(dμ/dr) for the O–H bonds should naturally be higher. In the present work, it is not possible to calculate the exact values from the O–H band intensities, because of the overlapping bands arising from self-association effects and that of two other symmetrical bands resulting from H-bond isomerism as explained by Fritzsche. However, the magnitude of Δμ, the interaction moment along the O–H ⋅⋅⋅ O bond, can be estimated from the (dμ/dr) value for the C=O bond reported here for the 1:1 complexes.

The value of (dμ/dr) for 1:1 complexes of the carbonyl systems considered here varies from about 5 × 10⁻¹⁰ esu cm⁻¹ to 8 × 10⁻¹⁰ esu cm⁻¹. If one of the oxygen sp²-hybrid orbitals is almost collinear with the O–H ⋅⋅⋅ O axis, it will be in a most favorable position for maximum interaction between the O–H bond and the lone pair forming an atomic dipole. Using minimized distances of 1.03 Å and 1.04 Å for free and H-bonded O–H +, and a maximum displacement of 0.025 Å along the O ⋅⋅⋅ O distance, one obtains a Δμ of about 0.10–0.15 D, owing to the polarization of the C=O bond. A similar or slightly higher value would also be expected for the induced moment for the O–H bond. So a total Δμ of about 0.3–0.4 D may be explained by considering the vibrations of the lone pair of electrons together with the vibrations of the O–H bond. The estimation of Δμ from the dielectric polarization method confirms this order of interaction moment. In the present study, only a weak H-bonding interaction is considered. In many complexes such as triethylamine + hydrobromic acid, the H-bonding interaction is much stronger and is due to proton-transfer effect. Ratajczak et al., found that Δμ in triethylamine + phenol complexes in nonpolar solvents changes continuously within a wide range from 0.30 to about 10.00 D. To account for such high polarity they suggested the possibility of partial proton-transfer species. In weak H-bonded complexes, the partial proton transfer is hindered due to the existence of resonance structure of type O–H ⋅⋅⋅ H-O⁻.

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SYNTHETIC STUDIES IN 2-ARYLBENZOIURANS

Among the methods employed for the synthesis of 2-arylbenezfurans, the method of Whalley and Lloyd using Pd–C in mild acetic acid medium has greater applicability on account of its simplicity and easy availability of the intermediate desoxybenzoins. These workers have, however, reported that the cyclization does not proceed well in a few cases. Dann et al. have extended the method more successfully for the cyclization of many desoxybenzoins to 2-arylbenezfurans using the demethylation mixture of aluminium bromide and benzene.

As can be seen, this method has two variables namely:

(a) The demethylation agent,
(b) The solvent.

With a view to develop a convenient procedure and appropriate conditions for the synthesis of 2-arylbenezfurans from desoxybenzoins, a comparative study of these two variables has been made using a few demethylation agents in different solvents. The following reagents in the chronological order have been studied: (A) AlCl₃–CH₂CN, (B) HBr–AcOH, (C) HF–AcO, (D) AlCl₃–C₂H₅NO₂ and (E) AlCl₃–C₂H₅. Using these reagents the following 2-arylbenezfurans (i) 6-methoxy-2 (2', 4'-dimethoxyphenyl)benzofuran I (methyl ether of naturally occurring signa-
A comparative study (Table I) indicates that the demethylation employing hydrobromic acid in acetic acid and hydroiodic acid in acetic anhydride followed by methylation gives poor yields of the product. The use of aluminium chloride in nitrobenzene, however, is found to be more useful with consequent improvement in yields. Demethylation with aluminium chloride in dry benzene, followed by methylation, provides a more convenient procedure of synthesis. The aluminium chloride in dry benzene effects demethylation of 2'-methoxy group (and possible other groups).

<table>
<thead>
<tr>
<th>Compounds</th>
<th>(A)</th>
<th>(B)</th>
<th>(C)</th>
<th>(D)</th>
<th>(E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Nil</td>
<td>18</td>
<td>21</td>
<td>39</td>
<td>49</td>
</tr>
<tr>
<td>III</td>
<td></td>
<td>16</td>
<td>17</td>
<td>34</td>
<td>45</td>
</tr>
<tr>
<td>V</td>
<td></td>
<td>19</td>
<td>22</td>
<td>40</td>
<td>51</td>
</tr>
</tbody>
</table>

The above results are tabulated in the form of percentage yields of the products using reagents A, B, C, D and E.

Thus, the reagent (E), i.e., aluminium chloride in dry benzene, seems to be the most convenient reagent for the synthesis of 2'-arylsulfonamides from the corresponding 2'-methoxydesoxybenzoin.

**Vignaefuran N-methyl ether (I)**

It crystallized from aqueous methanol, m.p. 87–88° (Found: C, 72·3; H, 5·8% C₁₈H₁₈O₂ requires C, 71·9; H, 5·7%). M+ 284; λ max OH 280, 316, 332 nm (log ε 3·95, 4·25, 4·20); λ max 1600, 1580, 1375, 1295, 1290, 1210, 1110, 1010, 950, 840, and 780 cm⁻¹. NMR (CDCl₃, δ) 3·55 (s, 6H, 2 × -OCH₃), 3·92 (s, 3H, -OCH₃), 6·60 (m, 2H, H-3', 5') 6·85 (q, 1H, J = 2·8 and 9 Hz, H-3), 7·08 (m, 2H, H-3, 7) 7·43 (d, 1H, J = 9 Hz, H-4) and 7·92 (d, 1H, J = 9·2 Hz, H-6').

**Pterofuran dimethyl ether (III)**

It crystallized from methanol as needles, m.p. 86° (lit.,² m.p. 86°) (Found: C, 68·5; H, 6·2; C₁₈H₁₈O₂ requires C, 68·8; H, 5·8%). M+ 314; λ max 284, 314, 328 nm (log ε 3·98, 4·29, 4·24). NMR (CDCl₃, δ) 3·88 (s, 6H, 2 × -OCH₃), 3·91 (s, 3H, -OCH₃), 3·98 (s, 3H, -OCH₃), 6·75 (d, 1H, J = 9 Hz, H-5'), 6·83 (q, 1H, J = 3 and 9 Hz, H-5'), 7·09 (d, 1H, J = 2 Hz, H-7), 7·20 (s, 1H, H-3), 7·48 (d, 1H, J = 9 Hz, H-4) and 7·70 (d, 1H, J = 8·5 Hz, H-6'), 6-Methoxy-2', 4', 6'-trimethoxyphenylbenzofuran (v)

It crystallized from aqueous alcohol as cuboids, m.p. 128° (Found: C, 69·0; H, 6·0; C₁₈H₁₈O₂ requires C, 68·8; H, 5·8%). M+ 314; λ max 295, 305 nm (log ε 4·05, 4·10). NMR (CDCl₃, δ) 3·73 (s, 6H, 2 × -OCH₃), 3·83 (s, 6H, 2 × -OCH₃), 6·22 (s, 2H, H-3', 5'), 6·70-7·10 (m, 3H, H-3, 5, 7) and 7·42 (d, 1H, J = 8·5 Hz, H-4).

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