

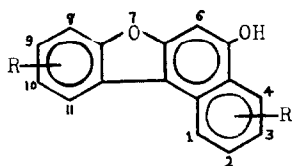
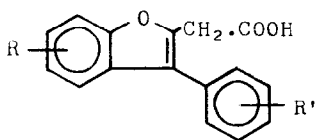
A SYNTHESIS OF 5-HYDROXY BENZO[b]NAPHTHO[1,2-d]FURAN. REVISION OF STRUCTURES OF COMPOUNDS REGARDED EARLIER AS 5-HYDROXY BENZO[b]NAPHTHO[1,2-d]FURANS.

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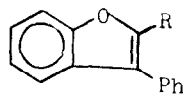
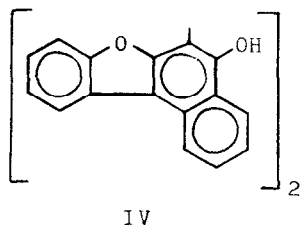
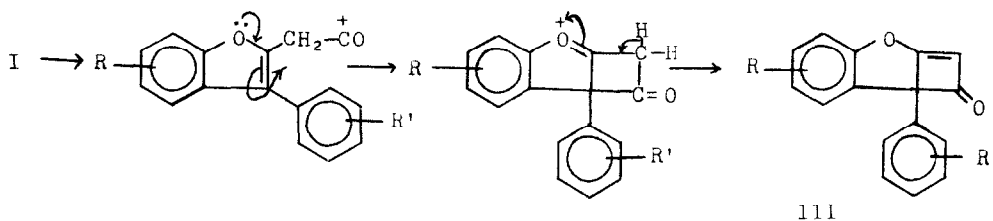
P.C.Johnson and A.Robertson¹ reported the synthesis of 5-hydroxy-benzo[b]naphtho[1,2-d]furans (II) by the cyclodehydration of 3-arylbenzo[b]furan-2-acetic acids (I) with phosphoric anhydride in benzene. They reported that these α -naphthols readily formed azo-dyes with diazonium chloride but they could be readily distinguished from the isomeric β -naphthols, 6-hydroxy-benzo[b]naphtho[1,2-d]furans by their failure to give the striking blue colour with warm alcoholic potassium hydroxide containing a little chloroform. Some of the naphthols were characterised as their *p*-nitrobenzoates. In an earlier communication it was observed by one of us² that 5-hydroxy-2,3,8,9-tetra-methoxy benzo[b]naphtho[1,2-d]furan showed a carbonyl absorption at 1740 cm^{-1} which is too high if the naphthol exhibited a keto-phenol tautomerism (expected ca $1665-1685\text{ cm}^{-1}$). It was found that all 5-hydroxybenzo[b]naphtho furans prepared in this laboratory had absorption at $1750-1765\text{ cm}^{-1}$ and Johnson and Robertson's 5-hydroxy-3,9-dimethoxy benzo[b]naphtho[1,2-d]furan also showed a similar carbonyl absorption. The results are given in the Table.



T A B L E

Serial No.	Compound	m.p.	i.r. absorption in cm^{-1}	References
1.	Parent compound	150-52 ^o	1753	3
2.	9-Methoxy-8-methyl-	164-65 ^o	1752	4
3.	10,11-Benzo-	188 ^o	1765	5
4.	9-Methyl-1,2-benzo-	150-51 ^o	1765	6
5.	3,9-Dimethoxy-	182-84 ^o	1748	1

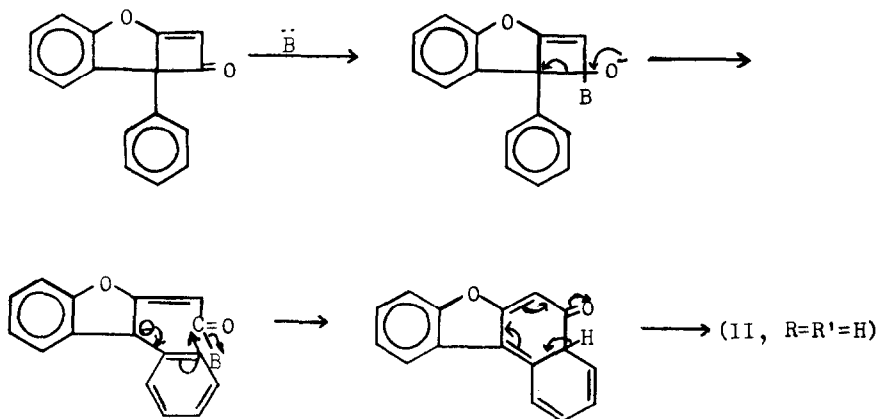
A reinvestigation showed that the parent compound (M^+ , $m/e = 234$) should be represented by the cyclobutenone structure (III, $R=R'=H$) arising by the mechanism shown. Thus the i.r. absorption is consistent with cyclobutenone structure⁷; the N.M.R. spectrum in CDCl_3 showed nine aromatic protons around $\tau 2.4$ and one proton at $\tau 5.66$ and the U.V. absorption at 248 $m\mu$ ($\log \epsilon$, 4.43) further supported the structure^{7,9}.



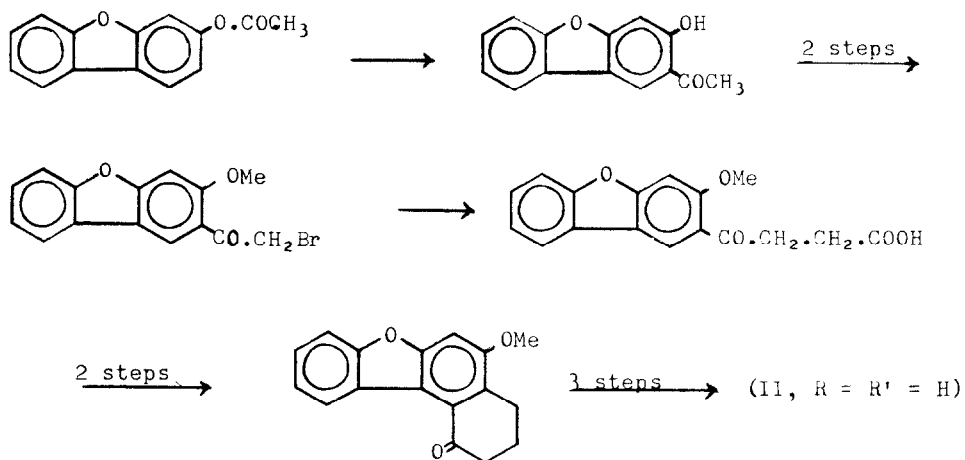
V, $R = \text{CH}_2 \cdot \text{CONH}_2$
 VI, $R = \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$
 VII, $R = \text{CH}_2 \cdot \text{C}(\text{Me})_2 \cdot \text{OH}$

On treatment with warm aqueous alcoholic sodium carbonate the compound gave a mixture of 3-phenylbenzo[b]furan-2-acetic acid, m.p. 144-46^o

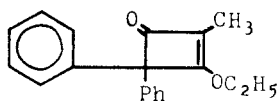
and a compound, m.p. $> 360^{\circ}$ analysing for $C_{32}H_{18}O_4$ (M^+ , $m/e = 466$) which is provisionally assigned the structure (IV). This compound is also formed by the action of bases on the authentic phenol (II, $R=R'=H$) in the presence of air. Catalytic reduction of (III, $R=R'=H$) was not possible using palladised charcoal under different conditions; experiments on reduction with Raney nickel in alcohol led to the formation of the phenol (II, $R=R'=H$) arising obviously by the action of traces of alkali in the catalyst. With aqueous alcoholic ammonia, 3-phenylbenzo[b]furan-2-acetamide (V), m.p. $180-82^{\circ}$ was formed (56 %) together with the related acid (14 %). Treatment with lithium aluminium hydride gave a mixture of the alcohol (VI), m.p. $79-81^{\circ}$ and authentic 5-hydroxybenzo[b]naphtho[1,2-d]furan (II, $R=R'=H$), m.p. $158-60^{\circ}$ (phenolic OH at 3320 cm^{-1} ; acetate, m.p. $137-39^{\circ}$) along with traces of (IV). Methylmagnesium iodide gave a mixture of the tertiary alcohol (VII), the naphthol (II, $R=R'=H$) and the compound (IV). Johnson and Robertson's 5-hydroxy-3,9-dimethoxybenzo[b]naphtho[1,2-d]furan also behaved in a similar manner. The formation of (II, $R=R'=H$) from (III, $R=R'=H$) under the influence of basic catalysts possibly follows the course:-



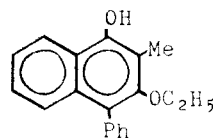
The authentic naphthol was unambiguously synthesised as follows:



As expected the naphthol gave a bluish green colouration with chloroform-alkali and was further characterised by oxidation with Fremy's salt to γ -brazanquinone (quinoxaline derivative with α -phenylene diamine, m.p. $242-44^{\circ}$). The cyclobutenones gave a faint reaction obviously on account of rearrangement to the related naphthols.



VIII



IX

The base-catalysed cyclobutenone-naphthol rearrangement is remarkable and recalls similar rearrangement brought about by heat of the cyclobutenone (VIII) to the naphthol (IX) by Arens and co-workers⁸ (cf. Woodward *et al.*⁹).

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