2. **NBS in CCl_4.** A solution containing 0.20 g of the acetate in 10 ml of CCl_4 was placed in a Pyrex flask with 0.18 g of N-bromosuccinimide and irradiated with a GE 275-W sunlamp for 16 hr; the reaction mixture was maintained at 26° during this time. The mixture was then filtered and solvent removed, and the residue was dissolved in $CDCl_3$. The nmr spectrum of this solution indicated that it contained only starting material.

Acknowledgment. We wish to thank the National Science Foundation for a grant (No. GP-6536X) in support of this work.

---

whose nmr spectrum was identical with the compound obtained from bromine and the *cis,trans*-acetate. The geometry of this product has not been determined. A competition experiment in which a 55:45 mixture of *threo*- and *erythro*-bromo ketones was treated (during 12 hr) with a limited quantity of bromine showed that dibromide resulted at the expense of the *erythro* isomer; also, it will be recalled that *no* dibromide resulted from reaction of *trans,trans*-acetate with bromine.

The Norrish Type II Process in α-Keto Acids. Photolysis of α-Ketodecanoic Acid in Benzene[1]

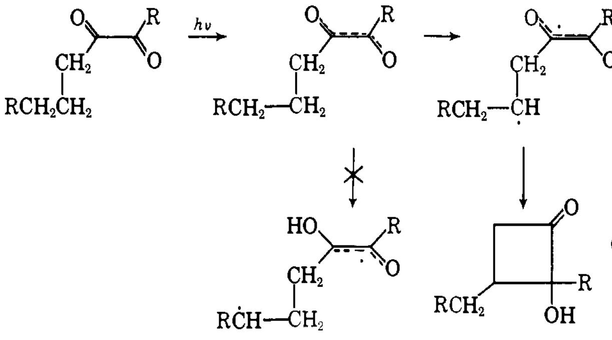
Ted R. Evans and Peter A. Leermakers[2]

Contribution from the Department of Chemistry, Wesleyan University, Middletown, Connecticut 06457. *Received December 1, 1967*

Abstract: Irradiation of α-ketodecanoic acid in benzene affords 1-heptene and pyruvic acid *via* a Norrish type II elimination (this being the first demonstrated example of the type II process in α-keto acids). The quantum yield for the process is 0.2. Quenching experiments indicate that α-ketodecanoic acid reacts only in the triplet state and has about the same reactivity in the photoelimination as an aliphatic ketone. A consequence of this fact demands a very fast rate of intersystem crossing in this compound. Relative rate constants for intersystem crossing and triplet hydrogen abstraction have been compared with other classes of carbonyl compounds, revealing the unique character of the excited states of α-keto acids.

In the condensed phase the major reaction pathway for aliphatic and aromatic ketones with γ-hydrogens is the Norrish type II photoelimination.[3] A minor, competing, pathway is cyclization to form a cyclobutanol.[3,4] The present evidence suggests that the initial abstraction is reversible and can occur from either the first excited singlet state or from the triplet state.[5-10] Although there are some ambiguities concerning the processes leading to cyclobutanol formation,[7,11-13] the elimination reaction apparently proceeds directly from the diradical intermediate.

In contrast α-diketones give only products of cyclization and no observable photoelimination.[14,15] The most striking thing about this reaction is that abstraction occurs by the "distant" keto group to yield hydroxycyclobutanones rather than abstraction by the "near" keto group to give 1-alkanoylcyclobutanols (eq 1). The reaction most probably occurs through the triplet state but there may be some radical chain reaction since the unsensitized quantum yield is 1.0 or higher and the quantum yield for the benzophenone-sensitized reaction is about 1.6.[15]



(1)

Although several types of photoreactions have been reported for α-keto acids and α-keto esters,[16-19] no examples of Norrish type II photoelimination or cyclobutanol formation are known.

Photolysis of α-ketodecanoic acid in benzene could lead to several types of products (Chart I). Photoelimination and/or cyclization, path a, would be analogous to that found for aliphatic and aromatic ketones. Photoreaction by path b would parallel the photochemistry of α-diketones. Although hydrogen atom abstraction by the acid group, as required in path b, is not well known, it has been observed in the photolysis of *n*-butyric acid.[20]

---

[1] Photochemistry of α-Keto Acids and α-Keto Esters VI. Part V: D. S. Kendall and P. A. Leermakers, *J. Am. Chem. Soc.*, **88**, 2766 (1966).

[2] Alfred P. Sloan Fellow, 1967-1969.

[3] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, pp 377-427.

[4] N. C. Yang and D. D. H. Yang, *J. Am. Chem. Soc.*, **80**, 2913 (1958).

[5] P. J. Wagner, *Tetrahedron Letters*, 1753 (1967).

[6] P. J. Wagner, *J. Am. Chem. Soc.*, **89**, 5898 (1967).

[7] D. R. Coulson and N. C. Yang, *ibid.*, **88**, 4511 (1966).

[8] P. J. Wagner and G. S. Hammond, *ibid.*, **88**, 1245 (1966).

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

[10] T. J. Dougherty, *ibid.*, **87**, 4011 (1965).

[11] A. Padwa, D. Crumrine, R. Hartman, and R. Layton, *ibid.*, **89**, 4435 (1967).

[12] I. Orban, K. Schaffner, and O. Jager, *ibid.*, **85**, 3034 (1963).

[13] K. Schulte-Elte and G. Ohloff, *Tetrahedron Letters*, 1143 (1964).

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

[15] W. H. Urry, D. J. Trecker, and D. A. Winey, *Tetrahedron Letters*, 609 (1962).

[16] See ref 1 and previous papers.

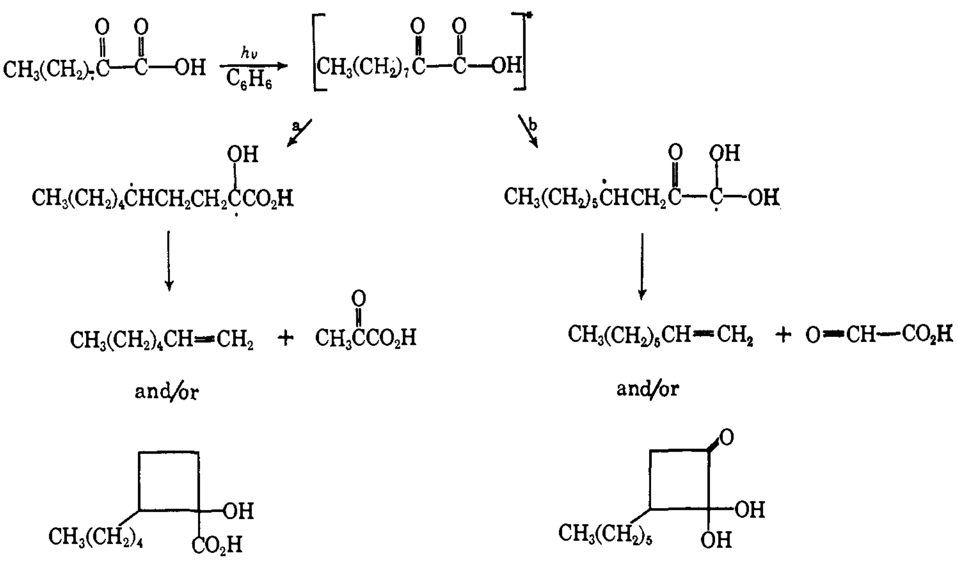
[17] E. S. Huyser and D. C. Neckers, *J. Org. Chem.*, **29**, 276 (1964).

[18] N. C. Yang and A. Marduchowitz, *ibid.*, **29**, 1654 (1964).

[19] S. P. Pappas, B. C. Pappas, and J. E. Blackwell, Jr., *ibid.*, **32**, 3066 (1967).

[20] P. Borrell and R. G. W. Norrish, *Proc. Roy. Soc.* (London), **A262**, 19 (1961).

Chart I



Results and Discussion

A. Irradiation Products. When α-ketodecanoic acid is photolyzed in benzene solution 1-heptene and pyruvic acid are produced as the only major products. Since pyruvic acid and α-ketodecanoic acid have essentially identical absorption spectra, complete photochemical conversion is difficult and 88% conversion to 1-heptene was only achieved after prolonged irradiation. At low conversions (about 8%) in either benzene or deuteriochloroform the yields of 1-heptene and pyruvic acid were found to be equal. Although pyruvic acid is stable in benzene,[21] decomposition of pyruvic acid is evident in deuteriochloroform at moderate conversion (>30%). In benzene, pyruvic acid and 1-heptene were the only products observed although others may be present in small amounts.

The quantum yield for 1-heptene formation for this process is 0.21. The quantum yield for pyruvic acid formation was not measured but it is reasonable to assume that it is the same since the chemical yields are identical at low conversion.

B. Mechanism. Figure 1 shows the plot of Φ_0/Φ for 1-heptene production against the concentration of 1,3-cyclohexadiene in benzene. The usual Stern–Volmer analysis gives $kq/kr = 9.1$ l. mol^{-1} for the keto acid photoelimination. Slightly different kq/kr values were found using naphthalene or myrcene as the quencher. For naphthalene ($E_T = 60.9$ kcal),[22] $kq/kr = 3.9$ l. mol^{-1}, and for myrcene (E_T = about 60 kcal),[23,24] $kq/kr = 2.3$ l. mol^{-1}. The rate of quenching is expected to drop off as the triplet energy of the acceptor approaches that of the donor.[25,26] Since the triplet energy of α-ketodecanoic acid is 64.3 kcal, the energy transfer to naphthalene and myrcene is exothermic by only about 3–4 kcal but energy transfer to cyclohexadiene ($E_T \simeq 53$ kcal)[23,24] is exothermic by approximately 11–12 kcal.

In contrast to aliphatic ketones,[8-10] we find that the photoelimination of α-ketodecanoic acid is completely quenchable. With 1.58 M 1,3-cyclohexadiene Φ_0/Φ equals 28.8 (not shown in the figure), giving a kq/kr value of 17 l. mol^{-1}, well within the experimental error for a linear Stern–Volmer relationship at such high concentrations. Since a value of 28.8 for Φ_0/Φ corresponds to quenching of approximately 97% of the reaction and since no leveling off in the Stern–Volmer plot is observed, all of the reaction proceeds *via* a triplet (quenchable) rather than a singlet (unquenchable) mechanism.

Table I gives the kq/kr values for intramolecular hydrogen abstraction by several carbonyl compounds including α-ketodecanoic acid. In all of these experiments the quenching reaction is exothermic by at least 9 kcal. Examination of Table I shows that whenever the carbonyl is conjugated with either an aryl or another keto group the rate of photoelimination is relatively low, as manifested by high kq/kr ratios. However the kq/kr value for α-ketodecanoic acid is about the same as that found for aliphatic ketones. This is rather surprising since excitation delocalization might be expected to occur with the α-keto acid as it does with α-diketones. Evidently I is a better representation of the excited state than is II for α-keto acids.

Table I

	kq/kr, l. mole^{-1}
2-Pentanone[a]	50
2-Hexanone[a]	10
n-Butyrophenone[a]	1850
n-Valerophenone[a]	100
2,7-Dimethyl-4,5-octanedione[b]	2800
α-Ketodecanoic acid	9.1

[a] Taken from ref 8 and 9. [b] Calculated from data for anthracene quenching given in ref 14. We should note that the hydrogen which is abstracted in this case is a tertiary hydrogen whereas the data given for all the other compounds refers to secondary or primary hydrogen abstraction. The value of kq/kr should be much larger than 2.8×10^3 l. mol^{-1} for abstraction of a secondary or primary hydrogen.

---

(21) P. A. Leermakers and G. F. Vesley, *J. Am. Chem. Soc.*, **85**, 3776 (1963).

(22) See ref 3, p 298.

(23) D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

(24) R. S. H. Liu, N. J. Turro, Jr., and G. S. Hammond, *J. Am. Chem. Soc.*, **87**, 3406 (1965).

(25) A. J. Fry, R. S. H. Kiu, and G. S. Hammond, *ibid.*, **88**, 4781 (1966).

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

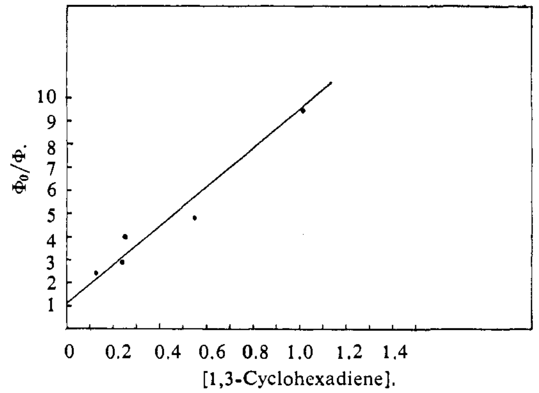
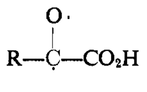
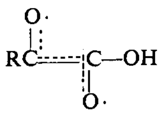


Figure 1. Stern–Volmer plot of relative quantum yield for heptene production *vs.* quencher concentration.



$R{-}\dot{C}(O\cdot){-}CO_2H$

I



II

C. Competition between Singlet Reaction and Intersystem Crossing. Aliphatic ketones possessing a secondary γ-hydrogen undergo 20–40% of the photoelimination from the singlet state. Those having primary γ-hydrogens show only about 10% unquenchable photoelimination.[8–10] The amount of singlet reaction will always depend upon the relative values of k_s and k_{ic}, the rate of singlet-state reaction and the rate of intersystem crossing from the singlet manifold to the triplet state. For any homologous series, k_{ic} may be presumed to remain constant. Thus the different amounts of unquenchable photoelimination with aliphatic ketones is a reflection on the different rates of k_s. For α-ketodecanoic acid, however, the complete lack of singlet elimination most probably indicates an increase in k_{ic} rather than a decrease in k_s. Since the triplet state of α-ketodecanoic acid shows the same reactivity as that of aliphatic ketones there is no reason to assume that its singlet state would be less reactive.

Rates of intersystem crossing depend upon both singlet–triplet energy splittings and the extent of spin–orbit interaction connecting singlet and triplet states. Singlet–triplet splittings for alkyl ketones and α-keto acids are comparable. The higher value of k_{ic}, then, implies that there is a greater amount of spin–orbit coupling than in simple ketones. This may be due to the energetic location of π,π* triplet state between the n,π* singlet and the n,π* triplet[27,28] for aliphatic α-keto acids.

Conclusions

Table II lists some approximate rates for intersystem crossing and intramolecular hydrogen abstraction for several types of carbonyl compounds. As can be seen, each type of carbonyl compound qualitatively fits into a separate classification with respect to the relative values of k_{ic} and k_r (the latter being the rate constant for abstraction by the triplet). Since there is no example where both k_{ic} and k_r have been measured for the same compound under the same conditions, an absolute comparison of these rates is probably not reliable.

Table II

	α-Keto acids	α-Diketones	Ketones	
			Aliphatic	Aromatic
k_{ic},	High	Low[a]	Low[b]	High[a]
sec^{-1}	$\gg 10^9$	$\sim 10^7$	$\sim 10^7$	$>10^{10}$
k_r,[c]	High	Low	High	Low
sec^{-1}	$\sim 10^9$	$<10^5$	10^8–10^9	10^6–10^7

[a] N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1967, p 75. [b] R. F. Borkman and D. R. Kearns, *J. Chem. Phys.*, **44**, 945 (1966). [c] Values of k_r were calculated from the kq/kr values in Table I assuming kq is 1×10^{10} l. mol^{-1} sec^{-1}.

In summary, this experiment, together with our previous conclusions on the pyruvic acid system,[1,12] indicates that α-keto acids exhibit a behavior different from that of any other class of carbonyl compounds. Namely, aliphatic α-keto acids may be characterized by *high rates of both intersystem crossing and photoreaction.*

Experimental Section

All compounds were used as commercially obtained except for myrcene which was distilled immediately before use. All photolyses were run with a merry-go-round apparatus to ensure equal irradiation of all of the samples. The light source was a 450-W Hanovia with several Corning 7-60 filters surrounding the lamp. Pyruvic acid was identified by comparison of its nmr with authentic material. 1-Heptene was identified by comparison of its ir, nmr, and vpc retention time with that of authentic material. All vpc analyses were performed using a 25-ft 1,2-bis(2-cyanoethoxy)ethane column maintained at room temperature.

Acknowledgments. We are grateful to the National Institutes of Health (Grant GM 13592) and to the Petroleum Research Fund for financial support. We also wish to thank Dr. A. A. Lamola for a critical analysis of our original manuscript.

---

[27] S. K. Lower and M. A. El-Sayed, *Chem. Rev.*, **66**, 199 (1966).

[28] V. G. Plotnikou, *Opt. Spectry USSR*, **6**, 401 (1967).