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THE MECHANISM OF THE NORRISH TYPE II REACTION OF α-KETO-ACIDS AND ESTERS

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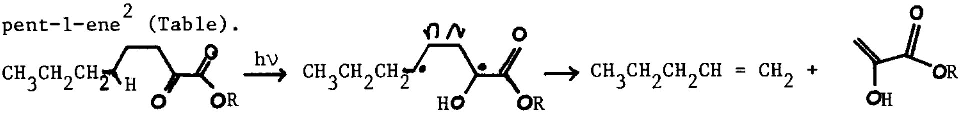
Summary

Methyl-α-keto-octanoate undergoes a Type II reaction to give pent-1-ene and photophysical measurements show that this and the Type II reactions of α-keto-acids occur, contrary to previous claims, from the excited singlet state.

It has been shown that α-keto-decanoic acid undergoes a Type II elimination reaction to give hept-1-ene[1]. We now report that α-keto-octanoic acid, its methyl ester and 2-(2-naphthyl)ethylester undergo a similar reaction to give pent-1-ene[2] (Table).



R = -H, $-CH_3$ or $-CH_2CH_2Np$*

These reactions are relatively insensitive to the presence of triplet quenchers such as oxygen and naphthalene. Even with the naphthyl ester, which contains a naphthalene group ideally situated to deactivate the triplet ester by energy transfer, the yield of pent-1-ene is quite high.

TABLE

YIELDS OF PENT-1-ENE FROM IRRADIATION(a) OF α-KETO-OCTANOIC ACID AND ESTERS IN BENZENE

R	Conditions	% Pent-1-ene(b)
-H	Argon purged	46
-H	Argon purged(c)	45
-H	Oxygen purged	38
$-CH_3$	Argon purged	52
$-CH_3$	Argon purged(c)	49
$-CH_3$	Oxygen purged	39
$-CH_2CH_2Np$*	Argon purged	40
$-CH_2CH_2Np$*	Oxygen purged	32

(a) Reactant concentration, 5 x 10^{-2}M; 18hr. irradiation using Black-light lamps (λmax. 350nm)
(b) Yield determined by g.l.c. and identified by g.l.c. and GC/MS.
(c) Naphthalene [1 x 10^{-3}M] added.

* Np = 2-Naphthyl

That naphthalene quenches the triplet state of alkyl pyruvates has been shown by use of the technique of nanosecond laser flash photolysis. Methyl pyruvate was found to have a triplet-triplet absorption spectrum similar to that of pyruvic acid[3,4]. The triplet lifetime is concentration dependent ($k_{sq} = 2 \times 10^8 M^{-1} s^{-1}$) and at concentrations of 5×10^{-2}M the lifetime was found to be 125 ns. From these lifetime measurements, the presence of oxygen at a concentration of 8×10^{-3}M should reduce the yield of pent-1-ene ~20-fold if the triplet ester is responsible for the reaction. Furthermore, laser flash photolysis of 2-(2-naphthyl)ethyl pyruvate showed that the naphthalene group leads to almost total triplet quenching of the ester and that this is attended by the formation of triplet naphthalene. Thus the formation of pent-1-ene from 2-(2-naphthyl)ethyl-α-keto-octanoate cannot have arisen via the triplet state of the ester.

Recently we showed that the triplet state of pyruvic acid is efficiently quenched by oxygen and by naphthalene[3]. Since α-keto-octanoic acid gives pent-1-ene in good yield in the presence of oxygen it can be surmised that the triplet state of the acid is not responsible for reaction.

We conclude that the Type II reaction of α-keto-acids and esters occurs from the excited singlet state. This conflicts with that of Evans and Leermakers[1] who showed that cyclohexa-1,3-diene at concentrations > 0.1M quench the Type II reaction of α-keto-decanoic acid. However, it has now been appreciated that the excited singlet states of ketones are quenched by high concentrations of dienes[5] including cyclohexa-1,3-diene. It has also been shown that α-keto-esters react with alkenes to give [2+2] cycloaddition products[6,7], and that the excited singlet state of methyl pyruvate is quenched by cyclohexa-1,3-diene.[7] It would appear that the quenching observed by Evans and Leermakers[1] was due to quenching of the excited singlet state.

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