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The Chemistry and Reactivity of Aryl Radicals — The C-C bond Formation from *o*-Bromobenzylphenylethers with Tin Hydride and Azobisisobutyronitrile

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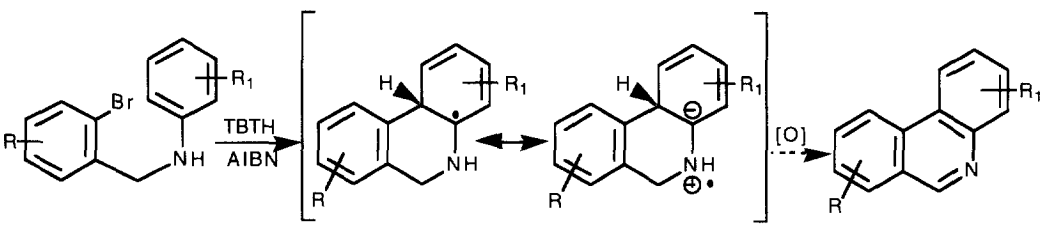
Abstract: Treatment of *o*-bromobenzylphenylethers and a two fold excess of *n*-tributyltin hydride (TBTH) with 0.5 to 0.6 mol equiv. of AIBN induces an inefficient C_{aryl}-C_{aryl} bond formation. The structures of the products resulting from a 1,5 and/or a 1,6 additions were found to be largely determined by the presence or absence of the substituent and its position in the phenyl ring. Copyright © 1996 Elsevier Science Ltd

The cyclisation of radicals derived from N-*o*-bromobenzylanilines to phenanthridines in preparatively useful yields was recently described.[1] The results were discussed in terms of possible reversibility of the primary radical reactions (Scheme 1).

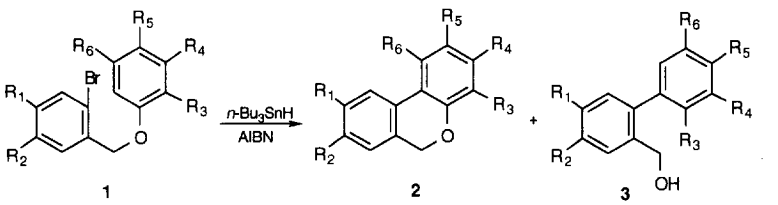


Scheme 1

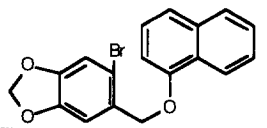
It was therefore considered to be of interest to examine the chemistry of similar aryl radicals produced from *o*-bromobenzylphenylethers. An earlier report had described[2] the photochemical generation of a similar radical and its very inefficient ring closure. As a consequence new methods involving the use of organopalladium compounds[3] and higher order organocopper derivatives[4] were developed with success to overcome this problem. The ethers required for the present study were readily prepared from *o*-bromobenzylhalide and phenols

(K_2CO_3/acetone) or the corresponding phenolates (from the phenol and NaH) by alkylation in CH_3CN. The various phenylethers, thus prepared, are collected in Table 1.

Table 1. Preparation and Reaction of 2-Bromobenzylarylethers **2** with Stannylhydride.



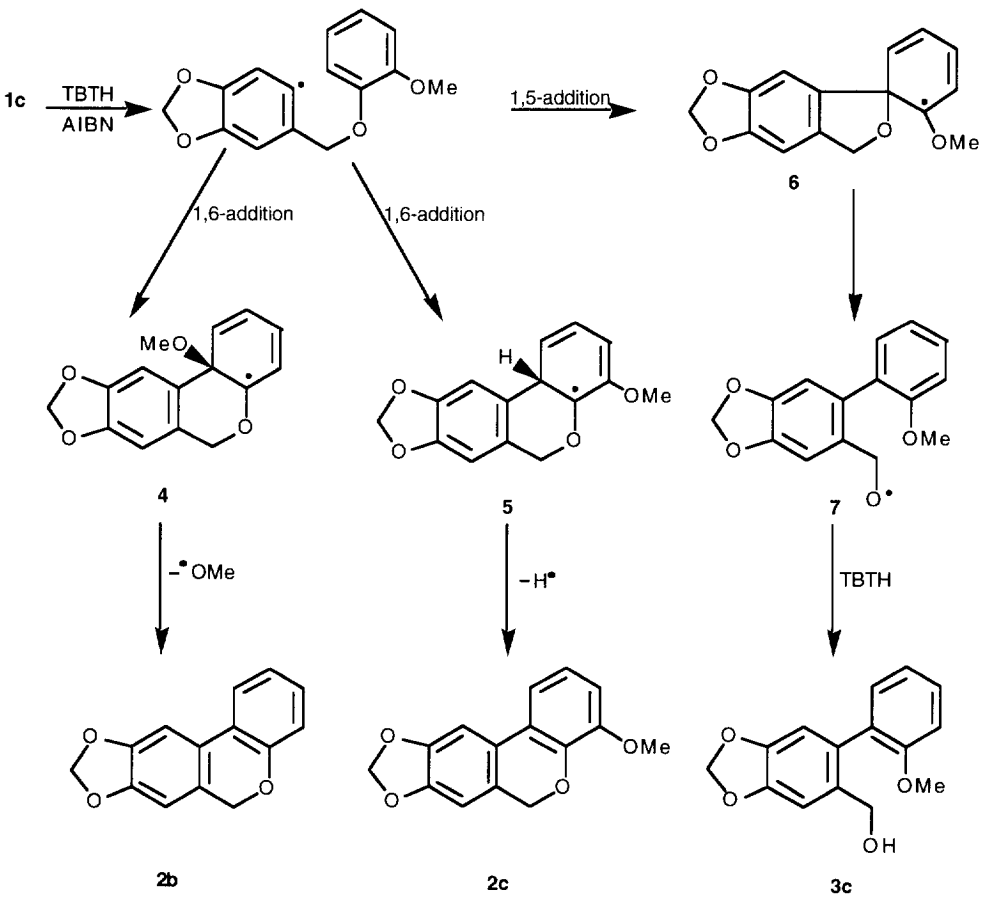
1 2 3

		1 Yield, %	2 Yield, %	3 Yield, %	Others Yield, %
a	R_1=R_2=R_3=R_4=R_5=R_6=H	55	48	—	—
b	R_1,R_2=OCH_2O; R_3=R_4=R_5=R_6=H	49	47	—	—
c	R_1,R_2=OCH_2O; R_3=OMe; R_4=R_5=R_6=H	82	5.2	18	**2b**, 6.8
d	R_1,R_2=OCH_2O; R_4=OMe; R_3=R_5=R_6=H	54	20	—	—
e	R_1,R_2=OCH_2O; R_5=OMe; R_3=R_4=R_6=H	73	22	6.9	—
f	R_1,R_2=OCH_2O; R_3=R_4=OMe R_5=R_6=H	56	23	—	**2c**, 18
g	R_1,R_2=OCH_2O; R_3=R_5=OMe R_4=R_6=H	74	7.4	19	**2d**, 30
h	R_1,R_2=OCH_2O; R_4=R_6=OMe R_3=R_5=H	74	4.9	—	**9**, 27
i	R_1,R_2=OCH_2O; R_3=CO_2Me R_4=R_5=R_6=H	64	30	—	**2b**, 0.97
j	R_1,R_2=OCH_2O; R_3=CO_2H R_4=R_5=R_6=H	78 (from **1i**)	19	1.9	**2b**, 1.2
k		48	napthobenzopyran 46	—	—

RESULTS AND DISCUSSION

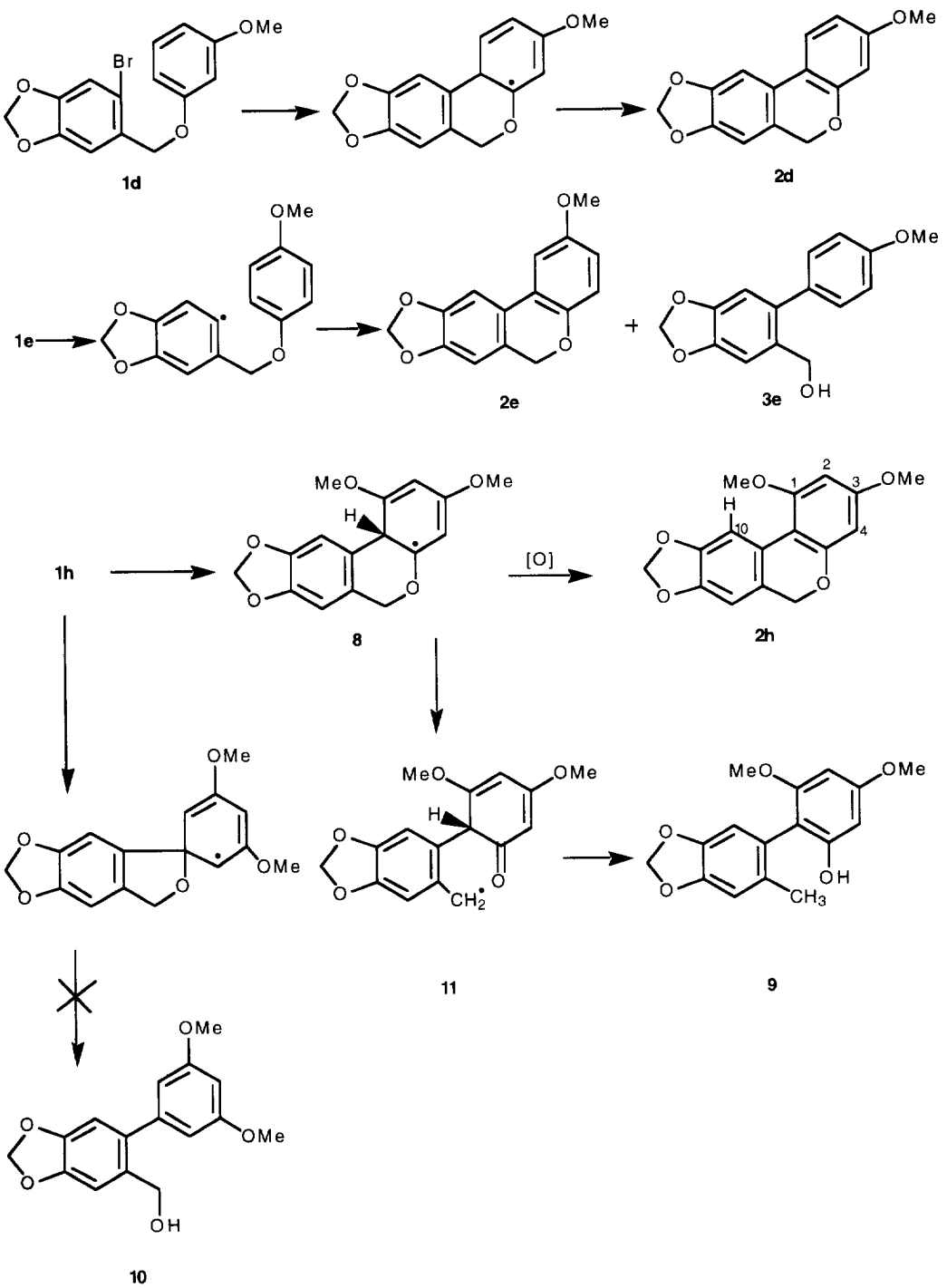
Compounds **1a**, **1b** and **1k**, carrying no substituent in the phenoxyl ring, when heated with *n*-tributyltin hydride (TBTH) (1-2 equiv.) and azobisisobutyronitrile (AIBN) (0.5~0.6 mol equiv.) in benzene under reflux, afforded the corresponding pyran derivatives **2a**, **2b**, and **2k**, respectively in modest yield (*ca.* 45%). Introduction of a

MeO group in the 2-position of the phenoxyl ring, as in **1c**, led to a mixture of compounds from which the methoxypyran **2c** (*ca.* 5%), the demethoxylated compound **2b** (*ca.* 7%) and the biphenyl alcohol **3c** (18%) were isolated by column chromatography. The placement of the same substituent in the 4-position, e.g, **1e**, also gave the pyran **2e** (22%) and the alcohol **3e** (*ca.* 7%). However, the 3-methoxy isomer **1d** yielded the pyran **2d** (20%) as the sole isolable product. It thus became apparent that the position of the methoxy group governs the nature of the various possible reactions that occur, namely cyclisations with or without loss of substituent and/or the cleavage of the C-O bond. Referring to the reaction of **1c**, the various radical intermediates that could, in principle, form on the homolysis of the C-Br bond, can be represented as shown below (Scheme 2).



Scheme 2

The three cyclohexadienyl radicals **4**, **5** and **6** produced on cyclisation[5a,b] involving the 1,6 and the 1,5 [5c] modes of addition respectively, all benefit from the additional stabilisation[6] offered by the adjacent oxygen



Scheme 3

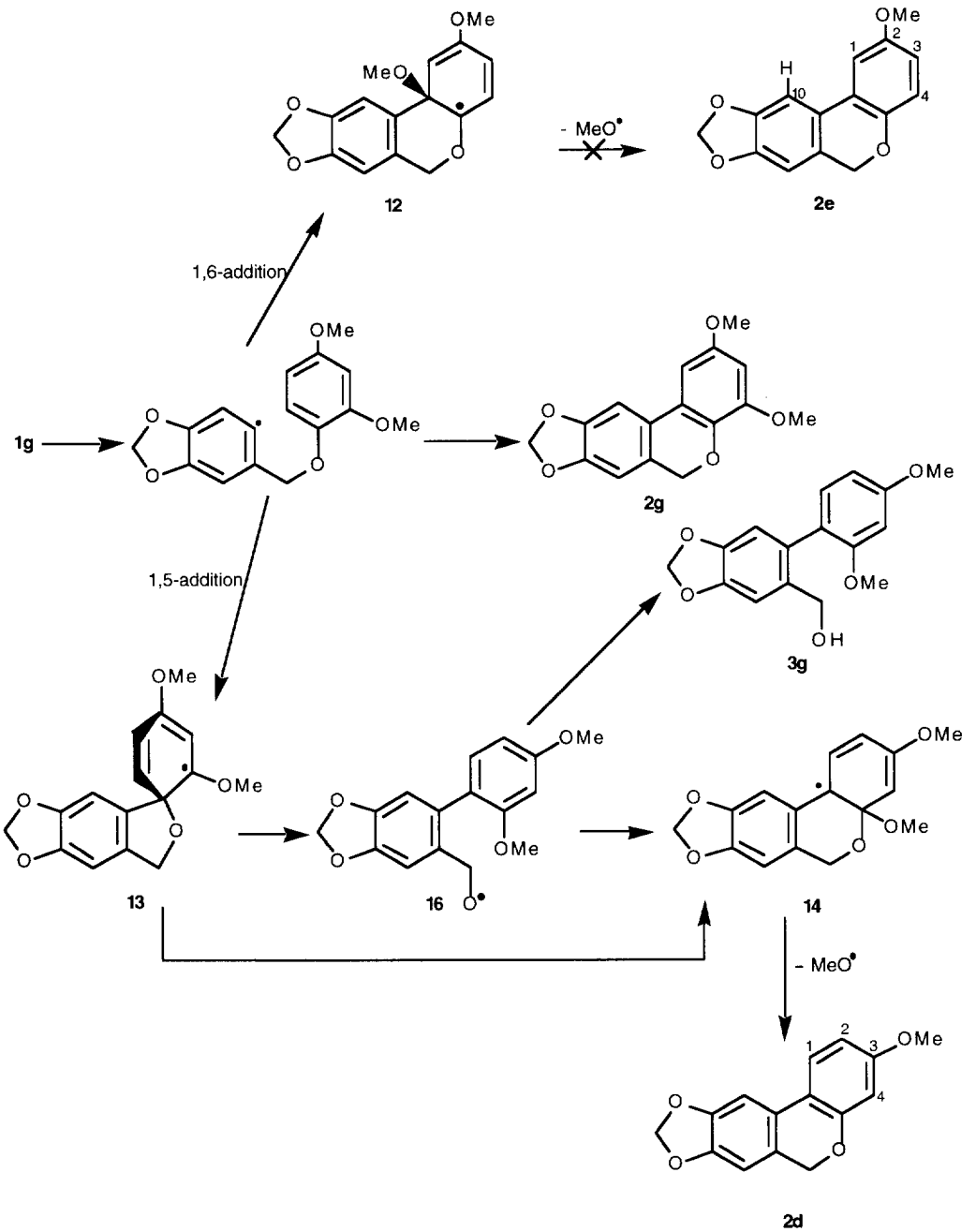
atom. While a formal loss[7] of H atom from **5** leads to the pyran **2c**, aromatisation of **4** by ejection of •OMe (β-scission) produces the demethoxy compound[8] **2b**. A similar β-scission from the spirocyclohexadienyl radical **6** generates the benzyloxy radical **7** quenched in a subsequent fast reaction[9] with TBTH to form the alcohol **3c**. The regeneration of aromaticity is assumed to provide the necessary driving force[10] for these reactions. For compound **1d** (Scheme 3), with the substituent in the 3 position, the product of the 1,6 addition **2d**, where the intermediate radical corresponding to **5** finds stabilisation from both the oxygens, was the only isolable substance. Siting the OMe group at the 4-position, as in **1e**, resulted in the formation of the pyran **2e** (22%) as the major product, the benzylalcohol **3e** being formed in 6.9% yield. The placement of two MeO groups at the 3 and 5 positions (compound **1h**), so as to permit all the oxygen atoms involved to act in concert to stabilise the radical **8** formed by 1,6 attack, led to an interesting result. The pyran **2h** (5%) was produced along with the phenol **9** (27%). There was no evidence for the formation of the benzyl alcohol **10**.

The structure of the phenol **9** was established by its elemental composition and analysis of its NMR spectrum. It contained a total of only four aromatic protons, two singlets at δ 6.81 and 6.66 (1H each), a doublet at δ 6.21 (1H, J_m 2.4 Hz) and 6.14 (1H, J_m 2.4 Hz) and more importantly a 3H singlet at δ 2.01. Resonances in the region (δ 4.30-4.50) characteristic of the Ar-CH_2-OH were not observed. Acetylation (Ac_2O; 4-dimethylaminopyridine) afforded the corresponding O-acetyl derivative possessing a strong carbonyl absorption at 1770 cm^{-1} in its IR spectrum. The formation of the phenol[11] reveals yet another mode of decomposition available for the radical **8**. Instead of the usual oxidative removal of H•, there seems to be a large preference[12a] for fragmentation to the ketobenzyl radical[12b] **11** and thence to **9** by prototropy and reduction or vice-versa. The structure assigned to the pyran **2h** was supported by the appearance of an aromatic proton (H_{10}) at a relatively low field (δ 7.8) due to anisotropicity of the *peri* OMe group.

The attention was next turned to determine the effect, if any, of two MeO groups located in such a way as to encourage the 1,5 attack. Accordingly the substance **1g** was selected and, when subjected to the combined action of TBTH and AIBN, it gave the monomethoxypyran **2d** (30%), the benzylalcohol **3g** (19%), and the dimethoxypyran **2g** (7.4%). As anticipated the combined yields of the products derived from the 1,5 process (**2d+3g** *ca.* 49%) (vide infra) significantly outweighed that resulting from the 1,6 substitution (**2g**, 7.4%).

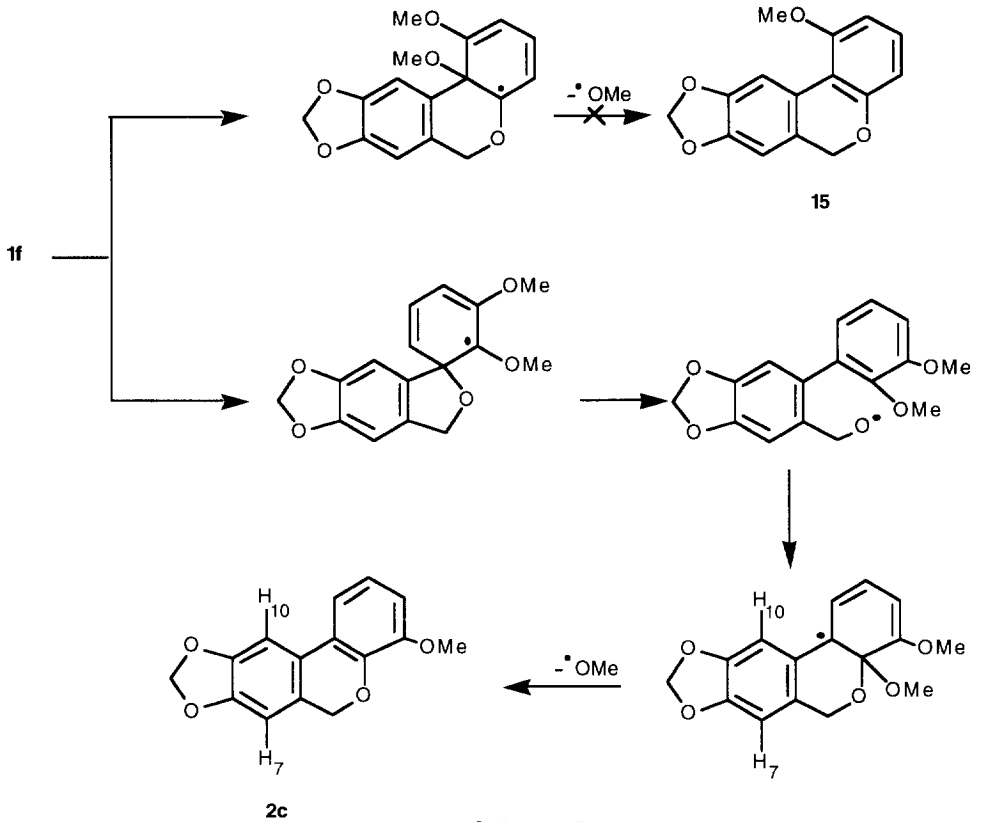
On the mechanism of demethoxylation: Compounds **1c**, **1f** and **1g**, that were found to suffer demethoxylation, all possessed an alkoxyl group ortho to the phenoxyl oxygen and two reasonable mechanisms could be written for such a loss. Taking the dimethoxy compound **1g** as the example, the two relevant cyclohexadienyl radicals from which demethoxylation could occur can be represented by the structures **12** and **13** (*cf.* Scheme 4).

A β-fragmentation from **12** should lead to the 2-methoxy[*b,d*]dibenzopyran (**2e**). If, on the other hand, a 1,2-oxygen migration[13a] takes place in the spiro radical **13** to form directly the isomeric radical **14**, then the loss of MeO• would furnish 3-methoxy-8,9-methylenedioxy[*b,d*]dibenzopyran (**2d**). It is more likely, however, that the generation of the radical **14** is the result of the reactive alkoxyl radical **16**, before its reduction to **3g**, attacking[13b] the aryl ring at the carbon bearing the methoxy group. In fact the product from **1g** was identical in all respects (NMR, IR, mp and mmp) with that derived from the cyclisation of the monomethoxy compound **1d**. Further support for the formal oxygen migration occurring prior to the loss of OMe group comes from the results


OMe
MeO
12
- MeO•
OMe
H
10
2e
1,6-addition
1g
OMe
OMe
2g
1,5-addition
OMe
OMe
3g
OH
OMe
OMe
13
OMe
OMe
16
O•
OMe
OMe
14
- MeO•
OMe
2d

Scheme 4

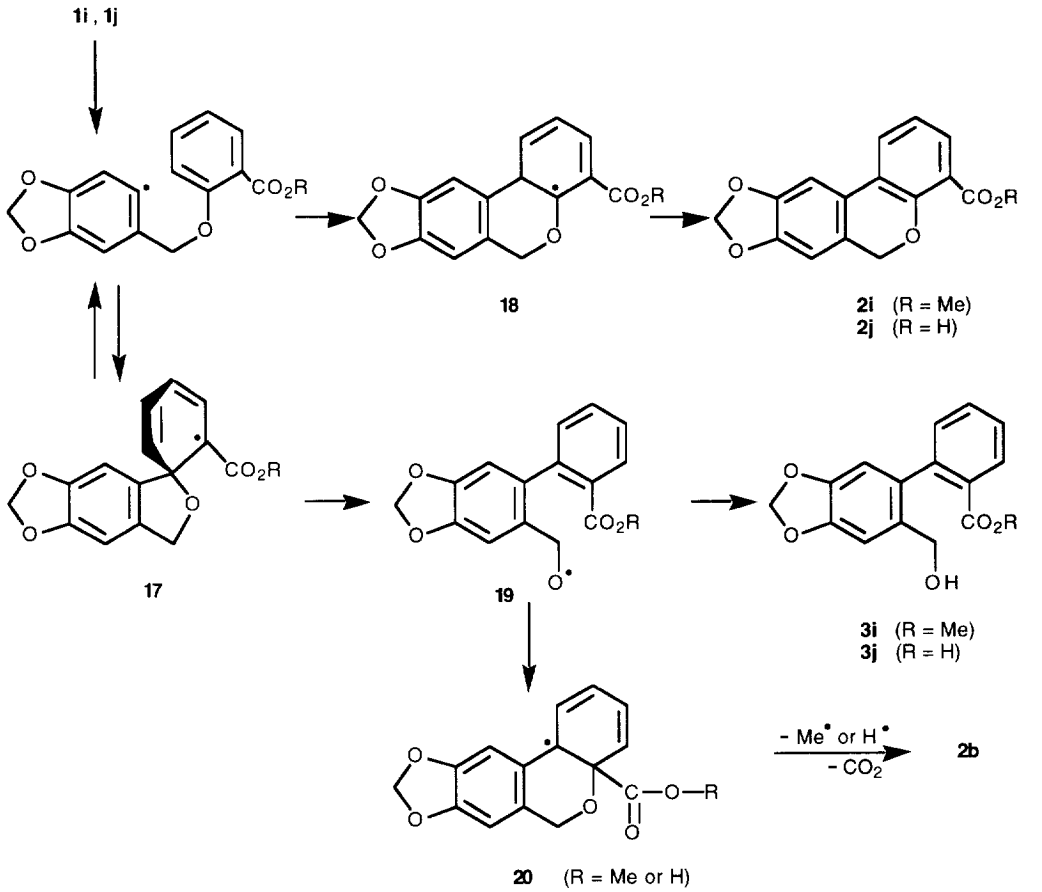
obtained for the dimethoxyphenylether **1f** (Scheme 5). The NMR spectrum of the monomethoxy compound **2c**



Scheme 5

formed from it, contained, in addition to the two singlets (7-H; 10-H; one H each), a 3H multiplet showing the presence of three contiguous hydrogens (1-H; 2-H; 3-H) in the phenoxyl ring. The absence of any low field resonance at δ *ca.* 7.80 (as observed for **2h**) precluded the alternative structure **15**, thus uniquely defining the structure of the product to be 4-methoxy-8,9-methylenedioxy-6H-dibenzo[*b,d*]pyran (**2c**).

Finally, the chemistry of the radical derived from the ester **1i** was studied (Scheme 6). The product of the 1,5 attack, anticipated by virtue of its electronic demand and its position in the phenoxyl ring, was isolated in only small amounts. Instead the pyran ester **2i**, a consequence of a 1,6 addition, formed as the major product (30%), was accompanied by traces of the decarbomethoxy compound (0.97%; identical with **2b**). Similarly, the free carboxylic acid **1j** afforded the pyran acid **2j** (19%), trace amounts of the benzyl alcohol **3j** (1.9%) and the decarboxylated product (**2b**; 1.2%). A plausible explanation for the seemingly anomalous results could be that the expected spiro radical **17** (Scheme 6) is indeed generated, as attested by the isolation, albeit in very poor yield of **3i, 3j** and **2b**. However, the very stability (increased $t_{1/2}$) of the former perhaps permits its conversion via a reversible process[14] into the isomeric radical **18**, which then suffers oxidative aromatisation to **2i** at a rate faster than the unimolecular decomposition of **17**. The formation of the pyran **2b** from both **1i** and **1j** can be rationalised by assuming that the alkoxyl radical **19** produces the new radical **20** (as in the case of **1g**) and thence leads to the observed product by loss of carbondioxide and either a methyl radical or a hydrogen atom.



Scheme 6

In conclusion, the aryl σ radicals generated from *o*-bromobenzylethers are found to undergo inefficient 1,6 and 1,5 ring closures to provide, in general, benzopyrans and biphenyl alcohols respectively. The formation of products and their relative proportions are discussed in terms of the stability of the radicals formed. The incursion of reversibility of the primary radical reaction is invoked to explain certain unusual reactions observed during the present study.

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EXPERIMENTAL

General. Melting points were determined with a microscopic hot-stage Reichert Thermovar and are uncorrected. Preparative thin layer chromatography (PTLC) were performed on plates precoated with silica gel (0.5 mm or 2 mm). Infrared (IR) spectra were obtained on potassium bromide discs with a Perkin-Elmer 157G and 683 grating infrared spectrophotometer and the frequencies reported in cm^{-1}. Proton nuclear magnetic resonance spectra (^1H NMR) were obtained at 300 MHz with a Brücker CXP 380 or General Electric GE-NMR and those at 60 MHz with a Perkin Elmer R 12 B instrument. Chemical shifts are reported in ppm down field from tetramethylsilane and $CDCl_3$ used as solvent unless stated otherwise. High and low resolution mass spectra (HREIMS and EIMS) were measured in a Kratos MS-25RF instrument using electron impact at 70 e V. All solvents were purified by standard methods.

General Procedure for the Preparation of *o*-Bromobenzylphenylethers.

Method A. The appropriate *o*-bromobenzylbromide or chloride (6 mmol) in dry acetone (30~45 ml), and the phenol, when readily available (30 mmol), were heated under reflux (10-19 h) in the presence of anhydrous K_2CO_3 (30 mmol) until the reaction was adjudged to be complete (tlc control). The solvent was evaporated under reduced pressure, water added to the residue and the compounds extracted with ether. The ethereal phase was washed with NaOH (10%), then with H_2O and dried (Na_2SO_4). Evaporation of solvent led to the phenylethers. For phenols which are not commercially available the following alternative alkylation method B was used.

Method B. The phenol (0.016 mol) and NaH (0.016 mol) in acetonitrile (20 ml) was stirred (RT, 30 min) and the mixture then cooled in an ice-bath. The *o*-bromobenzyl halide (0.016 mol) in CH_3CN (15 ml) was slowly added and the solution heated under reflux (3~15 h) until the reaction was complete (tlc control). The product was worked up as described in method A.

By method A:

2-Bromobenzylphenylether (1a). had mp: 36-40°C (from *n*-hexane), lit[15] mp: 38-40°C. ^1H NMR ($CDCl_3$; 60 MHz) δ 5.15 (s, 2H, CH_2O), 6.80-7.70 (m, 9H, Ar-*H*).

2-Bromo-4,5-methylenedioxybenzylphenylether (1b) had mp: 38-40°C (from *n*-hexane); ^1H NMR ($CDCl_3$; 60 MHz) δ 5.10 (s, 2H, CH_2O), 6.05 (s, 2H, OCH_2O), 6.80-7.70 (m, 7H, Ar-*H*). Anal. Calcd. for $C_{14}H_{11}BrO_3$: C, 54.75; H, 3.61. Found: C, 54.91; H, 3.54%.

2-Bromo-4,5-methylenedioxybenzyl-2'-methoxyphenylether (1c) had mp: 93-95°C (from CH_2Cl_2-*n*-hexane); ^1H NMR ($CDCl_3$; 60 MHz) δ 3.90 (s, 3H, O*Me*), 5.10 (s, 2H, CH_2O), 5.95 (s, 2H, OCH_2O), 6.80-7.20 (m, 6H, Ar-*H*). Anal. Calcd. for $C_{15}H_{13}BrO_4$: C, 53.43; H, 3.89. Found: C, 53.25; H, 3.80%.

2-Bromo-4,5-methylenedioxybenzyl-3'-methoxyphenylether (1d) had mp: 54-55°C ($CHCl_3$-*n*-hexane); ^1H NMR ($CDCl_3$; 60 MHz) δ 3.80 (s, 3H, O*Me*), 5.05 (s, 2H, CH_2O), 6.00 (s, 2H, OCH_2O), 6.40-7.40 (m, 6H, Ar-*H*). Anal. Calcd. for $C_{15}H_{13}BrO_4$: C, 53.43; H, 3.89. Found: C, 53.40; H, 3.90%.

2-Bromo-4,5-methylenedioxybenzyl-4'-methoxyphenylether (**1e**) had mp: 73-75°C (from $CHCl_3$-*n*-hexane); ^1H NMR ($CDCl_3$; 60 MHz) δ 3.80 (s, 3H, O*Me*), 5.05 (s, 2H, CH_2O), 6.05 (s, 2H, OCH_2O), 6.95 (s, 4H, Ar-*H*), 7.10 (s, 2H, Ar-*H*). Anal. Calcd. for $C_{15}H_{13}BrO_4$: C, 53.43; H, 3.89. Found: C, 53.30; H, 3.81%.

By method B:

2-Bromo-4,5-methylenedioxybenzyl-2',3'-dimethoxyphenylether (**1f**) had mp: 72-74°C (from CH_2Cl_2-*n*-hexane); ^1H NMR ($CDCl_3$; 300 MHz) δ 3.872 (s, 3H, O*Me*), 3.899 (s, 3H, O*Me*), 5.086 (s, 2H, CH_2O), 5.997 (s, 2H, OCH_2O), 6.58 (d, 1H, *J*=8.3Hz, Ar-*H*), 6.608 (d, 1H, *J*=8.3Hz, Ar-*H*), 6.963 (t, 1H, *J*=8.3Hz, Ar-*H*), 7.027 (s, 1H, Ar-*H*), 7.071 (s, 1H, Ar-*H*). Anal. Calcd. for $C_{16}H_{15}BrO_5$: C, 52.34; H, 4.12. Found: C, 52.45; H, 4.24%.

2-Bromo-4,5-methylenedioxybenzyl-2',4'-dimethoxyphenylether (**1g**) had mp: 115-116°C (from CH_2Cl_2-*n*-hexane); ^1H NMR ($CDCl_3$; 60 MHz) δ 3.8 (s, 3H, O*Me*), 3.90 (s, 3H, O*Me*), 5.05 (s, 2H, CH_2O), 6.00 (s, 2H, OCH_2O), 6.40 (dd, 1H, *J*=8 and 3.3 Hz, Ar-*H*), 6.6 (d, 1H, *J*=3.3Hz, Ar-*H*), 6.85 (d, 1H, *J*=8.0 Hz, Ar-*H*), 7.05 (s, 1H, Ar-*H*), 7.10 (s, 1H, Ar-H). Anal. Calcd. for $C_{16}H_{15}BrO_5$: C, 52.34; H, 4.12. Found: C, 52.36; H, 4.07%.

2-Bromo-4,5-methylenedioxybenzyl-3',5'-dimethoxyphenylether (**1h**) had mp: 91-93°C (from CH_2Cl_2-*n*-hexane); ^1H NMR ($CDCl_3$; 300 MHz) δ 3.774 (s, 6H, 2xO*Me*), 5.00 (s, 2H, CH_2O), 5.982 (s, 2H, OCH_2O), 6.106-6.160 (m, 3H, Ar-*H*), 7.018 (s, 1H, Ar-*H*), 7.029 (s, 1H, Ar-*H*). HREIMS Calcd. for $C_{16}H_{14}BrO_5$ (M^+-1): 367.0004. Found: 366.9962.

Methyl O-(2-bromo-4,5-methylenedioxybenzyl)salicylate (**1i**) had mp: 114-117°C (from CH_2Cl_2-*n*-hexane); ^1H NMR ($CDCl_3$; 60 MHz) δ 3.95 (s, 3H, O*Me*), 5.15 (s, 2H, CH_2O), 6.00 (s, 2H, OCH_2O), 6.90-8.00 (m, 6H, Ar-*H*). Anal. Calcd. for $C_{16}H_{13}BrO_5$: C, 52.63; H, 3.59. Found: C, 52.44; H, 3.53%.

O-(2-Bromo-4,5-methylenedioxybenzyl)salicyclic acid (**1j**) obtained by saponification (8N KOH) of **1i** in methanol at room temperature, followed by acidification, had mp: 153-155°C (from Et_2O-*n*-hexane); ^1H NMR ($CDCl_3$; 60 MHz) δ 5.30 (s, 2H, CH_2O), 6.05 (s, 2H, OCH_2O), 7.0~8.4 (m, 7H, Ar-*H* + CO_2H, 1H exchangeable in D_2O). Anal. Calcd. for $C_{15}H_{11}BrO_5$: C, 51.30; H, 3.16. Found: C, 51.25; H, 3.04%.

2-Bromo-4,5-methylenedioxybenzyl-1'-naphthylether (**1k**) had mp: 79-82°C (from CH_2Cl_2-*n*-hexane); ^1H NMR ($CDCl_3$; 60 MHz) δ 5.25 (s, 2H, CH_2O), 6.00 (s, 2H, OCH_2O), 6.80-8.00 (m, 8H, Ar-*H*), 8.40 (m, 1H, Ar-*H*). Anal. Calcd. for $C_{18}H_{13}BrO_3$: C, 60.53; H, 3.67. Found: C, 60.47; H, 3.61%.

General Method for Reaction of *o*-bromobenzylphenylethers with *n*-Bu_3SnH (TBTH) and AIBN. The appropriate bromide (1 equiv.), and TBTH (1 to 2 mol equiv.) in dry benzene (240 ml), under reflux, was treated with AIBN (0.5~0.6 mol equiv.) in benzene (58 ml), in portions during *ca.* 16 h.

Evaporation of the solvent under reduced pressure left an oily residue which was processed in one of the following three methods to isolate the products:

i. The residue remaining, after being repeatedly washed with *n*-pentane to remove organotin species, was submitted to column chromatography (SiO_2).

ii. The residue dissolved in Et_2O was treated with an aqueous solution of KF, the solid formed removed by filtration and the products in the filtrate isolated by chromatography.

iii. The residue was dissolved in acetonitrile and the solution washed several times with *n*-hexane, the combined *n*-hexane fractions extracted once with CH_3CN. Evaporation of the combined CH_3CN solutions yielded a residue which was subjected to column chromatography.

The ether **1a** (0.8 g), after work-up (method iii), gave: **6H-dibenzo[*b,d*]pyran** (**2a**; 0.27 g) as a colourless, viscous oil, lit[12] b.p 108-110°C/2 mm); ^{1}H NMR ($CDCl_3$, 60 MHz) δ 5.05 (b, 2H, CH_2O), 6.70-7.90 (m, 8H, Ar-*H*).

The ether **1b** (0.75 g), after work-up (method i or ii) and chromatography (*n*-hexane-EtOAc 9:1), gave: **8,9-methylenedioxy-6H-dibenzo[*b,d*]pyran** (**2b**; 0.26 g); mp: 83-85°C (from *n*-hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.01 (s, 2H, CH_2O), 5.986 (s, 2H, OCH_2O), 6.636 (s, 1H, Ar-*H*), 6.983 (t, 1H, *J*=7.5 Hz, Ar-*H*), 7.046 (d, 1H, *J*=7.5 Hz, Ar-*H*), 7.167 (s, 1H, Ar-*H*), 7.192 (t, 1H, *J*=7.5 Hz, Ar-*H*), 7.569 (d, 1H, *J*=7.5 Hz, Ar-*H*). Anal. Calcd. for $C_{14}H_{10}O_3$: C, 74.33; H, 4.46. Found: C, 74.23; H, 4.42%.

The ether **1c** (1 g), after work-up (method i or ii) and chromatography, gave: *a)* **8,9-Methylenedioxy-6H-dibenzo[*b,d*]pyran** (**2b**; 6.8% yield). *b)* **8,9-Methylenedioxy-4-methoxy-6H-dibenzo[*b,d*]pyran** (**2c**; 0.04 g); mp: 130-132°C (from CH_2Cl_2-*n*-hexane); ^{1}H NMR ($CDCl_3$, 60 MHz) δ 3.90 (s, 3H, O*Me*), 5.10 (s, 2H, CH_2O), 6.00 (s, 2H, OCH_2O), 6.60-7.25 (m, 5H, Ar-*H*). Anal. Calcd. for $C_{15}H_{12}O_4$: C, 70.29; H, 4.72. Found: C, 70.06; H, 4.58%. *c)* **4,5-Methylenedioxy-2-hydroxymethyl-2'-methoxybiphenyl** (**3c**; 0.13 g), oil IR (neat) 3405 (OH); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.15 (bs, 1H, O*H*, exchangeable in D_2O), 3.769 (s, 3H, O*Me*), 4.256 (d, 1H, *J*=11.7 Hz, CH_2OH), 4.333 (d, 1H, *J*=11 Hz), 5.991 (s, 2H, OCH_2O), 6.682 (s, 1H, Ar-*H*), 6.977 (d, 1H, *J*=7.8 Hz, Ar-*H*), 7.022 (s, 1H, Ar-*H*), 7.022 (t, 1H, *J*=7.8 Hz, Ar-*H*), 7.142 (dd, 1H, *J*=7.8 and 1.8 Hz, Ar-*H*), 7.352 (dd, 1H, *J*=7.8 and 1.8 Hz, Ar-*H*); HREIMS Calcd. for $C_{15}H_{14}O_4$: 258.08921. Found: 258.08869.

The ether **1d** (1 g) after work-up (method i or ii) and chromatography (CH_2Cl_2) gave: **8,9-methylenedioxy-3-methoxy-6H-dibenzo[*b,d*]pyran** (**2d**; 0.15 g); mp: 122-124°C (from CH_2Cl_2-*n*-hexane); ^{1}H NMR ($CDCl_3$; 60 MHz) δ 3.85 (s, 3H, O*Me*), 5.05 (s, 2H, CH_2O), 6.00 (s, 2H, OCH_2O), 6.55-6.88 (m, 3H, Ar-*H*), 7.15 (s, 1H, Ar-*H*), 7.55 (d, H, *J*=9 Hz, Ar-*H*). Anal. Calcd. for $C_{15}H_{12}O_4$: C, 70.29; H, 4.72. Found: C, 70.21; H, 4.99%.

The ether **1e** (1 g), after work-up (method iii) and chromatography (*n*-hexane-EtOAc 9:1 and EtOAc) gave: *a)* **8,9-Methylenedioxy-2-methoxy-6H-dibenzo[*b,d*]pyran** (**2e** ; 0.17 g, 22% yield), mp: 111-114°C (from Et_2O-*n*-hexane); ^{1}H NMR ($CDCl_3$, 60 MHz) δ 3.85 (s, 3H, O*Me*), 5.00 (s, 2H, CH_2O), 6.00 (s, 2H, OCH_2O), 6.60-7.25 (m, 5H, Ar-*H*). Anal. Calcd. for $C_{15}H_{12}O_4$: C, 70.29; H, 4.72. Found: C, 70.13;

H, 4.24%. *b)* **4,5-Methylenedioxy-2-hydroxymethyl-4'-methoxybiphenyl** (**3e**; 0.533 g, 6.9% yield), mp: 147-149°C (from EtOAc-*n*-hexane); IR (KBr) 3340-3230 (OH); ^{1}H NMR (CD_3COCD_3, 300 MHz) δ 2.868 (s, 1H, O*H* exchangeable in D_2O), 3.821 (s, 3H, O*Me*), 4.409 (s, 2H, CH_2OH), 5.998 (s, 2H, OCH_2O), 6.690 (s, 1H, Ar-*H*), 6.950 (dd, 1H, *J*=6.9 and 2.4 Hz, Ar-*H*), 6.957 (dd, 1H, *J*=8.7 and 1.9 Hz, Ar-*H*), 7.064 (s, 1H, Ar-*H*), 7.28 (dd, 1H, *J*=9.0 and 2.4 Hz, Ar-*H*), 7.288 (dd, 1H, *J*=6.9 and 1.9 Hz, Ar-*H*); HREIMS Calcd. for $C_{15}H_{14}O_4$: 258.08921. Found: 258.08963.

The ether **1f** (1g), after work-up (method iii) and chromatography (CH_2Cl_2 and CH_2Cl_2-MeOH 95:5) gave: *a)* **8,9-Methylenedioxy-4-methoxy-6H-dibenzo[*b,d*]pyran** (**2c**; 0.12 g, 18% yield). *b)* **8,9-Methylenedioxy-3,4-dimethoxy-6H-dibenzo[*b,d*]pyran** (**2f**; 0.18 g, 23% yield), mp: 161-163°C (from CH_2Cl_2-*n*-hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.896 (s, 6H, 2xO*Me*), 5.044 (s, 2H, CH_2O), 5.975 (s, 2H, OCH_2O), 6.626 (d, 1H, *J*=8.4 Hz, Ar-*H*), 7.094 (s, 1H, Ar-*H*), 7.268 (d, 1H, *J*=8.4 Hz, Ar-*H*). Anal. Calcd. for $C_{16}H_{14}O_5$: C, 67.13; H, 4.93. Found: C, 66.94; H, 4.94%.

The ether **1g** (1 g) after work-up (method iii) and chromatography (eluotropic mixture involving CH_2Cl_2 and CH_2Cl_2-MeOH 95 :5) gave: a) **8,9-Methylenedioxy-3-methoxy-6H-dibenzo[*b,d*]pyran** (**2d**; 0.21 g, 30% yield). *b)* **8,9-Methylenedioxy-2,4-dimethoxy-6H-dibenzo[*b,d*]pyran** (**2g**; 0.057 g, 7.4% yield), mp: 148-150°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.849 (s, 3H, O*Me*), 3.889 (s, 3H, O*Me*), 5.018 (s, 2H, CH_2O), 5.994 (s, 2H, OCH_2O), 6.463 (d, 1H, *J*=2.7 Hz, Ar-*H*), 6.659 (s, 1H, Ar-*H*), 6.686 (d, 1H, *J*=2.7 Hz, Ar-*H*), 7.119 (s, 1H, Ar-*H*). Anal Calcd for $C_{16}H_{14}O_5$: C, 67.13; H, 4.93. Found: C, 67.15; H, 4.93%. *c)* **4,5-Methylenedioxy-2-hydroxymethyl-2',4'-dimethoxybiphenyl** (**3g**; 0.15 g, 19% yield), mp: 113-115°C (from EtOAc - Et_2O); IR (KBr) 3530 (O*H*); ^{1}H NMR ($CDCl_3$, 60 MHz) δ 3.95 (s, 3H, O*Me*), 4.05 (s, 3H, O*Me*), 4.05 (bs, 1H, O*H*, exchangeable in D_2O), 4.50 (s, 2H, CH_2OH), 6.20 (s, 2H, OCH_2O), 6.60-7.30 (m, 5H, Ar-*H*). Anal. Calcd. for $C_{16}H_{16}O_5$: C, 66.66; H, 5.59. Found: C, 66.42; H, 5.90%.

The ether **1h** (1 g) after work-up (method iii) and chromatography (CH_2Cl_2) gave: *a)* **8,9-Methylenedioxy-1,3-dimethoxy-6H-dibenzo[*b,d*]pyran** (**2h**; 0.038 g, 4.9% yield), mp: 227-230°C (from *n*-hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.802 (s, 3H, O*Me*), 3.901 (s, 3H, O*Me*), 4.87 (s, 2H, CH_2O), 5.956 (s, 2H, OCH_2O), 6.226 (s, 2H, Ar-*H*), 6.637 (s, 1H, Ar-*H*), 7.803 (s, 1H, Ar-*H*); HREIMS Calcd. for $C_{16}H_{14}O_5$: 286.084124. Found: 286.083951. *b)* **4,5-Methylenedioxy-2-methyl-2'-hydroxy-4',6'-dimethoxybiphenyl** (**9**; 0.21 g, 27% yield), mp: 131-132°C (from CH_2Cl_2-*n*-hexane); IR (KBr): 3470 (OH); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.011 (s, 3H, CH_3), 3.706 (s, 3H, O*Me*), 3.818 (s, 3H, O*Me*), 4.829 (bs, 1H, O*H*, exchangeable in D_2O), 5.964 (d, 1H, *J*=5.7 Hz, OCH_AH$_B$O), 5.969 (d, 1H, *J*=5.7 Hz, OCH$_A$$H_B$O), 6.145 (d, 1H, *J*=2.4 Hz, Ar-*H*), 6.214 (d, 1H, *J*=2.4 Hz, Ar-*H*), 6.662 (s, 1H, Ar-*H*), 6.817 (s, 1H, Ar-*H*). Anal. Calcd. for $C_{16}H_{16}O_5$: C, 66.66; H, 5.59. Found: C, 66.78; H, 5.67%.

Methyl 8,9-methylenedioxy-6H-dibenzo[*b,d*]pyran-4-carboxylate (2i) The ester **1i** (1 g), after work-up (method iii) gave **2i** (0.23g ; 30% yield), mp: 155-158°C (from CH_2Cl_2-*n*-hexane); IR (KBr): 1728

(C=O); ^{1}H NMR δ 3.95 (s, 3H, CO_2Me), 5.10 (s, 2H, CH_2O); 6.05 (s, 2H, OCH_2O); 6.60-7.90 (m, 5H, Ar-*H*). Anal. Calcd. for $C_{16}H_{12}O_5$: C, 67.60; H, 4.25. Found: C, 67.38; H, 4.30%

The ether **1j** (0.5 g) after work-up (method iii), gave: a) **2b** (0.0039 g; 1.2% yield), mp: 82-84°C (from *n*-hexane). *b)* **8,9-Methylenedioxy-6H-dibenzo[*b,d*]pyran-4-carboxylic acid** (**2j**; 0.073 g, 19% yield), mp: 274-277°C (from EtOAc); IR (KBr): 3165 (OH), 1740 (C=O); ^{1}H NMR ($CDCl_3$-DMSO-d_6, 60 MHz) δ 5.10 (s, 2H, CH_2O), 6.05 (s, 2H, OCH_2O), 6.80-8.05 (m, 6H, Ar-*H*, COO*H*, the latter exchangeable in D_2O). HREIMS Calcd. for $C_{15}H_{10}O_5$: 270.052824. Found: 270.052443. *c)* **4,5-Methylenedioxy-2-hydroxymethylbiphenyl -2'-carboxylic acid** (**3j**; 7.4 mg, 1.9% yield), mp: 150-152°C (from CH_2Cl_2-*n*-hexane); IR (KBr): 3387 (OH), ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.592 (bs, 1H, O*H*, exchangeable in D_2O), 4.854 (d, 1H, *J*=11.7 Hz, CH_AH_BO), 4.950 (d, 1H, *J*=11.7 Hz, CH_AH_BO), 6.064 (s, 2H, OCH_2O), 6.929 (s, 1H, Ar-*H*), 7.099 (s, 1H, Ar-*H*), 7.48 (dt, 1H, J=7.8 and 1.2 Hz, Ar-*H*), 7.520 (dd, 1H, *J*=7.8 and 1.2 Hz, Ar-*H*), 7.630 (dt, 1H, *J*=7.8 and 1.5 Hz, Ar-*H*), 7.956 (dd, 1H, *J*=7.8 and 1.5 Hz, Ar-*H*), 9.778 (s, 1H, COO*H*, exchangeable in D_2O). HREIMS Calcd. for $C_{14}H_{11}O_4$ (M^+-OH): 255.06573. Found: 255.06520.

The compound **1k** (0.5 g) led to, by the workup (method i) and chromatography (*n*-hexane-EtOAc 9:1), **8,9-methylenedioxy-6H-napthobenzo[*b,d*]pyran** (**2k**; 0.18 g); mp: 146-151°C (from *n*-hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.195 (s, 2H, CH_2O), 5.999 (s, 2H, OCH_2O), 6.706 (s, 1H, Ar-*H*), 7.221 (s, 1H, Ar-*H*), 7.480 (dt, 2H, *J*=6.6 and 2.7 Hz, Ar-*H*), 7.514 (d, 1H, *J*=8.4 Hz, Ar-*H*), 7.688 (d, 1H, Ar-H, *J*=8.4 Hz, Ar-H),7.784 (dd, 1H, *J*=6.6 and 2.7 Hz, Ar-*H*), 8.230 (dd, 1H, *J*=6.6 and 2.7 Hz, Ar-*H*). Anal. Calcd. for $C_{18}H_{12}O_3$: C, 78.25; H, 4.38. Found: C, 78.18; H, 4.33%.

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