Light-induced Isomerisation of a Quinone Epoxide

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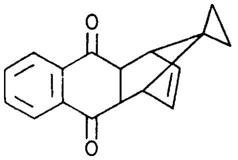
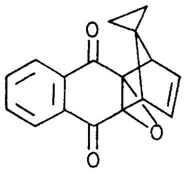
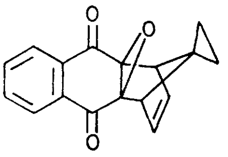
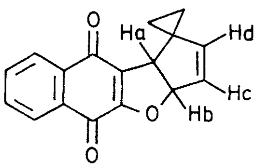
Summary The *endo*-epoxide of the quinonoid derivative of a bicyclo[2,2,1]heptadiene isomerises either photochemically or on heating it in alcohol to a furanonaphthoquinone.

TREATMENT of the naphthoquinone–spirocyclopentadiene adduct (I) with methanolic sodium hydroxide in the presence of air afforded a mixture of the two isomeric epoxides (II) and (III) as major products, together with a third isomer in low yield (*vide infra*). One of the epoxides, m.p. 169°, was isolated by successive recrystallisation and assigned the *exo*-epoxide structure (III) on the basis of changes in the chemical shifts of protons in both this compound and the epoxide mixture on addition of the reagent Eu(fod)$_3$.


(I)


(II)


(III)



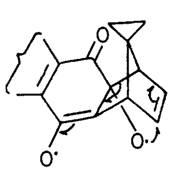
(IV)

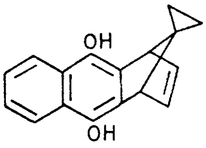
Exposure of the epoxide mixture in benzene solution to sunlight effected isomerisation of the *endo*-component in 90% yield to the quinone (IV), m.p. 204°, while leaving (III) unchanged. The ^{1}H n.m.r. spectrum (CDCl$_3$) of (IV) included signals at τ 6·02 (d, J 9 Hz, Ha), 3·78 (dd, J 9 and 2·5 Hz, Hb), 4·10 (dd, J 2·5 and 5·5 Hz, Hc), and 4·38 (d, J 5·5 Hz, Hd). Pure (III), when similarly irradiated, remained unchanged.

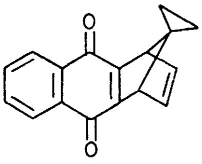
The third product obtained from the reaction of (I) with methanolic base was shown to be identical with the quinone (IV). Its presence must result from the action of methanol on the *endo* epoxide (II) since heating the epoxide mixture in either methanol or ethanol in the dark converts (II) [but not (III)] into (IV) in high yield.

Although other possibilities are not excluded, a reasonable mechanism for the photorearrangement (II) → (IV) involves ring opening of the epoxide ring of the $\alpha\beta$-epoxyketone to give a diradical[1] which could rearrange as indicated in the part structure (V). For the alcohol-induced reaction, nucleophilic ring opening of the epoxide followed by a related ionic rearrangement would give (IV).

That the formation of the epoxide mixture from adduct (I) arises from initial enolisation to the corresponding quinol (VI) is supported by the fact that (VI) gave rise to the epoxide mixture on reaction with methanolic sodium hydroxide in air. The quinone (VII) under these conditions did not react, but gave the epoxides on treatment with alkaline hydrogen peroxide. The quinol (VI) was obtained from (I) with potassium t-butoxide in tetrahydrofuran under nitrogen, and was oxidised to (VII) with silver oxide. The epoxidation of (VI) is presumably of a type already investigated by Hewgill.[2]


(V)


(VI)


(VII)

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[1] See *e.g.* O. Jeger and K. Schaffner, *Pure Appl. Chem.*, 1970, **21**, 247.

[2] F. R. Hewgill and S. L. Lee, *J. Chem. Soc.* (*C*), 1968, 1549.