

$(d\mu/dr)$ 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 Fritzche⁶. However, the magnitude of $\Delta\mu$, the interaction moment along the O-H...O bond, can be estimated from the $(d\mu/dr)$ value for the C=O bonds reported here for the 1:1 complexes.

The value of $(d\mu/dr)$ 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 favourable 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-H⁶⁻⁸, and a maximum displacement of 0.025 Å⁹, along the O...O distance, one obtains a $\Delta\mu$ 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 $\Delta\mu$ 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 $\Delta\mu$ from the dielectric polarization method confirms this order of interaction moment¹⁰. 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.*¹¹ found that $\Delta\mu$ in triethylamine + phenol complexes in nonpolar solvents changes continuously within a wide range from 0.30 to about 10.00 D. To account 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-O⁺.

Department of Physics,
 Rajah Serfoji Government
 College,
 Thanjavur 613 005,
 October 3, 1978.

S. R. M. MEYYAPPAN.
 M. SUBRAMANIAN.

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SYNTHETIC STUDIES IN 2-ARYLBENZOFURANS

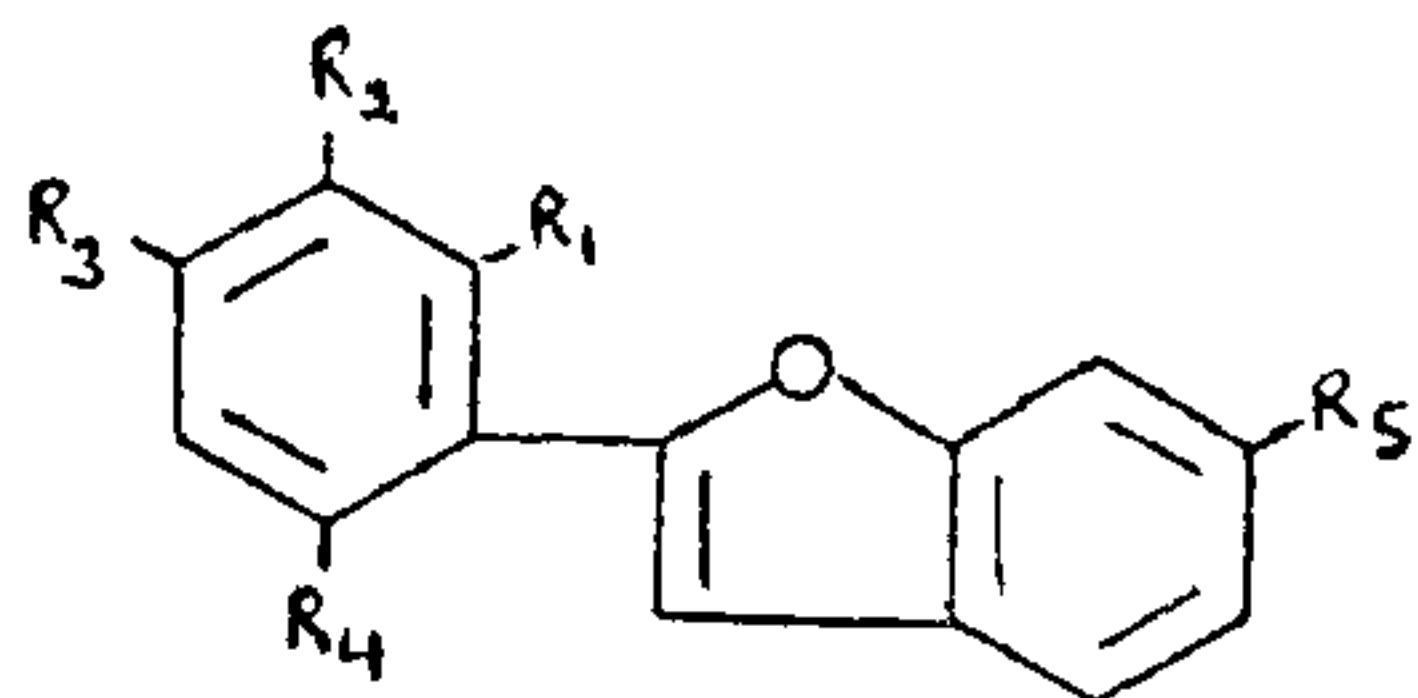
AMONG the methods employed for the synthesis of 2-arylbenzofurans, the method of Whally and Lloyd¹ using Pd-C in mild acetic acid medium has greater applicability on account of its simplicity and easy availability of the intermediate desoxybenzoins. These workers¹ have, however, reported that the cyclization does not proceed well in a few cases. Dann *et al.*² have extended the method more successfully for the cyclization of many desoxybenzoins to 2-arylbenzofurans using the demethylation mixture of aluminium bromide and benzene.

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

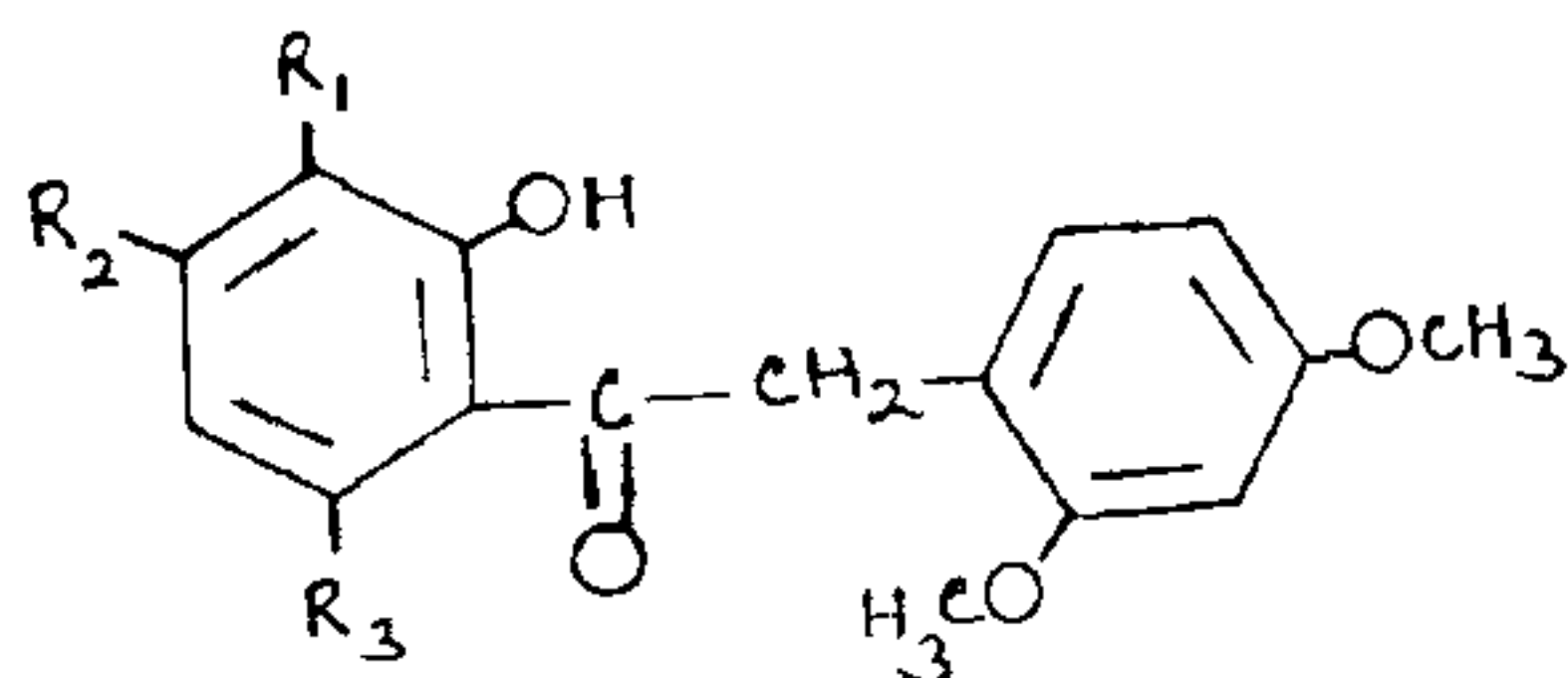
- (a) The demethylation agent,
- (b) The solvent.

With a view to develop a convenient procedure and appropriate conditions for the synthesis of 2-arylbenzofurans 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-CH₃CN, (B) HBr-AcOH, (C) HI-Ac₂O, (D) AlCl₃-C₆H₅NO₂ and (E) AlCl₃-C₆H₆. Using these reagents the following 2-arylbenzofurans (i) 6-methoxy-2 (2', 4'-dimethoxyphenyl)-benzofuran I (methyl ether of naturally occurring vignafuran³, II), (ii) 6-methoxy-2- (2', 3', 4'-trimethoxyphenyl)-benzofuran III (dimethyl ether of naturally occurring pterofuran^{4,5} IV) and (iii) 6-methoxy-2 (2', 4', 6'-trimethoxyphenyl)-benzofuran V, have been prepared from the desoxybenzoins (i) 2-hydroxy-4-methoxyphenyl-2', 4'-dimethoxybenzyl ketone⁶ VI, (ii) 2-hydroxy-3, 4-dimethoxyphenyl-2', 4'-dimethoxybenzyl ketone⁷ VII and 2-hydroxy-4, 6-dimethoxyphenyl-2', 4'-dimethoxybenzyl ketone⁸ VIII.

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	R ₁	R ₂	R ₃	R ₄	R ₅
I	OCH ₃	H	OCH ₃	H	OCH ₃
II	OCH ₃	H	OCH ₃	H	OH
III	OCH ₃	OCH ₃	OCH ₃	H	OCH ₃
IV	OCH ₃	OH	OCH ₃	H	OH
V	OCH ₃	H	OCH ₃	OCH ₃	OCH ₃



	R ₁	R ₂	R ₃
VI	H	OCH ₃	H
VII	OCH ₃	OCH ₃	H
VIII	H	OCH ₃	OCH ₃

A comparative study (Table I) indicates that the demethylation employing hydrobromic acid in acetic

TABLE I

Compounds	(A)	(B)	(C)	(D)	(E)
I	Nil	18	21	39	49
III	..	16	17	34	45
V	..	19	22	40	51

acid and hydriodic 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 more convenient procedure of synthesis. The aluminium chloride in dry benzene effects demethylation of 2'-methoxy group (and possible other groups

oo). It also provides appropriate conditions for a smooth and effective cyclization involving 2'-hydroxy group and the carbonyl to give 2-arylbenzofurans in good yields.

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-arylbenzofurans from the corresponding 2'-methoxydesoxybenzoins.

Vignafuran methyl ether (I)

It crystallized from aqueous methanol, m.p. 87-88° (Found: C, 72.3; H, 5.8 C₁₇H₁₆O₄ requires C, 71.9; H, 5.7%). M⁺ 284; λ_{max}^{MeOH} 280, 316, 332 nm (log ε 3.95, 4.25, 4.20); ν_{max}^{Nujol} 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-5), 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.^{4,5} m.p. 86°) (Found: C, 68.5; H, 6.2. C₁₈H₁₈O₅ requires C, 68.8; H, 5.8%). M⁺ 314; λ_{max}^{MeOH} 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 (2', 4', 6'-trimethoxyphenyl)-benzofuran (v)

It crystallized from aqueous alcohol as cubes, m.p. 128° (Found: C, 69.0; H, 6.0. C₁₈H₁₈O₅ requires C, 68.8; H, 5.8%). M⁺ 314; λ_{max}^{MeOH} 295, 305 nm (log ε 4.05, 4.10); ν_{max}^{Nujol} 1620, 1590, 1485, 1150, 1410, 1375, 1320, 1300, 1275, 1210, 1150, 1125, 1050, 1010, 1000, 940 and 825 cm⁻¹. 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).

Department of Chemistry,
University of Delhi,
Delhi 110 007,
May 31, 1978.

S. K. SANDUJA *
A. S. KUKLA.

- * Present address: Department of Chemistry, Ramjas College, University of Delhi, Delhi 110 027;
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