Oxidative Cyclisation of 2′-Hydroxychalcones to Aurones using Mercury(II) Acetate in Dimethyl Sulphoxide

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Summary In dimethyl sulphoxide (DMSO) solution, 2′-hydroxychalcones react stereospecifically with mercury(II) acetate to give cyclic oxymercuration adducts (coumaranones) which are converted cleanly into (*Z*)-aurones by an *E*2-type oxidative-demercuration process.

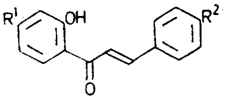
ALTHOUGH a variety of reagents will effect oxidation of 2′-hydroxychalcones (**1**),[1] these reactions usually afford mixtures of products such as those of oxidative cyclisation, *e.g.* flavones,[1a,b] isoflavones, [1c,d] and aurones.[1e,f] We now report a novel procedure by which the chalcones (**1**) can be converted into (*Z*)-aurones (**4**) as the sole organic products.

In an extension of our work on the asymmetric cyclisation of *o*-allylphenols using an oxymercuration reaction,[2] we found that treatment of the chalcone (**1a**) with mercury(II) acetate suspended in CH_2Cl_2–tetrahydrofuran (30 : 1) containing a trace of an acid catalyst (*e.g.* aq. $HClO_4$) gave a mixture[3] of the *cis*- and *trans*-isomers of the oxymercurial adduct (2a) which underwent reductive demercuration ($NaBH_4$–HO^-) to the flavanone (**2b**). In marked contrast, equimolar amounts of (**1a**) and mercury(II) acetate reacted slowly in acid-free DMSO solution at room temperature giving mercury(I) acetate (precipitated), the adduct (**3a**) (a *single* diastereoisomer), and the aurone (**4a**). The formation of (**3a**) is noteworthy in that addition of ArO–HgOAc to the carbon–carbon double bond has occurred exclusively in an anti-Markovnikov sense;[4] no trace of isomeric six-membered ring adducts, *e.g.* (**2a**), was found in this or later experiments.

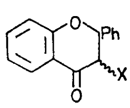
The adduct (3a), which was characterised by conversion into the bromide (**3b**), gave the coumaranone (**3c**) on borohydride reduction and the aurone (**4a**) on treatment with mercury(II) acetate in DMSO. This latter observation suggested that (3a) is an intermediate in the conversion of (**1a**) into (**4a**) and this was confirmed by spectroscopic (^1H n.m.r., u.v.) analysis of the course of the chalcone-mercury(II) acetate reaction.

From a study of the reactions of several ring-substituted chalcones (**1b**—**e**), it appears that the transformation (**1**) → (**3**) → (**4**) is of general synthetic use although the reactivity of the chalcone and the proportions of (**3**) and (**4**) formed vary considerably. Thus, quantitative conversion of (**1b**) into (**4b**) was achieved using a 2 : 1 molar excess of mercury(II) acetate over chalcone. At the other extreme, (**1c**) gave mainly the adduct (**3d**) which could be converted into the aurone (**4c**) (*ca.* 54% overall yield), however, by further treatment in DMSO with an insoluble base, *e.g.* CaO.

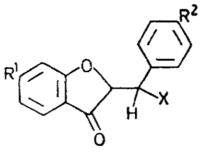
The following results were obtained from an investigation of the kinetics of the oxidation. (i) The rates of both the oxymercuration [(**1**) → (**3**)] and demercuration [(**3**) → (**4**)] steps are enhanced by an electron-withdrawing *para*-substituent in the styryl ring of the chalcone ($R^2 = NO_2 > Cl > H > OMe$; $\rho \leqslant ca. + 0{\cdot}9$). (ii) A *para*-methoxy substituent in the aroyl ring (**1c**) enhances the rate of cyclisation but retards the demercuration of the resulting adduct (**3d**). (iii) The conversion of (**3a**) into (**4a**) is most rapid in the *absence* of mercury(II) acetate or acids (*e.g.* HOAc) and is slower in alcoholic solutions than in DMSO.



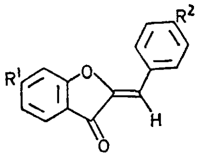
(1) a; $R^1 = R^2 = H$
b; $R^1 = H, R^2 = NO_2$
c; $R^1 = OMe, R^2 = H$
d; $R^1 = H, R^2 = OMe$
e; $R^1 = H, R^2 = Cl$



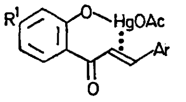
(2) a; X = HgOAc
b; X = H



(3) a; $R^1 = R^2 = H$, X = HgOAc
b; $R^1 = R^2 = H$, X = HgBr
c; $R^1 = R^2 = X = H$
d; $R^1 = OMe, R^2 = H$, X = HgOAc



(4) a; $R^1 = R^2 = H$
b; $R^1 = H, R^2 = NO_2$
c; $R^1 = OMe, R^2 = H$



(5)

The substituent and medium effects on the decomposition of the oxymercurials (**3**) indicate that the process is of the *E*2-type with ionised acetate functioning as internal base. The effect of substituents on the rate of oxymercuration of (**1**) was unexpected[3] and is more in harmony with a mechanism involving formation and cyclisation of an aryloxymercury(II) acetate (**5**) than with a 'normal' electrophilic-addition pathway, *i.e.* activation of the alkene bond by $(HgOAc)^+$ and 2′-hydroxy participation. It has not yet been established whether the addition of ArO–HgOAc to the double bond is stereospecifically *cis* or *trans*. If the (*Z*)-aurone products (**4**) result from antiperiplanar elimination, however, the precursors (**3**) must be formed by a *cis*-addition mechanism, in accord with an intermediate of the type (**5**).

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