A Type 2 Photoelimination Reaction of 1-Naphthyl Ketones

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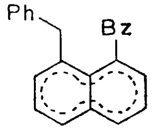
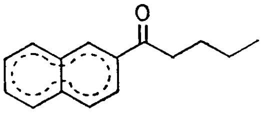
1-(Alkoxyacetyl)naphthalenes undergo a type 2 photoelimination reaction with a low but significant quantum efficiency. The reaction does not occur from the lowest-energy excited-triplet state but from a higher energy (probably a singlet) state.

ACYLNAPHTHALENES have lowest triplet excited states which are relatively low in energy and (π,π*) in electronic character. Intermolecular photoreduction is slow and inefficient unless a very good hydrogen donor such as tributyltin(IV) hydride is present.[1] This low reactivity is normally attributed to an electron distribution in the (π,π*) state which is unfavourable for hydrogen abstraction. The ready hydrogen abstraction by (n,π*) excited states of carbonyl compounds reflects the relatively electron-deficient character of the oxygen atom in these states, but the oxygen atom in (π,π*) states is not electron-deficient. The ' residual ' reactivity of naphthyl ketones towards such hydrogen donors as propan-2-ol in intermolecular hydrogen abstraction is explained in terms of a mixing of states,[2] so that the lowest energy and reacting state is not a ' pure ' (π,π*) state but has some (n,π*) character.

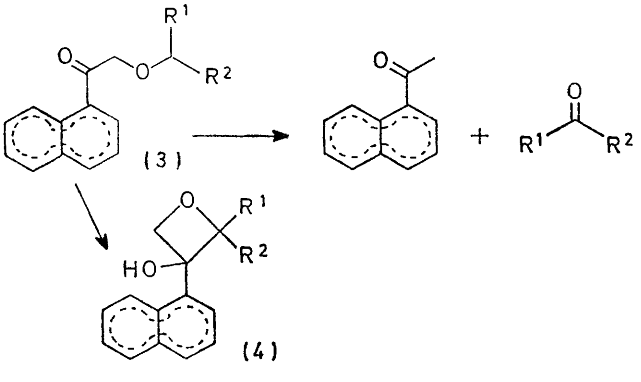
Efficient, though relatively slow, intramolecular hydrogen abstraction and cyclisation occurs in 1-benzoyl-8-benzylnaphthalene (1), and this reaction can be quenched by *trans*-stilbene.[3] However, the inefficient ($\phi = 0{\cdot}002$) type 2 photoelimination reaction of 2-pentanoylnaphthalene (2) appears not to occur through the lowest excited-triplet state,[4] since penta-1,3-diene does not affect the reaction although it does quench intermolecular photoreduction.



(1)



(2)



(3)

(4)

In the present work the photochemistry of 1-(alkoxyacetyl)naphthalenes (3) was studied in order to observe the effect of having a relatively weak C–H bond at the site of reaction and to identify the excited state responsible for reaction. The products expected from intramolecular hydrogen abstraction in the excited state are 1-acetylnaphthalene and a simple aldehyde or ketone, and possibly an oxetanol (4) by analogy with α-alkoxyacetophenone systems.[5]

RESULTS AND DISCUSSION

Acylnaphthalenes (3; R^1, R^2 = H or Me) were synthesised and then irradiated at 313 nm in benzene solution. The major products observed by g.l.c. were 1-acetylnaphthalene and formaldehyde, acetaldehyde, or acetone in approximately equal molar quantities, 1·0 : 1·1 (±0·2). At 70% conversion no oxetanol (4) was detected under the analytical conditions used. The estimated quantum yields for formation of 1-acetylnaphthalene are as follows:

R^1	R^2	ϕ
H	H	0·0016 ± 0·0003
Me	H	0·010 ± 0·002
Me	Me	0·015 ± 0·003

Irradiations under identical conditions with a solution of cyclopentadiene or penta-1,3-diene in benzene (1·0 mol l^{-1}) gave quantum yields for formation of 1-acetylnaphthalene identical to those listed above. Since the triplet energy of the (*s-cis*) dienes (*ca.* 220 kJ mol^{-1}) is well below that of the lowest triplet state of the ketones (*ca.* 240 kJ mol^{-1}) the absence of a quenching effect suggests that the reaction does not occur through this lowest triplet state. This conclusion is supported by the observation that diene dimers were formed in the irradiations in benzene–diene solvent similar to those formed in control experiments by triplet-energy transfer from 1-acetylnaphthalene to the dienes. This indicates that the triplet state of the (alkoxyacetyl)naphthalene is formed and is quenched by diene, but it does not take part in the reaction sequence leading to the type 2 elimination products.

The reactive excited state must be a higher-energy state, and it is probably a singlet state. Support for this assignment is twofold. First, if reaction occurs through an upper triplet state it should still be quenched to a measurable extent by conjugated diene unless the excited state lifetime is extremely short ($<10^{-10}$ s).

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[1] G. S. Hammond and P. A. Leermakers, *J. Amer. Chem. Soc.*, 1962, **84**, 207.

[2] N. C. Yang and R. L. Dusenbery, *J. Amer. Chem. Soc.*, 1968, **90**, 5899; H. Lutz, M.-C. Duval, E. Breheret, and L. Lindqvist, *J. Phys. Chem.*, 1972, **76**, 821.

[3] A. G. Schultz, C. D. DeBoer, W. G. Herkstroeter, and R. H. Schlessinger, *J. Amer. Chem. Soc.*, 1970, **92**, 6086.

[4] N. C. Yang and A. Shani, *Chem. Comm.*, 1971, 815.

[5] F. D. Lewis and N. J. Turro, *J. Amer. Chem. Soc.*, 1970, **92**, 311.

Secondly, the lack of cyclisation product is more in keeping with a singlet than with a triplet precursor. The singlet states of aliphatic ketones give little cyclobutanol product,[6] but the triplet states of α-alkoxyacetophenones are known to give high yields of oxetanol.[5]

The lack of reactivity in the lowest triplet state may result from the unfavourable electron distribution in a state with considerable (π,π*) character, but it may also reflect the endothermic nature of the primary reaction step. It is not always recognised that thermodynamic factors may play an important role in determining the reactivity of excited states. In the particular case of intermolecular photoreduction involving the lowest triplet state of an acylnaphthalene (AcNap) and propan-2-ol the primary reaction step (5) is slightly endothermic, and on thermodynamic grounds the rate constant is expected to be somewhat low. When the hydrogen donor is tributyltin(IV) hydride the primary step (6) is exothermic, and on thermodynamic grounds fast and efficient photoreduction might be expected despite the fact that the electron distribution in the lowest triplet state is not favourable.

$$(\mathrm{AcNap})^* + \mathrm{Me_2CHOH} \longrightarrow (\mathrm{AcNap})\mathrm{H}\cdot + \mathrm{Me_2\dot{C}OH},\ \Delta H \sim +13\ \mathrm{kJ\ mol^{-1}} \quad (5)$$

$$(\mathrm{AcNap})^* + \mathrm{Bu_3SnH} \longrightarrow (\mathrm{AcNap})\mathrm{H}\cdot + \mathrm{Bu_3Sn}\cdot,\ \Delta H \sim -63\ \mathrm{kJ\ mol^{-1}} \quad (6)$$

The enthalpy terms in the primary reaction step from the lowest triplet state of 1-(isopropoxyacetyl)naphthalene (3; $R^1 = R^2 = Me$) are very similar to those for the intermolecular hydrogen-abstraction step (5), and the intramolecular process is probably also slightly endothermic. It is likely that both electronic and thermodynamic factors influence the reactivity of an excited state in a particular process.

The inability of dienes to quench the reaction rules out a mechanism in which the upper excited state is populated by thermal activation of molecules in the lowest triplet state, though such a mechanism may operate in other systems particularly where there is an (n,π*) triplet state slightly higher in energy than the lowest (π,π*) triplet state.[7] The low quantum yields of reaction must therefore result, at least in part, from competition between intramolecular reaction of the higher-energy state and radiationless decay of this state to the lowest-energy triplet state. On this basis it is understandable that intermolecular photoreduction of acylnaphthalenes does not involve a higher-energy excited state, since intermolecular hydrogen abstraction by an upper state would compete less effectively with internal deactivation processes than would intramolecular abstraction.

EXPERIMENTAL

The 1-(alkoxyacetyl)naphthalenes were prepared from 1-(diazoacetyl)naphthalene.[8] Irradiations were carried out using radiation from a medium-pressure mercury-arc filtered through Pyrex glass and through a potassium chromate–potassium carbonate solution to isolate the 313 nm region. Quantum yield estimates were obtained using valerophenone in benzene as a secondary standard actinometer.[9] The naphthyl ketone and the actinometer solutions were irradiated successively under identical conditions, and the unknown quantum yield was calculated on the basis of a value of 0·33 for the quantum yield for production of acetophenone in the actinometer solution. The extent of reaction was kept below 10% to reduce errors caused by competitive absorption of radiation by the products of reaction. The temperature of the irradiated solutions was maintained at 25(±2) °C. G.l.c. analysis was carried out on a column made up as 10% Carbowax C20M on Kieselghur.

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[8] M. S. Newman and P. Beal, *J. Amer. Chem. Soc.*, 1950, **72**, 5161.

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