

ACID DEGRADATION STUDIES OF 2-AROYL-3(2H)-BENZOFURANONES AND 3-PHENYL-4-HYDROXY COUMARINS

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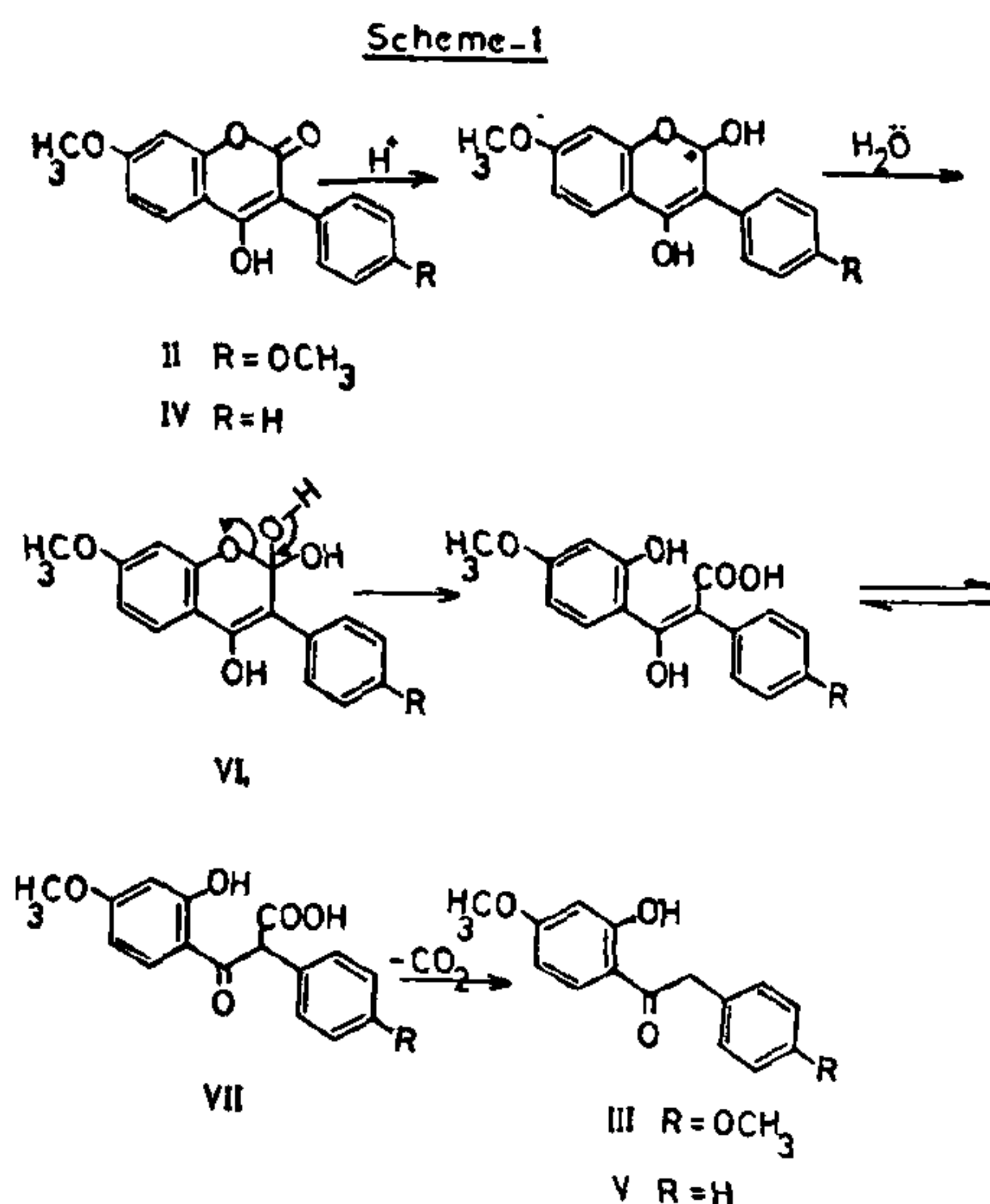
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ABSTRACT

In an attempted acid-catalysed rearrangement of 2-aryl-3(2H)-benzofuranones, the compounds have been found to cleave to yield 3(2H)-benzofuranones and aryl carboxylic acids. 3-Phenyl-4-hydroxy-coumarins, too, have been found to be unstable to acid treatment and degrade readily to phenyl benzyl ketones. Mechanisms for the above degradations are discussed.

In an attempted acid catalysed rearrangement of 2-aryl-3(2H)-benzofuranones to 3-phenyl-4-hydroxy coumarins, 6-methoxy-2-(4-methoxybenzoyl)-3(2H)-benzofuranone¹ (I) was refluxed with aqueous ethanolic sulphuric acid (40%). The product was a mixture (on TLC) which on careful purification yielded two compounds A and B. Compound A, m.p. 120° showed carbonyl at 1700 cm⁻¹ indicating its 3(2H)-benzofuranone nature; NMR (CDCl₃): δ 3.94 (s, 3H, -OCH₃); 4.67 (s, 2H, -O-CH₂-C=), 6.53-6.82

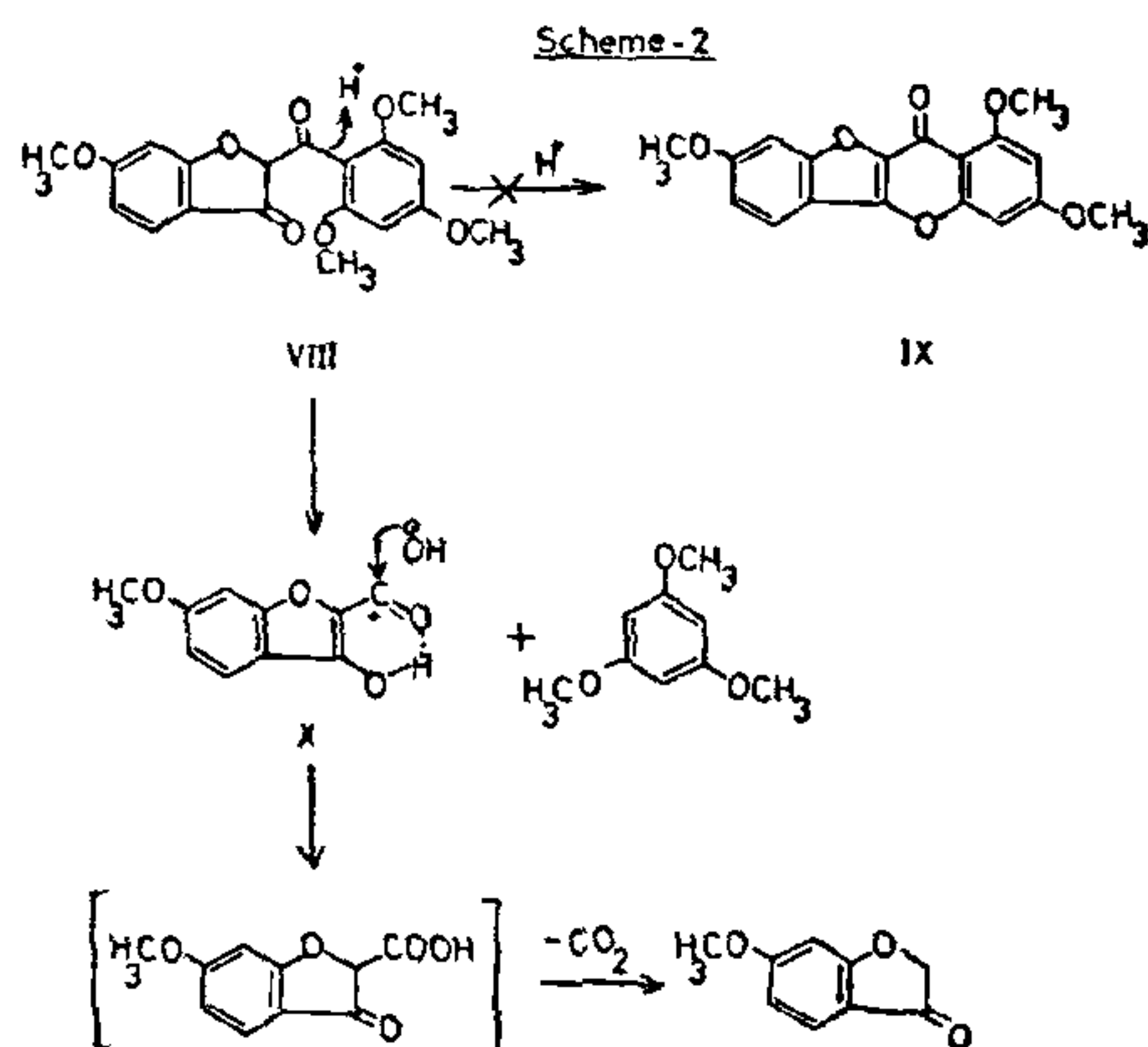
(2H, H-5 and H-7); 7.63 (d, 1H, J=8Hz, H-4), revealed it to be 6-methoxy-3(2H)-benzofuranone, identity of which was confirmed by comparison with an authentic sample². Compound B, m.p. 180°, on a similar study was found to be 4-methoxybenzoic acid. Modification of the reaction conditions failed to show any substantial formation of the desired products. It was then considered that 3-phenyl-4-hydroxy coumarins might be unstable under the reaction conditions and may cleave to give rise to other reaction products. 7, 4'-Dimethoxy-3-phenyl-4-hydroxycoumarin³ (II) was next refluxed with aqueous ethanolic sulphuric acid (40%) and the progress of the reaction studied on TLC. After 30 min, another spot (higher R_f) appeared. The reaction was continued till original spot disappeared (22 hr). The product (UV, IR and NMR) revealed itself to be identical with 2-hydroxy-4-methoxyphenyl 4-methoxybenzyl ketone⁴ (III). This acid cleavage of 3-phenyl-4-hydroxycoumarins has been found to be of a general nature, as 7-methoxy-3-phenyl-4-hydroxy coumarin³ (IV) on similar treatment gave 2-hydroxy-4-methoxyphenyl benzyl ketone⁴ (V). Incidentally this is the first report of the acid degradation of 3-phenyl-4-hydroxy coumarins, which is likely to have been initiated by the protonation of the carbonyl at position 2 followed by an attack of a water molecule to give an intermediate (VI) (Scheme 1). Ring opening followed by decarboxylation of the resulting β keto acid derivative (VII), would then give rise to phenyl benzyl ketone.



A search of literature showed that Bryant and Haslam⁵ had reported the cleavage of 6-methoxy-2-(2, 4, 6-trimethoxy benzoyl)-3(2H)-benzofuranone (VIII) to 6-methoxy-3(2H)-benzofuranone and 1, 3, 5-trimethoxybenzene on treatment with aluminium chloride-dioxan or hydrochloric acid-acetic acid during their attempted synthesis of chromono-(2', 3': 3, 2)-benzofuran (IX) according to Scheme 2.

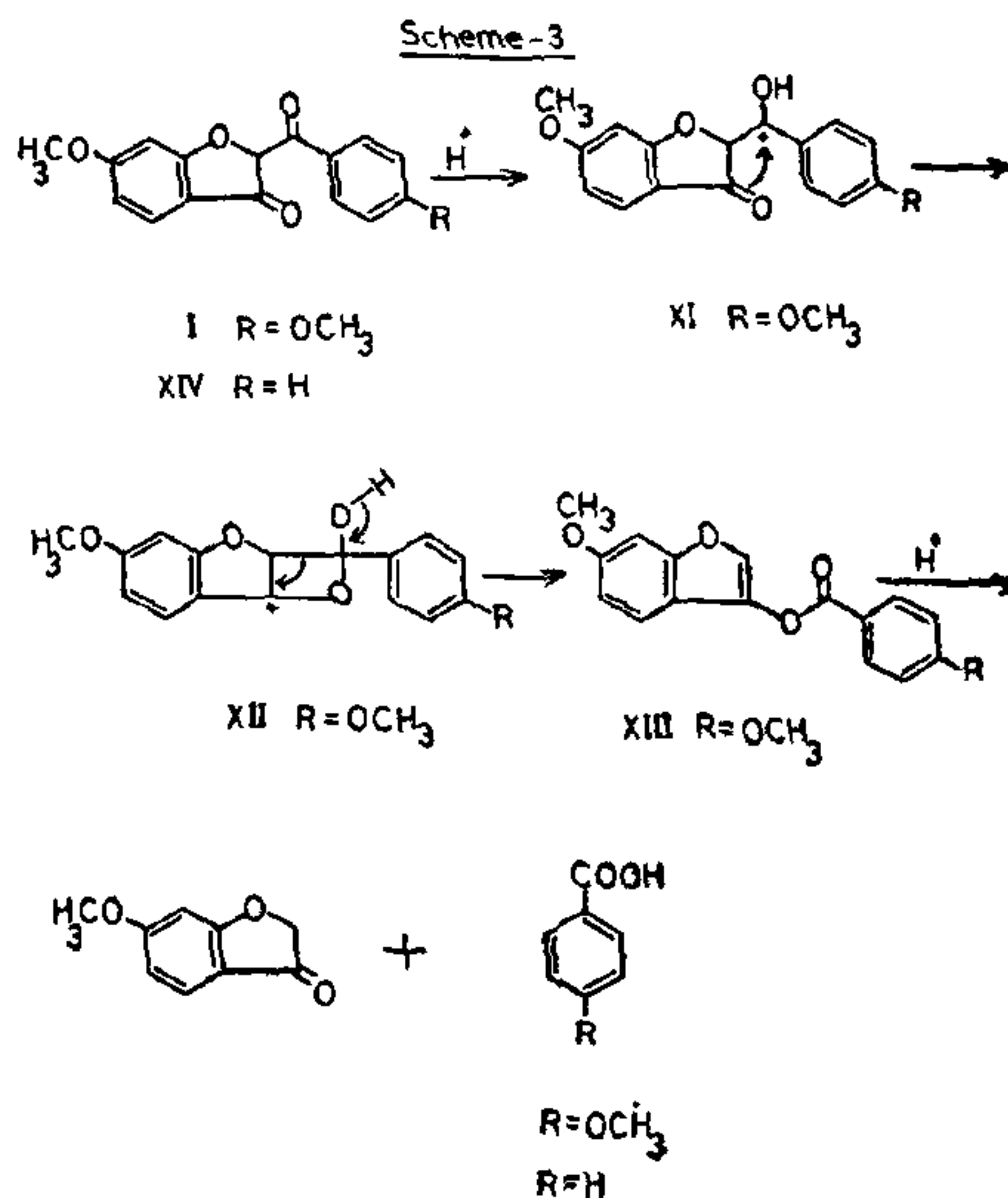
This mechanism of Bryant and Haslam fails to explain the products, *i.e.* 6-methoxy-3(2H)-benzofuranone and 4-methoxy benzoic acid, now obtained by us during the acid rearrangement of 6-methoxy-2-(4-methoxybenzoyl)-3(2H)-benzofuranone (I). The above mechanism (Scheme 2) also seems improbable on the basis that (i) carbonium ion (X) (Scheme 2) has no stabilizing factor, (ii) electrons on the oxygen of the carbonium ion (X) are more likely to be delocalised towards positive carbon and hence not readily

available for hydrogen bonding with adjacent hydroxyl group and (iii) the medium of the reaction is acidic and hence attack by a hydroxide ion as proposed is very unlikely.



It is quite likely, however, that the carbonium ion (XI) formed by protonation of α -carbonyl in 6-methoxy-2-(4-methoxybenzoyl)-3(2H)-benzofuranone (I) undergoes rearrangement to carbonium-ion (XII) (Scheme 3) because of the neighbouring group participation of the carbonyl group at position-3, situated at a favourable location for such an anchimeric assistance. Carbonium ion (XII) then could lose a proton as shown to give an enol-benzoate (XIII). Further degradation of enol-ester (XIII) in acid medium would give rise to 6-methoxy-3(2H)-benzofuranone and 4-methoxybenzoic acid.

Further evidence of the degradation of 2-aryyl-3(2H)-benzofuranones according to the general pattern given in Scheme 3 has been obtained by reacting 6-methoxy-2-benzoyl-3(2H)-benzofuranone (XIV) under the conditions described above when 6-methoxy-3(2H)-benzofuranone and benzoic acid were obtained.



Products obtained by Bryant and Haslam⁵ in their attempted synthesis of chromono-(2', 3': 3, 2)-benzofuranone (IX) can also be explained on the mechanism now advanced in Scheme 3. 6-Methoxy-2-(2, 4, 6-trimethoxy benzoyl)-3(2H)-benzofuranone (VIII) would thus be expected to yield 6-methoxy-3(2H)-benzofuranone and 2, 4, 6-trimethoxybenzoic acid. The latter is an unstable acid and is known to degrade readily to 1, 3, 5-trimethoxybenzene⁶.

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