Photochemistry of β-Naphthyl Alkyl Ketones in Solution

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Summary β-Naphthyl n-butyl ketone was photolysed to β-acetonaphthone and propene from the *n*,π* singlet state only.

CARBONYL compounds with γ-hydrogens undergo the "Norrish type II process" to give an enol and an olefin (equation 1).[1] The nature of photoreactive states for this reaction depends on the structure of carbonyl compounds. Alkyl ketones will react in both the *n*,π* singlet and the *n*,π* triplet states,[2–4] while phenyl alkyl ketones do so only in the *n*,π* triplet state.[2] The nature of the first singlet excited state for acetonaphthone is *n*,π*, while its lowest triplet state is π,π*.[5] Since "type II" reactions may proceed through the *n*,π* singlet state, it is of interest to investigate the photochemical behaviour of naphthyl alkyl ketones with γ-hydrogens (I; R¹ = β-naphthyl) to see whether they will undergo such reactions.

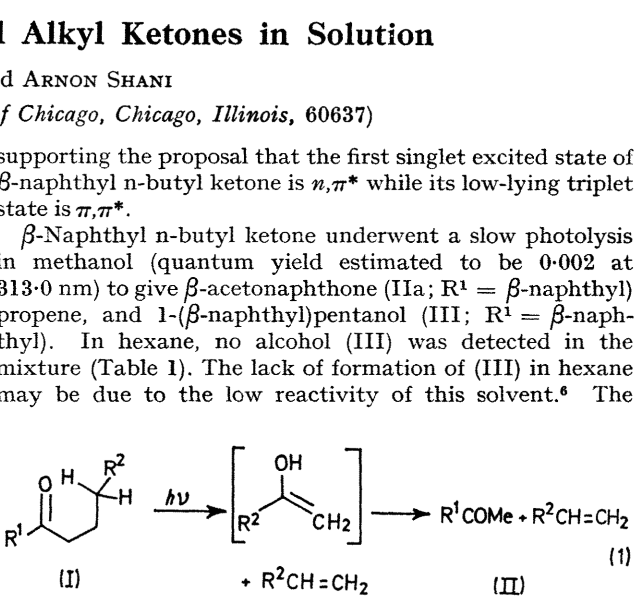
(I) (II) (1)

TABLE 1[a]

Solvent	t/h	Recovery of (Ia) (%)	Products (%) (II)	(III)	(VI)	(IV) and (VII)
Methanol[b]	7	88	7	3		
Methanol[b]	24	60—66	12—13	10	2—3	1—3
Hexane	24	93	6			

[a] Irradiation (Hanovia 450 W, Vycor-filtered) of (Ia) (2 g) in 100 ml solvent.
[b] In addition, a highly insoluble compound was obtained (0·5—1·0%), m.p. 215—217°.

In its u.v. spectrum, naphthyl n-butyl ketone (Ia; R^1 = β-naphthyl, R^2 = Me) has λ_{max} (hexane) 341 nm (log ε 3·17) [338 (3·17) in methanol] and in the phosphorescence emission spectrum an O–O band appears at 483 nm (τ 0·9 s). Both spectra are very similar to those of β-acetonaphthone supporting the proposal that the first singlet excited state of β-naphthyl n-butyl ketone is *n*,π* while its low-lying triplet state is π,π*.

β-Naphthyl n-butyl ketone underwent a slow photolysis in methanol (quantum yield estimated to be 0·002 at 313·0 nm) to give β-acetonaphthone (IIa; R^1 = β-naphthyl) propene, and 1-(β-naphthyl)pentanol (III; R^1 = β-naphthyl). In hexane, no alcohol (III) was detected in the mixture (Table 1). The lack of formation of (III) in hexane may be due to the low reactivity of this solvent.[6] The photolysis was then performed in *p*-methoxytoluene which was selected for its high reactivity in photoreduction and its miscibility with penta-1,3-diene.[6] The photochemical reaction of (Ia) in *p*-methoxytoluene was complex: in addition to (IIa) and (III), at least five other products were formed; among them were the secondary products derived from β-acetonaphthone (IIa) such as the diol (VII; $R^1 = \beta$-naphthyl). Complete separation of (IV), (V), (VII), and (VIII) could not be achieved chromatographically (g.l.c. or column). The assignment of probable structures for (V) and (VII) was based on spectral data (n.m.r. and i.r.) of the purified fractions, and for (IV) and (VII) on a positive periodic acid test in addition to their spectra.

The effect of adding penta-1,3-diene to β-naphthyl n-butyl ketone was then determined. The results are summarised in Tables 2 and 3. The reaction in hexane (see Table 2) was followed by g.l.c. and the experimental error was ±0·7%. In all experiments, *ca.* 90% of the starting ketone was recovered and no product was detectable. The data illustrated that penta-1,3-diene had no measurable effect on this reaction. The products of reaction of (Ia) in *p*-methoxytoluene (see Table 3) were analysed by chromatography on alumina. That the yields of acetonaphthone increased with increasing penta-1,3-diene concentration may be attributed to the quenching of secondary reactions; the formation of (III) and other products is readily quenched.

TABLE 2[a]

Irradiation of β-naphthyl alkyl ketone in hexane with penta-1,3-*diene*

[Penta-1,3-diene]/M	Yield of acetonaphthone (%) 20 h	48 h
0	2·8	6·6
0·01	3·4	6·0
0·06	2·9	6·9
0·10	2·6	5·8
0·40	4·0	6·0
0·50	2·7	6·4
1·0	3·7	5·5
2·0	2·7	6·6
8·0	4·0	6·2
average	3·2 ± 0·8	6·2 ± 0·7

[a] Irradiation (Hanovia lamp, Pyrex-filtered) of 0·05M-solutions (20 ml) at 25°.

$$\underset{\text{(I)}}{R^1CO\cdot[CH_2]_3Me} + \underset{\text{(solvent)}}{R^2H} \xrightarrow{h\nu} \underset{\text{(III)}}{R^1Bu^nCH(OH)} + \underset{\text{(IV)}}{R^1Bu^nC(OH)\cdot C(OH)R^1Bu^n} + \underset{\text{(V)}}{R^1R^2Bu^nC(OH)} \quad (2)$$

$$\underset{\text{(II)}}{R^1COMe} + \underset{\text{(solvent)}}{R^2H} \xrightarrow{h\nu} \underset{\text{(VI)}}{R^1MeCH(OH)} + \underset{\text{(VII)}}{R^1MeC(OH)\cdot C(OH)R^1Me} + \underset{\text{(VIII)}}{R^1R^2MeC(OH)} \quad (3)$$

TABLE 3[a]

Irradiation of β-naphthyl alkyl ketone in p-*methoxytoluene containing penta*-1,3-*diene*.

[Penta-1,3-diene]/M	Products (%) Recovered (I)	(II)	(III)	(VI)	(IV), (V), (VII), and (VIII)
0	16 ± 1	5—6	15	2	35—40
0·04	30	9	14	1	37
0·08	38	9—10	11		22
0·20	55	9	5		12
1·0	75	11	4		2
8·0	80	15	1—2		

[a] Irradiation (Hanovia lamp, Pyrex-filtered) of 0·05M-solutions (10 ml) at 25°

Therefore, we suggest that the type II process for β-naphthyl n-butyl ketone proceeds through the n,π^* singlet state, while the formation of (III) and other products proceeds *via* the triplet state. Also no cyclobutanol formation was detected even though this is a major process for the corresponding aliphatic[7] and aromatic ketones.[8,9] A possible explanation is that cyclobutanol formation may proceed mainly *via* the triplet state.

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