

Photochemical Oxidative Dimerisation of 4-Phenylazo-1-naphthol in Organic Solvents

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The photo-oxygenation of 4-phenylazo-1-naphthol (**1**) gives the dimer 4,4'-bis(phenylazo)-2,2'-binaphthyl-1,1'-diol (**2**) in organic solvents, with a particularly good yield (28%) in chloroform.

The photo-oxygenation of arylazonaphthols in organic solvents has been reported.^{1,2} In particular, Griffiths and Hawkins¹ have reported that the photo-oxygenation of (**1**) in methanol gives 1,4-naphthoquinone (21%) and the phenyldiazonium ion (0.3%). We also have identified the dimer as a major product, with 1,4-naphthoquinone and a trace of phenyldiazonium ion as primary products in the photo-oxygenation of (**1**) in some organic solvents by h.p.l.c. The dimerisation of arylazonaphthols has not previously been

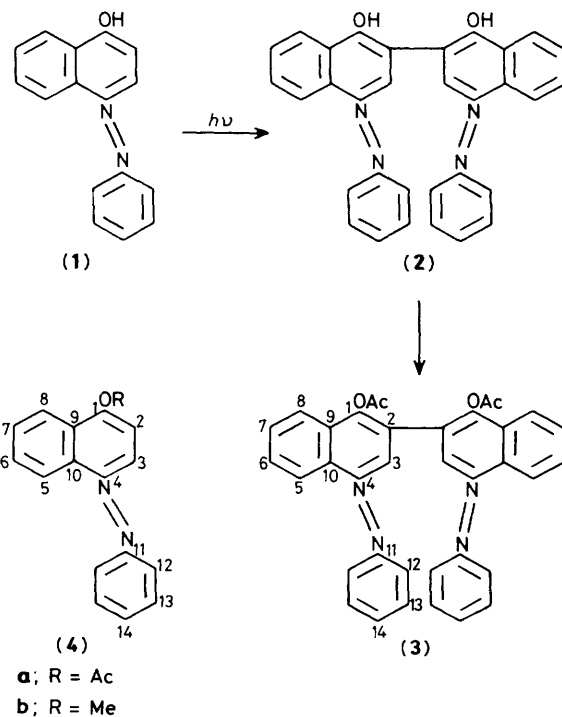


Table 1. Yield of the oxidative dimer (**2**) in various organic solvents.

Solvent	Predominant tautomer ^a	Irradiation time/h	Yield(%) ^b
Methanol	A	25	3.9
Isopropyl alcohol	A	25	1.5
Acetone	A	6	6.3
		25	0.0
Ethyl acetate	A	25	2.3
Benzene	A-H	25	15.9
Dichloromethane	H	25	16.5
		6	5.5
Chloroform	H	25	28.4
		6	12.6

^a A = azo form, H = hydrazone form. ^b Isolated yield.

described. We now report that irradiation of 4-phenylazo-1-naphthol (**1**) (m.p. 210–212 °C)³ in air-saturated organic solvents affords a dimer. Irradiation of (**1**) in air-saturated methanol through a Pyrex filter with a 400 W high-pressure mercury lamp for 25 h at 20 ± 5 °C gave a precipitate which could be easily isolated by filtration, washed with methanol, and recrystallized from dimethylformamide (yield 3.9%, m.p. 250–253 °C) (**2**).⁴ The structure of this photoproduct (**2**) was assigned on the basis of its acetylated derivative, (**3**),^{4†} [m.p. 267–270 °C, $\nu(\text{KBr})$ 3070–40, 1750, 1355, 1225, 1215, 860, 760, 745, and 690 cm^{-1} ; m/z 578(M^+), 536, 494, 389, 283, 105, 77, and 43; $\delta_{\text{C}}(\text{CDCl}_3)$ 128.0, 129.2(C-1 or C-2), 114.5(C-3), 145.7(C-4), 124.0(C-5), 127.4(C-6 and C-7), 123.2(C-8), 127.6(C-9), 132.1(C-10), 153.3(C-11), 123.3(C-12), 129.2(C-13), 131.2(C-14), 168.7(–OCO–), 20.6(–CH₃)]. The elemental and mass spectrometric analysis of (**3**) corresponded to $\text{C}_{36}\text{H}_{26}\text{N}_4\text{O}_4$ i.e. two molecules of 1-acetoxy-4-phenylazonaphthalene (**4a**) (m.p. 126–128 °C) minus two hydrogen atoms. The i.r. spectrum of (**3**) was similar to that of (**4a**) except for the lack of a band at 840 cm^{-1} (KBr, 2 adjacent hydrogens) and the presence of a band at 860 cm^{-1} (KBr, isolated hydrogen). The position of the coupling in (**3**) was elucidated by comparison of its ¹³C n.m.r. spectrum with that of (**4a**).[‡] All the signals in the n.m.r. spectrum of (**3**) compared with those in (**4a**), except for δ_{C} 128.0 and 129.2 in the spectrum of (**3**) which corresponded to C-1 and C-2. These resonances are at higher frequency than that of C-2 in (**4a**) (δ

111.9) therefore we conclude that (**3**) is a dimer joined at the C-2 position.

The photoreactions of (**1**) were examined in various air-saturated solvents. The results are summarized in Table 1, and they show that the dimer (**2**) is formed in higher yield in solvents where the hydrazone form of (**1**) predominates in comparison with solvents in which the azo tautomer predominates.⁵ However irradiation of (**1**) in acetone for a short period (6 h) gives (**2**) in good yield despite the predominance of the azo tautomer (suggesting that hydrogen atom abstraction is important). However (**2**) is not obtained on prolonged irradiation (25 h). No dimeric product was obtained with (**4b**).³ These results suggest that keto–enol tautomerisation of (**1**) plays an important role in this dimerisation reaction.

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† Satisfactory elemental analysis was obtained for (**3**).

‡ ¹³C N.m.r. data for (**4a**); $\delta_{\text{C}}(\text{CDCl}_3)$ 149.0(C-1), 111.9(C-2), 118.2(C-3), 145.6(C-4), 123.9(C-5), 126.9(C-6 and C-7), 121.3(C-8), 127.3(C-9), 132.5(C-10), 153.2(C-11), 123.2(C-12), 129.1(C-13), 131.1(C-14), 169.0(–OCO–), and 21.0(–CH₃).