The Configuration of Aurones and Aurone Epoxides[1]

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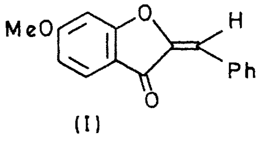
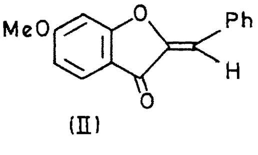
Summary Configurations are assigned to aurones and their epoxides on the basis of chemical and n.m.r. evidence.

IN order to elucidate the stereochemistry of aurone epoxide derivatives[2,3] a study was undertaken to determine the configurations of aurones and their epoxides.

Two geometrical isomers may result from the condensation of a coumaran-3-one and an aromatic aldehyde since the β-aryl group in the resulting aurone (2-arylidene-coumaran-3-one) may be either *cis* (as in I) or *trans* (as in II) to the carbonyl group. In all cases reported to date for the preparation of aurones by this method only one isomer was obtained. In the present work it was found that u.v. irradiation of 6-methoxyaurone, prepared by condensation of 6-methoxycoumaran-3-one with benzaldehyde, gave its geometrical isomer. The isomerisation was carried out in benzene solution by means of a high-pressure mercury-vapour lamp using a Pyrex filter to give a *ca.* 1 : 1 equilibrium mixture of the *cis*- and *trans*-isomers which was separated on an alumina column.



(I)

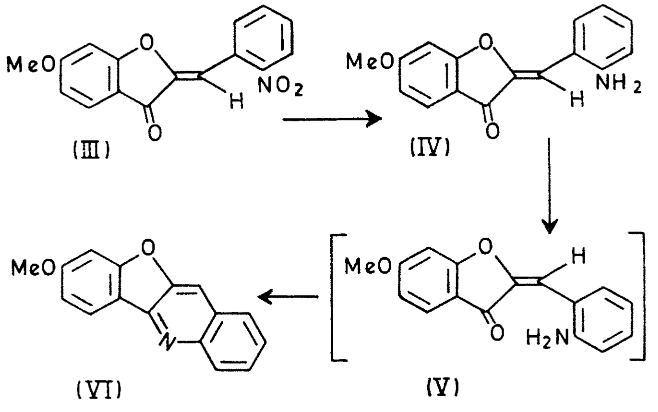


(II)

It was possible, in the case of the geometrical isomers of certain $\alpha\beta$-unsaturated ketones,[4] to make configurational assignments on the basis of the chemical shifts of the β-protons. In the *trans*-isomers, due to the deshielding influence of the carbonyl group, the β-proton gave a signal at considerably lower field than the signal of the corresponding proton in the *cis*-isomer. This method of assignment was not applicable to the isomers of 6-methoxyaurone because of the close values of the β-proton chemical shifts which were τ 3·20 for the synthetic product, and τ 3·14 for the product of irradiation. However, the lower τ-value (1·85) (deshielding by the carbonyl group) of the 2′,6′-protons in the latter, compared with a value of τ 2·10 in the former, indicated that this compound was the *cis*-(I) and the synthetic product was the *trans*-isomer (II). The *cis*-isomer, which was a yellow-green compound, m.p. 136—137°, was quantitatively isomerised to the *trans*-isomer on treatment with hot ethanolic sodium hydroxide.

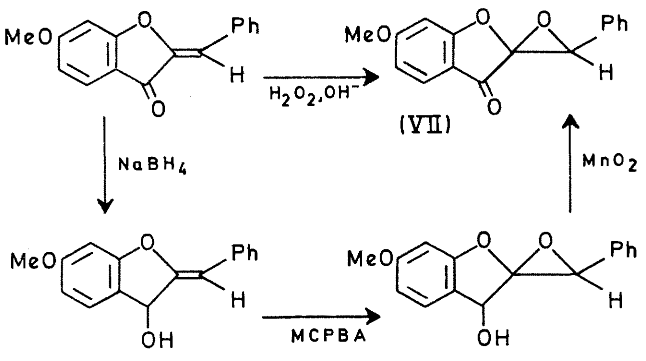
The assigned geometrical structures were confirmed by a chemical method outlined below (Scheme 1). Aurone (III) on reduction with stannous chloride and hydrochloric acid gave the 2′-aminoaurone (IV). The latter on irradiation with u.v. light gave the quinoline (VI), presumably via the *cis*-aminoaurone (V), which on formation cyclised immediately. Isolation of the quinoline (VI) rather than *cis*-aminoaurone (V) indicated that the aminoaurone (IV) and consequently the nitroaurone (III) were both *trans*-isomers. The reactions described are similar to a series of reactions carried out by Bell and Cromwell to define the stereochemistry of benzylidene-tetralones.[5]

Both *cis*- and *trans*-6-methoxyaurones on treatment with alkaline hydrogen peroxide afforded the same aurone epoxide (VII). That this epoxide had the *trans*-configuration was shown when it was found to be identical with the epoxide resulting from the stereospecific synthesis[6] using *m*-chloroperbenzoic acid as outlined in Scheme 2. When *cis*-6-methoxyaurone (I) was the starting material *cis*-6-methoxyaurone epoxide was obtained by a similar sequence of reactions involving the peracid epoxidation.



SCHEME 1

The double bond of $\alpha\beta$-unsaturated carbonyl compounds is generally unreactive[7] towards the electrophilic[8] peracid reagent and reaction at the carbonyl group (Baeyer–Villiger reaction) predominates.[9] When it was found that 3-benzylideneflavanones were epoxidised directly with *m*-chloroperbenzoic acid,[10] the method was applied to aurones and found to be equally successful. Thus both *cis*- and *trans*-aurone (I and II) on reaction with this reagent gave *cis*- and *trans*-6-methoxyaurone epoxides respectively.



SCHEME 2. MCPBA = *m*-chloroperbenzoic acid.

All new compounds gave elemental analyses and spectroscopic data consistent with the structures shown.

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[4] See *e.g.* A. Hassner and T. C. Mead, *Tetrahedron*, 1964, **20**, 2201; D. N. Kevill, E. D. Weiler, and N. H. Cromwell, *J. Org. Chem.*, 1964, **29**, 1276.

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[7] D. Swern, *Chem. Rev.*, 1949, **45**, 1.

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