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PHOTOELIMINATION IN N-SUBSTITUTED BENZAMIDES

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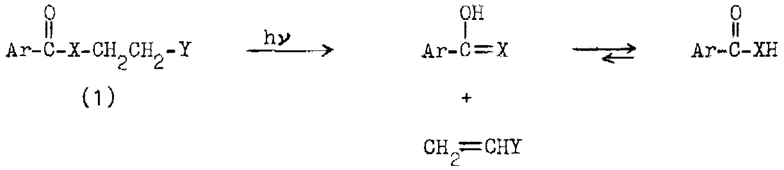
One of the typical photochemical reactions of aromatic carbonyl compounds (1) is the Norrish type 2 photoelimination:



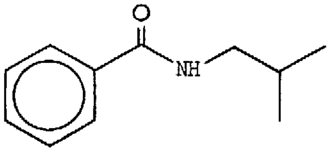
$$\underset{(1)}{Ar-\overset{O}{\overset{\|}{C}}-X-CH_2CH_2-Y} \xrightarrow{h\nu} Ar-\overset{OH}{\overset{|}{C}}{=}X + CH_2{=}CHY \rightleftarrows Ar-\overset{O}{\overset{\|}{C}}-XH$$

Aromatic ketones (1; $X = CH_2$) have been studied extensively.[1] For these compounds the reaction generally occurs from the (n,π^*) triplet excited state by way of a hydrogen-abstraction mechanism and an intermediate biradical species $Ar\dot{C}(OH)CH_2CH_2\dot{C}HY$. If the (n,π^*) triplet is the lowest energy triplet state, the quantum yield for reaction is usually high (up to 1.0); if there is a lower energy (π,π^*) triplet state, the quantum yield is much lower (often less than 0.01). Dialkylamino-substituted ketones of the type $ArCOCH_2N(CH_2R)_2$ undergo reaction with moderate efficiency (ϕ = 0.05 - 0.15) by way of an electron-transfer mechanism, and the efficiency is not markedly dependent on the electronic character (n,π^* or π,π^*) of the lowest excited state.[2] Dialkylaminoketones (1; $X = CH_2$, $Y = NMe_2$ or $N(CH_2Ph)_2$) seem to react by two mechanisms.[3,4] In a hydrocarbon solvent there is a hydrogen-abstraction mechanism and the overall quantum yield is quite low (< 0.03); in methanol there is an electron-transfer mechanism and a higher overall efficiency ($\phi > 0.15$). In the hydrocarbon solvent electron transfer accounts for much of the decay of the excited state but does not seem to be responsible for product formation.

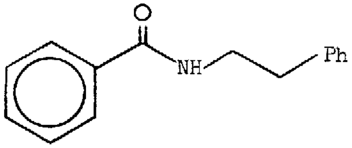
Much less work has been reported for benzoate esters (1; X = O).[5-7] The lowest excited states are (π,π^*) and reaction is inefficient for ordinary alkyl benzoates ($\phi < 0.01$).[5] However, introduction of an electron-donor substituent such as dialkylamino (1; X = O, $Y = NR_2$) or methylthio (1; X = O, Y = SMe) leads to a big increase in reaction efficiency

(ϕ up to 0.2) by opening up the possibility of an electron-transfer mechanism.[8]

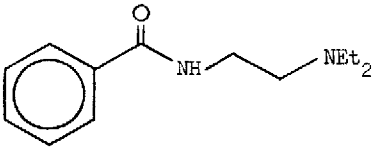
We now report that substituted benzamides (1; X = NH) can take part in the Norrish type 2 reaction and that the pattern of their reactivity is similar to that of the benzoate esters except that the absolute quantum yields are lower. Aliphatic amides (RCONHR') are reported[9] to react on irradiation almost exclusively by α-cleavage and hardly at all by a photoelimination route. Reports of intramolecular hydrogen abstraction by an amide carbonyl group are rare (though there are several involving imides[10]) - two of the few concern N,N'-diethyluracil[11] and a substituted pyridone.[12] The present work is the first, to our knowledge, which involves a simple amide grouping.



(2)



(3)



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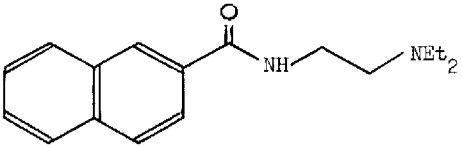


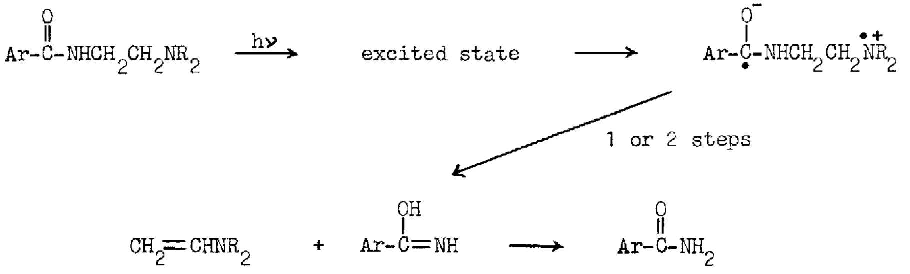
(5)

Amides (2) - (5) were irradiated (254 nm), and the unsubstituted amide produced in the photoelimination process (benzamide from 2, 3 or 4, and 2-naphthamide from 5) was estimated quantitatively by g.l.c. (10% cyanosilicone oil on Kieselguhr, with eicosane or octacosane as internal standard). The quantum yields for production of the amide were determined using 1-propyl benzoate as actinometer, and the results are displayed in Table 1.

Table 1 Quantum yields for Norrish type 2 reaction of amides (2) - (5)

Amide	2	3	4	4	5
Solvent	*c*-C_6H_{12}	EtOH/*c*-C_6H_{12}	*c*-C_6H_{12}	EtOH/*c*-C_6H_{12}	EtOH/*c*-C_6H_{12}
ϕ	0.0006	0.0004	0.023	0.053	0.009

The quantum yield values are lower than those for related esters (for example, ϕ = 0.009 for $PhCOOCH_2CHMe_2$ in acetonitrile), but the variation of quantum yield follows a similar pattern for amides as for esters. The alkyl-substituted compound (2) undergoes reaction with very low efficiency, and this is not improved by the introduction of a phenyl substituent (in 3) which is capable of stabilising an adjacent radical centre. A dramatic increase occurs, nearly 40-fold in hydrocarbon solvent, when a dialkylamino substituent is present, and the increase is larger in a more polar solvent. The quantum yield for the naphthamide (5) is high in comparison with that of the alkyl amide (2); on the basis of results for esters[5] a 50-fold reduction in quantum yield is expected on going from a phenyl to a naphthyl compound when the mechanism involves hydrogen abstraction. These results suggest[13] that the primary step in the excited state reactions of the amino-substituted amides involves electron transfer from nitrogen to the excited chromophore:



In order to identify the lowest excited states, luminescence measurements were carried out on the amides, and the results are shown in Table 2.

Table 2 Luminescence properties of amides (2) - (5)

Amide	τ_p/s (a)	triplet energy /kJ mol^{-1}(kcal mol^{-1})	τ_s/ns (b)	$\phi_{fluor.}$
2	1.6	325 (78)	0.2	0.002
3	1.8	325 (78)	(0.4)	0.004
4	1.4	325 (78)	(0.1)	0.001
5	2.1	245 (59)	4.5	0.038

(a) phosphorescence lifetime at 77 K in 3-methylpentane glass

(b) singlet lifetime in degassed cyclohexane solution - values in parentheses are estimated

The fluorescence of the benzamides is very weak, and the singlet lifetimes are difficult to measure. In the absorption spectra there is no sign of $n \rightarrow \pi^*$ absorption at longer wavelengths than the intense $\pi \rightarrow \pi^*$ bands. The phosphorescence lifetimes are long, typical of (π,π^*) triplet states, and the triplet energies are similar to the (π,π^*) triplet energies of other phenyl and naphthyl compounds. The benzamides show only very weak transient (triplet) absorption in flash photolysis studies at room temperature, but the naphthamide (5) gives a transient of lifetime 83 μs whose spectrum is very similar to the triplet-triplet absorption spectrum of 2-(dimethylamino)ethyl 2-naphthoate.[8] The luminescence results suggest that the lowest excited states are (π,π^*) in character, and this is consistent with the low quantum yields for Norrish type 2 reaction and with the large increase in quantum yield when an electron-transfer mechanism is available.

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