Photo-induced Dimerization of 1-Naphthoxide Anion: a New Type of Photochemical Reaction

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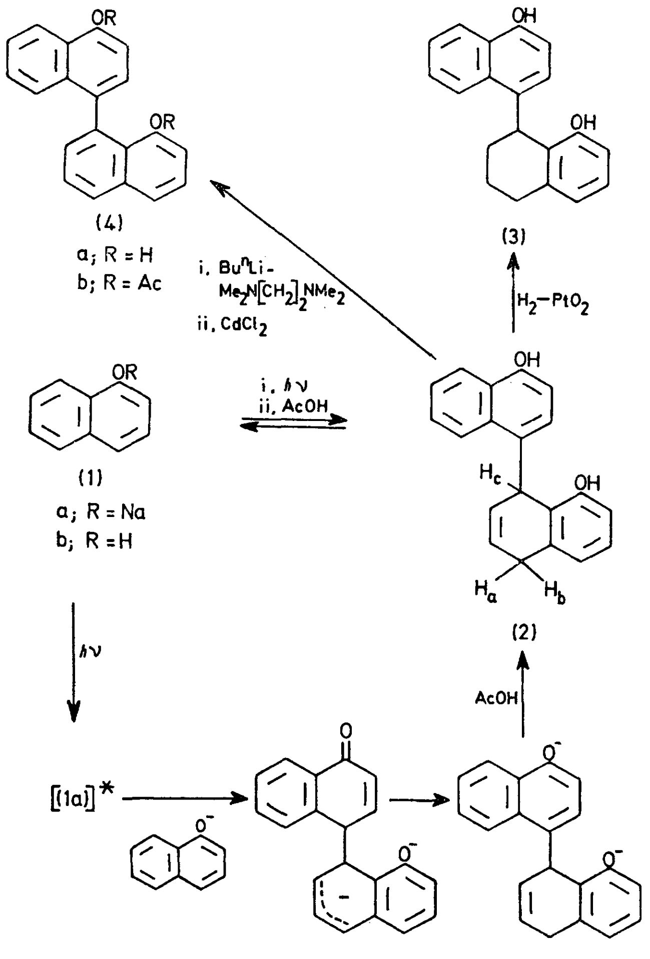
Summary Irradiation of the 1-naphthoxide anion (**1**) gave 5′,8′-dihydro-4,8′-bi-1-naphthol (**2**) probably *via* photo-induced nucleophilic addition.

Although irradiation of phenol gives all five possible *ortho* and *para* C–C and C–O coupled dimers,[1] 1- and 2-naphthols do not undergo photodimerization. We now report that irradiation of 1-naphthoxide anion (**1a**) furnishes a dimer having a 1,4-dihydrobenzene unit probably *via* a photo-induced nucleophilic addition reaction.



Irradiation of (**1a**) in MeOH with a high pressure Hg lamp gave the photodimer (**2**) in 47% yield, after acidification with AcOH followed by chromatographic separation (SiO_2) from recovered (**1b**). On being heated to its decomposition point (184 °C), (**2**) reverted to (**1b**).

^{13}C- and ^{1}H-n.m.r. spectroscopy showed that the substance contained a 1,4-dihydrobenzene structure (J_{ac} and J_{bc} *ca.* 4·5 Hz).[2] Hydrogenation of (**2**) (1 mol. equiv. of H_2, PtO_2) gave a tetralin derivative (**3**) [m.p. 230 °C (decomp.)]. Dehydrogenation[3] afforded an unsymmetrical binaphthol (**4a**) [m.p. 185 °C (decomp.)].

The coupling position in (**4a**) was elucidated by comparison of its ^{1}H-coupled ^{13}C-n.m.r. spectrum† with that of (**1b**).‡ From the long-range ^{13}C–^{1}H coupling pattern [dd, ^3J(C-2–H-4) $7\cdot_2$, ^2J(C-2–H-3) $2\cdot_7$ Hz] of the C-2 signals of (**1b**), one of the two corresponding signals in (**4a**) lacks the 7 Hz coupling due to ^3J(C-2–H-4), thus indicating a substituent at one of the two 4-positions. From the broadened ^2J(C-1–H-2) doublet of doublets [^3J(C-1–H-3) $8\cdot_2$ and ^3J(C-1–H-8) $4\cdot_0$ Hz] of the C-1 signal of (**1b**), the 4 Hz coupling is missing in one of the two corresponding signals in the dimer (**4a**), indicative of a substituent at one of the 8-positions. These observations are compatible with only the 4,8′-bi-1-naphthol structure of the possible binaphthol structures. Additionally, one of the acetyl–methyl signals in the ^{1}H-n.m.r. spectrum of the binaphthol diacetate (**4b**) is unusually shielded (δ 1·12 p.p.m.), which is strong support for the coupling site being the 8- and not the 5--position. This structure (**4a**) indicates that the original product is 5′,8′-dihydro-4,8′-bi-1-naphthol (**2**). The formation of (**2**) can be rationalized by attack of an excited state of (**1a**) on the 8-position of (**1a**) in the ground state. This must be a nucleophilic attack because: (i) the 8-position in the ground state of anion (**1a**) has the largest value of $S_r(N)$ for nucleophilic attack based on Hückel molecular orbital calculations[4] and (ii) the structure of the product is quite different from analogous structures which are possible from the photodimerization of a phenol *via* a phenoxyl radical.

This type of reaction has no precedent. The difference in the photochemical behaviour of the anion (**1a**) from that of the neutral species (**1b**) is remarkable. Sodium phenoxide and 2-naphthoxide, however, were unreactive under the same conditions.

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† ^{1}H-Coupled spectra were obtained using a CFT-20 spectrometer with a 16 k memory using the gated mode over 1202 Hz (digital resolution 0·3 Hz).

‡ To the best of our knowledge this treatment is the first adaptation to the elucidation of the structure of an unknown compound, although several reports have mentioned its possibility; C. Chang, *J. Org. Chem.*, 1976, **41**, 1881, and refs. cited therein.

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[2] R. G. Harvey, D. F. Lindow, and P. W. Rabideau, *Tetrahedron*, 1972, **28**, 2909.
[3] R. G. Harvey and H. Cho, *J. Amer. Chem. Soc.*, 1974, **96**, 2434.
[4] For parameters see L. H. Klemm, J. Shabtai, and D. R. Taylor, *J. Org. Chem.*, 1968, **33**, 1480.