Mechanisms of Photochemical Reactions in Solution. XXXVIII.[1] Quenching of the Type II Photoelimination Reaction

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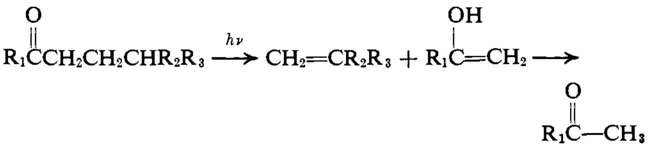
Received September 23, 1965

Abstract: Piperylene has been used to quench photoelimination of several ketones in dilute (0.2 *M*) solution. Aliphatic ketones apparently undergo the reaction from both singlet and triplet excited states. Aromatic ketones undergo the reaction only from their triplet states, and then only if they possess an n,π^* rather than a π,π^* configuration. Rate constants were estimated for various ketones in their triplet states: 2-hexanone, 1×10^9 sec^{-1}; 2-pentanone, 2.0×10^8 sec^{-1}; *n*-valerophenone, 5×10^7 sec^{-1}; *n*-butyrophenone, 3×10^6 sec^{-1}. It is proposed that reactivities of n,π^* carbonyl singlets and triplets are similar in these reactions.

Ketones and aldehydes that possess a hydrogen-bearing γ-carbon atom undergo a facile photoelimination reaction, commonly called the Norrish Type II process, to yield olefins and smaller carbonyl compounds.[3] Several elegant studies have verified Noyes's early suggestion[4] that the reaction proceeds by intramolecular hydrogen transfer to yield an olefin and an enol, followed by rearrangement of the latter to a carbonyl compound.

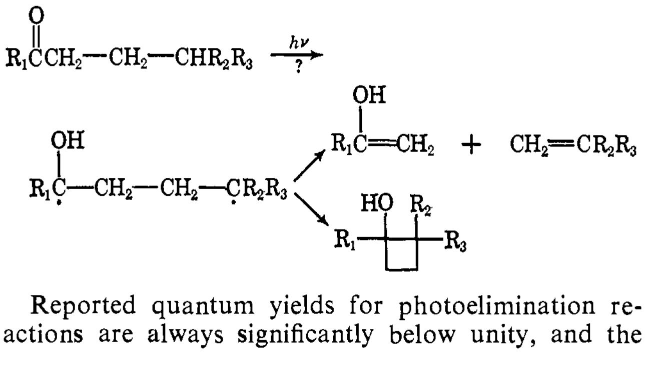


$$R_1\overset{\overset{O}{\|}}{C}CH_2CH_2CHR_2R_3 \xrightarrow{h\nu} CH_2{=}CR_2R_3 + R_1\overset{\overset{OH}{|}}{C}{=}CH_2 \longrightarrow R_1\overset{\overset{O}{\|}}{C}{-}CH_3$$

Srinivasan found an appreciable amount of acetone-d_1 resulting from photolysis of 2-hexanone-5,5-d_2.[5] More recently the enol form of acetone resulting from irradiation of 2-pentanone has actually been observed by infrared spectroscopy.[6]

Although the identity of the last intermediate in this reaction is now well established, most other aspects of the mechanism are far from clear. Of major interest is identification of the excited state(s) responsible for the reaction. Noyes found that high pressures of oxygen do not quench photoelimination of 2-hexanone,[7] and Srinivasan found only slight quenching of methoxyacetone.[8] Both authors concluded that the reaction proceeds from an excited singlet state. However, Ausloos found that oxygen does quench photoelimination from 2-pentanone,[9] and inferred that the reaction proceeds from an excited triplet state. Noyes, meanwhile, found that biacetyl also quenches 2-pentanone, but suggested that transfer of singlet energy might be responsible.[10] More recently, Ausloos and Rebbert have provided very convincing proof that both 2-pentanone and *n*-butyraldehyde undergo photoelimination from their triplet states. Biacetyl quenches the elimination reaction of 2-pentanone *without disturbing* the weak *fluorescence of the latter compound.*[11] Furthermore, elimination from *n*-butyraldehyde can be sensitized very efficiently by triplet energy transfer from acetone.[12]

Aside from its intrinsic interest, the question of which excited state(s) is (are) involved has a large bearing on the as yet unresolved problem of elucidating the nature of the primary photochemical process occurring in photoelimination. One can picture hydrogen transfer from carbon to oxygen and cleavage of the α,β bond as either discrete steps or as occurring simultaneously. Reaction from a triplet would probably produce a spin-unpaired (biradical) intermediate that has to undergo spin inversion to produce products in their singlet ground states, while there would be no *a priori* reason for not formulating the reaction from the singlet as a completely concerted process. Cyclobutanol formation frequently accompanies elimination,[13] especially in solution, making the intermediacy of a 1,4-biradical, from which both types of products could result, especially appealing. However, the different pressure dependencies for acetone and cyclobutanol production from 2-pentanone are as yet impossible to explain.[14]



Reported quantum yields for photoelimination reactions are always significantly below unity, and the

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(1) Part XXXVII: P. J. Wagner, C. A. Stout, S. Searles, Jr., and G. S. Hammond, submitted for publication.

(2) National Science Foundation Postdoctoral Fellow, 1964–1965.

(3) C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, 1504 (1935).

(4) W. Davis, Jr., and W. A. Noyes, Jr., *J. Am. Chem. Soc.* **69**, 2153 (1947).

(5) R. Srinivasan, *ibid.*, **81**, 5061 (1959).

(6) G. R. McMillan, J. G. Calvert, and J. N. Pitts, Jr., *ibid.*, **86**, 3620 (1964).

(7) V. Brunet and W. A. Noyes, Jr., *Bull. Soc. Chim. France*, 121 (1958).

(8) R. Srinivasan, *J. Am. Chem. Soc.*, **84**, 2475 (1962).

(9) R. P. Borkowski and P. Ausloos, *J. Phys. Chem.*, **65**, 2257 (1961).

(10) J. L. Michel and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **85**, 1027 (1963).

(11) R. E. Rebbert and P. Ausloos, *ibid.*, **86**, 4803 (1964).

(12) P. Ausloos and R. E. Rebbert, *ibid.*, **86**, 4512 (1964).

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(14) P. Ausloos and R. E. Rebbert, *ibid.*, **83**, 4897 (1961).

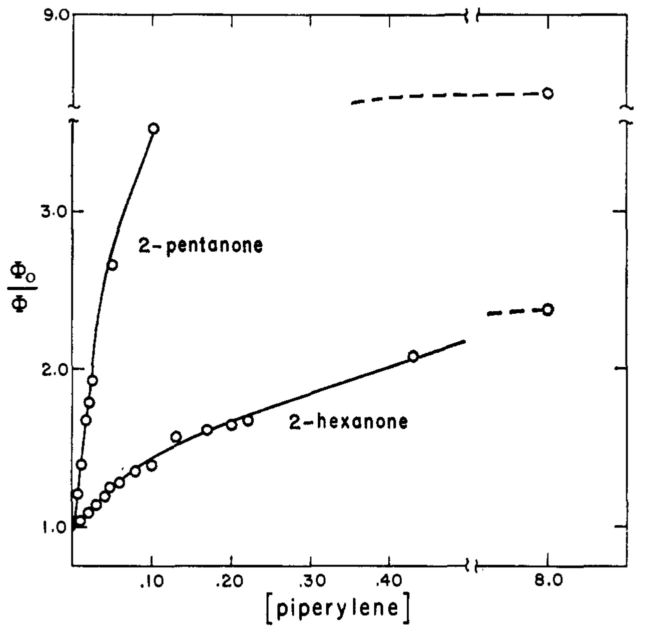

Figure 1. Quantum yields as a function of piperylene concentration.

nature of the process whereby the balance of the excited molecules lose their excitation energy is completely unknown.

Ausloos has reported that irradiation of 4-methyl-2-hexanone gives 13 times more 2-butene than 1-butene.[15] Consequently we expected that ketones bearing secondary C–H bonds at the γ position would be much less susceptible to quenching than those bearing primary C–H bonds and undertook some quenching studies to test this hypothesis.[16]

Results

Aliphatic Ketones. Preliminary experiments indicated that piperylene partially quenches the photoreactions of 2-pentanone, 2-hexanone, and methoxyacetone in solution. The former two were studied in greater detail. Degassed *n*-hexane solutions 0.20 *M* in ketone and 0.10–0.15 *M* in chlorobenzene or *m*-dichlorobenzene and containing various concentrations of piperylene were irradiated in parallel experiments with 3130-A light. The amounts of ketone reacted and acetone produced then were determined by vapor phase chromatographic (vpc) analysis. It is known that in solution, Type II processes account for almost the entire photochemistry of these ketones, the quantum yield for Type I cleavages to radicals being a maximum of 0.01.[14] With 2-hexanone and no quencher we observed an 88% yield of acetone and two other small product peaks in the vpc traces, attributed to the isomeric 1,2-dimethylcyclobutanols, which amount to approximately 10% of the reacted ketone. With 2-pentanone a 65% yield of acetone was obtained, together with a vpc peak, attributed to 1-methylcyclobutanol, with an area corresponding to approximately 30% of the reacted ketone.[17] At conversions below 50% no other product peaks were visible in the vpc traces, although at large conversions (>60%) several unknown side products begin to appear. Piperylene quenches the formation of both acetone and the peaks attributed to cyclobutanols and at high concentrations yields photodimers. Unfortunately, the sensitivity of our analytical conditions was not sufficient to permit us to assess accurately the quenching effects on the competition between alcohol and acetone production. However, at different quencher concentrations the ratio of the quantum yield for production of acetone to that for loss of the starting material is roughly constant.

Tables I and II contain the quantum yields for disappearance of ketone at each quencher concentration relative to those at zero quencher for 2-pentanone and 2-hexanone, respectively. The scatter in the acetone data was too large to permit ready analysis. Figure 1 is a plot of the Φ_0/Φ values against piperylene concentration for the two ketones. With low concentrations of piperylene the plot is approximately linear but in each case the quenching effect levels off and a limiting, residual quantum yield is reached at high concentrations of quencher. The Stern–Volmer formulation for quenching a unimolecular reaction of an excited state (rate constant = k_r) results in the following familiar expression:

$$\Phi_T^0/\Phi_T = 1 + \frac{k_q[Q]}{k_r}$$

Table I. Quenching Effects on Relative Quantum Yields of 2-Pentanone

[Piperylene], *M*	$-[K]/-[K]_0$[a]	Φ_0/Φ	Φ_T^0/Φ_T[b]
0	1.00	1.00	1.00
0.005	0.82	1.22	1.26
0.010	0.72	1.39	1.47
0.015	0.60	1.67	1.83
0.020	0.56	1.78	2.00
0.025	0.52	1.93	2.20
0.050	0.38	2.65	3.38
0.10	0.28	3.53	5.50
8.0	0.12	8.35	...

[a] Each value represents the average of two runs; in one conversion at zero quencher was 45%, in the other 28%. [b] $\Phi_T = \Phi_{total} - \Phi_{singlet}$.

Table II. Quenching Effects on Relative Quantum Yields of 2-Hexanone

[Piperylene], *M*	$-[K]/-[K]_0$[a]	Φ_0/Φ	Φ_T^0/Φ_T[b]
0	1.00	1.00	1.00
0.01	0.96	1.04	1.07
0.02	0.92	1.09	1.16
0.03	0.87	1.14	1.29
0.04	0.84	1.19	1.38
0.05	0.80	1.25	1.52
0.06	0.78	1.28	1.62
0.08	0.74	1.35	1.81
0.10	0.72	1.39	1.93
0.13	0.64	1.56	2.64
0.17	0.62	1.61	2.90
0.20	0.60	1.67	3.22
0.22	0.58	1.72	3.62
0.43	0.48	2.08	9.70
8.0	0.42	2.38	...

[a] Each value represents the average of two runs, one to 50% conversion, the other to 27%. [b] $\Phi_T = \Phi_{total} - \Phi_{singlet}$.

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(15) P. Ausloos, *J. Phys. Chem.*, **65**, 1616 (1961).

(16) P. J. Wagner and G. S. Hammond, *J. Am. Chem. Soc.*, **87**, 4009 (1965).

(17) Ausloos[14] reported the ratio of alcohol to acetone as 0.48.

Since piperylene is a very efficient acceptor for the triplet energy of high-energy ketone triplets, but does not quench their excited singlet states,[18] it is apparent that *these two ketones undergo photoelimination from both excited triplet states and unquenchable excited singlets.*

The linear portions of the two plots in Figure 1 indicate that triplet 2-pentanone reacts eight times slower than triplet 2-hexanone, and thus is quenched more efficiently. The actual slopes of Φ_T^0/Φ_T plots are 50 and 10 l. mole^{-1}. Since the triplet excitation energy of aliphatic ketones is around 75 kcal, and that of piperylene is ~58 kcal, the rates of triplet quenching ought to be diffusion controlled. We shall assume that k_q equals 1×10^{10} l. mole^{-1} sec^{-1} in *n*-hexane. The actual value predicted by the Debye theory is 2×10^{10}.[19] However, diffusion-controlled rate constants for triplet energy transfer in benzene, which has twice as large a coefficient of viscosity as hexane, average 5×10^9 l. mole^{-1} sec^{-1},[20] while theory predicts 10^{10}.[21] Consequently, we estimate the rate constants at which the excited triplet states of 2-pentanone and 2-hexanone undergo chemical reaction as 2.0×10^8 and 1×10^9 sec^{-1}, respectively.[22] If acetone and cyclobutanols are formed from a common biradical intermediate, the k_r values are rate constants for formation of this intermediate. If, however, the products come from two separate processes, the k_r values represent the sum of their individual rate constants.

With no quencher present 2-pentanone disappears 84% as fast as 2-hexanone. If we take the quantum yield of 2-hexanone as 0.50,[23] then it is 0.42 for 2-pentanone. In 8 *M* piperylene the corresponding quantum yields would be 0.21 and 0.05 (0.18 and 0.04 for formation of acetone). The lower figures must represent quantum yields for reaction from the excited singlets. Therefore, 2-hexanone is four times more reactive than 2-pentanone in their singlet states, if we make the very reasonable assumption that the two have nearly equal rates of intersystem crossing.

It is thus apparent why Ausloos is able to quench 2-pentanone so readily; very little reaction occurs from the singlet, and the triplet does not react excessively fast. Conversely, one can see why 2-hexanone is not readily quenched in the vapor phase; almost half the reaction occurs in a singlet state and the triplet reacts extremely rapidly.

Only one experiment was performed with methoxyacetone. Four 0.51 *M* samples, two in hexane and two in piperylene, were subjected to equal amounts of 3130-A irradiation. The methoxyacetone in piperylene disappeared 60% as fast as that in hexane, indicating that only 40% of photoelimination to yield formaldehyde and acetone occurs in the triplet state.

Aliphatic Aldehydes. Degassed hexane solutions 0.3 *M* in butyraldehyde and valeraldehyde were irradiated in the presence of various concentrations of piperylene. The aldehydes disappear much faster than do the ketones, as would be expected if decomposition is a chain process.[24] Piperylene quenches disappearance of the aldehydes inefficiently, and at high concentrations begins to increase the rate and promote formation of new products, probably because radicals formed by addition to the diene participate in the chain decomposition reaction. Consequently, no attempt was made to sort out the Type II process. The occurrence of a minimum in the total rate of decomposition, as the concentration of piperylene is varied, may indicate that chain initiation involves both excited singlets and triplets.

Phenyl Ketones. Solutions of *n*-butyrophenone or *n*-valerophenone and varying amounts of piperylene in benzene were irradiated with 3130-A light. The solutions also contained *m*-dichlorobenzene to serve as an internal standard in the vpc analysis for acetophenone produced in the photoelimination reaction. In the first series of experiments relatively large concentrations of piperylene were used and irradiation was carried on so long that reaction was virtually complete in the piperylene-free control. The only reaction observed in the samples containing piperylene as solvent was photodimerization of the quencher.[25] Although the data could not be subjected to quantitative analysis, they showed very clearly that elimination occurs exclusively from triplet states of the ketones. The rates of formation of acetophenone were slower than the rates of disappearance of the parent ketones. The relative rates, 0.77 for butyrophenone and 0.80 for valerophenone, were unaffected by the addition of piperylene. In both cases products believed to be cyclobutanols appeared as additional peaks in the vpc traces with peak areas ~25% of those due to acetophenone.

Tables III and IV show data gathered using lower concentrations of piperylene. The reactions were

Table III. Quenching Effects on Butyrophenone[a]

[Piperylene], *M*	[Acetophenone],[b] *M*	ΦIt	Φ_0/Φ
0	0.0333	0.0366	1.0
0.001	0.0139	0.0144	2.54
0.002	0.0077	0.0078	4.66
0.003	0.0058	0.0059	6.16
0.004	0.0044	0.0044	8.32
0.006	0.0029	0.0029	12.62

[a] Initially 0.20 *M* in benzene. [b] Concentration in final solution.

Table IV. Quenching Effects on Valerophenone[a]

[Piperylene], *M*	[Acetophenone],[b] *M*	ΦIt	Φ_0/Φ
0	0.0384	0.0423	1.0
0.005	0.0249	0.0264	1.66
0.010	0.0203	0.0213	1.99
0.015	0.0160	0.0166	2.55
0.020	0.0137	0.0141	3.00
0.030	0.0097	0.0099	4.27

[a] Initially 0.20 *M* in benzene. [b] Concentration in final solution.

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(18) G. S. Hammond, P. A. Leermakers, and N. J. Turro, *J. Am. Chem. Soc.*, **83**, 2396 (1961).

(19) P. J. W. Debye, *Trans. Electrochem. Soc.*, **82**, 265 (1942).

(20) As measured by flash spectroscopic techniques: W. B. Herkstroeter, Thesis, California Institute of Technology, 1965.

(21) The effect of viscosity on k_q/k_r values showed up in preliminary orientating experiments performed in cyclohexane. Quenching was approximately half as efficient as in *n*-hexane.

(22) In our preliminary communication we estimated slightly different values because we used the benzene value of k_Q.

(23) N. C. Yang, private communication.

(24) W. H. Urry and D. J. Trecker, *J. Am. Chem. Soc.*, **84**, 118 (1962).

(25) The column used in analysis did not separate the *cis* and *trans* isomers of piperylene.

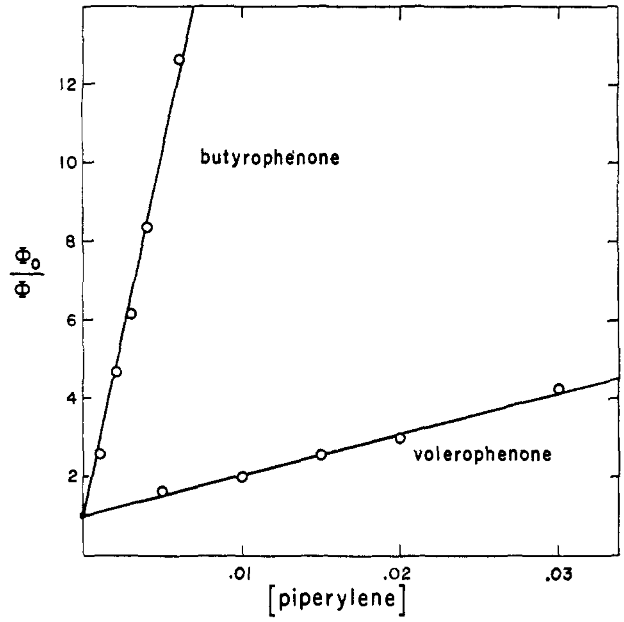

Figure 2. Quantum yields as a function of piperylene concentration.

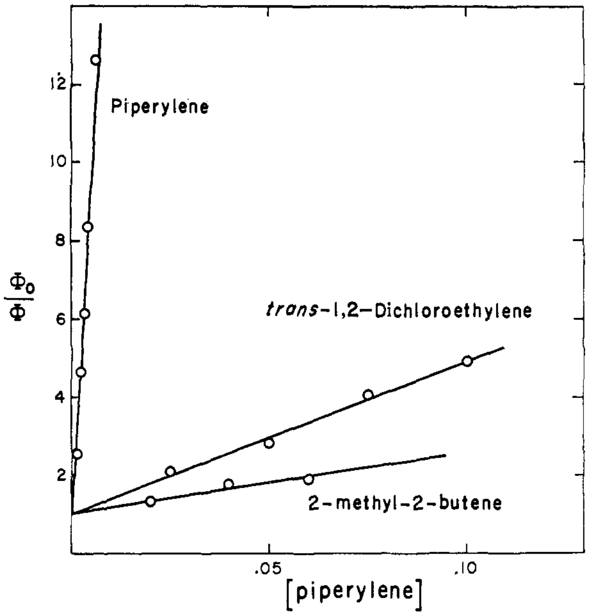

Figure 3. Stern–Volmer plots for quenching of acetophenone formation from butyrophenone.

carried to 25% conversion so correction was made for competitive absorption by the acetophenone produced. The relationship between the quantum yield and the fraction reacted is given by the following equation.

$$\Phi I_t = \left(1 - \alpha\frac{\epsilon_A}{\epsilon_K}\right)[A] + \frac{\epsilon_A}{\epsilon_K}\alpha^2[K]_0 \ln\left(\frac{\alpha[K]_0}{\alpha[K]_0 - [A]}\right)$$

where I = light intensity, A = acetophenone, K = valerophenone or butyrophenone, and α = fraction of K reacted that yields A.

The correction is not exact because a filter system, rather than a monochromator, was used to select light from the source. However, the error should be small because the shapes of the absorption spectra are very similar.[26] The calculated values of ΦIt are listed in the tables, as are the values of Φ_0/Φ. Figure 2 shows the plots of Φ_0/Φ against piperylene concentration.

Pitts has measured the triplet excitation energy of butyrophenone and finds it to be somewhat lower than that of acetophenone.[27] Consequently, acetophenone should not quench butyrophenone triplets, but may be able to sensitize it under the proper conditions. It is unlikely that our experimental conditions would favor much such sensitization, and even if all energy absorbed by acetophenone were transferred to the parent ketone the slopes in Figure 2 would be changed by no more than 10%.

Least-squares analysis of the data yields values of k_q/k_r of 1850 and 100 for butyrophenone and valerophenone, respectively. Since the solvent was benzene, we assume that $k_q = 5 \times 10^9$ l. mole^{-1} sec^{-1}, in which case the rates at which the excited triplets of the two ketones undergo Type II photoelimination are 2.7×10^6 sec^{-1} and 5×10^7 sec^{-1}. Pitts has reported that 10^{-3} M naphthalene lowers the quantum yield for photoelimination of butyrophenone by 65%,[28] in excellent agreement with our results.

Absolute values of the quantum yields were estimated using the reaction of acetophenone with 2-propanol as an actinometer. Although the results are consistent with the value of 0.41 for butyrophenone determined independently by Baum, Wan, and Pitts,[28] we will not report the results in detail because the method used by the Riverside group is probably inherently more accurate. The quantum yield for valerophenone is apparently about 10% higher than that for butyrophenone.

Two other aryl ketones, α-naphthyl butyl ketone and *o*-methylvalerophenone, were irradiated but underwent no measurable reaction in a period sufficient to effect 25% reaction of valerophenone.

Quenching by Olefins. A single set of samples was irradiated in parallel to determine the efficiency of quenching of butyrophenone by various concentrations of *trans*-1,2-dichloroethylene and 2-methyl-2-butene, with the results shown in Table V and plotted in Figure 3. The slopes of the Stern–Volmer plots are 38 and 16 l. mole^{-1}, indicating k_q values $^1/_{50}$ and $^1/_{115}$ that of piperylene, or 1×10^8 and 4×10^7 l. mole^{-1} sec^{-1} in benzene for dichloroethylene and 2-methyl-2-butene, respectively. Dougherty has found that dichloroethylene quenches 2-octanone triplets with $^1/_{60}$ the efficiency of piperylene.[29]

α,β-Unsaturated Ketones. Solutions of 2-methyl-2-octen-4-one (**1**) and 2-methyl-2-hepten-4-one (**2**) were irradiated for periods long enough to produce substantial reaction with the other aliphatic ketones. No loss of starting material was detected and no mesityl oxide appeared.

$CH_3CH_2CH_2CH_2COCH{=}C(CH_3)CH_3$
1

$CH_3CH_2CH_2COCH{=}C(CH_3)CH_3$
2

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[26] The value of ϵ for acetophenone is 90% of that for the other two ketones at 3130 A.

[27] E. J. Baum and J. N. Pitts, Jr., to be published.

[28] E. J. Baum, J. K. S. Wan, and J. N. Pitts, Jr., Abstracts, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, p 7S.

[29] T. J. Dougherty, *J. Am. Chem. Soc.*, **87**, 4011 (1965).

Table V. Quenching of *n*-Butyrophenone[a] by Olefins

Quencher	[Quencher], *M*	Φ/t	Φ_0/Φ
2-Methyl-2-butene	0	0.0314	1.00
2-Methyl-2-butene	0.020	0.0233	1.35
2-Methyl-2-butene	0.040	0.0177	1.77
2-Methyl-2-butene	0.060	0.0167	1.88
2-Methyl-2-butene	2.0	~0	>30
trans-1,2-Dichloroethylene	0.025	0.0150	2.09
trans-1,2-Dichloroethylene	0.050	0.0110	2.86
trans-1,2-Dichloroethylene	0.075	0.0078	4.04
trans-1,2-Dichloroethylene	0.10	0.0064	4.90

[a] Originally 0.20 *M* in benzene.

Discussion

Mechanism. The following scheme contains all we know at present about the steps involved in Type II processes.

$$^1K_0 \xrightarrow{h\nu} {}^1K_m^* \longrightarrow {}^1K_1^*$$

$$^1K_1^* \xrightarrow{k_1} \text{products}$$

$$^1K_1^* \xrightarrow{k_{ic}} {}^3K_n^* \longrightarrow {}^3K_1^*$$

$$^3K_1^* \xrightarrow{k_3} \text{products}$$

$$^3K_1^* \xrightarrow{k_d} {}^1K_0$$

$$^3K_1^* + Q \xrightarrow{k_q} {}^1K_0 + Q^*$$

The scheme is incomplete because of the omission of nonradiative return from the excited singlet to the ground state. This step is ordinarily considered to be negligible with carbonyl compounds[30] although direct documentation is not abundant.

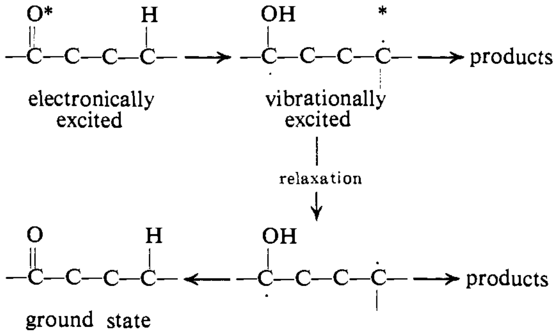
One clear-cut conclusion from our results is that the over-all quantum yield for photoelimination is not a very sensitive indicator of the inherent reactivity of excited states. A highly reactive ketone, such as 2-hexanone, has a total quantum yield only slightly higher than that for butyrophenone. The pertinent data are summarized in Table VI.

Table VI. Estimated Rate Constants and Quantum Yields

Ketone	k_3, sec^{-1}	Φ
2-Hexanone	1×10^9	0.50[a]
2-Pentanone	2.0×10^8	0.42[b]
n-Valerophenone	5×10^7	~0.45[c]
n-Butyrophenone	2.7×10^6	0.41[d]

[a] Reference 23. [b] Measured relative to 2-hexanone. [c] Measured relative to *n*-butyrophenone. [d] Reference 28.

Part of the source of the leveling effect is obvious. If a compound is not sufficiently reactive to do chemistry while in its excited singlet, another opportunity will be provided after intersystem crossing. In fact, it is surprising that the quantum yields are not close to unity in all cases since, with the exception of butyrophenone, all triplets have rates of reaction high enough to compete very effectively with even the highest known rates of radiationless decay. We suspect that the inefficiencies are due to the occurrence of trivial chemical processes. A clue to the nature of the decay mechanism is found in the report that irradiation of ketones in which the γ-carbon atom is a center of optical activity leads to rapid racemization.[31] It is also known that photocyclization of an optically active ketone produces products that retain some activity.[32] The results indicate that the chemistry of intermediates in the photoelimination and cyclization is complex. Apparently, ring closure, inversion of the γ-carbon atom, return of an abstracted hydrogen atom to its original site, and fragmentation are all closely competitive processes. Reversal of hydrogen transfer provides a mechanism for radiationless decay of an excited state if the reaction produces the ground state of the original molecule. A key step in the decay would be vibrational relaxation of the intermediate biradical.



Although we have established that both excited singlets and triplets can participate in elimination and cyclization, we do not yet know whether they give rise to identical intermediates. Studies designed to effect further dissection of the mechanism are in progress.

Reactivity Relationships. Hydrogen abstraction reactions, most commonly encountered in photoreduction reactions of aldehydes and ketones, are commonly associated with excited triplets. However, in one of the first mechanistic studies in the field, Porter and Windsor[33] concluded that photoreduction of duroquinone involved the lowest excited singlet state. We have now found very strong evidence that the intramolecular reaction can occur in both excited singlets and triplets. There seems to be no reason for assuming that singlets and triplets having the same configuration, in this case n,π^*, have inherently different chemical reactivity. Those compounds, such as the aryl ketones, that give no detectable reaction from singlets also have relatively low rate constants for reaction from the triplets. It is also very possible that the rate of intersystem crossing is faster with the aryl ketones. Probably the only reason for the predominance of triplet mechanisms in bimolecular reactions is the relatively long lifetime of triplets. Although we have no direct evidence, we suspect that the same ideas apply to the photoaddition of carbonyl compounds to carbon–carbon double bonds.[34] Recognition of the principle may have some

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(30) M. Kasha, *Discussions Faraday Soc.*, **9**, 14 (1950).

(31) K. H. Schulte-Elte and G. Ohloff, *Tetrahedron Letters*, 1143 (1964).

(32) I. Orban, K. Schaffner, and O. Jeger, *J. Am. Chem. Soc.*, **85**, 3033 (1963).

(33) N. K. Bridge and G. Porter, *Proc. Roy. Soc.* (London), **A244**, 259, 276 (1958).

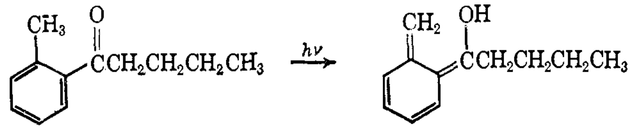
(34) D. R. Arnold, R. L. Hinman, and A. Glick, *Tetrahedron Letters*, 1425 (1965).

practical significance since in some instances the lowest lying excited singlet states of carbonyl compounds may have much higher inherent reactivity than the lowest triplets. This will occur when the lowest singlet has the n,π^* configuration and a π,π^* state lies lowest in the triplet manifold. In such cases it may be possible to carry out bimolecular photoreactions *via* excited singlets by using high concentrations of cosubstrates.

At least two factors appear important in determining the relative reactivities of excited triplets in cyclization and elimination reactions. Comparison of 2-hexanone with 2-pentanone and of valerophenone with butyrophenone shows in the first case a factor of 6 and in the second a factor of 18 favoring reaction at a γ-methylene group in preference to a γ-methyl group. The results are, of course, similar to those obtained by the internal competitive method.[15] The preference is analogous to the selectivity of alkoxy radicals in hydrogen abstraction reactions.[35] The result is not at all surprising since Walling has shown that the selectivity of benzophenone triplets in bimolecular hydrogen abstraction reactions is very similar to that of the *t*-butoxy radical.[36] The very reasonable nature of the correlation increases the credibility of the formulation of both elimination and cyclization reactions as involving biradical intermediates.

The second significant comparison shows that triplets of the two aliphatic ketones react 20 to 75 times more rapidly than their aryl alkyl analogs. This indicates that significant refinement of current notions concerning the reactivity of carbonyl triplets is both feasible and desirable. Gradations in reactivity that have been previously discussed are a major decrease in reactivity as the triplet configuration is changed from n,π^* to π,π^*,[37,38] and a further dramatic decrease in reactivity when extensive charge transfer character is introduced in π,π^* triplets.[39] The lowest triplets of all four compounds listed in Table VI would be classified as n,π^*. One way to account for the difference in reactivity is to relinquish the rigid classification of states and describe the triplets of aryl ketones as having mixed n,π^* and π,π^* character.[40]

Introduction of an *o*-methyl group in valerophenone leads to disappearance of the reactions involving abstraction of γ-hydrogen atoms. During irradiation the solution developed a yellow color and so we presume that photoenolization[41] occurred.



The result is highly informative. No simple correlation with reactivities in bimolecular hydrogen abstraction reactions would lead to the prediction that abstraction of a primary benzylic hydrogen atom should be overwhelmingly predominant over attack on an aliphatic, secondary position. The very high reactivity of the methyl group may be due to the fact that the reaction product, which is completely conjugated, may be produced in an electronically excited state.[42] Alternatively, the result can be attributed to conformational effects, perhaps indicating that the time allowed for reaction of excited states is too short to allow them to explore all possible rotational arrangements.

The failure of α-naphthyl butyl ketone and the two α,β-unsaturated ketones to undergo reaction is unexceptional. Apparently the excited compounds decay to unreactive π,π^* states before they can undergo elimination or cyclization reactions. Study of the naphthyl ketone was stimulated by the report that some naphthoyl compounds undergo photoaddition to olefins with respectable quantum yields.[44] A long extrapolation of the two results suggests that the photoaddition reaction does not depend upon the trapping of one of the higher excited states of the systems. Similarly, study of the α,β-unsaturated ketones was a response to Yang's very reasonable suggestion[45] that the failure of mesityl oxide to undergo reaction is because the lowest excited state has a π,π^* configuration with a twist about the carbon–carbon double bond. Our results are entirely consistent with this explanation and imply furthermore that the stabilization occurs much faster even than the very rapid intramolecular hydrogen transfer possible in any prior n,π^* state, either singlet or triplet.

The reactivity of various unsaturated compounds as quenchers is also of interest. Dichloroethylene and 2-methyl-2-butene are both much less effective than piperylene. The value of the $S_0 \rightarrow T_1$ transition energy of dichloroethylene has been estimated as 72 kcal mole^{-1}.[46] Evans has estimated that the band head for the singlet–triplet transition of ethylene lies at about 82 kcal mole^{-1}.[47] The value would probably be lowered by methyl substitution[48] so the vertical excitation energies of the two substrates may be comparable. The excitation energy of butyrophenone triplets is about 72 kcal mole^{-1}, so energy transfer to the olefinic compounds may be inefficient merely because the process is nearly isoenergetic[49] or because nonvertical excitation of the energy acceptors is required.[50] Further studies designed to clarify this question are in progress.

Experimental Section

Chemicals. 2-Pentanone and 2-hexanone were distilled commercial materials. The aromatic ketones were prepared from the

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(35) C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108 (1960); C. Walling and A. Padwa, *ibid.*, **85**, 1597 (1963).

(36) C. Walling and M. J. Gibian, *ibid.*, 86, 3902 (1964).

(37) G. S. Hammond and P. A. Leermakers, *ibid.*, **84**, 207 (1962).

(38) J. N. Pitts, Jr., H. W. Johnson, and T. Kuwana, *J. Phys. Chem.*, **66**, 2456 (1962).

(39) G. Porter and P. Suppan, "Organic Photochemistry," International Union of Pure and Applied Chemistry, London, 1965.

(40) A simple way to describe the situation is to say that in a "pure" n,π^* state the excitation would be localized in the carbonyl group, and in a π,π^* state the excitation would be primarily in the part of the system containing no heteroatoms. In a mixed state the excitation would be partially delocalized between the two-part systems.

(41) E. F. Zwicker, L. I. Grossweiner, and N. C. Yang, *J. Am. Chem. Soc.*, **85**, 2671 (1963).

(42) Formation of an electronically excited state of the product would minimize the requirement of coupling vibrational and electronic changes of state.[43]

(43) G. W. Robinson and R. P. Frosch, *J. Chem. Phys.*, 38, 1187 (1963).

(44) N. C. Yang, M. Nussim, M. J. Jorgenson, and S. Murov, *Tetrahedron Letters*, 3657 (1964).

(45) N. C. Yang and M. J. Jorgenson, *ibid.*, 1203 (1964).

(46) G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, **66**, 2100 (1944).

(47) D. F. Evans, *J. Chem. Soc.*, 1735 (1950).

(48) R. S. Mulliken, *J. Chem. Phys.*, 33, 1596 (1960).

(49) K. Sandros and H. L. J. Bäckstrom, *Acta Chem. Scand.*, **16**, 958 (1962).

(50) G. S. Hammond, *et al.*, *J. Am. Chem. Soc.*, **86**, 3197 (1964).

arylmagnesium bromide and butyronitrile or valeronitrile.[51] Both 2-methyl-2-octen-4-one and 2-methyl-2-hepten-4-one were prepared from dimethylacrylic acid *via* the acid chloride and the dialkylcadmium.[52] Both benzene and hexane were washed with sulfuric acid, dried, and distilled from phosphorus pentoxide.

Apparatus. All relative quantum yields were measured in a precisely machined "merry-go-round" apparatus so that each sample received the same amount of light. In the center was a 450-w Hanovia lamp in a quartz immersion well surrounded by a quartz filter jacket containing 46 g of $NiSO_4 \cdot 6H_2O$ and 14 g of $CoSO_4 \cdot 7H_2O$ per 100 ml of water. The water solution permitted the following wavelength distribution to pass through the 1-mm walls of the Pyrex tubes employed: 6% 2967 A, 20% 3025 A, 62% 3130 A, 10% 3340 A.

Procedure. All reactions were run in 13-mm Pyrex tubes. After solutions of the proper concentrations had been prepared, 3.4 ml of each was placed in a tube with a syringe, and the tubes were degassed three or four times to 2×10^{-4} mm in freeze-thaw cycles and finally sealed *in vacuo*. For any given run, two samples containing no quencher and one sample for each quencher concentration were irradiated for the same length of time, and then stored in the dark until vpc analysis. The aliphatic ketones were analyzed with 5-ft columns packed with 25% Carbowax 20M on 42-60 Firebrick. Injector temperature was 180°, and the columns were programmed upward from 100° at 10°/min. The aromatic ketones were analyzed on 6-ft columns containing 5% Carbowax 20M on Chromosorb G, programmed upward from 125° at 10°/min. All analyses were performed on a Loenco Model 70 dual column-dual thermal detector machine with helium flows of 150 ml/min.

Acknowledgment. This work was supported by a grant from the National Science Foundation.

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Acid-Catalyzed Isomerization in the Peptide Part of Ergot Alkaloids[1]

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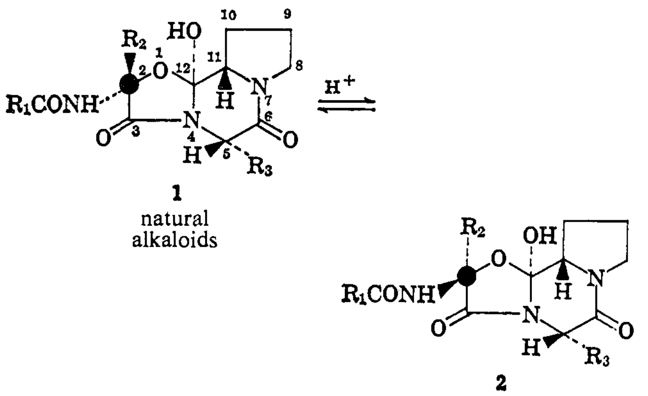
Abstract: Chemical evidence and a probable reaction mechanism for the acid-catalyzed isomerization at C-2 of the peptide part of ergot alkaloids is presented.

From X-ray crystal-structure analysis[2] it has become evident that the reversible acid-catalyzed isomerization of the peptide ergot alkaloids, as described for the first time in 1961 by Schlientz, Brunner, Thudium, and Hofmann,[3] represents an epimerization at position 2 of the peptide part as depicted by the stereo formulas **1** and 2 (Chart I).

Chart I



1
natural alkaloids

2
aci isomers

R_1CO = lysergyl or 9,10-dihydrolysergyl
R_2 = CH_3 (ergotamine group) or $CH(CH_3)_2$ (ergotoxine group)
R_3 = $CH_2C_6H_5$, $CH(CH_3)_2$, or CH_2-$CH(CH_3)_2$

This result prompts us to report some of our chemical investigations in connection with this problem, since these findings gave the clue to the interesting mechanism of this acid-catalyzed isomerization called, in short, "*aci* isomerization."

The *aci* isomerization is not the only reaction observed when natural ergot peptide alkaloids are heated in aqueous acidic solution, but it is accompanied by the long known epimerization at C-8 of lysergic acid,[4] thus leading to a mixture of four isomers. If, however, one of the corresponding $\Delta^{9,10}$-dihydro alkaloids is refluxed in dilute acetic acid, an equilibrium solely between the dihydro alkaloid and its *aci* isomer is established and almost no irreversible cleavage products can be detected. The same holds true for cyclols (**1**) in which R_1CO stands for a simple acyl group like acetyl, benzoyl, *p*-nitrobenzoyl, or *p*-iodobenzoyl.

The reversibility of this epimerization in dilute acetic acid at C-2 of the peptide part is well documented by the observation that, no matter whether one starts with compound **1** or **2**, the same approximate 1:1 mixture of the two isomers is formed as an end result. The rate by which this equilibrium is reached depends mainly on reaction temperature, pH of the reaction

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[1] (a) This is our 65th publication on ergot alkaloids; 64th communication: D. Stauffacher, H. Tscherter, and A. Hofmann, *Helv. Chim. Acta*, **48**, 1379 (1965). (b) Research Laboratories, Sandoz Ltd., Basle, Switzerland.

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[3] W. Schlientz, R. Brunner, F. Thudium, and A. Hofmann, *Experientia*, **17**, 108 (1961).

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