were not observed. Cyclization of 1,4 diradicals is often not favored in competition with elimination.[6, 20]

The type I photochemical cleavage has also been reported for a seven-membered ring compound electronically related to **1**, **2a**, and **2b**. Irradiation of 3,6-dihydro-3,3,6,6-tetramethyl-2*H*-azepin-2-one (**9**) in hexane gives in 20% yield *cis*-2,2-dimethyl-3-isobutenyl-cyclopropyl isocyanate (**10**).[21]

(20) F. D. Lewis and T. A. Hilliard, *J. Amer. Chem. Soc.*, **94**, 3852 (1972).

(21) T. Susaki, S. Eguchi, and M. Ohno, *ibid.*, **92**, 3192 (1970).
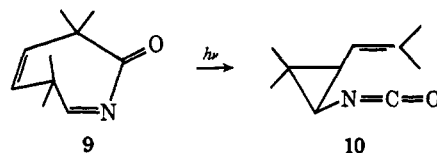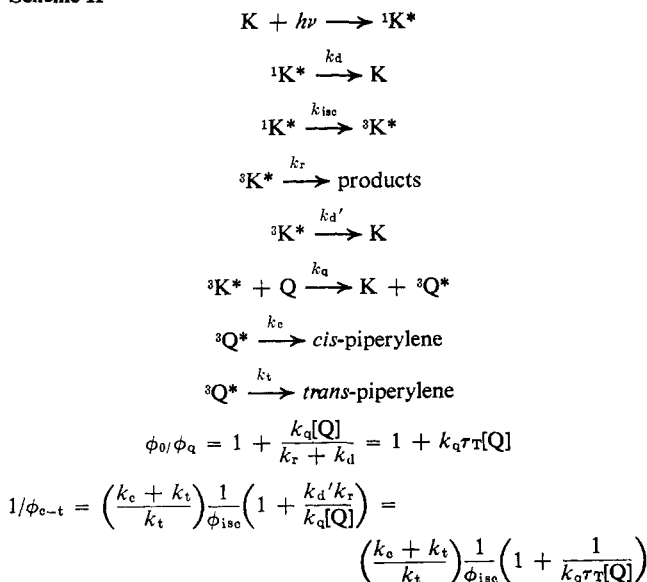
A mechanism for the formation of glutarimide with analogy in ketone photochemistry is the Norrish type II process. By this mechanism an electron-deficient nitrogen of excited **2a** or **2b** would abstract a γ hydrogen from the alkoxy side chain yielding a 1,4 diradical. Subsequent elimination of ethene or propene, respectively, would generate glutarimide. The observation of propene as a product of the photochemistry of **2b** supports this mechanism. However, the lack of precedent for photochemical hydrogen atom abstraction by the nitrogen of a C–N double bond[8, 9] prompts us to initiate an investigation of more complex mechanisms.
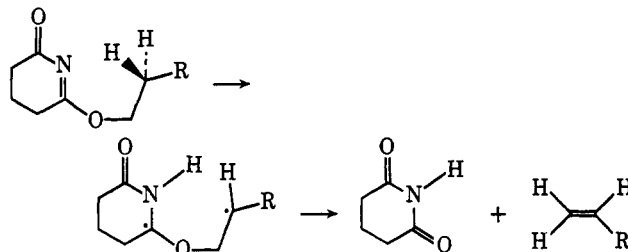
Quenching studies were employed to determine the multiplicity of the reactive excited states of **1** and **2a**. The slopes of the Stern–Volmer plots obtained with *cis*-piperylene as a quencher of carbamate and glutarimide formation are given in Table I. The magnitude of the slopes suggests that the reactions occur via an excited singlet state or a short-lived triplet state. The fact that *trans*-piperylene was observed in the irradiated quantum yield samples suggests that triplet states of **1** and **2a** are formed. If we assume then that the type I and type II reactions occur via a short-lived triplet state, a kinetic mechanism as shown in Scheme II is applicable. Consistent with this scheme,
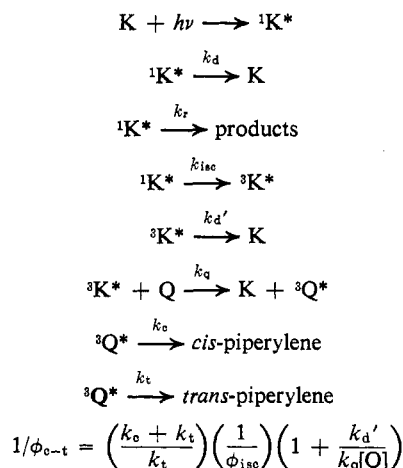
Scheme II

$$K + h\nu \longrightarrow {}^1K^*$$

$$^1K^* \xrightarrow{k_d} K$$

$$^1K^* \xrightarrow{k_{isc}} {}^3K^*$$

$$^3K^* \xrightarrow{k_r} \text{products}$$

$$^3K^* \xrightarrow{k_d'} K$$

$$^3K^* + Q \xrightarrow{k_q} K + {}^3Q^*$$

$$^3Q^* \xrightarrow{k_c} cis\text{-piperylene}$$

$$^3Q^* \xrightarrow{k_t} trans\text{-piperylene}$$

$$\phi_0/\phi_q = 1 + \frac{k_q[Q]}{k_r + k_d} = 1 + k_q\tau_T[Q]$$

$$1/\phi_{c-t} = \left(\frac{k_c + k_t}{k_t}\right)\frac{1}{\phi_{isc}}\left(1 + \frac{k_d'k_r}{k_q[Q]}\right) =$$

$$\left(\frac{k_c + k_t}{k_t}\right)\frac{1}{\phi_{isc}}\left(1 + \frac{1}{k_q\tau_T[Q]}\right)$$

plots of reciprocal of quantum yield for isomerization of *cis*-piperylene to *trans*-piperylene (ϕ_{c-t}) vs. reciprocal

of *cis*-piperylene concentration are linear. From the slopes and intercepts of these plots, values of $k_q \tau_T$ can be calculated. If the reactions occur from short-lived triplet keto imino ethers the values of $k_q \tau_T$ from the piperylene isomerization plots should equal the slopes of the Stern–Volmer plots. As shown in Table I, this is not the case well beyond experimental error. We conclude, therefore, that the type I and type II reactions occur at least predominantly *via* the n,π* singlet states of **1** and **2a** as shown in the kinetic mechanism in Scheme III. The lack of acetone sensitiza-

Scheme III

$$K + h\nu \longrightarrow {}^1K^*$$

$${}^1K^* \xrightarrow{k_d} K$$

$${}^1K^* \xrightarrow{k_r} products$$

$${}^1K^* \xrightarrow{k_{isc}} {}^3K^*$$

$${}^3K^* \xrightarrow{k_d'} K$$

$${}^3K^* + Q \xrightarrow{k_q} K + {}^3Q^*$$

$${}^3Q^* \xrightarrow{k_c} cis\text{-piperylene}$$

$${}^3Q^* \xrightarrow{k_t} trans\text{-piperylene}$$

$$1/\phi_{c-t} = \left(\frac{k_c + k_t}{k_t}\right)\left(\frac{1}{\phi_{isc}}\right)\left(1 + \frac{k_d'}{k_q[Q]}\right)$$

tion of the rearrangement of **1** as shown in Table II is also consistent with a reactive singlet state. The small amount of quenching of the reactions of the keto imino ethers reflected in the Stern–Volmer slopes (Table I) may result from endothermic singlet quenching.[22]

The fact that *cis*-piperylene is isomerized in the presence of excited keto imino ethers suggests that **1** and **2a** do in fact intersystem cross, and the intersystem crossing efficiencies can be calculated from the quantum yield data. If we assume that $\phi_{c-t} + \phi_{t-c} = 1$ for sensitized piperylene isomerization in *tert*-butyl alcohol as observed for sensitized piperylene isomerization in benzene solvent,[23] we can calculate $\phi_{c-t} = k_t/(k_c + k_t)$ from the benzophenone sensitized *trans/cis*-piperylene photostationary state in *tert*-butyl alcohol ([trans]/[cis]$_{pss}$ = 1.34). From this information and the intercepts of plots of ϕ_{c-t}^{-1} *vs.* reciprocal of *cis*-piperylene concentration, intersystem crossing efficiencies of 0.19 and 0.10 were calculated for **1** and **2a**, respectively.

As noted earlier, α cleavage is an uncommon reaction of α,β-unsaturated ketones structurally related to **1** and **2a**. Photodimerization and photocycloaddition to olefins are generally the observed reactions. The difference in reactivity of **1** and **2a** compared with cyclic α,β-unsaturated ketones may be simply a matter of energetics. The n,π* singlet energies of **1** and **2a** are considerably higher than n,π* singlet energies of α,β-unsaturated ketones. Hence, for **1** and **2a** and presumably not for most α,β-unsaturated ketones, sufficient energy is available along the reaction coordinate for α cleavage, and this mode of reactivity

is then competitive with the various modes of energy dissipation available to the excited state. Consistent with this explanation is the fact that 2-cyclopentenones substituted in the 5 position α cleave. Although substitution probably has little effect on the singlet energies, it weakens the bond α to the carbonyl and should lower the activation energy required for α cleavage.

In conclusion, we have observed photochemical reactions of keto imino ethers which resemble the Norrish type I and type II photoreactions of ketones. For both reactions the n,π* singlet state has been shown to be the predominant reactive state. 2 + 2 cyclo-additions of electron-rich or electron-neutral olefins to either the carbon–nitrogen or carbon–oxygen double bonds of these systems are not competitive.

Experimental Section

Melting points and boiling points are uncorrected. Melting points were measured with a Thomas-Hoover Unimelt apparatus. Perkin-Elmer 337 and Cary 14 spectrophotometers were used to determine ir and uv spectra, respectively. Nmr spectra were recorded with Varian A-60A and HA-100 spectrometers and a JEOL PS-100 spectrometer, and chemical shifts are reported in δ units from internal tetramethylsilane. The mass spectra were obtained with Varian Mat CH-5 and CH-7 spectrometers. Glpc analyses and isolations were performed with Varian Aerograph (Model 200 and 1700) gas chromatographs equipped with thermal conductivity detectors, and peak areas were measured by Disc integration. Microanalyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich., and Atlantic Microlab, Atlanta, Ga.

2-Ethoxypyrrolin-5-one (1) was prepared by the O-alkylation of the silver salt of succinimide with ethyl iodide using the procedure reported by Comstock and Wheeler.[10] A yield of 48% of **1** was obtained after distillation: bp 72–74° (0.05 mm) (lit. bp 144–146° (20 mm)); ir (neat) 3.4, 5.72, and 6.40 μ; nmr (CDCl₃) δ 1.4 (t, *J* = 7 Hz, 3 H), 2.40–3.0 (m, 4 H), and 4.45 ppm (q, *J* = 7 Hz, 2 H); mass spectrum *m/e* 127 (M⁺, 60%) and 99 (base); uv λ$_{max}$ (cyclohexane) 273 nm (ε 55) and λ$_{max}$ (absolute ethanol) 265 nm (ε 45).

6-Ethoxy-4,5-dihydro-2(3H)-pyridone (2a). A solution containing 50 g (0.29 mol) of silver nitrate in 50 ml of distilled water was combined with 20 g (0.19 mol) of anhydrous sodium carbonate in 50 ml of distilled water. The resulting yellow silver carbonate precipitate was collected by vacuum filtration. In 300 ml of ethanol, the silver carbonate, 29.4 g (0.260 mol) of glutarimide, and 1.0 g of silver nitrate were refluxed in the dark for 12 hr. The reaction mixture was filtered and the filtrate dried at 100° (0.1 mm) for 4–5 hr. In 300 ml of dry chloroform (distilled from phosphorus pentoxide), 46.5 g (0.30 mol) of ethyl iodide and the dried filtrate were refluxed for 48 hr. After the mixture was filtered, the solvent was rotary evaporated and the dark, oily residue distilled under reduced pressure. A second distillation at 60–61° (0.01 mm) yielded 13.7 g (38%) of **2a**: ir (neat) 3.4, 5.90, and 6.30 μ; nmr (CDCl₃) δ 1.35 (t, *J* = 7 Hz, 3 H), 1.8–2.25 (m, 2 H), 2.3–2.7 (m, 2 H), and 4.35 ppm (q, *J* = 7 Hz, 2 H); mass spectrum *m/e* 141 (M⁺, 76%) and 98 (base); uv λ$_{max}$ (cyclohexane) 275 (ε 60) and λ$_{max}$ (*tert*-butyl alcohol) 275 sh (ε 128).

Anal. Calcd for C₇H₁₁NO₂: C, 59.55; H, 7.85; N, 9.92. Found: C, 59.63; H, 7.84; N, 9.90.

6-Propoxy-4,5-dihydro-2(3H)-pyridone (2b). The silver salt of glutarimide was prepared and dried as described in the procedure for the preparation of **2a**. To a 250-ml three-necked flask containing the dried silver salt prepared from 6.0 g of glutarimide were added 10.02 g of iodopropane and 50 ml of dry chloroform (distilled from calcium hydride). The reaction mixture was refluxed for 48 hr with magnetic stirring. The silver iodide was then removed by vacuum filtration through Celite. Upon rotary evaporation of the solvent, glutarimide precipitated. Benzene was added and the unreacted glutarimide (0.88 g) was removed by a second vacuum filtration. The benzene was rotary evaporated and the residual oil rough distilled at reduced pressure (bp 79–81° (0.02 mm)) giving 1.7 g of product. The product was analyzed by glpc with a 0.95 cm × 3 m column of 5% FS-1265 on 60–80 mesh Haloport F at 200°. The analysis indicated that the product contained 73% 6-propoxy-4,5-dihydro-2(3H)-pyridone (**2b**). An analytical sample of **2b** was prepared by preparative glpc with the same column.

(22) F. S. Wettack, G. D. Renkes, M. G. Rockley, N. J. Turro, and J. C. Dalton, *J. Amer. Chem. Soc.*, **92**, 1793 (1970).
(23) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

Spectroscopic data: ir (neat) 5.9 and 6.3 μ; nmr (100 MHz, DCCl₃) δ 0.97 (t, $J = 7$ Hz, 3 H), 1.74 (sextet, $J = 7$ Hz, 2 H), 1.84 to 2.13 (m, 2 H), 2.50 (t, $J = 7$ Hz, 2 H), 2.50 (t, $J = 6$ Hz, 2 H), 4.27 ppm (t, $J = 7$ Hz, 2 H); mass spectrum m/e 113 (51), 86 (100), 85 (39), 84 (60), no parent ion appeared.

Anal. Calcd for $C_8H_{13}NO_2$: C, 61.91; H, 8.44; N, 9.03. Found: C, 61.86; H, 8.49; N, 8.96.

Irradiation of 2-Ethoxypyrrolin-5-one (1) in *tert*-Butyl Alcohol. A solution containing 9.55 g (0.075 mol) of **1** in 130 ml of dry *tert*-butyl alcohol (distilled from sodium) was degassed with a stream of nitrogen before and during the irradiation. The degassed solution was irradiated with a Vycor filtered, 450-W mercury lamp for 24 hr. At this time all the starting material was destroyed as indicated by glpc with a 2 m × 0.64 cm column of 5% FS-1265 on 60–80 mesh Haloport F at 150° (He, 78 cc/min). After rotary evaporation of the solvent, the residue was distilled at 67° (0.1 mm) to yield 10.9 g (70%) of 2-methyl-2-propyl *N*-(ethoxycyclopropyl)carbamate (**3**): ir 3.00, 3.4, and 5.70 μ; nmr (CDCl₃) δ 0.80–1.15 (m, 4 H), 1.13 (t, $J = 7$ Hz, 3 H), 1.47 (s, 9 H), 3.68 (q, $J = 7$ Hz, 2 H), and 5.75 ppm (broad, 1 H); mass spectrum m/e 145 (M⁺, 65%) and 57 (base).

Anal. Calcd for $C_{10}H_{19}NO_3$: C, 59.67; H, 9.52; N, 6.96. Found: C, 59.58; H, 9.30; N, 6.97.

Irradiation of 2-Ethoxypyrrolin-5-one (1) and Dimethoxyethene in *tert*-Butyl Alcohol. A solution of 2.01 g (0.015 mol) of 2-ethoxypyrrolin-5-one and 7.0 g (0.08 mol) of dimethoxyethene in 130 ml of dry *tert*-butyl alcohol (distilled from sodium) was degassed with nitrogen and irradiated with a Corex filtered, 450-W mercury lamp. The irradiation was continued until all the starting material was destroyed (16 hr). Gas chromatographic analysis of the irradiated solution indicated that only 2-methyl-2-propyl *N*-(ethoxycyclopropyl)carbamate (**3**) was formed. Work-up in the manner described yielded 2.3 g of **3** (70% yield, bp 67° (0.1 mm)).

Irradiation of 2-Ethoxypyrrolin-5-one (1) in Tetrahydrofuran. A solution containing 9.21 g (0.073 mol) of **1** in 130 ml of dry THF (distilled from lithium aluminum hydride) was degassed with nitrogen and irradiated for 24 hr with a Vycor filtered, 450-W mercury lamp. The solvent was removed by distillation at atmospheric pressure and the residue vacuum distilled yielding 7.12 g (78%) of ethoxycyclopropyl isocyanate (**4**): bp 88–89° (196 mm); ir (neat) 4.40 6.90, 7.70 μ; nmr (CDCl₃) δ 0.8–1.4 (m, 4 H), 1.2 (t, $J = 7$ Hz, 3 H), and 3.7 ppm (q, $J = 7$ Hz, 2 H).

Irradiation of 6-Ethoxy-4,5-dihydro-2(3H)-pyridone (2a) in *tert*-Butyl Alcohol. 6-Ethoxy-4,5-dihydro-2(3H)-pyridone (4.45 g) in 130 ml of dry *tert*-butyl alcohol was degassed with nitrogen and irradiated for 19 hr with a Vycor filtered, 450-W mercury lamp. After this period the starting material was completely destroyed and two products were formed as indicated by glpc with a 2 m × 0.64 cm column of 5% FS-1265 on 60–80 mesh Haloport F at 165° (He, 78 cc/min). After rotary evaporation of the solvent, the reaction mixture was vacuum distilled yielding 0.85 g (15%) of 2-methyl-2-propyl *N*-(ethoxyethylidene)carbamate (**5a**): bp 75–76° (5 mm); ir (neat) 5.80, 6.00, and 8.0 μ; nmr (CDCl₃) δ 1.00 (s, 9 H), 1.25 (t, $J = 7$ Hz, 3 H), 2.10 (s, 3 H), and 4.10 ppm (q, $J = 7$ Hz, 2 H); mass spectrum m/e 187 (M⁺, 4%) and 114 (base).

Anal. Calcd for $C_9H_{17}NO_3$: C, 57.73; H, 9.15; N, 7.48. Found: C, 57.82; H, 9.11; N, 7.52.

The second photoproduct remained in the distillation pot at 5-mm pressure. The pot residue was dissolved in hot benzene and the solution allowed to cool. The crystals that precipitated were collected by filtration (0.185 g, 23%) and identified as glutarimide (**7**) by comparison with an authentic sample.

Irradiation of 6-Propoxy-4,5-dihydro-2(3H)-pyridone (2b) in *tert*-Butyl Alcohol. A sample of **2b** (0.32 g) was purified by preparative glpc using the conditions described above. The sample was dissolved in 15 ml of dry *tert*-butyl alcohol (distilled from calcium hydride) in a quartz test tube, degassed with nitrogen, and irradiated at 2537 Å in a Rayonet reactor for 1100 min at 25°. The solvent was rotary evaporated giving 0.35 g of crude product. Gas chromatographic analysis indicated that two major volatile products were formed. One product was identified as glutarimide by comparison with an authentic sample. The other was identified as a mixture of the Z and E isomers of *tert*-butyl *N*-(propoxyethylidene)carbamate (**5b** and **6b**, respectively) by nmr spectroscopy. Glutarimide and the mixture of carbamates were formed in 9 and 19% yields, respectively, by glpc relative to cinnamaldehyde as an internal standard using a 0.64 cm × 2 m column of 5% FS-1265 on 60–80 mesh Haloport F at 160°. An analytical sample of the carbamate mixture was prepared by preparative glpc with a 0.95 × 3 m column of 5% FS-1265 on 60–80 mesh Haloport F

at 170°. Spectroscopic data: ir (CHCl₃) 5.85 and 6.0 μ; nmr (100 MHz, DCCl₃) of the major carbamate **5b**, δ 0.94 (t, $J = 7$ Hz, 3 H), 1.52 (s, 9 H), 1.60 (sextet, $J = 7$ Hz, 2 H), 2.07 (s, 3 H), 4.02 ppm (t, $J = 7$ Hz, 2 H); of the minor carbamate **6b**, δ 0.94 (t, $J = 7$ Hz, 3 H), 1.50 (s, 9 H), 1.60 (sextet $J = 7$ Hz, 2 H), 2.40 (s, 3 H), 3.62 ppm (t, $J = 7$ Hz, 2 H); mass spectrum m/e 201 (M⁺, 0.5%) 159 (21), 127 (75), 85 (100). The ratio of the major to the minor carbamate products was 12:1 by nmr integration.

Anal. Calcd for $C_{10}H_{19}NO_3$: C, 59.67; H, 9.52; N, 6.96; Found: C, 59.64; H, 9.54; N, 6.93.

Irradiation of 6-Propoxy-4,5-dihydro-2(3H)-pyridone (2b) on the Vacuum Line. A sample of **2b** (0.064 g) was collected from a gas chromatograph using a 0.95 cm × 3 m column of 5% FS-1265 on 60–80 mesh Haloport F at 200°. The sample was dissolved in 1.5 ml of *tert*-butyl alcohol (distilled from calcium hydride) and placed in a quartz tube. The tube was attached to a vacuum line and degassed by two freeze (liquid nitrogen)–pump (5 × 10⁻⁵ mm)–thaw cycles. The sample tube was then filled with prepurified nitrogen and irradiated on the vacuum line with low-pressure mercury lamps for 2400 min at ambient temperature. During the irradiation gaseous products were collected in a liquid nitrogen cooled trap. At the end of the irradiation additional gaseous products were collected by a partial distillation of the irradiated sample on the vacuum line at room temperature. The gaseous products were analyzed by mass spectrometry. Both propene and ethene were observed giving the following fragmenation patterns: propene, m/e 42 (65%), 41 (100), 40 (25), 39 (60), and 38 (20); ethene, 28 (100%), 27 (62), 26 (52), 25 (10). The ratio of the intensity of the base peak of ethene to the base peak of propene was 6:1.

Irradiation of 6-Ethoxy- and 6-Propoxy-4,5-dihydro-2(3H)-Pyridone (2a and 2b) in an Infrared Solution Cell. A 0.2-mm path length ir solution cell was filled with a glyme (distilled from lithium aluminum hydride) solution of 6-ethoxy-4,5-dihydro-2-(3H)-pyridone (**2a**) of appropriate concentration for infrared spectroscopy. The initial spectrum *vs.* a glyme filled reference cell showed a carbonyl stretching band at 5.85 μ and a more intense carbon–nitrogen double bond stretch at 6.28 μ. The ratio of the absorbance of the carbon–nitrogen to carbon–oxygen double bond stretch was 2:1. The solution cell was then irradiated at ambient temperature with CS-056 (Corning) filtered light from a Bausch and Lomb, 200-W super-pressure mercury lamp for 10 min. Subsequent scanning of the ir spectrum showed a strong isocyanate band at 4.45 μ (assigned to the vinyl isocyanate **8a**). The carbonyl stretching band of glutarimide in glyme solvent overlaps with the carbonyl band of **2a** (5.85 μ). The formation of glutarimide was detected by observing a change in the ratio of the absorbance of the 5.85-μ band to the 6.28-μ band. Glutarimide does not have an ir absorption band at 6.28 μ, and hence the 6.28-μ band intensity is a measure of the amount of **2a** remaining after irradiation. After the 10-min irradiation, the ratio of the absorbance of the 5.85-μ band to the 6.28-μ band was 1:1 compared with the initial ratio of 2:1. Hence a product with a 5.85-μ carbonyl band was formed, and it was assigned as glutarimide. A similar result was obtained when **2b** was irradiated in an ir solution cell in glyme solvent.

Irradiation of 2-Ethoxypyrrolin-5-one (1) and 6-Ethoxy-4,5-dihydro-2(3H)-pyridone (2a) in the Presence of Olefins in an Infrared Solution Cell. A glyme solution of **2a** and approximately twice as much of either dimethoxyethene or cyclohexene was placed in an ir solution cell. The concentration of **2b** was appropriate for ir spectroscopy. The infrared spectrum obtained of the solution after irradiation for 5 min with CS-056 filtered light from the 200-W mercury lamp was identical with a superposition of the spectrum obtained in the absence of olefin and the spectrum of the olefin in glyme solvent. A similar result was obtained when **1** was irradiated in an ir solution cell in glyme solvent in the presence of either dimethoxyethene or cyclohexene.

Reagents Used for Quantum Yield Measurements. Reagent grade *tert*-butyl alcohol was distilled through a 1-m Todd column packed with glass helices. A prefraction was taken until the distillate showed no uv absorption between 230 and 400 nm for a 1.0-cm path length. The purified *tert*-butyl alcohol was then dried by a subsequent simple distillation from sodium prior to use. 2-Ethoxypyrrolin-5-one (**1**) was purified by vacuum distillation as described and was pure by glpc analysis with a 2 m × 0.64 cm column of 5% FS-1265 on Haloport F at 150° (He, 78 cc/min). 6-Ethoxy-4,5-dihydro-2(3H)-pyridone (**2a**) was purified by preparative glpc with a 3 m × 0.95 cm column containing 5% FS-1265 on 60–80 mesh Haloport F at 165° (He, 70 cc/min) followed by molecular distillation at room temperature, 10⁻⁵-mm pressure. Spectrograde acetone, dried over molecular sieves, was used without further

purification. cis-Piperylene (Chemical Samples) was purified by preparative glpc with a silver nitrate–ethylene glycol column as described by Hammond.[24]

Quantum Yield Measurements. Quantum yield experiments were performed in a Rayonet photochemical reactor Model RPR-100 using RPR-2537 A lamps. The lamps were powered from an Isotran Model MVR 2000 constant-voltage power supply. Inside the Rayonet reactor was mounted a rotating wheel constructed from a black, anodized aluminum drum 17.8 cm in diameter by 5.7 cm thick. On the perimeter of the drum were located 30 cylindrical compartments 13 mm in diameter. Each compartment was exposed to the lamps through a slit 0.635 cm × 1.78 cm. The drum was mounted on a central shaft of a 1.78 cm aluminum rod. At the base and top of the shaft are ball bearings rigidly attached to the Rayonet reactor. The wheel was rotated at 48 rpm. The quantum yield apparatus was cooled with air which had passed through a water cooled heat exchanger. The apparatus was thermostated at 30 ± 0.1° with a temperature control mechanism employing a thermistor sensor. Calibration of the compartments of the wheel with potassium ferrioxalate actinometry demonstrated that each compartment received identical quantities of light ±1%.

Samples (3.0 ml) of the appropriate concentrations (Table I) of 2-ethoxypyrrolin-5-one (1), 6-ethoxy-4,5-dihydro-2(3H)-pyridone (2a), cis-piperylene, and acetone in tert-butyl alcohol solvent were placed in oven-dried 13-mm quartz test tubes and degassed by four freeze (liquid nitrogen)–pump (2 × 10⁻⁵ mm)–thaw cycles and sealed. The concentrations of the keto imino ethers (1 and 2a) were such that greater than 99% of the incident light below 300 nm was absorbed. During the irradiations the lamp intensity was monitored with potassium ferrioxalate actinometry and averaged 5.7 × 10¹⁵ quanta/sec. Quantum yields were corrected for the small emission impurities above 300 nm reported for the 2537 A lamps by Southern New England Ultraviolet Co., Middletown, Conn. Analyses of product formation from the irradiation of 1 and 2a were obtained by glpc with a 2 m × 0.64 cm column of 5% FS-1265 on 60–80 Haloport F at 140° (He, 75 cc/min) relative to external cinnamaldehyde and at 135° (He, 48 cc/min) relative to external isophorone, respectively. The quantum yields of glutarimide formation were corrected for the small amount of glutarimide formed by hydrolysis by residual water. This correction was obtained from the analysis of an unirradiated blank sample. Isomerization of cis-piperylene was measured by glpc with a 5 m × 0.64 cm column of 25% β,β-oxydiproprionitrile on 80–100 mesh Chromosorb P at ambient temperature (He, 46 cc/min). Quantum yields of cis–trans isomerization of piperylene were corrected for back reaction.[23] Gas chromatographic data were corrected for differences in detector response, and quantum yield irradiation times were adjusted such that no more than 10% of the starting materials were destroyed during the irradiation.

Piperylene Photostationary State in tert-Butyl Alcohol. A 50-ml Pyrex test tube was filled with 30 ml of tert-butyl alcohol solution, 2.0 g of cis-piperylene, and 0.50 g of benzophenone. The solution was irradiated external to a 450-W mercury lamp until the ratio of trans- to cis-piperylene did not change (12 hr) as measured by glpc with a 5 m × 0.64 cm column of 25% β,β-oxydiproprionitrile on 80–100 mesh Chromosorb P at ambient temperature. At the photostationary state the ratio of trans- to cis-piperylene was 1.34.

(24) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, J. Amer. Chem. Soc., **86**, 3197 (1964).

Norrish Type II Rearrangement from π,π* Triplet States

Charles D. DeBoer,*[1] William G. Herkstroeter, Alfred P. Marchetti, Arthur G. Schultz, and Richard H. Schlessinger[2]

Contribution from the Research Laboratories, Eastman Kodak Company, Rochester, New York 14650. Received October 18, 1972

Abstract: The photochemical rearrangement of 1-benzoyl-8-benzylnaphthalene (BBN) to cis- and trans-7,8-diphenylacenaphthen-7-ol has been shown to occur from the lowest triplet state which is a π–π* state having less than 10% mixing with the lowest n–π* state (8.9 kcal higher). The 4.7-kcal/mol activation energy for the rearrangement step is consistent with only partial localization of the excitation in the transition state. A novel quenching of the long-lived BBN triplet state has been observed with several ketones of higher triplet energy. For lack of a more precise explanation, this has been called "exciplex" quenching.

The Norrish type II rearrangement is one of the most well-studied photochemical reactions known.[3,4] The elegant work of Wagner, et al., has elucidated the detailed steps of the reaction, showing that it proceeds through a reversible intermediate diradical.[5] Turro and coworkers determined many of the factors which control the multiplicity of the reactive state.[6] More recent reports showed the diverse structural variations which are possible in the Norrish type II rearrangement.[7] Almost all these studies were done with n–π* triplets, i.e., ketones in which the lowest excited state is n–π*. A recent report by Wagner, Kemppainen, and Schott suggested that in cases where ketones with lowest π,π* triplets undergo the Norrish type II reaction, the mechanism of the reaction involves thermal excitation of the π,π* state to a slightly higher n,π* state, from which reaction actually occurs.[8]

A preliminary communication on the Norrish type II photorearrangement of 1-benzoyl-8-benzylnaphthalene (BBN) through a seven-membered ring transition state was recently reported by some of us.[9] We

(1) Author to whom correspondence should be addressed.
(2) Alfred P. Sloan Fellow, 1970–1974.
(3) P. J. Wagner and G. S. Hammond, Advan. Photochem., **5**, 94 (1968).
(4) P. J. Wagner, P. A. Kelso, and R. G. Zepp, J. Amer. Chem. Soc., **94**, 7480 (1972), and references therein.
(5) (a) P. J. Wagner and T. Jellinek, J. Amer. Chem. Soc., **93**, 7328 (1971), see also ref 4; (b) P. J. Wagner and R. G. Zepp, ibid., **93**, 4958 (1971); (c) P. J. Wagner and A. E. Kemppainen, ibid., **90**, 5896 (1968).
(6) N. J. Turro and F. D. Lewis, Tetrahedron Lett., 5845 (1968).

(7) J. C. Dalton and N. J. Turro, J. Amer. Chem. Soc., **93**, 3569 (1971).
(8) P. J. Wagner, A. E. Kemppainen, and H. N. Schott, J. Amer. Chem. Soc., **92**, 5280 (1970).
(9) A. G. Schultz, C. D. DeBoer, W. G. Herkstroeter, and R. H. Schlessinger, J. Amer. Chem. Soc., **92**, 6086 (1970).