

ELECTROCHEMICAL SYNTHESIS OF HETEROCYCLIC COMPOUNDS-IV.¹ SYNTHESIS WITH NASCENT QUINONES

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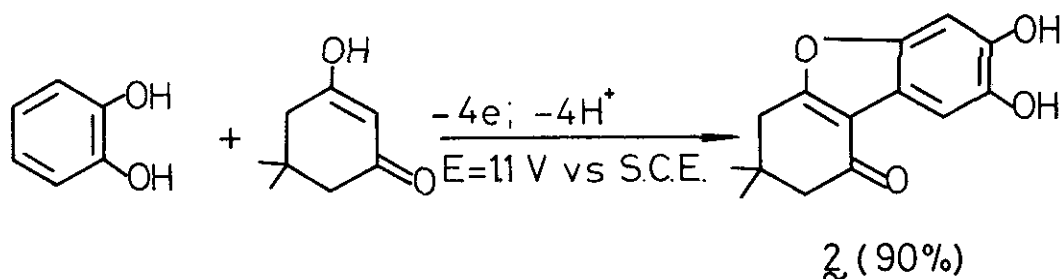
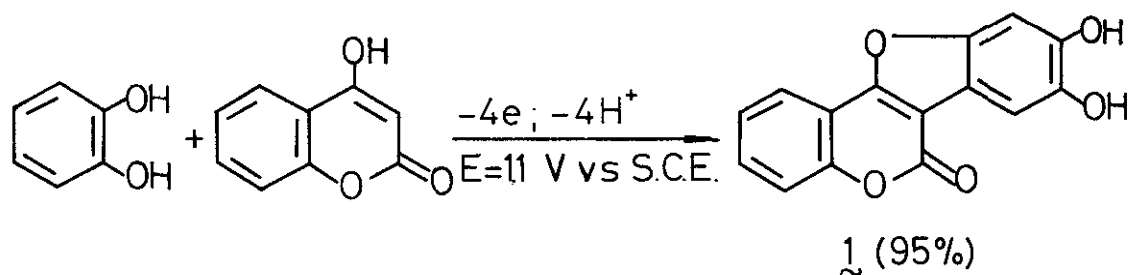
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Many biosyntheses are known to pass through quinoid intermediates. The literature on the chemical and enzymatic oxidation of phenolic compounds has been summarised in several books and reviews²⁻⁶.

The wide range of possible syntheses with nascent quinones in the presence of a nucleophilic reagent has been reviewed⁷. The electrochemical oxidation of the hydroquinones and catecholes was described in review papers^{8,9}.

In view of the great biosynthetic importance and preparative utility of the formation of o-quinones, we have investigated the anodic oxidations of the catechole in the presence of the 4-hydroxycoumarin and dimedone as a nucleophiles. We now wish to report the new electrochemical method for the synthesis of the 11,12-dihydroxycoumestan, **1**, and dihydroxybenzofuran derivative, **2**, which were obtained in high yield, according to the scheme.



Although the method for this conversion is known¹⁰, the electrochemical synthesis described here provides a convenient preparative route

to the corresponding heterocyclic products 1 and 2. Both electrochemical syntheses were carried out in an undivided cell at a graphite anode and Pt-cathode by electrolysis at controlled potential. The compound 1 had correct elemental analyses with m.p. 308-10°dec. (lit.¹⁰ m.p. 310°dec.): IR (KBr): 3350, 1700, 1640, 1470, 1350, 1270, 1240, 1200, 1085 cm⁻¹. MS, m/e: 268, 250, 240, 222, 212, 194, 178, 147, 134, 120, 92. The compound 2 had correct elemental analyses and showed m.p. 280°dec. (lit.⁷ 280°dec.). IR (KBr): 3470, 2950, 1650, 1580, 1295, 1150, 1110, 1050, cm⁻¹. MS, m/e: 246, 238, 222, 208, 192, 190, 178, 162, 152, 119, 103, 89, 76

In a typical procedure, catechol (0.002 mole) and 4-hydroxycoumarin or dimedone (0.002 mole) are dissolved in 100 ml of 0.15 M CH₃COONa water solution. The anodic potential was maintained at 1.1 V vs. S.C.E. with initial currents generally 400-500 mA. The electrolysis was discontinued until 4 electrons/catechol were transferred¹¹. The solution was left in the refrigerator after electrolysis for one hour. The precipitated solid was collected by filtration.

References

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11. During controlled potential electrolyses an electronic integrator was used to record the quantity of electricity passed.