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GENERATION OF ∝- ACYLCARBENIUM IONS : A NOVEL UNCATALYSED C-C BOND FORMATION AT ROOM TEMPERATURE

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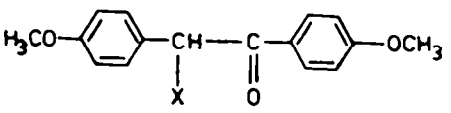
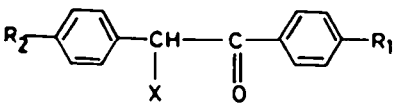
Abstract : Reactions of substituted desyl chloride 1 and 5 with phenol at room temperature in benzene results in C-alkylation. The reaction is shown to proceed through a benzylic ∝-acylcarbenium ion. This contention is supported by (i) the failure of this reaction with haloketones 8 and 22 and (ii) the different nature of products obtained when these haloketones were allowed to react in the presence of K_2CO_3.

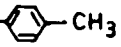
A great deal of current interest is evident in the generation of ∝-acylcarbenium ions[1]. Benzylic∝-acylcarbenium ions have been generated[2,3] by reaction of (i) halides with $AgSbF_6$ in SO_2, (ii) mesylates or trifuluoroacetates in acidic or alcoholic medium. The reactions of compounds in the second group are usually carried out in acetic acid at temperatures ranging from 50-90°. We report herein, a room temperature reaction between suitably substituted desyl chloride and phenols proceeding through ∝-acylcarbenium ion resulting in an uncatalysed C-C bond formation. To the best of our knowledge, this is the only example of an uncatalysed formation of ∝-acylcarbenium ion in a non-polar medium.

Reaction of the haloketone 1 with p-cresol in 1:1 ratio in excess benzene (30 hrs room temperature) afforded a product $C_{23}H_{20}O_3$, m.p. 119-20°. The spectral properties [IR : absence of hydroxyl and carbonyl groups ; NMR ^1H : 2.4 (3H, s), 3.76 and 3.83 (each 3H, s), 6.78, 6.95, 7.39 and 7.55 (each 2H, d, J=9 Hz), 7.00 (1H, bs), 7.15 (1H, bd, J=9 Hz) and 7.37 (1H, d, J=9 Hz); NMR ^{13}C : two quartets (21.45, 55.19 for 2C on basis of height of peak), seven doublets (110.23, 113.73 for 2C, 114.28 for 2C, 119.33, 125.23, 128.08 for 2C, 130.76 for 2C) and nine singlets (159.33, 158.72, 152.3, 150.39, 132.03, 130.76, 125.23, 123.46, 115.3)] suggested structure 2 for this compound and ruled out alternate structures such as 2a and 2b. The structure of the product is supported by the similarity of the reported m.p. (126°)[4].

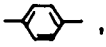
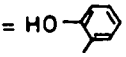
The structure 2 was also confirmed by its synthesis. Reaction of p-cresol with 1 in presence of K_2CO_3 gave three products which were separated by chromatography. These were identified as 2 (45%), 3 (20%) and 4 (15%) by their spectral properties. The identities of 2 and 4 were also

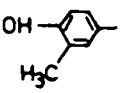
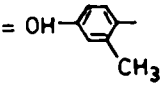


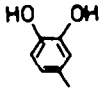


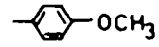
1 X = Cl , 3 X = O- 

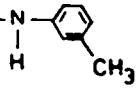
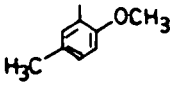
4 X = OH , 10 X = HO- 

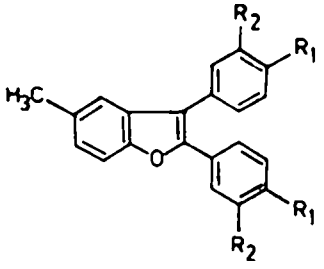
11 X = AcO-  , 12 X = HO- 

13 X = OH-  , 14 X = OH- 

18 X = OH-  , 21 X = 

29 X = OCH_3 , 30 X = - 

31 X = -  , 32 X = 



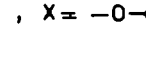
2 $R_1 = OCH_3$, $R_2 = H$

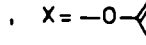
7 $R_1 - R_2 = O-CH_2-O$

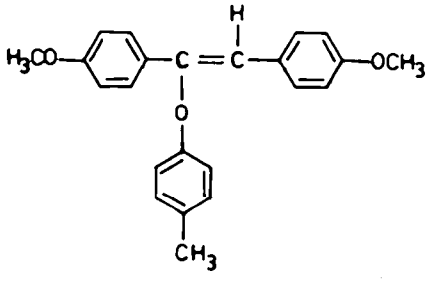
8 $R_1 = R_2 = H$, X = Cl

9 $R_1 = R_2 = H$, X = OH

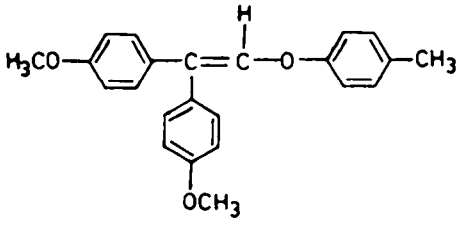
22 $R_1 = OCH_3$, $R_2 = H$, X = Cl

27 $R_1 = R_2 = H$, X = -O- 

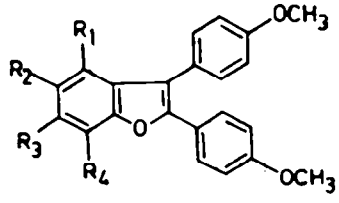
28 $R_1 = OCH_3$, X = -O- 
$R_2 = H$



2a



2b

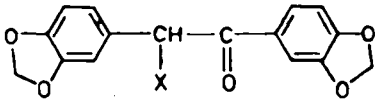


15 $R_1 - R_2 = -CH = CH - CH = CH-$, $R_3 = R_4 = H$

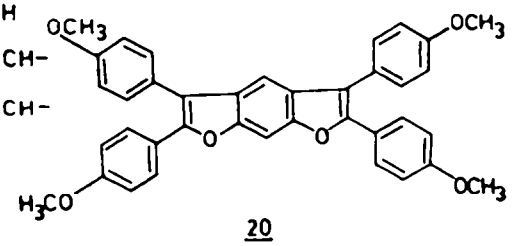
16 $R_1 = R_4 = H$, $R_2 - R_3 = -CH = CH - CH = CH-$

17 $R_1 = R_2 = H$, $R_3 - R_4 = -CH = CH - CH = CH-$

19 $R_1 = R_2 = R_4 = H$, $R_3 = OH$



5 X = Cl , 6 X = OH



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confirmed by direct comparison (TLC, IR, mmp). The ether 3, on keeping in benzene at room temperature was recovered unchanged. However, when reaction was carried out in presence of conc. HCl in benzene (10 hrs, room temperature) 3 was smoothly converted into a product identical (m.p., mmp, TLC, IR) with 2. This not only confirmed the structure 2, but suggested that conversion of 1 to 2 might involve 3 as an intermediate. The acid formed in the conversion of 1 to 3 could then be responsible for conversion of 3 into 2. However, as K_2CO_3 is in excess, the HCl formed is obviously neutralized. Hence, formation of benzofuran 2 obviously does not proceed through formation of ether 3 and must be formed by a competing pathway (vide infra).

The chloride 5 m.p. 77-78°, prepared from 6 using pyridine-$SOCl_2$, on reaction with p-cresol in benzene (24 hrs, room temperature) furnished a product, m.p. 161-62°. This could be readily characterized as the unknown benzofuran 7 from its spectral properties (vide experimental). From the reaction of p-cresol and desyl chloride 8 in benzene in presence or absence of acid at room temperature starting materials were recovered unchanged. This clearly suggested that oxygen substituent in the aromatic ring of the haloketone is essential for formation of benzofuran at room temperature. The reaction of p-cresol with different benzoins 4, 6 or 9 were then attempted (in benzene at room temperature). The failure of these reactions indicated that a good leaving group such as chlorine is essential for benzofuran formation at room temperature in benzene.

Reaction of the haloketones with other phenols : On reaction of 1 with phenol at room temperature in benzene, a product $C_{22}H_{20}O_4$, m.p. 158-60° was obtained. This was identified by its spectral data (vide experimental) as the hitherto unknown phenol 10. The insolubility in NaOH and absence of $FeCl_3$ colouration cast doubts on its phenolic nature. This led to the possibility that the hydroxyl could be alcoholic. The easy formation of acetate and its spectral properties [IR : 1770 and 1680 : NMR ^1H : new signal at 2.28 (3H, s) and no significant shift of Ar-C<u>H</u>-CO] ruled out that hydroxyl was alcoholic. The compound m.p. 158-60° and its acetate should then be represented by structures 10 and 11 respectively. The alternate phenolic structure 12 was ruled out since the PMR of compound m.p. 158-60° showed six doublets in aromatic region (at 6.7, 6.82, 6.85, 6.95, 7.15 and 7.97, each 2H with J=9 Hz). Similar reaction of 1 with ortho and meta cresols furnished products m.p. 129-31° and 138-40° identified by their spectral properties as the unknown phenols 13 and 14 respectively. The identities were confirmed by examination of spectral properties of acetates as well as by direct comparison (IR, mmp, TLC) with synthetic samples prepared from 1 under Friedel-Craft's conditions ($AlCl_3$-CH_3NO_2/room temperature). It was interesting that both phenols 13 and 14 are insoluble in dilute alkali and did not give positive test with $FeCl_3$.

Reaction of 1 with phenol, o-cresol and m-cresol in absence of K_2CO_3 had furnished phenols 10, 13 and 14, whereas reaction of 1 with p-cresol had furnished benzofuran 2 at room temperature in benzene. Thus the requirement for formation of benzofuran was a blocked para position to the phenolic hydroxyl group. Furthermore as 10, 13 and 14 are C-alkylated products, benzofuran formation should also involve initial C-alkylation ortho to phenolic hydroxyl group followed by cyclization. The alternate usual pathway of O-alkylation followed by cyclization ortho to oxygen could now be excluded.

If this assumption is correct then the reaction of 1 with β-naphthol should furnish the angular naphthofuran 15 rather than linear naphthofuran 16, since β-naphthol is expected to undergo C-alkylation at C-1 rather than at C-3. Reaction of β-naphthol with 1 provided a compound m.p. 115-17°. This compound from its spectral features was obviously a naphthofuran. Though the NMR features could not differentiate between 15 and 16 as the peaks appeared in a cluster (vide experimental) it was assumed that the product was 15, based on reasoning mentioned above. The product from reaction of anisoin with β-naphthol in presence of an acid is reported[4] to have m.p. 116°. These workers have also assigned structure 15 to the product but have not ruled out structure 16.

Since α-naphthol is reported[5] to give a coupling reaction with diazotized aniline at both C-2 and C-4, it was anticipated that the reaction of α-naphthol with 1 should result in alkylation at C-2 and C-4. The former would undergo cyclization to the naphthofuran 17 and the latter would not react further. In agreement with this expectation reaction of α-naphthol with 1 afforded two products m.p. 120° and 166-68°. These could be identified (IR, NMR, analysis) as the naphthofuran 17[6] and the unknown C-alkylated product 18 respectively. This compound was clearly the product substituted at C-4 in α-naphthol since the C-2 proton was clearly seen as an ortho coupled doublet at a considerably upfield position (vide experimental).

The results obtained so far, suggested that if initial alkylation occurs ortho to a phenolic hydroxyl then benzofuran formation would result, whereas if initial alkylation occurs at para position then obviously furan formation is prevented. This finding was confirmed by carrying out reactions with resorcinol and catechol.

Reaction of resorcinol with 1 in 1:1 molar ratio furnished a product m.p. 137°, characterized (IR, NMR) as the benzofuran 19[4]. Reaction of resorcinol with 1 in 1:2 ratio resulted in the formation of a compound m.p. 202° which was tentatively characterized as the hitherto unknown furan 20. Since the required two singlets are not clearly seen in the mass of NMR signals the alternate 1,2,3,4 tetrasubstituted structures could not be ruled out. However, since resorcinol is known[4] to undergo 4,6 dialkylation rather than 2,4 dialkylation the compound was assigned structure 20. On reaction of 1 with catechol (1:1) the product obtained was shown (spectral properties) to be the expected hitherto unknown C-alkylated phenol 21. Significantly both the compounds 19 and 21 were soluble in NaOH and gave positive colour reaction (greenish and reddish brown respectively) with $FeCl_3$.

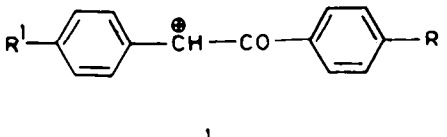
Thus, in the present work, six benzofurns 2, 7, 15, 17, 19 and 20 were obtained in one step. Though, 2, 15, 17 and 19 are known, their reported preparation involves ether formation followed by acid catalysed cyclization[4,10-12] whereas in the present study these are obtained in a single step at room temperature.

STUDIES ON MECHANISM OF REACTION

The failure of reaction of p-cresol with 8 and the positive reaction with 1 and 5 suggested that a suitably placed oxygen function in the haloketone is essential for the reaction under these conditions. In order to support this argument the reaction was tried on the haloketone 22. Under similar conditions, reaction of this haloketone 22 with p-cresol in benzene resulted in recovery of unchanged starting compound, further confirming the need of an

oxygen substituent para to the CHCl grouping for the success of the reaction. This result could be rationalized since cation 23 (derived from 1) is stabilized by p-methoxy group. Similar stabilization of cations 24 and 25 (derived from 8 and 22) is not possible. It may be pointed out that the PMR and CMR of cation 24 (generated from corresponding bromides by reaction with $AgSbF_6$ in SO_2) has been reported[19]. The PMR and CMR chemical shift indicated that positive charge in cation 24 is mainly on the carbon alpha to the carbonyl.

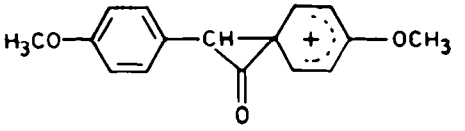
Another plausible mode of stabilization of cation 23 was through the bridged structure 26. However, since both 22 and 8 did not undergo reaction, it was obvious that this mode of stabilization was not significant. Recently Creary and Geiger[7] had also ruled out this mode of stabilization in their study of reactions of mesylates.



23 $R = R^1 = OCH_3$

24 $R = R^1 = H$

25 $R = OCH_3$, $R^1 = H$



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It had been suggested[8] that electron donors attached to carbonyl group decrease the positive character of carbonyl carbon and hence decrease the destabilization of α-acylcarbenium ions. Such considerations would envisage facile reactions of cation 23 and 25 derived from 1 and 22. The facile reaction of p-cresol in benzene, with 1 and failure of rection of p-cresol with 22 clearly suggested that the methoxyl group para to the carbonyl does not play any significant role in the reaction.

The products of reaction of haloketones 8 and 22 with p-cresol in presence of K_2CO_3 were readily identified (spectral data and mode of formation) as the corresponding ethers 27 and 28 respectively. Since haloketones 8 and 22 had not undergone reaction with p-cresol (in the absence of K_2CO_3), it was obvious that reaction with K_2CO_3 of 1, 8 and 22 to give ethers 3, 27 and 28 was a displacement reaction. This displacement was due to the formation of low concentration of phenoxide ion which is a more powerful nucleophile and hence results in ether formation from all these substrates. By contrast reaction of 1 with p-cresol in absence of K_2CO_3 involved a different mechanism presumably the formation of an α-acylcarbenium ion.

Another fact confirming the formation of cation 23 was that reaction of 1 with p-cresol and K_2CO_3 not only gave ether 3 but also the benzofuran 2. Since benzofurans are not formed from the haloketones 8 and 22, it appeared reasonable to conclude that the benzofuran formation in the K_2CO_3 reaction of 1 involves cation 23 (Scheme 1). An alternative mechanism to explain the formation of ether 3 and benzofuran 2 from the reaction of 1 with p-cresol and K_2CO_3 would require that both products are formed from cation 23. This seems unlikely as the reaction of 1 with p-cresol in absence of K_2CO_3

gives only benzofuran 2 and no detectable quantity of the ether 3.

Thus the contention that reaction of 1 proceeds through cation 23 is supported by (i) the failure of the reaction (in absence of K_2CO_3) with 8 and 22 (ii) the different nature of products obtained when haloketones 1, 8 and 22 were allowed to react in the presence of K_2CO_3 (iii) the fact that in the reaction of 1 in presence of K_2CO_3 a phenyl ether 3 (displacement) and a benzofuran 2 (α-acylcarbenium ion) are obtained through two competing parthways.

Reaction of haloketone 1 with other nucleophiles was then examined. The reaction of 1 with methanol (in benzene, room temperature) afforded a syrupy liquid identified as methoxy ketone 29. Significantly a similar reaction of haloketone 8 with methanol even under reflux resulted in recovery of unchanged 8. This suggested that conversion of 1 to 29 is not a displacement reaction but involves cation 23 as an intermediate. Based on this reasoning it was expected that similar reaction of 1 with anisole should afford 30. However, in actual practice this reaction led to recovery of starting material.

This led to conclusion that in the reaction in benzene as solvent, conversion of 1 to cation 23 may need presence of a proton. This proton presumably, serves as an electrophilic catalyst for the rupture of C-Cl bond. In order to confirm this, reaction of 1 with m-toluidine was investigated. It was expected that under these reaction conditions (benzene, room temperature) the proton from the amino group would be sufficiently acidic to convert 1 into cation 23. In agreement with this reasoning reaction of 1 with m-toluidine did afford a product m.p. 122-24° which was identified as the N-alkylated product 31.

In order to check whether a acidic proton is needed for the conversion of 1 to cation 23, it was planned to carry out reaction of p-cresyl methyl ether with 1 in presence of p-nitrophenol. The latter would provide the electrophilic catalyst whereas the greater nucleophilicity of p-cresyl methyl ether as compared to p-nitrophenol should result in the formation of 32. In actual practice the reaction gave back only starting material. It was then obvious that failure of reaction of anisole and p-cresyl methyl ether was not due to the absence of acidic proton.

A plausible rationalization, for the failure of reaction with anisole would be the reversibility of the formation of the σ-complex 34. This suggestion was supported by the work of Okamoto et al[8]. In case of the reaction with phenol the reversibility of formation of 33 is low (Scheme 1).

CONCLUSIONS

1. α-Acylcarbenium ions are generated for the first time in a non-polar medium*, at room temperature in an uncatalysed reaction.
2. A novel uncatalysed C-C bond formation at room temperature is observed for the reaction of desyl chlorides substituted by oxygen para to -CH-Cl group and phenols unsubstituted at para position.
3. A one step synthesis of suitably substituted benzofurans is reported. The usual synthesis of benzofuran from these substrates involved two step i.e. O-alkylation followed by cyclization.

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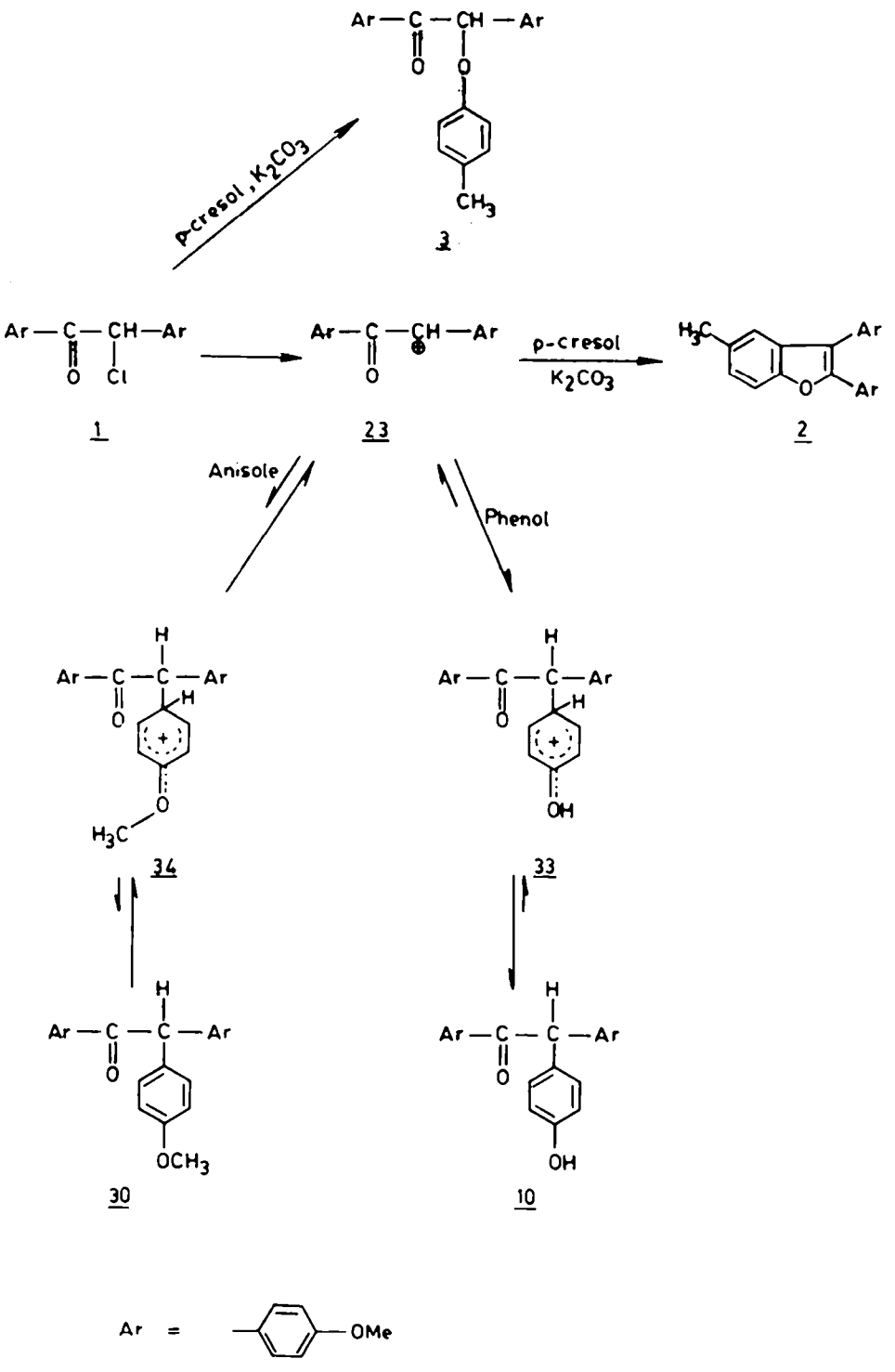
* The dielectric constant of 5% (v/v) phenol in benzene is 2.6 as against 2.2 for benzene. The present experiments use ~ 2.5% solutions.



Scheme 1 - Mechanism of reaction

EXPERIMENTAL

All melting points and boiling points are uncorrected. All solvents were distilled and dried. Elemental analysis were obtained using Hosli's rapid carbon-hydrogen analyser. IR spectra were recorded (in cm^{-1}) on Perkin-Elmer infracord model 337 and Beckmann IR-20 spectrophotometers. PMR spectra were recorded on Perkin-Elmer R-32 (90 MHz) instrument. PMR shifts are reported in δ values using tetramethylsilane as internal standard. CMR spectra were scanned on JEOL FX 100.

General procedure : Reaction of haloketone 1 with different phenols

A mixture of chloro compound (1, 0.005 M) and phenol (0.005 M) in benzene (20 ml) was kept at room temperature for 30-40 hrs. After evaporation of benzene the reaction mixture was extracted with $CHCl_3$. The chloroform layer was washed with 2 N NaOH (10 x 2 ml) and then with H_2O. After evaporating solvent the product was recrystallized from different solvents to give either substituted benzofuran or the corresponding C-alkylated product. However in case of α-naphthol two products 17 and 18 were isolated by chromatography. Resorcinol (1 M) gave benzofuran 19 which was soluble in dil. NaOH, whereas resorcinol (0.5 M) gave benzofuran 20. The results and spectral properties are summarized below.

Table 1 : Results obtained by the reaction of haloketone 1 with different phenols.

Compound	Yield (%)	m.p. (lit. m.p.) [°C]	Molecular formula	Elemental analysis calculated C %	H %	found C %	H %
2	65[a]	119-20 (126)[4]	-	-	-	-	-
15	70[a]	115-17 (116)[4]	-	-	-	-	-
17	16[b]	129 (120)[6]	-	-	-	-	-
19	72[a]	137 (136)[4]	-	-	-	-	-
20	75[a]	202	$C_{38}H_{30}O_6$	78.33	5.19	78.02	5.08
10	74[b]	158-60	$C_{22}H_{20}O_4$	75.85	5.79	76.03	5.55
13	65[b]	129-31	$C_{23}H_{22}O_4$	76.22	6.12	76.02	6.16
14	65[b]	138-40	$C_{23}H_{22}O_4$	76.22	6.12	76.32	6.02
18	48[b]	166-68	$C_{26}H_{22}O_4$	78.37	5.57	78.01	5.66
21	52[b]	186-88	$C_{22}H_{20}O_5$	72.51	5.53	72.67	5.57

a - reaction time 30 hrs. b - reaction time 48 hrs.

IR and NMR ^1H Data of compounds

Compound 20 :
IR: 1600, 1500; NMR ^1H : 3.77 and 3.82 (each 6H, s, Ar-OCH_3), 6.72 to 6.97 (7H, m, Ar-H), 7.27 to 7.58 (11H, m, Ar-H).

Compound 10 :
IR: 3350, 1680, 1600, 1505; NMR ^1H : 3.73 and 3.8 (each 3H, s, Ar-OCH_3). 5.72 (1H, bs, Ar-OH, exchanges with D_2O), 5.88(1H, s, Ar-CH-CO), 6.63 to 7.23 (10H, m, Ar-H), 7.99 (2H, d, J=9 Hz, Ar-H, ortho to carbonyl).

Compound 13 :
IR: 3360, 1670, 1600, 1500; NMR ^1H : 2.15 (3H, s, Ar-OCH_3), 3.72 and 3.8 (each 3H, s, Ar-OCH_3), 5.6 (1H, bs, Ar-OH, exchanges with D_2O), 5.82 (1H, s, Ar-CH-CO), 6.5 to 7.0 (7H, m, Ar-H), 7.15 (2H, d, J=9 Hz, Ar-H, meta to methoxyl), 7.99 (2H, d, J=9 Hz, Ar-H, ortho to carbonyl).

Compound 14 :
IR: 3250, 1640, 1600, ; NMR ^1H : 2.22 (3H, s, Ar-C$\underline{H}_3$), 3.76 and 3.82 (each 3H, s, Ar-OC$\underline{H}_3$), 5.58 (1H, s, Ar-O$\underline{H}$, exchanges with D_2O). 5.95 (1H, s, Ar-C$\underline{H}$-CO), 6.42 to 6.99 (7H, m, Ar-$\underline{H}$), 7.05 (2H, d, J=9 Hz, Ar-$\underline{H}$, meta to methoxyl), 7.88 (2H, d, J=9 Hz, Ar-$\underline{H}$, ortho to carbonyl).

Compound 18 :
IR: 3250,1650; NMR ^1H : 3.76 and 3.79 (each 3H, s, Ar-OC$\underline{H}_3$), 6.52 (1H, s, Ar-C$\underline{H}$-CO), 6.8 (1H, d, J=7 Hz, Ar-$\underline{H}$,ortho to hydroxyl), 6.82 and 7.2 (each 2H, d, J=9 Hz, Ar-$\underline{H}$, ortho to methoxyl), 7.0 (1H, d, J=7 Hz, Ar-$\underline{H}$, meta to hydroxyl), 7.34 and 7.85 (each 2H, d, J=9 Hz, Ar-$\underline{H}$, meta to methoxyl), 7.4 (3H, m, Ar-$\underline{H}$), 8.32 (1H, d of d, J=3 and 8 Hz, C-8 H of naphthalene), 9.35(1H, bs, Ar-O$\underline{H}$, exchanges with D_2O).

Compound 21 :
IR: 3300, 1655, 1600, 1500; NMR ^1H : 3.77 and 3.82 (each 3H, s, Ar-OC$\underline{H}_3$), 5.81 (1H, s, Ar-C$\underline{H}$-CO), 6.52 to 6.9 (7H, m, Ar-$\underline{H}$), 7.15 (2H, d ,J=9 Hz, Ar-$\underline{H}$, meta to methoxyl), 7.75 (2H, bs, Ar-O$\underline{H}$, exchanges with D_2O), 7.96(2H, d, J=9 Hz, Ar-$\underline{H}$, ortho to carbonyl).

Acetyl derivatives of phenols, 10, 14 and 21

The phenols, 10, 14 and 21 were converted to the corresponsding acetates. The results obtained are given below.

Yield, IR and NMR ^1H data of acetates.

Acetate of 10 :
Yield 71%, IR : 1770, 1680, 1600, 1500; NMR ^1H : 2.28 (3H, s, -OCOC$\underline{H}_3$), 3.69 and 3.85 (each 3H, s, Ar-OC$\underline{H}_3$), 5.91 (1H, s, Ar-C$\underline{H}$-CO), 6.61 to 7.3 (10H, m, Ar-$\underline{H}$), 7.97 (2H, d, J=9 Hz, Ar-$\underline{H}$, ortho to carbonyl).

Acetate of 14 :
Yield 83%; IR : 1770, 1680, 1600; NMR ^1H : 2.2 (3H, s, Ar-C$\underline{H}_3$), 2.28 (3H, s,-OCO-C$\underline{H}_3$), 3.76 and 3.78 (each 3H, s, Ar-OC$\underline{H}_3$), 5.8 (1H, s, Ar-C$\underline{H}$-CO), 6.7 to 6.9 (7H, m, Ar-$\underline{H}$), 7.05 (2H, d, J=9 Hz, Ar-$\underline{H}$, meta to methoxyl), 7.85 (2H, d, J=9 Hz, Ar-$\underline{H}$, ortho to carbonyl).

Acetate of 21 :
Yield 77%; IR : 1770, 1640, 1600; NMR ^1H : 2.22 (6H, s,-OCO-C$\underline{H}_3$), 3.75 and 3.8 (each 3H, s, Ar-OC$\underline{H}_3$), 5.9 (1H,s , Ar-C$\underline{H}$-CO), 6.55 to 7.22 (9H, m, Ar-$\underline{H}$), 7.95 (2H, d, J=9 Hz, Ar-$\underline{H}$, ortho to carbonyl).

2,3-bis-(3',4'-Methylenedioxyphenyl)-5-methyl-benzofuran 7

A mixture of haloketone 5 (1.592 g, 0.005 M), p-cresol (0.54g, 0.005 M) in benzene (20 ml) was kept at room temperature for 24 hrs. Usual work (as described in general proceedure) gave shining needles in 63% yield, m.p. 161-62°. NMR ^1H : 2.38 (3H, s, Ar-C$\underline{H}_3$), 5.88 and 5.95 (each 2H, s, Ar-O-C$\underline{H}_2$-O), 6.66 to 7.45 (9H, m, Ar-$\underline{H}$). Analysis : Found : C; 73.98, H; 4.42%, calculated for $C_{23}H_{16}O_5$, C; 74.18, H; 4.33%.

1,2-bis-(4-Methoxyphenyl)-2-(4'-methylphenoxy)ethanone 3

A mixture of chloroanisoin 1 (2.905 g, 0.01 M), p-cresol (1.08 g, 0.01 M) and potassium carbonate (2 g) in dry acetone (20 ml) was refluxed for 3 hrs. The reaction mixture after chromatography gave three products identified as 2, m.p. 119-20° (lit[4] m.p.126) in 45% yield, ether 3, m.p. 75-76° in 20% yield and anisoin 4, m.p. 112-13° (lit[18] m.p. 113) in 15% yield.

Compound 3 :
IR : 1695, NMR ^1H : 2.2 (3H, s, Ar-C$\underline{H}_3$), 3.7 and 3.72 (each 3 H, s, Ar-OC$\underline{H}_3$), 6.2 (1H, s, Ar-C$\underline{H}$-CO), 6.72 to 7.02 (8H, m, Ar-$\underline{H}$), 7.45 (2H, d, J=8 Hz, Ar-$\underline{H}$, ortho to -CH-CO), 8.00 (2H, d, J=8 Hz, Ar-$\underline{H}$, ortho to carbonyl). Analysis : Found : C; 76.25, H; 6.12%, calculated for $C_{23}H_{22}O_4$, C; 76.22, H; 6.12%.

p-Cresyloxydeoxybenzoin 27

A mixture of desyl chloride 8 (2.305 g, 0,01 M), p-cresol (1.08g 0.01 M) and potassium carbonate (2.8 g, 0.02 M) in dry acetone (30 ml) was refluxed for 3 hrs. The reaction mixture after usual work up gave white crystals from hexane in 66% yield. m.p. 88-89° (lit[9] m.p. 90-91)

1-(4-Methoxyphenyl)-2-phenyl-2-(4'-methylphenoxy)ethanone 28

Similar reaction on the haloketone 22 (0.26 g, 0.001 M), furnished a solid, characterised as 28, m.p. 103-5°, in 53% yield. IR : 1700, 1605, 1505 NMR ^1H : 2.25 (3H, s, Ar-C$\underline{H}_3$), 3.8 (3H, s, Ar-OC$\underline{H}_3$), 6.2 (1H, s, Ar-C$\underline{H}$-CO), 6.78 to 7.6 (11H, m, Ar-$\underline{H}$), 8.04 (2H, d, J=9 Hz, Ar-$\underline{H}$, ortho to carbonyl). Analysis : Found C; 79,34, H; 6.05%, calculated for $C_{22}H_{20}O_3$, C; 79,51, H; 6.02%.

1,2-bis-(4-Methoxyphenyl)-2-methoxyethanone 29 :

A mixture of haloketone 1 (0.29 g, 0.001 M) and methanol (2 ml) in benzene (5ml) were kept at room temperature. After complete removal of methanol and benzene, a gummy liquid was obtained which was characterised as 29 in 72% yield. IR : 1700, 1605; NMR ^1H : 3.4 (3H, s, -OC$\underline{H}_3$), 3.73 and

3.79 (each 3H, s, Ar-OC$\underline{H}_3$), 5.41 (1H, s, Ar-C$\underline{H}$-CO), 6.82 (4H, d, J=9 Hz, Ar-$\underline{H}$, ortho to methoxyl), 7.35 (2H, d, J=9 Hz, Ar-$\underline{H}$, ortho to -CH), 7.95 (2H, d, J=9 Hz, Ar-$\underline{H}$, ortho to carbonyl) Analysis : Found C; 70.97, H; 6.46, Calculated for $C_{17}H_{18}O_4$, C; 71.31, H; 6.34%.

Reaction of m-toluidine with haloketone 1

A mixture of m-toluidine (0.1 g, 0.01M) and haloketone 1 (0.29 g, 0.01 M) in benzene (10 ml) was kept for 24 hrs at room temperature. After evaporation of benzene, the reaction mixture was worked up by the usual way. This gave 31 in 70% yield, m.p. 122-24°, IR : 3365, 1680, 1640, 1525, NMR δ : 2.18 (3H,s, Ar-C$\underline{H}_3$), 3.62 and 3.73 (each 3H, s, Ar-OC$\underline{H}_3$), 4.7 (1H, bs, Ar-N$\underline{H}$, exchanges with D_2O), 5.87 (1H,s, Ar-C$\underline{H}$), 6.35 to 7.0 (8H, m, Ar-$\underline{H}$) , 7.28 (2H, d, J-9 Hz, Ar-$\underline{H}$ meta to methoxyl), 7.92 (2H, d, J=9 Hz, Ar-$\underline{H}$, ortho to carbonyl). Analysis : Found : C; 76.22, H; 6.30, Calculated for $C_{23}H_{23}NO_3$, C; 76.43, H; 6.41%.

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