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ELECTROCHEMICAL TRANSFORMATIONS OF 2`-HYDROXYCHALCONES INTO FLAVANOIDS[1]

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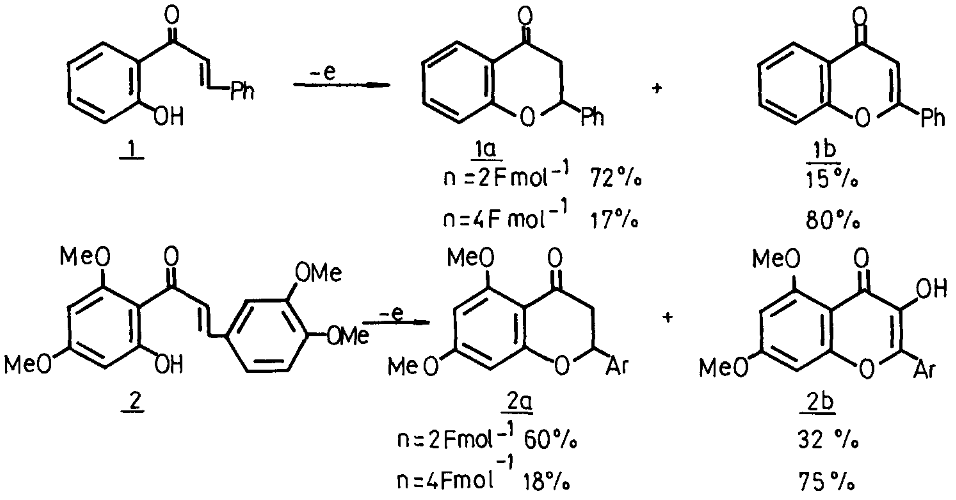
Abstract: 2`-Hydroxychalcones are cyclized to flavanones, and flavone, or flavonol, by electrochemically generated tris-(4-bromophenyl)amine cation radical as homogeneous electron-transfer agent.

Substituted 2`-hydroxychalcones are widely distributed in plants[2] and they also serve as biosynthetic precursors to all the other classes of flavanoid and isoflavanoid pigments[3]. The equilibrium between isomeric flavanones and 2`-hydroxychalcones raises the question of the flavanones as true intermediates in flavanoid biosynthesis[4]. The chemical oxidation of 2`-hydroxychalcones leading to the various flavanoid compounds have been effected by several oxidants[5-9].

In view of the biomimetic importance and preparative utility we have investigated the oxidation of 2`-hydroxychalcones by electrochemically generated tris-(4-bromophenyl)amine cation radical as homogeneous electron-transfer agent. The oxidation of 2`-hydroxychalcones 1 or 2 were performed in divided cell by controlled potential electrolysis at carbon felt anode. The yields of flavanones, 1a and 2a, and flavone, 1b, or flavonol, 2b, are dependent upon the charge passed, as indicated in the scheme.

In a typical procedure, 2`-hydroxychalcone (o,4 g) and tris-(4-bromophenyl)amine (o,o5 g) were dissolved in 1oo ml of CH_3OH-CH_2Cl_2(3:1) - o.2 M $LiClO_4$ solution. The anodic potential was maintained at 1.2 V vs. SCE and the electrolysis was continued until 2 or 4 F mol^{-1} were transfered[1o]. The solution was evaporated to a volume of about 1o ml and 1oo ml of water was added. The mixture was extracted with chloroform and after evaporation of solvent the residue was subjected to column chromatography over column of silica gel using benzene-ethyl acetate-petroleum ether (3:1-1) mixture as an eluant[11].

Our results show that the transformation of 2`-hydroxychalcones, mediated by electrochemically generated tris-(4-bromophenyl)amine cation radical occurs through flavanone as an intermediate. The mechanism, the influence of the substituents on the ring closure and synthetic utility is now under further investigation.



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10. During controlled potential electrolysis an electronic integrator was used to record the quantity of electricity passed.
11. The first elution afforded the unreacted 2`-hydroxychalcone, the second the flavanone and the third flavone 1b or flavonol 2b. The structures of all products are confirmed by comparison of their m.p.and spectroscopic data with authentic samples.

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