Type II Photoreaction of Epoxynaphthoquinones

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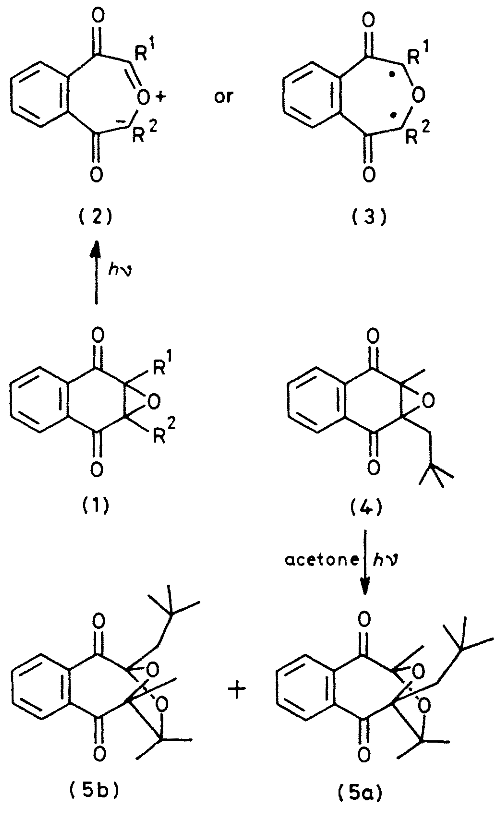
Summary Type II photoreaction of the epoxynaphthoquinone (**6**) proceeds without oxiran ring opening to give the cyclobutanol (**12**) which, on further irradiation, is converted into a new class of polycondensed ring system.



RECENTLY the photochemical generation of the carbonyl ylide (**2**) or 1,3-diradical (**3**) from several epoxynaphthoquinones (**1**) was reported. These products were successfully trapped by olefins,[1] ketones,[2] and aldehydes.[2] We now describe some experiments demonstrating that a type II photoreaction is preferred to the generation of (**2**) or (**3**) and that a type II cyclisation provides an interesting precursor (**12**) for a new class of ring compounds (**11**), (**13**), and (**15**).

After a benzene solution (0·02 M) of (**6a**) had been irradiated† with a 300 W high-pressure Hg lamp for up to 65% conversion, separation of the products by silica gel chromatography gave the cyclobutanol (**12a**) (m.p. 143—144 °C, 25%), the phthiocol (**10a**) (17%), the β-diketone (**13a**) (m.p. 196 °C, 40%), and the β-alkoxy enone (**15a**) (m.p. 155—156 °C, 15%).‡ The structure of (**15a**) was confirmed by reductive acetylation, which yielded (**14a**) in 75% yield. Controlled experiments readily showed that (**12a**) and (**10a**) were initially produced in a 10:1 ratio, and on further irradiation (**12a**) gave (**10a**), (**13a**), and (**15a**) in the ratio 1:6·5:2·5. Similarly (**6b**) afforded (**12b**) (m.p. 198 °C, 51%), (**10a**) (15%), and (**13b**) (m.p. 220—222 °C, 22%), but the corresponding β-alkoxy enone (**15b**) was not obtained. Irradiation of the 2-alkylepoxynaphthoquinones (**6c**) and (**6d**) gave similar results. In these cases, however, the β-diketones (**13c**) and (**13d**) were readily dehydrated on silica gel to give the indenone derivatives

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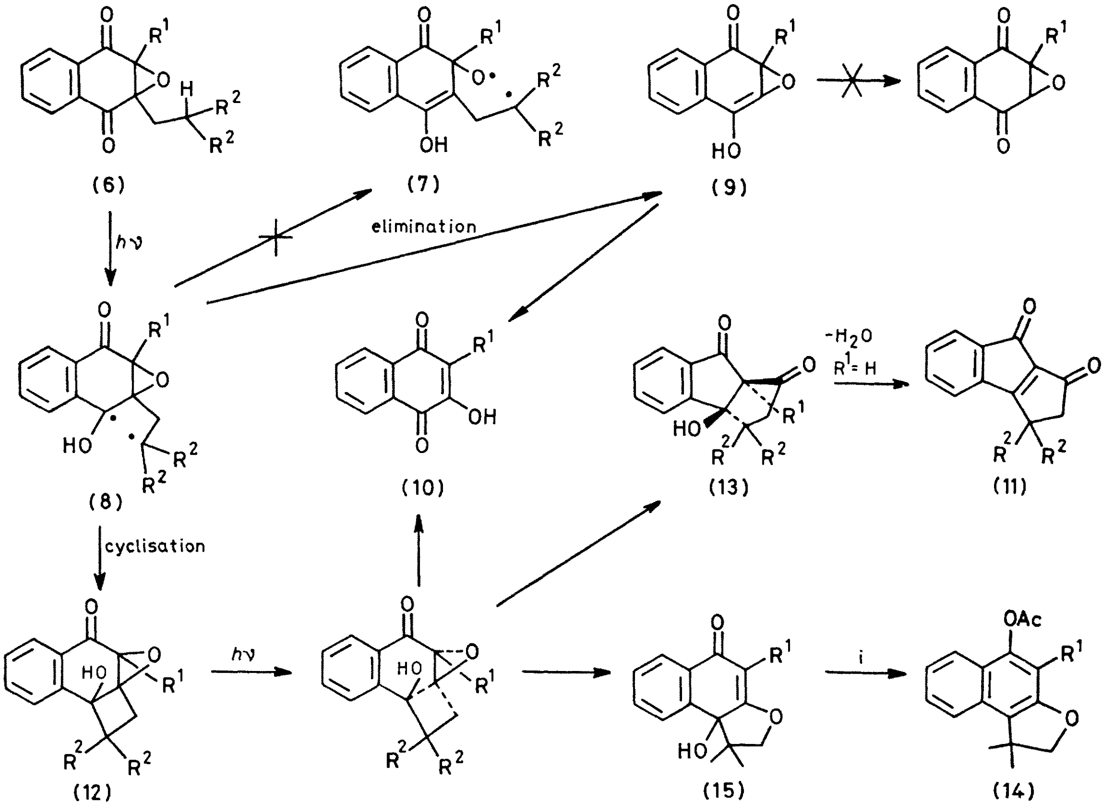
† Irradiation was carried out in a Pyrex vessel under N_2 at room temperature.

‡ All new compounds were fully characterised by appropriate i.r., ^1H and ^{13}C n.m.r., and mass spectra, and elemental analyses.

(**11c**) and (**11d**), respectively, supporting the structure assigned to the β-diketones (**13**). Comparison of the chemical shift due to the methyl protons of (**13b**) (δ 1·36) with that of its acetate (δ 1·36) showed the stereochemistry of the ring junction to be *trans*. While irradiation of (**6a**) in acetone also led to the above-mentioned type II photoreaction, the epoxynaphthoquinone (**4**) which had no γ-hydrogen atom gave two 1,3-dioxolans (**5a**) (m.p. 130—131 °C; 39%) and (**5b**) (m.p. 121—122 °C; 41%).

It is well known that a type II biradical collapses to another biradical and type II elimination is suppressed when one of the radical sites is allylic or conjugated with a three-membered ring.[3] However, type II cyclisation and elimination from (**8**) are apparently faster processes than epoxy carbinyl radical rearrangement to give the radical (**7**). As indicated in the Scheme, type II elimination yields the enol (**9**) as a transient intermediate, which is transformed into (**10**) *via* a 1,4-hydrogen shift; the expected keto–enol tautomerisation was not observed.

Aside from the synthetic utility for the preparation of a new class of polycondensed ring compounds, the photorearrangement of (**12**) is of mechanistic interest in view of the fact that the benzyl group migrates only to an α-carbon with retention of the configuration and the methylene group migrates only to oxygen. To the best of our knowledge, the photorearrangement of an $\alpha\beta$-epoxy ketone to a β-alkoxy enone is unprecedented. A reasonable explanation for the selective migrations may be that the reaction proceeds in such a concerted manner that the migrating groups have to be attached to the back side lobe of the bond to be cleaved.



a; R^1 = Me, R^2 = Me
b; R^1 = Me, R^2 = Ph
c; R^1 = H, R^2 = Me
d; R^1 = H, R^2 = Ph

Scheme. i, Zn, Ac$_2$O

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