Thermal Rearrangement of *o-cis*-Butadienylphenol to 2-Methyl-2*H*-1-benzopyran

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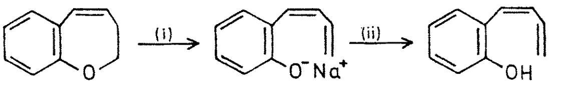
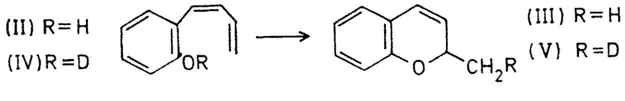
Summary Evidence is presented which suggests that the isomerization of *o-cis*-butadienylphenols to benzopyrans proceeds *via* 2-allylidenecyclohexadienones.

WE have suggested a mechanism for the cyclization of butadienylphenols[1] and have endeavoured to relate this reaction to the thermal and photochemical interconversions of benzopyrans and 2-allylidenecyclohexadienones.[2] We have found that 2,3-dihydro-1-benzoxepin (I) can be prepared in high yields,[3] and that treatment of (I) with an excess of sodium methoxide in dimethylformamide (DMF) (110°, 10 hr.) gave pure *o-cis*-butadienylphenol (II) in high yield. The interest in these reactions,[4] and the suggestion of a mechanism by H.-J. Hansen[5] prompt us to communicate our results.



SCHEME 1. Reagents (i) NaOMe–DMF, (ii) H_3O.

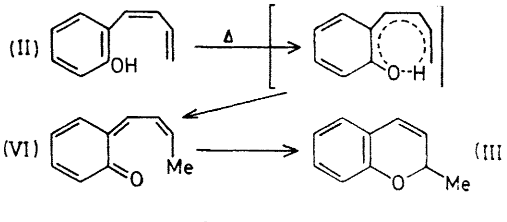
The *o*-butadienylphenol (II) was quantitatively isomerized into 2-methyl-2*H*-1-benzopyran (III) by heating in DMF (110°, 24 hr.). Kinetic investigations show that the reaction is faster in less polar solvents and that the rate is unaffected by catalytic amounts of acid or base. The first-order rate constants (n.m.r., 68°) in $(CD_3)_2SO$, C_2D_5OD, and C_6D_6 are 1·36, 10·4, and 118 × 10^{-6} sec.$^{-1}$, respectively: $\Delta H^\ddagger$ 23 kcal./mole and $\Delta S^\ddagger$ −17 e.u. [$(CD_3)_2SO$].



SCHEME 2.

Only the monodeuteriated benzopyran (V) was formed on heating the *O*-deuteriated butadienylphenol (IV) in $(CD_3)_2SO$, C_6D_6, and CH_3OD. The result in the last solvent indicates that the hydrogen-transfer step is not reversible. High-dilution i.r. spectra reveal intramolecular hydrogen bonding of the phenol to the terminal double bond.

We suggest the following mechanism for the conversion of (II) into (III): a [1,7]-sigmatropic shift of the phenolic hydrogen in (II) to give (VI),[6] which rapidly cyclizes to (III) under the reaction conditions. A one-step mechanism where the -OH adds directly to the terminal double-bond, without involving the rest of the π-system, seems unlikely since *o*-allylphenols do not readily undergo a similar reaction.[7]



SCHEME 3.

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[6] This tautomerization is presumably antarafacial (R. B. Woodward and R. Hoffmann, *Accounts. Chem. Res.*, 1968, **1**, 17), but the exact conformation of the transition state and resulting stereochemistry of (VI) are unknown.

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