Photochemical Reactions of 1,8-Diacetylnaphthalene and 1,3-Dimethoxy-1,3-dimethyl-1*H*,3*H*-naphtho[1,8-*cd*]pyran[1]

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Summary The photochemical reaction of 1,8-diacetyl-naphthalene (1) involves an intramolecular proton migration from one acetyl group to the other followed by cyclization; that of the naphthopyran (6) results in the formation of dimethylacenaphthylene oxide (7).

SUBSTITUENTS located at *peri* positions of naphthalene interact strongly with each other, and unique intramolecular photochemical reactions between these substituents can be expected. We have studied the photocyclization of a *peri*-alkenylnaphthalene from this point of view.[1] We now report the photochemical reactions of 1,8-diacetylnaphthalene (1), and the napthopyran derivative (6).

Irradiation of (1) in acetonitrile, with argon bubbling, with a 450 W high pressure mercury arc lamp in a water-cooled Pyrex immersion well gave (4) (*ca.* 15%), (5) (*ca.* 25%), and (2) (*ca.* 20%) after silica-gel thick layer chromatography. Compounds (4) and (5) were identical with authentic samples.† The structure of the highly fluorescent product (2) is based on its spectral data; n.m.r. [(CD$_3$)$_2$CO] δ 7·5—8·6 (m, 6H, aromatic), 4·30 (d, *J* 4 Hz, 2H, CH$_2$), and 2·90 (s, 3H, Me); i.r. (KBr) 3260(OH) and 1600 (C=C) cm^{-1}; u.v. (MeOH) 240(sh), 302(sh), 310, and 326 nm; fluorescence (MeCN) 400 nm. Mass spectral analysis of (2) was unsuccessful because of its instability in air at room temperature. Decomposition of (2) gave (4) and intractable materials in air. This suggests that (4) is formed

† Compound (4) is commercially available and (5) was prepared by base catalysed intramolecular aldol condensation of (1).

from (2) by air oxidation during the isolation procedure. The products of the photo-reaction have u.v. spectra similar to that of (2) but different from (5) [λ_{max} 248, 255, 310(sh), 322, 350(sh), 358, and 380(sh) nm in MeOH] and they are highly fluorescent (fluorescence maximum at 400 nm in MeCN). This suggests that (5) is also produced during the isolation process. We think that (3) is the precursor of (5).

(1)

(2)   +   (3)

(4)   (5)
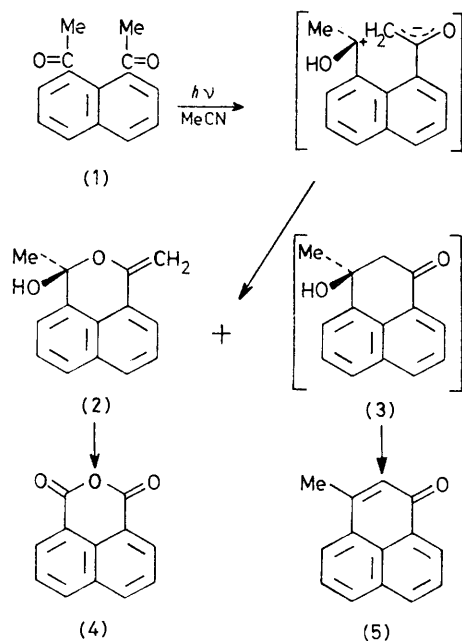
Scheme 1

The fact that the reaction takes place more effectively in polar solvents than in non-polar solvents suggests that it is not a radical reaction but an ionic one probably proceeding through intramolecular proton migration followed by cyclization as shown in Scheme 1. We believe that this reaction occurs from the lowest triplet state of (1), since it is quenched by piperylene and the rate is decreased to *ca.* one third by oxygen while in a heavy atom solvent such as PrBr–MeCN (1 : 1) the rate is doubled.‡ The lowest triplet has π–π^* character, since the phosphorescence life-time (*ca.* 1 s in ether–pentane–alcohol at 77 K) and the energy (*ca.* 56 kcal mol^{-1}) are almost the same as those of 1-acetylnaphthalene which has a π–π^* lowest triplet.

In methanol (1) is converted gradually into a 1 : 1 mixture of *cis* and *trans* (6) in the dark at room temperature; in refluxing solvent it gives predominantly (5) with a small amount of (6). Identification of (6) is based on the fact that it is hydrolysed to (1) and methanol by a trace of water

in CDCl$_3$ and its spectral data; n.m.r. (CDCl$_3$) δ 7·2—7·9 (m, 6H, aromatic), 3·25 (s, 6H, OMe), and 1·85 and 1·80 (s, 6H, *cis* and *trans* Me, respectively); i.r. (KBr) 1040—1210 cm^{-1} (acetal); u.v. (MeOH) 255(sh), 268(sh), 276, 286, 297, 306(sh), 310(sh), 315, and 320(sh); m/e 258 (M^+). Irradiation of (1) in methanol did not accelerate the formation of (6). The dark reaction was observed in other alcoholic solvents, except t-butyl alcohol, and was greatly accelerated by addition of a catalytic amount of acetic acid. This suggests that the reaction is autocatalytic being promoted by the proton which is formed by dissociation of (1) into the enolate ion. The dissociation is probably due to relief of steric strain arising from the two acetyl groups of (1).§

The photochemical reaction of (1) in methanol was almost the same as that in acetonitrile, although it was complicated by the competing dark reaction. However, irradiation of (6) in methanol under the same conditions as for (1) in acetonitrile gave 1,2-dimethyl acenaphthylene oxide (7), m.p. 123 °C, sublimable white needles (Scheme 2). The structure of (7) is based on its spectral data; n.m.r. (CDCl$_3$) δ 7·1—7·8 (m, 6H, aromatic) and 2·13 (s, 6H, Me); i.r. (KBr) 780, 790, and 800 cm^{-1} (epoxide); u.v. (MeOH) 224, 270(sh), 280(sh), 288, 297, 304(sh), 314, and 318(sh) nm; m/e 196

(1)   (6)

1:1 *cis, trans* mixture

(7)
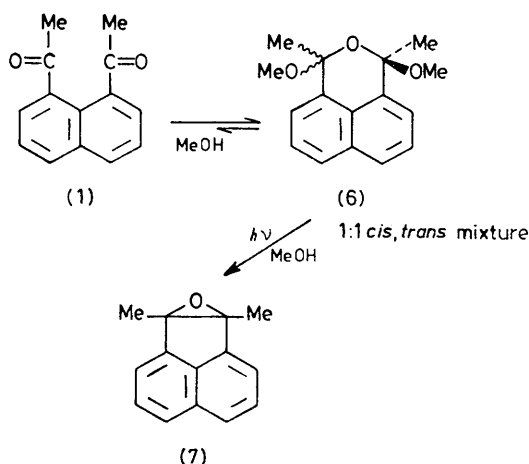
Scheme 2

(M^+). Although (7) is photoreactive,** it can be obtained in *ca.* 70% yield by controlled irradiation of (6). This reaction seems to be more useful for the preparation of (7) than oxidation of 1,2-dimethylacenaphthylene since synthesis of the latter requires many steps.[2]

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‡ The fluorescence of (1) is hardly quenched by saturated oxygen and piperylene (2·5 × 10^{-2} M).

§ Molecular models suggest restricted rotation of the two acetyl groups, but the following facts indicate free rotation; (i) no broadening of the ^{13}C n.m.r. peaks at 204·1 (C=O) and 29·3 (Me) p.p.m. was observed at *ca.* −100 °C; (ii) no appreciable change in the ^{1}H n.m.r. peak at δ 2·65 (Me) was observed after heating of a solution of (1) in benzene in a sealed tube at 80 °C; (iii) samples of (1) prepared from two synthetic precursors were identical [*cis* glycol + NaIO$_4$ and *trans* glycol + Pb(OAc)$_4$] J. K. Stille and R. T. Foster, *J. Org. Chem.*, 1963, **28**, 2703). Thus, we conclude that (1) has a considerably distorted structure.

** The photochemistry of (7) is under investigation.

[1] For previous papers in the series on photochemistry of *peri*-substituted naphthalenes, see K. Honda, A. Yabe, and H. Tanaka, *Bull. Chem. Soc. Japan*, 1975, **48**, 2062.
[2] A. Bosch and R. K. Brown, *Canad. J. Chem.*, 1968, **46**, 715; T. H. Kinstle and P. J. Ihrig, *J. Org. Chem.*, 1970, **35**, 257.