

Chromosorb G, the cyclobutanols invariably have retention times a few minutes shorter than their parent ketones. Since cyclobutanol retention times increase with increasing Carbowax loading faster than do ketone retention times, we occasionally analyzed samples on each of two columns containing different amounts of Carbowax to ensure that no cyclic alcohols were eluting under the ketone peak. Since flame detectors effectively count carbons, we assumed that cyclobutanols produce the same response as their parent ketones. All acetophenone-standard responses were calibrated with known mixtures of pure materials.

Cyclobutanols from γ -*tert*-Butylbutyrophenone. The ketone (2 g) in 25 ml of pentane was irradiated to 95% conversion with a 450-W medium-pressure mercury arc filtered by a Pyrex sleeve. Solvent was removed on a flash evaporator and the two products presumed to be cyclobutanols were collected by preparative vpc on a Carbowax 20M column.

Both products displayed similar ir, nmr, and mass spectra, including OH stretches at 3600 cm^{-1} and the $M - 18$, $M - 28$, and m/e 120 peaks characteristics of 1-phenylcyclobutanols. The product with the shorter retention time had the following nmr spectrum (very dilute in CCl_4 ; Varian T-60; chemical shifts relative to TMS) consistent with the *trans*-2-*tert*-butyl-1-phenylcyclobutanol structure: δ 7.2–7.6 (m, 5 H, phenyl), 1.7–2.7 (complex, 5 H, ring protons), 1.45 (s, 1 H, OH), 0.95 (s, 9 H, CMe_3). This product shows *no* hydrogen-bonded O–H stretches in the ir. The product with the longer retention time was assigned as the *cis* isomer on the basis of both free and H-bonded OH stretches in the ir and the upfield shift of the *tert*-butyl signal in the nmr (δ 0.5, s, (9 H)) which would be caused by the *tert*-butyl group being held in the shielding region of the neighboring benzene ring.

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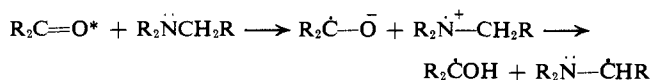
Type II Photoreactions of Phenyl Ketones. Competitive Charge Transfer in α -, γ -, and δ -Dialkylamino Ketones

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Abstract: α -Dimethylaminoacetophenone (I), γ -dimethylaminobutyrophenone (II), and δ -pyrrolidinovalerophenone (III) all undergo photoelimination in solution to yield acetophenone. Intersystem crossing yields are lower than unity for all three ketones, decreasing in the order $\text{III} > \text{II} > \text{I}$. For all three ketones, Φ_{isc} values are higher in methanol than in benzene or acetonitrile. Analysis of quantum yields and lifetimes suggests that all the photoelimination of II and III arises by direct triplet state γ -hydrogen abstraction. Rapid charge transfer quenching by the remote amino group is a competitive triplet reaction, being 3.5 times faster for II than for III and five times faster in benzene or acetonitrile than in methanol, but does not lead to photoelimination products. Triethylamine and dimethyl *tert*-butylamine quench triplet valerophenone at equal rates in a given solvent, the absolute rate constants being ten times higher in benzene and acetonitrile than in methanol. This behavior indicates a bimolecular charge transfer process which leads efficiently to radicals. The lack of a sizable rate increase in acetonitrile indicates that amine-triplet ketone interactions involve charge transfer but not full electron transfer. The decreases afforded by methanol reflect the decreased availability of hydrogen-bonded lone-pair electrons. The lack of biradical formation from the corresponding CT complexes formed from II and III reflects geometric restraints to transfer of a proton to oxygen in the cyclic complex. I is unusual in that all of its photoelimination in benzene and acetonitrile, two-thirds in methanol, arises from an unquenchable singlet state. This observation invalidates the suggestion that π, π^* triplets of α -dialkylamino ketones might be highly reactive. The singlet reaction of I may involve either singlet CT complexation or the fact that the $^1n, \pi^*$ state of I has $n(\text{O}), \sigma^*(\text{C}-\text{N})$ character, causing expulsion of the dimethylamide anion. Triplet I is formed only in methanol or by sensitization and is unusual in that it does not seem to undergo the rapid CT quenching noted for II and III but proceeds to product in high yields.

Photoreduction of ketones by amines has received considerable attention.^{2,3} Cohen first proposed that amines *reduce* ketone triplets and that the resulting radical ions collapse either to radicals by a proton shift or to ground states of reactants by a reverse electron shift.²



In our study of substituent effects on intramolecular hydrogen abstraction by triplet phenyl ketones, we

(1) Alfred P. Sloan Fellow, 1968–1972.

(2) (a) S. G. Cohen and R. J. Baumgarten, *J. Amer. Chem. Soc.*, **89**, 3741 (1967); (b) S. G. Cohen and H. M. Chao, *ibid.*, **90**, 165 (1968); (c) S. G. Cohen, N. Stein, and H. M. Chao, *ibid.*, **90**, 521 (1968); (d) S. G. Cohen and J. I. Cohen, *J. Phys. Chem.*, **72**, 3782 (1968).

(3) (a) R. S. Davidson and P. F. Lambeth, *Chem. Commun.*, 1265 (1967); 511 (1968); (b) S. G. Cohen and G. Parsons, *J. Amer. Chem. Soc.*, **92**, 7603 (1970).

have investigated the photochemistry of α -, γ -, and δ -dialkylamino substituted phenyl alkyl ketones with the hope of establishing how well intramolecular charge transfer interactions compete with intramolecular hydrogen abstraction, in particular, how the competition depends on the distance between the two groups and on the polarity of the solvent.

Results

We have studied three ketones: α -dimethylaminoacetophenone (Im), γ -dimethylaminobutyrophenone (II), and δ -pyrrolidinovalerophenone (III), as well as some ammonium salts of II and III. In all cases, the ketones and their salts undergo type II photoelimination to yield acetophenone. Small peaks presumably corresponding to cyclobutanols appear in vpc traces of II and III photosylates, but not from I. Acetophenone

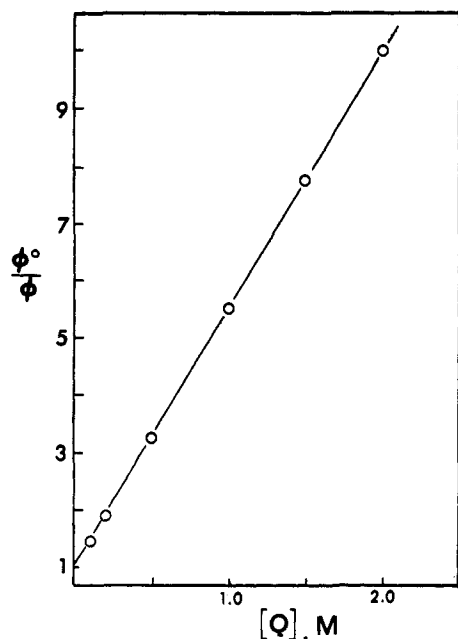
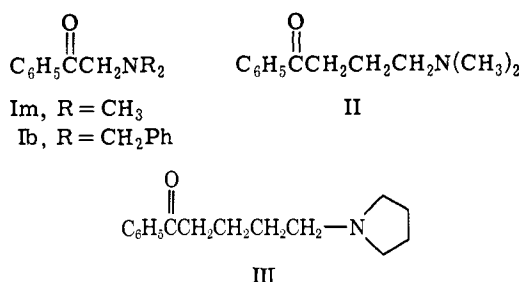


Figure 1. Stern-Volmer plot for 1,3-pentadiene quenching of acetophenone formation from γ -dimethylaminobutyrophenone in methanol.



accounts for 70–90% of the reacted ketone for I, II, and III. With II-HCl, however, the yield of acetophenone is only one-eighth the amount of ketone reacted. It is assumed that the rest of the ketone is photoreduced in the moderately reactive methanol solvent. Likewise, some of III-HCl is probably also photoreduced in methanol.

Quantum Yields and Quenching Studies. Degassed solutions 0.03 M in III or III-HCl, 0.1 M in Im, II, or II-HCl, and containing various concentrations of 1,3-pentadiene or 2,5-dimethyl-2,4-hexadiene were irradiated at 25° with the 313-nm region of a mercury arc in parallel with valerophenone actinometer solutions.³ Yields of acetophenone formation were determined by vpc analysis. Stern-Volmer plots of relative quantum yield vs. quencher concentration were linear for II, III, and their salts, Figure 1 displaying one example, II in methanol. Table I lists quantum yields and $k_q\tau$ values in three different solvents and in benzene containing enough pyridine to maximize the quantum yields.⁴

Ketone Im behaves differently from II and III in that its photoelimination is unquenchable in hexane and in acetonitrile, just as has been reported for Ib in benzene.⁵ However, small concentrations of diene

(4) P. J. Wagner, I. E. Kochevar, and A. E. Kemppainen, *J. Amer. Chem. Soc.*, **94**, 7489 (1972).

(5) A. Padwa, W. A. Eisenhardt, R. Gruber, and D. Pashayan, *ibid.*, **91**, 1857 (1969).

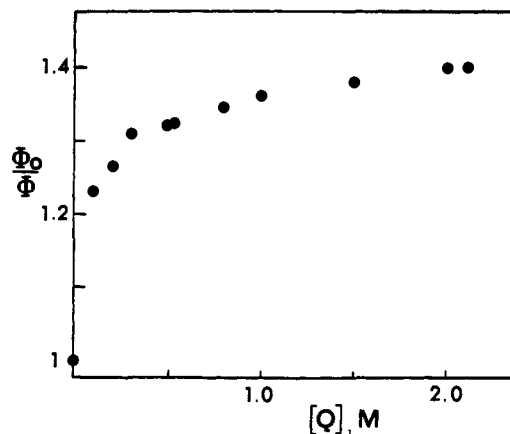


Figure 2. Stern-Volmer plot for 1,3-pentadiene quenching of acetophenone formation from α -dimethylaminoacetophenone in methanol.

Table I. Photoelimination of Phenyl ω -Dialkylaminoalkyl Ketones^a

Ketone	Solvent	Φ_{II}^b	$k_q\tau, M^{-1}$
Im	Benzene	0.056 (0.056)	<0.2
	Acetonitrile	0.056	<0.2
	Methanol	0.085	~20
II	Benzene	0.025 (0.056)	0.60
	Acetonitrile	0.050	1.5
	Methanol	0.25	4.5
II-HCl	Methanol	0.009	720
II-EtBr	Methanol	0.0008	
III ^c	Benzene	0.046 (0.050)	4.6
	Acetonitrile	0.024	4.8
	Methanol	0.08	33
III-HCl ^c	Methanol	0.38	570

^a [Ketone] = 0.1 M, irradiation at 313 nm, 25°. ^b Values in parentheses are those obtained in the presence of 0.5–1.0 M pyridine. ^c 0.03 M.

very efficiently quench one-third of the reaction of Im in methanol solvent, the remaining two-thirds being unquenchable. Figure 2 displays the quenching plot obtained for Im in methanol and Table II divides total

Table II. Solvent Dependence of Quantum Yields for α -Dimethylaminoacetophenone

Solvent	Φ_{total}	Φ_{T}	Φ_{S}	Φ_{sens}^a
Benzene	0.056	0	0.056	0.30
Acetonitrile	0.056	0	0.056	
Methanol	0.085	0.027	0.058	0.40

^a Corrected for only 80% absorption by sensitizer.

quantum yields into their triplet (quenchable) and unquenchable (singlet) components. Interestingly, the total quantum yield of Im is higher in methanol than in the aprotic solvents by exactly the amount of triplet reaction observed in methanol. An estimate of $k_q\tau$ obtained from the lowest concentration quenching points for Im is also listed in Table I.

Sensitization of Im Photoelimination. Benzene and methanol solutions containing 5 M 2-butanone and 0.025 M Im were irradiated at 313 nm, under which conditions the aliphatic ketone absorbs some 80% of the incident radiation. Quantum yields for formation of acetophenone are listed in Table II. Efficient triplet

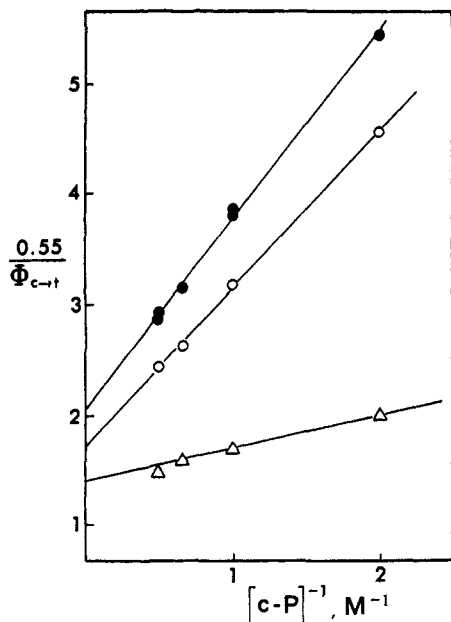


Figure 3. Dependence of quantum yields for γ -dimethylamino-butyrophenone sensitized cis-trans isomerization of 1,3-pentadiene on diene concentration: ●, in acetonitrile; ○, in benzene; △, in methanol.

energy transfer from the aliphatic ketone ($E_T = 78$ – 80 kcal/mol)⁶ to the phenone ($E_T = 72$ – 74 kcal/mol)⁷ would be expected. As in the direct irradiation, no product peaks attributable to cyclobutanols were detected during vpc analysis of these sensitized experiments.

Intersystem Crossing Yields. Since the sensitization experiments suggest a low intersystem crossing yield for Im, the efficiencies with which Im, II, and III sensitize the cis-trans isomerization of various concentrations of 1,3-pentadiene in different solvents were determined and compared to that of acetophenone ($\Phi_{isc} = 1$).⁸ Figures 3 and 4 show some typical results; Table III lists Φ_{isc} values obtained from the intercepts and $k_t\tau_t$ values obtained from the intercept/slope values.⁹ These $k_t\tau$

Table III. Kinetic Parameters for Amino Ketone Sensitized Cis-Trans Isomerization of 1,3-Pentadiene

Ketone	Solvent	Φ_{isc}	$k_t\tau_t$, M^{-1}	k_{ot}^a , 10^{11} sec^{-1}
Im	Benzene ^a	<0.01		>100
	CH ₃ CN ^a	<0.01		>100
	CH ₃ OH ^b	0.03	15	30
II	Benzene ^c	0.58	1.2	0.7
	CH ₃ CN ^c	0.50	1.2	1.0
	CH ₃ OH ^d	0.72	4.5	0.4
III	Benzene ^e	0.82		0.22
	CH ₃ CN ^e	0.80		0.25
	CH ₃ OH ^e	0.89		0.12

^a 2 M diene. ^b 0.04–0.2 M diene. ^c 0.5–2.0 M diene. ^d 0.05–2.0 M diene. ^e 0.5 M diene; Φ_{isc} corrected for less than 100% quenching by diene and for quenching by ground-state III.

(6) R. G. Borkman and D. R. Kearns, *J. Chem. Phys.*, **44**, 945 (1966).

(7) (a) J. Saltiel, H. C. Curtis, L. Metts, J. W. Wiley, J. Winterle, and M. Wrighton, *J. Amer. Chem. Soc.*, **92**, 410 (1970); (b) P. Wagner, M. May, and A. Haug, *Chem. Phys. Lett.*, **13**, 545 (1972).

(8) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

(9) P. J. Wagner in "Creation and Detection of the Excited State," Vol. 1A, A. A. Lamola, Ed., Marcel Dekker, New York, N. Y., 1971, p 173.

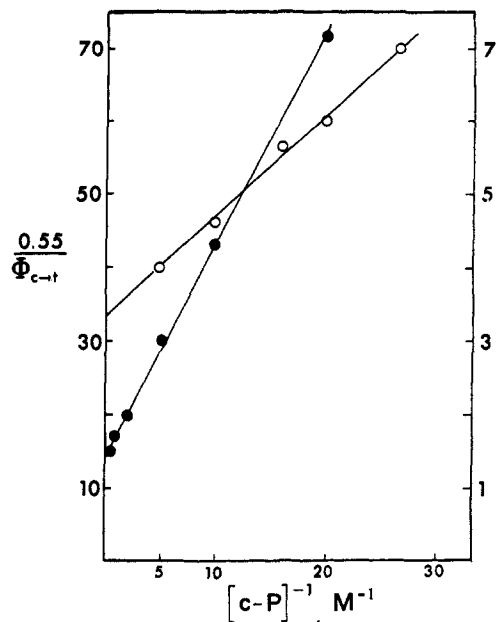


Figure 4. Dependence of quantum yields for amino ketone sensitized cis-trans isomerization of 1,3-pentadiene on diene concentration in methanol: ○ (left ordinate), Im; ● (right ordinate), II.

values agree closely with the $k_q\tau$ values obtained by quenching, except for ketone II in benzene. It is quite possible that, because of the low $k_q\tau$ and Φ_{isc} values, a slight amount of isomerization was sensitized by product acetophenone. With Im, we took particular pains to avoid this possibility by working at less than 1% conversion. In benzene, the amount of Im-sensitized diene isomerization is so small that most of what was actually observed could be attributed to acetophenone sensitization.

Amine Quenching of Valerophenone. Two different tertiary amines were employed to quench the photolimitation of valerophenone in solvents of different polarities. Table IV compares the $k_q\tau$ values so ob-

Table IV. Tertiary Amine Quenching of Triplet Valerophenone^a

Quencher	Solvent	$k_q\tau$, M^{-1}	k_q , $10^9 M^{-1} sec^{-1}$
Benzene-pyridine ^b	Diene ^c	36	5.0 ^d
	Benzene		
	Diene ^c	40	5.0
Acetonitrile	TEA ^e	25	3.1
	DMBA ^f	25	3.1
	Diene ^c	68	10.0 ^d
	TEA ^e	25	3.7
Methanol	DMBA ^f	22	3.2
	Diene ^c	100	7.5 ^{d,g}
	TEA ^e	5.5	0.4
	DMBA ^f	3.5	0.22
	Et ₃ N ⁺ Br ⁻	<0.1	<0.01

^a 0.1 M ketone irradiated at 25° with 313-nm light. ^b 0.6 M pyridine added. ^c 2,5-Dimethyl-2,4-hexadiene. ^d P. J. Wagner and I. Kochevar, *J. Amer. Chem. Soc.*, **90**, 2232 (1968). ^e Triethylamine. ^f Dimethyl-*tert*-butylamine. ^g P. J. Wagner, J. McGrath, and R. G. Zepp, *J. Amer. Chem. Soc.*, **94**, 6883 (1972).

tained with those for a "diffusion-controlled" diene quencher, from which τ values were estimated. Note that the presence of pyridine does not affect τ for valerophenone, so it is assumed that the other tertiary amines

have no solvent effect on τ either. Pyridine does enhance the quantum yield in benzene by a factor of 2.5, and it is assumed that the other amines would have a similar effect on the biradical intermediate.⁴ Consequently, the $k_q\tau$ values for benzene solvent in Table IV are 2.5 times the measured Stern–Volmer slopes. The k_q values for the amines must represent chemical quenching, since at 0.8 M triethylamine in benzene, the quantum yield for disappearance of valerophenone is 0.64 vs. 0.40 in the absence of amine. The negligible quenching found for tetraethylammonium bromide indicates that bromide quenching is not responsible for the low quantum yield of II–EtBr.

Spectroscopy. The absorption and emission spectra of II indicate no interaction between the amino group and the carbonyl. Its uv spectrum and its ir spectrum in the carbonyl region are identical with those of valerophenone. In its nmr spectrum, the chemical shifts of the protons α to nitrogen are almost identical with their values in model amines. Its phosphorescence spectrum in rigid hydrocarbon glasses at 77°K closely resembles those of other phenyl alkyl ketones with n, π^* lowest triplets and has a decay time of 4.7 msec.¹⁰ In ethanol glass, the spectra and decay times of II, II–HCl, and II–EtBr are very similar to those of valerophenone in ethanol.¹⁰ In the nonrigid isopentane at 77°K, however, the phosphorescence of II is broader and much longer lived, perhaps indicating intramolecular interaction between the amino group and the triplet carbonyl.

Padwa reports that the phosphorescence of Im is unexceptional.¹¹ We find that its uv spectrum is a little unusual in that the first $\pi \rightarrow \pi^*$ transition is red-shifted compared to acetophenone, so that the $n \rightarrow \pi^*$ transition appears as a shoulder, λ_{\max} at 335–340 nm instead of at 325 nm as in simple phenyl alkyl ketones. The lowest singlet probably is slightly mixed with $n \rightarrow \sigma^*$ states as in α -halo ketones.¹² Excitation at 313 nm populates both $^1n, \pi^*$ and $^1\pi, \pi^*$ (L_B) states approximately equally.

Finally, in our hands Im and other α -amino ketones are yellow when first distilled and get yellower rapidly as they undergo facile autoxidation. The γ - and δ -amino ketones can be distilled colorless but also oxidize fairly rapidly.

Discussion

Bimolecular Reactions. As indicated in Table IV, triethylamine and dimethyl-*tert*-butylamine quench triplet valerophenone with nearly identical rate constants in a given solvent. In even the most rapid free-radical hydrogen abstraction processes, secondary C–H bonds are significantly more reactive than primary C–H bonds. Therefore, our results are not consistent with hydrogen abstraction being the primary process involved in the quenching. This conclusion has, of course, been reached before, but on the basis of relative quantum yields.^{2,3} Our relative rates are less equivocal evidence.

As Cohen originally proposed,² the most likely interaction is some form of charge-transfer complexing,

(10) P. J. Wagner, M. May, A. Haug, and D. R. Graber, *J. Amer. Chem. Soc.*, **92**, 5269 (1970).

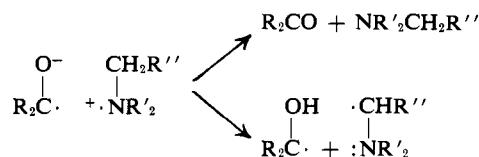
(11) A. Padwa, W. Eisenhardt, R. Gruber, and D. Pashayan, *ibid.*, **93**, 6998 (1971).

(12) N. L. Allinger, J. C. Tai, and M. A. Miller, *ibid.*, **88**, 4495 (1966).

which he pictured as a one-electron oxidation–reduction process. The actual magnitudes of the k_q values in different solvents are most interesting. In benzene, the reaction is almost diffusion controlled. A similar value has been measured by triethylamine quenching of benzophenone phosphorescence.¹³ Acetonitrile produces no change within experimental error, while methanol decreases reactivity by an order of magnitude. Ground-state reactions which proceed by electron transfer display tremendous rate enhancements in acetonitrile relative to benzene.¹⁴

The present solvent effects suggest the formation of a charge-transfer complex but not a pair of radical ions. Since the CT process creates a large dipole but no free charges, solvent effects can be expected to differ from those expected and observed in electron-transfer processes. Incomplete realization of this concept produced the hypothesis of vibrational energy transfer¹⁵ for some singlet quenching processes which now seem to involve exciplexes with considerable charge-transfer character.¹⁶ The rate decrease caused by methanol has also been observed, since our original report,^{17a} for water¹³ and presumably reflects the decreased availability of hydrogen-bonded amine lone pairs. The ultimate in such deactivation is exemplified by the negligible quenching ability of the quaternary ammonium salt.

In these bimolecular reactions the CT complex proceeds on to radicals and to radical-coupling products in high yield. Thus, 0.8 M triethylamine quenches 95% of triplet valerophenone in benzene, of which 60% does not return to ground-state valerophenone. Similar quantum yields, on the order of 60%, have been reported for the photoreduction of other ketones by tertiary amines.^{2,3} Proton transfer within the CT complex and reversion to ground-state ketone presumably are closely competitive.



Intramolecular CT Singlet Quenching. If amines can quench electrophilic n, π^* triplets so rapidly, they ought to be able to quench n, π^* singlets rapidly also. Such bimolecular singlet quenching has been observed for biacetyl¹⁸ and fluorenone,¹⁹ which undergo $S^* \rightarrow T^*$ intersystem crossing relatively slowly. The 10^{11} -sec⁻¹ intersystem crossing rate observed for benzophenone²⁰ and assumed for most simple phenyl ketones²¹ usually prevents bimolecular singlet reactions of phenones. However, we find that intramolecular quenching by

(13) S. G. Cohen and A. D. Litt, *Tetrahedron Lett.*, 837 (1970).

(14) E. M. Kosower and M. Mohammad, *J. Amer. Chem. Soc.*, **90**, 3271 (1968).

(15) S. Murov, R. S. Cole, and G. S. Hammond, *ibid.*, **90**, 2957 (1968).

(16) (a) B. S. Solomon, C. Steel, and A. Weller, *Chem. Commun.*, 927 (1969); (b) T. R. Evans, *J. Amer. Chem. Soc.*, **93**, 2081 (1971).

(17) (a) P. J. Wagner and A. E. Kemppainen, *ibid.*, **91**, 3085 (1969).

(b) γ -Dialkylaminobutyrophenones, as a class, are central nervous system depressants, some quite potent, and should be handled with due care.

(18) N. J. Turro and R. Engel, *J. Amer. Chem. Soc.*, **91**, 7113 (1969).

(19) G. A. Davis, P. A. Carapellucci, K. Szoc, and J. D. Gresser, *ibid.*, **91**, 2264 (1969).

(20) P. Rentzepis and C. J. Mitschele, *Anal. Chem.*, **42**, 20A (1970).

(21) R. M. Hochstrasser, *Accounts Chem. Res.*, **1**, 266 (1968).

tertiary amine groups does compete with intersystem crossing.

As Table III shows, the efficiency of this intramolecular quenching is very high for the α -amino ketone and decreases as the amino group moves down the alkyl chain away from the carbonyl. If it is assumed that the rate of intersystem crossing is 10^{11} sec^{-1} independent of amino substitution, the rate constants k_{ct} for singlet quenching listed in Table III result.

It is very interesting that the same general solvent effects noted for bimolecular triplet quenching recur in these estimated intramolecular singlet quenching rates, except that acetonitrile produces a slight rate increase and methanol only a 50% reduction. In fact, the solvent effects are identical with those reported for aniline quenching of polyacene fluorescence.²² We assume that a similar CT complexing occurs, except that with these ketones, a $^1n, \pi^*$ state rather than a $^1\pi, \pi^*$ state is involved.

It should be noted that in the only recorded cases of phenyl ketones with Φ_{isc} values substantially below unity, fluorenone^{19,23} and *p*-aminobenzophenone,²⁴ k_{isc} values are lower than in benzophenone itself and decrease with increasing solvent polarity. Therefore, our k_{ct} values, if anything, underestimate the solvent effect of methanol.

Before making further comparisons, we shall discuss the three ketones individually.

δ -Amino Ketone. Triplet III is formed in high yield. Unlike δ -methoxyvalerophenone,²⁵ III produces vpc-stable cyclization products in very low yield, their total quantum yield not exceeding 0.01. We have not ascertained whether they correspond to cyclobutanols, cyclopentanols, or both. As with δ -methoxyvalerophenone,²⁵ the type II quantum yield of III is increased only slightly by the addition of pyridine. Consequently, the low absolute Φ_{II} values for III are not due to a peculiar substituent effect on the biradical intermediate and must reflect competition from the expected intramolecular CT quenching. The high Φ_{II} value for the hydrochloride salt of III can only reflect the absence of competing CT quenching.

In Table III, the quantum yield and lifetime data are broken down into k_r and k_d values according to eq 1.⁹ The corresponding data for valerophenone (VP) are

$$\Phi_{max} = \Phi_{isc} k_r (k_r + k_d)^{-1} \quad (1)$$

also included. The decreases in reactivity (k_r) afforded by the δ -dialkylamino (pyrrolidino) and δ -dialkylammonium groups are consistent with the inductive effects of other δ substituents, which indicate a ρ_I value of -1.85 .²⁶ The σ_I value for amino groups of ~ 0.10 ²⁷ predicts the observed rate decrease of about half; a σ_I value of 0.65 for NHR_2^+ would predict the observed decrease in k_r for III-HCl. Literature values range from 0.6 for NH_3^+ to 0.9 for NR_3^+ .²⁷ The k_d value for III-HCl presumably reflects hydrogen abstraction

(22) (a) A. Weller, *Pure Appl. Chem.*, **16**, 115 (1968); (b) W. R. Ware and H. P. Richter, *J. Chem. Phys.*, **48**, 1595 (1968); (c) K. Kaneta and M. Koizumi, *Bull. Chem. Soc. Jap.*, **40**, 2254 (1967).

(23) (a) R. A. Caldwell, *Tetrahedron Lett.*, 2121 (1969); (b) J. B. Gutenplan and S. G. Cohen, *ibid.*, 2125 (1969).

(24) S. G. Cohen, M. D. Saltzman, and J. B. Gutenplan, *ibid.*, 4321 (1969).

(25) P. J. Wagner and R. G. Zepp, *J. Amer. Chem. Soc.*, **93**, 4958 (1971).

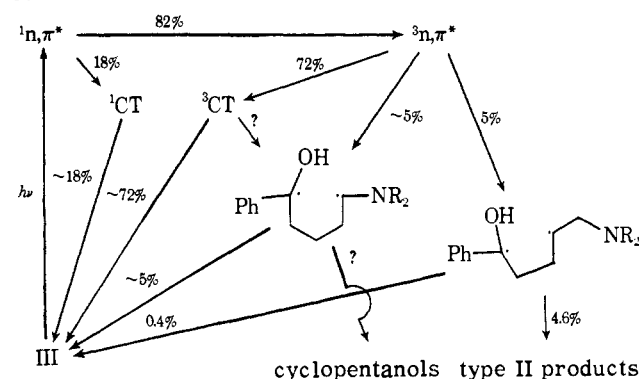
(26) P. J. Wagner and A. E. Kemppainen, *ibid.*, **94**, 7495 (1972).

(27) P. R. Wells, *Chem. Rev.*, **63**, 171 (1963).

from solvent, while the k_d values for III itself represent CT quenching of the triplet carbonyl by the δ -dialkylamino group. The usual solvent effects are manifest.

The behavior of III in benzene is summarized in Scheme I. The percentages are all relative to the orig-

Scheme I



inally formed n, π^* singlet. Since, if any cyclopentanols are formed, they are formed in very low yield, it is probable that the CT complexes—both singlet and triplet derived—undergo very little proton transfer to yield a 1,5 biradical. Some direct δ -hydrogen abstraction would be expected^{25,28} to yield the 1,5 biradical, but cyclization of 1,5 biradicals is often very inefficient.²⁸ There are at least three and probably four reversible chemical processes which cause radiationless decay in III, which must set some sort of record.

γ -Amino Ketone. Singlet excited II partitions itself about evenly between complexation and triplet formation. Φ_{II}^0 in benzene is probably only 0.015, since 0.1 *M* amine (*i.e.*, the amino ketone concentration) is sufficient to double Φ_{II} values.⁴ As with γ -methoxyvalerophenone,²⁶ the likely Φ_{max}/Φ_{II}^0 ratio for II is on the order of 4, indicating that dialkylamino and methoxy have similar substituent effects on the 1,4 biradical. Application of eq 1 to the low quantum yields and short triplet lifetimes yields the k_r and k_d values listed in Table V.

In our preliminary report^{17a} we mistakenly neglected the possibility of direct γ -hydrogen transfer competing with charge transfer.^{17b} The *maximum* k_r values for II, as calculated by eq 1, are no larger than what would be predicted²⁶ for direct hydrogen abstraction. Thus k_r for γ -methoxyvalerophenone²⁶ is $6 \times 10^8 \text{ sec}^{-1}$ and a nitrogen surely can stabilize a radical at least as well as an oxygen atom.²⁹ Therefore, we now conclude that most of the type II reaction of II in aprotic solvents proceeds by direct γ -hydrogen abstraction. The CT complex formed competitively with the biradical apparently undergoes little proton transfer. Rates of formation of the triplet CT complex are subject to the usual solvent effects.

γ -Hydrogen abstraction still occurs in II-HCl and II-EtBr, but at vastly reduced rates. We have calculated a ρ_I of -4.3 for γ substituents,²⁶ so the k_r values 1/750th and 1/8000th that of VP for II-HCl and II-EtBr are consistent with σ_I values of 0.67 and 0.90 for NHR_2^+ and NR_3^+ , respectively. It is assumed that tetravalent nitrogen, being isoelectronic with

(28) P. J. Wagner, P. A. Kelso, A. E. Kemppainen, and R. G. Zepp, *J. Amer. Chem. Soc.*, **94**, 7500 (1972).

(29) E. S. Huyser, "Free Radical Chain Reactions," Wiley-Interscience, New York, N. Y., 1970, p 156.

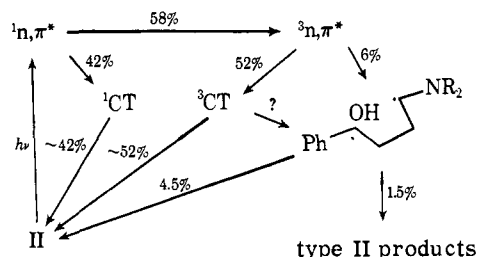
Table V. Summary of Triplet State Reactivities of Phenyl ω -Dialkylaminoalkyl Ketones

Ketone	Solvent	Φ_{isc}	Φ_{max}	Φ_{BR}^a	$1/\tau, 10^9 \text{ sec}^{-1}$	$k_r, 10^9 \text{ sec}^{-1}$	$k_d, 10^9 \text{ sec}^{-1}$
II	Benzene	0.58	0.056	0.10	8.0	0.8	7.2
	CH ₃ CN	0.50	0.050	0.10	7.4 ^b	0.7	6.7
	CH ₃ OH	0.72	0.25	0.35	1.7	≤ 0.60	≥ 1.1
II-HCl	CH ₃ OH	1 ^c	0.009	0.009	0.010	0.00009	0.01
II-EtBr	CH ₃ OH	1 ^c	0.0008	0.001	0.01 ^c	0.00001	0.01
III	Benzene	0.82	0.05	0.061	1.1	0.07	1.0
	CH ₃ CN	0.80	0.024	0.030	2.1	0.06	2.0
	CH ₃ OH	0.89	0.08	0.09	0.23	0.020	0.21
III-HCl	CH ₃ OH	1 ^c	0.38	0.38	0.013	0.005	0.008
Im	CH ₃ OH	0.03	0.027	0.90	~ 0.5	0.45	0.05
VP	Benzene	1	1	1	0.12	0.12	
	CH ₃ CN	1	1	1	0.15	0.15	
	CH ₃ OH	1	1	1	0.08	0.08 ^d	

^a Cyclobutanol formation ignored; k_r may be 10–20% higher for II and III. ^b Average from $k_q\tau$ and $k_r\tau$. ^c Assumed. ^d Note change from ref 17 because of lower value for k_q .

carbon, is equivalent to an alkyl group in stabilizing a radical center. Our results are self-consistent in that the inductive effect of a NHR_2^+ substituent in terms of a σ_1 value is the same for both γ and δ substitution.

Scheme II describes the behavior of II in benzene.

Scheme II

Again, each of three intermediates en route to type II elimination reverts to ground-state II with high efficiency.

In methanol, the k_r value calculated from the observed Φ_{II} value seems too large. Methanol decreases k_r for triplet III to one-third its benzene value. Part of the decrease probably involves a larger σ_1 for the hydrogen-bonded amino group. In II, a hydrogen-bonded γ -amino group should produce an even larger inductive deactivation. Moreover, hydrogen bonding should decrease the ability of a lone pair to stabilize a radical center. Therefore, it is likely that k_r for II in methanol is appreciably lower than $6 \times 10^8 \text{ sec}^{-1}$, that k_d is correspondingly larger (although still only $\sim 0.2k_d$ in benzene), and that much of the type II reaction comes from proton transfer in the CT complex.

As in the reported cases of bimolecular amine quenching of ketone singlets,^{18,19} II gives no indication of yielding stable products from its excited singlet. As Figure 1 shows, the triplet Stern-Volmer quenching plot of II in methanol is linear out to 90% quenching. That this experiment involves only triplet quenching is proven by the identical $k_q\tau$ value obtained from sensitization experiments. Since the overall type II quantum yield is 0.25, the maximum singlet quantum yield which would not have caused detectable curvature in Figure 1 is on the order of 0.003, which would account for only 1% of the singlets which do not cross over to the triplet manifold. The singlet charge-transfer interaction apparently is almost entirely a quenching process, *i.e.*, the CT complex undergoes decay to ground state

much faster than it can undergo a proton transfer. This rate difference probably involves geometric factors which slow down transfer (see below) and may also reflect the spin-allowed nature of the decay process.

Comparison of γ - and δ -Amino Ketones. The estimated rate ratio k^{γ}/k^{δ} for both singlet and triplet CT quenching is 3.5 ± 0.5 in all three solvents, with the singlet rates being 10–40 times larger than the analogous triplet rates. It is very interesting that the rate ratio for intramolecular triplet energy transfer in ω -styryl-alkyl phenyl ketones is also 3.3.³⁰ All three processes are apparently governed by the same conformational factors. The absolute values of k_d for III are lower than the bimolecular rate constants in Table IV. On a time average, a δ substituent does not approach the carbonyl closely as often as does an independent molecule during a solution encounter. A β substituent probably does so more often.³⁰ The γ substituent is the best model for a bimolecular solution encounter.

The fact that singlet k_{et} values are so much larger than triplet k_d values and less subject to deceleration by methanol suggests that the singlet n, π^* state is considerably more electrophilic than the triplet n, π^* state.

α -Amino Ketones. Like many α -substituted ketones, α -amino ketones show behavior which does not correlate with that of compounds with more carbons separating the two functional groups. In benzene and acetonitrile, Im undergoes no measurable intersystem crossing, so that the unquenchable photoelimination most likely arises from an excited singlet. The classic interpretation³¹ of the quenching data (Figure 2) would be that in methanol reaction occurs from both singlet and triplet states. In fact, the unquenchable quantum yield in methanol is the same as in other solvents, indicating that whatever process leads to product experiences the same solvent effect as the singlet quenching process.

The measured sensitized quantum yields for Im (Table II) definitely do not represent the total efficiency with which triplet Im reacts because triplet energy transfer from 2-butanone to Im cannot be 100% efficient. Even if the rate of energy transfer is diffusion-controlled, it must compete with the almost diffusion-controlled CT quenching of triplet 2-butanone by tertiary amine Im. Moreover, the intersystem crossing efficiency of 2-

(30) D. O. Cowan and A. A. Baum, *J. Amer. Chem. Soc.*, **93**, 1153 (1971).

(31) P. J. Wagner and G. S. Hammond, *ibid.*, **87**, 4009 (1965).

butanone may be less than 100%.³² Consequently, we conclude that triplet Im, when formed, undergoes photoelimination in very high efficiency. In methanol, the total quenchable triplet quantum yield is 90% of the measured Φ_{isc} . In this respect, Im resembles α -methoxyacetophenone.³³

What is most amazing is that the maximum k_d for triplet Im is less than one-tenth as fast as for the γ - and δ -amino ketones, whereas k_{ct} for singlet Im is extremely rapid. The triplet k_r value in Table V deduced from the $k_{t\tau}$ value in Table III is one-fourth as large as the rate of γ -hydrogen abstraction in α -methoxyacetophenone³³ and would seem to be the minimum that might be expected for direct hydrogen atom abstraction. Given the small solvent effects on k_r in the other amino ketones and in ketones in general,³⁴ τ_T values for Im in benzene and acetonitrile very likely are near 1 nsec, so that the inability of Im to sensitize diene isomerization in these solvents must be blamed on a near-zero Φ_{isc} and not on very low $k_{t\tau}$ values.

The absence of cyclobutanol formation from Im deserves comment since it may be compounded of a steric effect in any 1,4 biradical,³⁵ the normal low cyclization efficiency of singlet type II reactions,³⁶ and perhaps even a singlet elimination mechanism not involving a biradical. Two α -(*N*-amido)acetophenones, which react only from their triplets, produce azetidins in good yield.^{11,37}

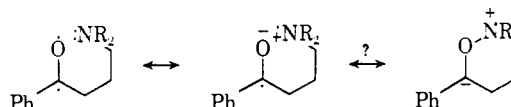
Our results for Im are of considerable importance with respect to the many photoreactions of α -amino ketones observed in Padwa's laboratory.³⁸ Most of these reactions probably take place by singlet CT processes.³⁹ The most significant modification required of published conclusions involves the suggestion that π, π^* triplets of α -amino ketones have high reactivity, comparable to that of n, π^* triplets.⁵ The comparable unquenchable photoelimination quantum yields of phenyl, biphenyl, and naphthyl α -dibenzylaminoalkyl ketones¹¹ presumably involve singlet reactions; the relative reactivities of these ketones' triplets remain to be determined but probably vary by as much as a factor of 10,000.⁴⁰

It is remarkably coincidental that the photoisomerization of α -(β -styryl)acetophenone²⁸ behaves very much like the photoelimination of Im in that the reaction is only partially quenchable and the quenchable portion indicates a surprisingly long triplet lifetime. Cowan and Baum²⁸ have suggested that the lowest singlet of the styryl ketone is of mixed character and can cross directly to a π, π^* triplet localized on the styrene chromophore. Although the lowest singlets of the α -amino ketones are probably also of mixed character, the unquenchable photoelimination resulting from direct irradiation cannot involve an "unquenchable" triplet, otherwise the quantum yields of the sen-

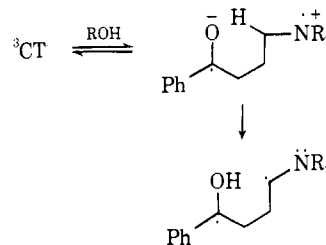
sitized reaction would be as low as those in direct irradiations. However, the mixed nature of the lowest singlet of Im may explain its unique behavior. Before we explore the mechanistic possibilities for singlet Im, it is best to discuss why triplet CT complexing is so slow for Im and does not lead to type II products for II.

Nature of CT Complexes. II and III. As we pointed out in our preliminary communication,^{17a} a special explanation is required for the very low efficiency with which the 3CT complex formed from II transfers a usually readily accessible γ proton to oxygen, since no such inefficiency interferes with bimolecular photo-reductions of triplet ketones by amines.^{2,3} The geometry of the CT complex from II must be such that the γ hydrogens are held away from the carbonyl oxygen. The CT bonding apparently holds the remote nitrogen close enough to the carbonyl that the overall complex is restricted to the conformational possibilities of a cycloalkane, none of which bring a γ hydrogen particularly close to oxygen. This conclusion is consistent with our conclusion that the CT process does not create a pair of free-radical ions. Similar effects would presumably impede biradical formation *via* the 3CT complex from III and the 1CT complexes from II and III.

Turro has presented evidence that CT quenching of n, π^* excited ketones by olefins involves attack primarily on the half-empty n orbital of oxygen.⁴¹ Since we have shown that rates of CT quenching by amines and olefins of the same ionization potential are the same,⁴² the CT processes in these amino ketones also probably involve approach of the lone pair of nitrogen toward the n orbital of oxygen. In the triplet, a covalently bonded zwitterion cannot be formed directly; in the singlet, a N-O bond may contribute to the CT complex and may provide the path for rapid, efficient decay to unreacted ground state.



It is well known that, although alcohols decrease rates of singlet exciplex formation, they enhance the decay rates of the exciplexes.²² As we noted above, II undergoes photoelimination in methanol in higher quantum efficiency than would be expected for exclusive γ -hydrogen abstraction. It is probable that some of the 3CT complex does undergo γ -proton transfer to yield the 1,4 biradical. Perhaps, in the protic solvent, the 3CT complex proceeds partially to a real zwitterionic biradical, in which methanol solvates the ketyl radical anion, allowing the positive nitrogen to move away and a γ hydrogen to approach the carbonyl.



(32) N. C. Yang, E. D. Feit, M. H. Hui, N. J. Turro, and J. C. Dalton, *J. Amer. Chem. Soc.*, **92**, 6974 (1970).

(33) (a) P. J. Wagner and A. E. Kemppainen, *ibid.*, **90**, 5896 (1968);

(b) N. J. Turro and F. D. Lewis, *ibid.*, **92**, 311 (1970).

(34) P. J. Wagner, *ibid.*, **89**, 5898 (1967).

(35) F. D. Lewis and T. R. Hilliard, *ibid.*, **92**, 6672 (1970).

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

(37) E. H. Gold, *J. Amer. Chem. Soc.*, **93**, 2793 (1971).

(38) A. Padwa, *Accounts Chem. Res.*, **4**, 48 (1971).

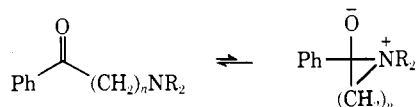
(39) For a preliminary communication, see P. J. Wagner and T. Jellinek, *J. Amer. Chem. Soc.*, **93**, 7328 (1971).

(40) S. G. Cohen, G. A. Davis, and W. D. K. Clark, *ibid.*, **94**, 869 (1972).

(41) N. J. Turro, J. C. Dalton, G. Farrington, M. Niemczyk, and D. M. Pond, *ibid.*, **92**, 6978 (1970).

(42) I. Kochevar and P. J. Wagner, *ibid.*, **94**, 3859 (1972).

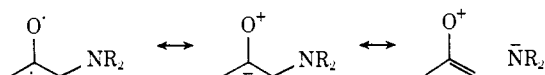
The most stable ground-state cyclic form of amino ketones is presumably the zwitterion corresponding to the intermediate involved in amine additions to carbonyls. The uv, nmr, and ir spectra of II indicate that its ground-state equilibrium lies totally on the side of the neutral form, unlike the situation with some azacycloalkanones.⁴³



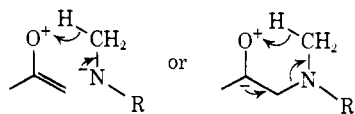
The geometry of the first formed excited CT complex is probably different from that of the ground-state zwitterion, but it is possible that one of the modes of radiationless decay involves electronic reorganization to the ground-state zwitterion.

CT in α -Amino Ketones. Whereas the relative behavior of the n, π^* singlets and triplets of the γ - and δ -amino ketones is reasonably understandable, such is not the case for Im. The slowness of ^3CT formation in triplet Im suggests that some conformational factor impedes close approach of the lone pair on nitrogen to the oxygen. Extensive information about the conformational preferences of carbonyl compounds⁴⁴ unfortunately indicates no obvious explanation.

Since CT formation is slow for triplet Im, the very rapid intramolecular decay of singlet Im may not even involve CT complexing. Both the chemical reactivity⁴⁵ and low dipole moment⁴⁶ of carbonyl n, π^* singlets suggest a partial negative charge on carbon. The mixing of π^* and σ^* levels deduced from the uv spectra of α -halo ketones¹² reflects the same phenomenon. We presume that the lowest singlet of I has its n, π^* excitation mixed with the σ^* C-N orbital. In that event,



the excited singlet may undergo a direct γ -hydride shift to give "type II" products or it may actually expel an amide anion which either re-adds to the unhappy enolate cation, regenerating ground-state amino ketone, or transfers a hydride ion to it. This process would be



analogous to the known ability of excited ketones to expel α substituents as anions.⁴⁷ The best conformation for such a reaction would find the C-N bond parallel to the carbonyl π bond (conformation B), the same conformation which produces uv-measurable interactions in α -halo ketones.¹² In fact, the photoreactivity of a tetracycline containing an axial α -dimethylamino group has been so interpreted.⁴⁸

(43) N. J. Leonard, D. F. Morow, and M. T. Rogers, *J. Amer. Chem. Soc.*, **79**, 5476 (1957).

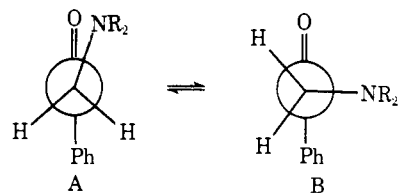
(44) G. J. Karabatsos and D. J. Fenoglio, *Top. Stereochem.*, **5**, 167 (1970).

(45) N. J. Turro, P. A. Wriede, J. C. Dalton, D. Arnold, and A. Glick, *J. Amer. Chem. Soc.*, **89**, 3950 (1967).

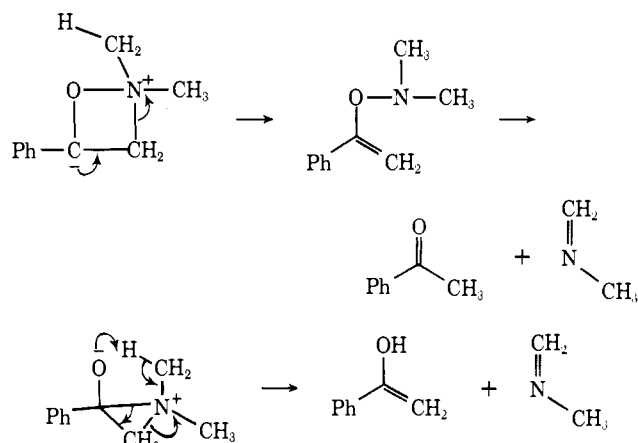
(46) (a) R. M. Hochstrasser and L. J. Noe, *J. Chem. Phys.*, **48**, 514 (1968); (b) D. E. Freeman and W. Klemperer, *ibid.*, **40**, 604 (1964).

(47) K. Schaffner, *Pure Appl. Chem.*, **16**, 75 (1968).

(48) J. J. Hlavka and P. Bitha, *Tetrahedron Lett.*, 3843 (1966).



Alternatively, it is possible that singlet Im does undergo rapid CT interaction in conformation A, which would be expected⁴⁴ to predominate in the ground state. The slow triplet CT interaction would then have to be blamed on a conformational change in the triplet strongly favoring B. Whether the singlet CT complex is written as a three- or four-membered ring, electronic reorganization could result in elimination of imine, unlike the situation in the other amino ketones.



Clearly, further work is required for a more exact understanding of the photoreactivity of α -amino ketones.

Experimental Section

Chemicals. Benzene, acetonitrile, and methanol were purified as described previously.^{4,49} Chemical Samples Co. 1,3-pentadiene and 2,5-dimethyl-2,4-hexadiene were used as received. Im, II, and III were prepared by addition of phenyl magnesium bromide to α -dimethylaminoacetonitrile, γ -dimethylaminobutyronitrile, and δ -pyrrolidinovaleronitrile (all from Aldrich), respectively. The ketones were purified by vacuum distillation just before use. Even in a freezer they all slowly turned yellow. They were identified by their mass spectra⁵⁰ and shown to be >99% pure by vpc analysis. II-HCl and III-HCl were prepared by bubbling HCl gas into benzene solutions of the ketones. The resulting crystals were washed with ethanol and dried. II-EtBr was prepared by allowing a solution of II and ethyl bromide in benzene to stand overnight. Triethylamine and dimethyl *tert*-butylamine (Aldrich) were distilled before use. Eastman 2-butanone was used as received.

Procedures. Sample preparation, irradiation, and analyses were performed as previously described.⁴ Mass balance measurements for II-HCl were performed by pipeting 1 ml of a methanol solution of the salt into 1 ml of methanol containing excess KOH. Free II was then analyzed by vpc. For intersystem crossing yield measurements, an acetophenone actinometer was irradiated in parallel with every amino ketone sample.

Phosphorescence. Phosphorescence of II was recorded as previously described.¹⁰ Uv spectra were recorded on a Cary 14.

Acknowledgment. This work was supported by the Alfred P. Sloan Foundation and by the National Science Foundation. We thank Professor Padwa for a preprint of his work on α -amino ketones.

(49) P. J. Wagner and D. J. Buebeck, *J. Amer. Chem. Soc.*, **91**, 5090 (1969).

(50) P. J. Wagner, *Org. Mass. Spectrom.*, **3**, 1307 (1970).