The Photoisomerisation of α-Tropolone

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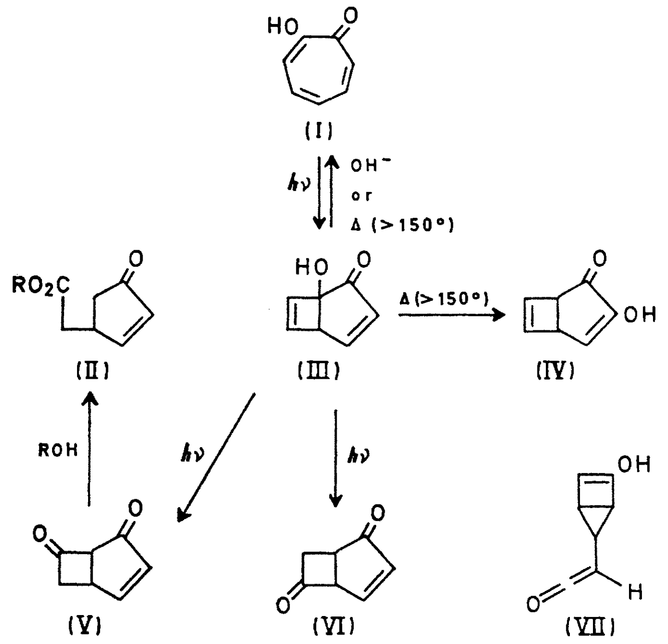
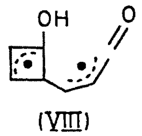
Summary α-Tropolone photoisomerises in hexane *via* 5-hydroxybicyclo[3,2,0]hepta-2,6-dien-4-one (III) to a mixture of bicyclo[3,2,0]hept-2-ene-4,6-dione and bicyclo[3,2,0]hept-2-ene-4,7-dione; the hydroxy-ketone (III) is also formed when α-tropolone is irradiated in water and in methanol.

ALTHOUGH detailed studies of the photochemistry of a number of troponoid compounds have been reported, the literature on α-tropolone (I) itself is apparently confined to the demonstration that irradiation in water and ethanol gives, respectively, 4-oxocyclopent-2-enylacetic acid (II; R=H) and the corresponding ethyl ester (II; R=Et).[1] We report here our studies of the photochemistry of α-tropolone in water, methanol, and hexane.

Irradiation of α-tropolone (I) in water (*ca.* 0·02M, medium-pressure mercury-arc lamp, Pyrex filter, room temperature) gave two major products, the keto-acid (II; R=H) and 5-hydroxybicyclo[3,2,0]hepta-2,6-dien-4-one (III), the ratio of (II; R=H) to (III) increasing as irradiation was continued. The acid (II; R=H)[1] and the hydroxy-ketone (III) (b.p. 90°/1 mm) could both be isolated in satisfactory yields. The hydroxy-ketone (III) reverted rapidly to α-tropolone upon treatment with dilute base (non-photochemically), and also underwent thermal isomerisation above 150° to a mixture of α-tropolone and 3-hydroxybicyclo[3,2,0]hepta-2,6-dien-4-one (IV).





(VIII)

Analogously, the irradiation of (I) in methanol gave (III) and, subsequently, the previously described[1,2] methyl ester (II; R=Me).

In hexane, the irradiation of (I) gave initially (III), which then photoisomerised to a 6:1 mixture of bicyclo[3,2,0]-hept-2-ene-4,6-dione (V) and bicyclo[3,2,0]hept-2-ene-4,7-dione (VI). Pure samples of (V) and (VI) could be isolated by g.l.c. The β-diketone (V) showed the expected high reactivity to protic solvents, giving (II; R=H) and (II; R=Me) with water and methanol, respectively. The isomeric diketone (VI) decomposed more slowly in methanol to give a mixture of three as yet unidentified products. The final monomeric product from the irradiation in hexane was phenol.

By analogy with the photoisomerisation of the methyl ether of (III) to a bicyclopentenylketen at low temperatures,[3] the diketone (V) probably arises *via* the keten (VII).† Ketens have been detected as intermediates in several recent studies and shown to rearrange thermally faster than they react with protic solvents;[4] and consequently it seems not unreasonable that (VII) could be the precursor of (V) even in water and methanol. Thus, it is very likely that the compounds (II) obtained in these solvents are formed by the following sequence:

$$(\mathrm{I}) \xrightarrow{h\nu} (\mathrm{III}) \xrightarrow{h\nu} (\mathrm{VII}) \xrightarrow{\Delta} (\mathrm{V}) \xrightarrow{\mathrm{ROH}} (\mathrm{II})$$

The dione (VI) may be produced from (III) either by a symmetry-allowed photochemical *supra,supra*-[1,3] sigmatropic shift[5] or by the equivalent biradical process *via* (VIII), followed by ketonisation. The latter possibility appears more attractive because the biradical (VIII) could serve as a common precursor of both (VI) and (VII). Rearrangements similar to the conversion of (III) into the enol of (VI) have recently been observed in the photochemistry of purpurogallin tetramethyl ether[6] and α-tropolone methyl ether.[7]

The enolic α-diketone (IV) was not produced photochemically from (I) or (III). (Contrast the cases of 5-phenyl-[8] and 5-chloro-α-tropolone.[9]) The thermal isomerisation of (III) to (IV) probably occurs by a Cope rearrangement, as in the case of the corresponding methyl ether.[10]

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† O. L. Chapman and M. A. Hems have also isolated the hydroxy-ketone (III) in room-temperature photolyses of α-tropolone. They have, further, obtained spectroscopic evidence (ν_{max} 2112 cm^{-1}) for the formation of the keten (VII) when the hydroxy-ketone (III) is irradiated at 77°K. Upon warming, the absorption at 2112 cm^{-1} disappears and is replaced by bands at 1783 (cyclobutanone C=O) and 1707 cm^{-1} (cyclopentenone C=O). We thank Professor Chapman and Dr. Hems for this unpublished information.

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