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PHOTOELIMINATION IN 2-(DIMETHYLAMINO)ETHYL BENZOATES

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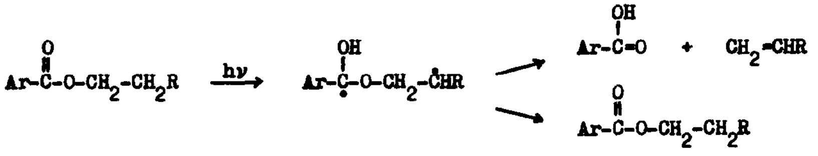
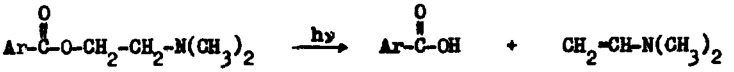
The Norrish type 2 photoelimination reaction in carbonyl compounds has been extensively studied for ketones, and it occurs also for aldehydes, carboxylic acids, carboxylate esters and many other classes of compound.[1] The reaction for alkyl esters of aromatic carboxylic acids is of low quantum yield (< 0.02), and it appears[2] to involve the rapid formation of an intermediate biradical which can break down to give products, but which largely reverts to the ground state of the starting ester by a reverse hydrogen-transfer step (1).



$$\mathrm{Ar\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}CH_2\text{-}CH_2R} \xrightarrow{h\nu} \mathrm{Ar\text{-}\overset{\overset{OH}{|}}{\dot{C}}\text{-}O\text{-}CH_2\text{-}\dot{C}HR} \begin{cases} \longrightarrow \mathrm{Ar\text{-}\overset{\overset{OH}{|}}{C}{=}O} + \mathrm{CH_2{=}CHR} \\ \longrightarrow \mathrm{Ar\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}CH_2\text{-}CH_2R} \end{cases} \qquad (1)$$

The intermediate must be short-lived, since an optically active starting ester is not racemised on irradiation,[3] which means that reversion of the biradical to the original ester is much faster than bond rotation.

We report here that an analogous, but much more efficient, process occurs on irradiation (254 nm) of aromatic esters in which there is a dimethylamino substituent in the alkyl chain (2).



$$\mathrm{Ar\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}CH_2\text{-}CH_2\text{-}N(CH_3)_2} \xrightarrow{h\nu} \mathrm{Ar\text{-}\overset{\overset{O}{\|}}{C}\text{-}OH} + \mathrm{CH_2{=}CH\text{-}N(CH_3)_2} \qquad (2)$$

$$\phi = 0.1 - 0.3$$

The higher quantum yield may arise because the lowering of the C-H bond strength at the site of hydrogen abstraction (because of the adjacent dimethylamino group) increases the rate constant for the primary abstraction step and, more significantly, decreases the rate constant for the reverse hydrogen-transfer step. This would alter the partitioning of the biradical intermediate in favour of product formation. However, comparison with esters substituted with a phenyl or alkoxy group (see Table 1) does not support this proposal, since these groups should also decrease the homolytic bond strength of the adjacent C-H bond by a similar or greater amount.

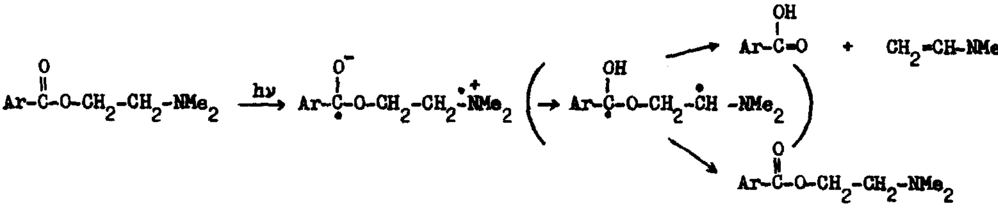
Table 1 Quantum yields for production of carboxylic acid:

$$\text{Ar-CO-O-CH}_2\text{-CH}_2\text{-Y} \xrightarrow{h\nu} \text{Ar-CO-OH}$$

Ar	Y	solvent	Φ (a)
C_6H_5	CH_3	c-C_6H_{12}	0.0057 (b)
C_6H_5	$N(CH_3)_2$	c-C_6H_{12}	0.24
C_6H_5	$N(CH_3)_2$	CH_3CN	0.21
p-F-C_6H_4	$N(CH_3)_2$	c-C_6H_{12}	0.19
C_6H_5	OCH_3	c-C_6H_{12}	0.038
C_6H_5	OC_2H_5	C_6H_{14}	0.009 (c)
C_6H_5	C_6H_5	c-C_6H_{12}	0.014
C_6H_5	$\overset{+}{N}H(CH_3)_2\ Cl^-$	CH_3CN	0.018
2-$C_{10}H_7$	$N(CH_3)_2$	c-C_6H_{12}	0.08

(a) converted to the methyl ester using diazomethane, and estimated by v.p.c.
(b) reference 2
(c) reference 4

A second possibility is that reaction is more efficient for the (dimethylamino)ethyl esters than for the other alkyl esters because an initial electron-transfer mechanism is involved in the former case (3).



(3)

The partitioning of the intermediate (to starting material or to products) in the electron-transfer mechanism can differ from that expected on the basis of a direct hydrogen-transfer mechanism if either (i) the electron transfer gives a zwitterion which goes directly to products, or (ii) the biradical is formed as a subsequent intermediate, but in a different state (e.g. of spin multiplicity or conformation) from the one which would be formed by direct hydrogen transfer.

For ketones of the type $Ph\text{-}CO\text{-}(CH_2)_3\text{-}NR_2$, an electron-transfer mechanism has been ruled out for the elimination reaction (although intramolecular charge-transfer is involved in the radiationless decay of the excited state),[5] but the following observations, taken together, provide strong support for an electron-transfer mechanism in the reaction of esters studied here:

(a) The comparison with alkoxyethyl and phenylethyl esters indicates that homolytic C-H bond strength at the site of abstraction is not the governing factor in producing a higher quantum yield for the (dimethylamino)ethyl esters.

(b) Neither penta-1,3-diene (a triplet quencher) nor biacetyl (a singlet and triplet quencher) quenches the reaction of 2-(dimethylamino)ethyl benzoate (see Table 2), whereas both can partly quench the reaction for alkyl benzoates.[2] This means that the excited state(s) responsible for reaction in the present systems are very short-lived ($\tau \leq 10^{-10}$s), probably because the primary electron-transfer step is very fast.

Table 2 Effect of quenchers

Ar	Y	quencher	ϕ
C_6H_5	$N(CH_3)_2$	none	0.24
C_6H_5	$N(CH_3)_2$	pentadiene (0.1 M)	0.26
C_6H_5	$N(CH_3)_2$	biacetyl (0.1 M)	0.23

(c) Protonation of the nitrogen atom by conversion to the ammonium salt leads to a value for the quantum yield which is comparable to those for the unsubstituted esters. The electron-transfer mechanism is not possible in the ammonium compound, and the reaction must occur by a hydrogen-transfer mechanism or from the free (dimethylamino)ethyl ester in equilibrium with the salt.

(d) The efficiency of elimination for the (dimethylamino)ethyl ester of 2-naphthoic acid is quite high (0.08, about one-third the value of the quantum yield for the ester of benzoic acid). This is in contrast to results for isobutyl naphthoate (ϕ = 0.00016, about 50 times lower than the quantum yield for isobutyl benzoate)[2]. This points to a mechanism for the nitrogen-containing ester which does not involve hydrogen transfer in the primary step.

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