# Regioselectivity in the Reactions of Methoxydehydrobenzenes with Furans. Part 2.[1] 2-Methoxyfuran and Methoxydehydrobenzenes

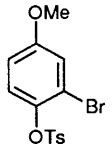
**Robin G. F. Giles,*[a] Andrew B. Hughes[a,b] and Melvyn V. Sargent*[b]**
[a] *School of Mathematical and Physical Sciences, Murdoch University, Murdoch, Western Australia, 6150*
[b] *Department of Organic Chemistry, The University of Western Australia, Nedlands, Western Australia, 6009*

Acid-induced ring opening of adducts of furan and methoxydehydrobenzenes gives the naphthalenols derived from the more stable carbocation. The cycloadditions of methoxydehydrobenzenes containing a 3-methoxy group and 2-methoxyfuran are highly regiospecific. The adducts, being strained acetals, undergo ring opening to provide a convenient synthesis of naphthalenols.

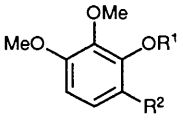
In Part 1 [1] we explored the cycloaddition of 3-methoxydehydrobenzene with 2-substituted furans and we now extend this work to the cycloaddition of methoxy-substituted dehydrobenzenes with both furan and 2-methoxyfuran. 2-Methoxyfuran is expected to be a more reactive diene than furan but there are few examples of its use in Diels–Alder reactions,[2,3] and only one record of its reaction with a dehydrobenzene.[4] Our interest in the cycloadducts of furan and 2-methoxyfuran with methoxydehydrobenzenes was as precursors to naphthalenols and we have investigated the regiochemistry of the acid-induced ring opening of the symmetrical furan adducts and the regiochemistry of the cycloaddition of unsymmetrical methoxydehydrobenzenes with 2-methoxyfuran.

The required dehydrobenzenes were usually generated from the appropriate 1,2-dibromo- or 1-bromo-2-tosyloxybenzene by treatment with butyllithium in tetrahydrofuran (THF) at −100 °C in the presence of either furan or 2-methoxyfuran, and then allowing the solution to slowly warm to room temperature. Certain of the required intermediates are new compounds and their preparation is now briefly discussed.

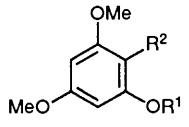
2-Bromo-4-methoxyphenyl toluene-*p*-sulphonate **1** was readily prepared by tosylation of 2-bromo-4-methoxyphenol.[5] For the preparation of 6-bromo-2,3-dimethoxyphenyl toluene-*p*-sulphonate **4**, the starting material was 2,3-dimethoxyphenol[6] **2**, which was converted into its tosyl ester **3**; bromination then supplied compound **4** as shown by its hydrolysis to the known 6-bromo-2,3-dimethoxyphenol **5**.[6] 2-Bromo-3,5-dimethoxyphenyl toluene-*p*-sulphonate **8** has been prepared previously by



**1**



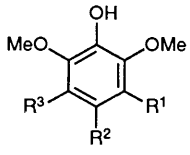
**2**; $R^1 = R^2 = H$
**3**; $R^1$ = Ts, $R^2 = H$
**4**; $R^1$ = Ts, $R^2$ = Br
**5**; $R^1 = H$, $R^2$ = Br



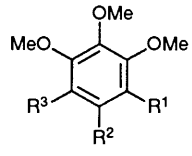
**6**; $R^1 = R^2 = H$
**7**; $R^1$ = Ts, $R^2 = H$
**8**; $R^1$ = Ts, $R^2$ = Br

Tochtermann *et al.*[7] by bromination of 3,5-dimethoxyphenol[8] **6** and tosylation of the product. We have found that it is more efficient to reverse these processes since the bromination of the tosylate **7** smoothly yields the required bromo tosylate **8**.

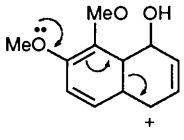
Kohn and Grün[9] reported that bromination of 2,6-dimethoxyphenol[10] **9** with 2 mol equiv. of bromine gave the dibromo compound **10**, which on methylation gave the dibromo compound **12** required for the generation of 3,4,5-trimethoxydehydrobenzene[11] **57**. We found that methylation of the dibromination product of 2,6-dimethoxyphenol **9** gave both the dibromo compounds **12** and **13**.[12] We have confirmed that the monobromination product of the phenol **9** is the monobromo compound[13] **11**, so that the former result is not surprising. Compound **12** is best prepared by bromination of the known 5-bromo-1,2,3-trimethoxybenzene **14**.[14]



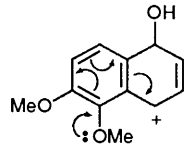
**9**; $R^1 = R^2 = R^3 = H$
**10**; $R^1 = R^2$ = Br, $R^3 = H$
**11**; $R^1$ = Br, $R^2 = R^3 = H$



**12**; $R^1 = R^2$ = Br, $R^3 = H$
**13**; $R^1 = R^3$ = Br, $R^2 = H$
**14**; $R^1 = R^3 = H$, $R^2$ = Br



**15**

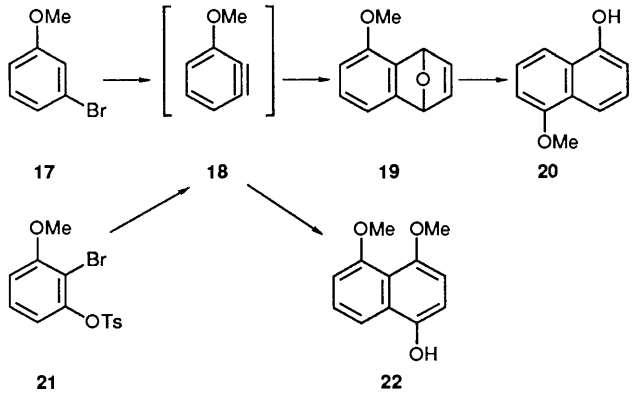


**16**

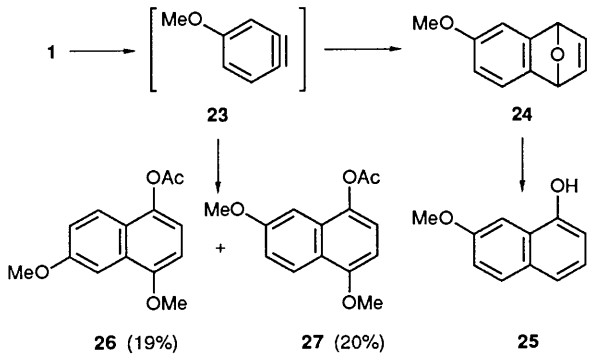
3-Methoxydehydrobenzene **18**, generated by treatment of 3-bromoanisole **17** with sodamide in the presence of furan, gave the cycloadduct[15] **19**, which on acid-induced ring-opening supplied the known 5-methoxynaphthalen-1-ol[16] **20** (Scheme 1). The direction of ring opening is that expected on the grounds of protonation of the oxygen of the epoxide bridge, followed by opening of the bridge to give the more stable carbocation. The same is true of the unsymmetrical cycloadducts of furan (**24**)[17] (Scheme 2), (**44**)[7] (Scheme 6), (**52**) (Scheme 7) and (**58**) (Scheme 8) which gave, on ring opening, as expected, as the sole or major products the known naphthalenols **25**,[18] **45**,[19] **53**[20] and **59**[21] respectively.

The case of the adduct **38** (Scheme 5) is worthy of special comment. The major product of ring opening is the known naphthalenol[22] **39** which would arise from the carbocation **15**. The minor product **40** must arise from the carbocation **16**. It is likely that in the carbocation **16** the *peri*-methoxy group is out of the plane of the conjugated system because of steric hindrance by the *ortho*-methoxy group. A similar reason has been advanced to account for the readily occurring demethylation of *peri*-methoxy groups in polymethoxynaphthalenes.[22]

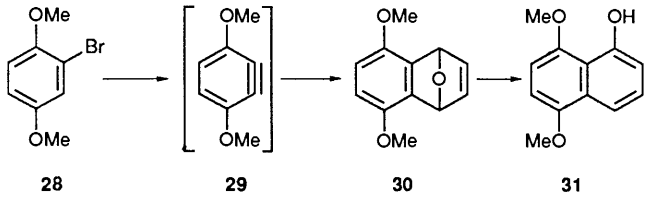
The naphthalenol **53** (Scheme 7) had previously been prepared by Brunner and Hawke[20] by a Haworth synthesis. The reported m.p. was 37 °C higher than that recorded by us. In order to verify our structural assignment we therefore converted this



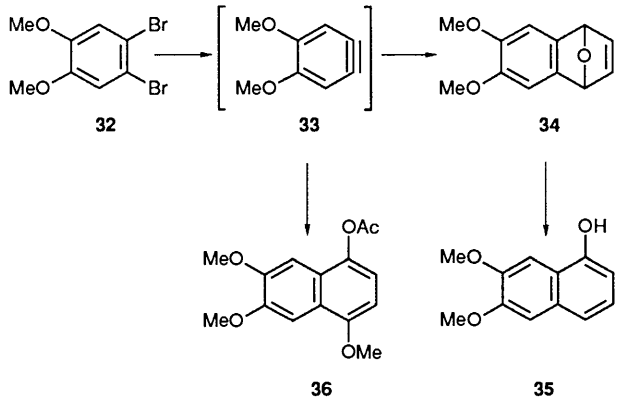

Scheme 1



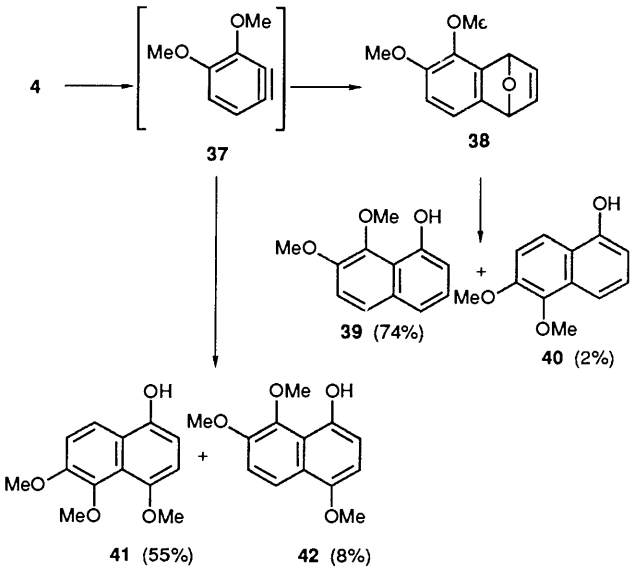

Scheme 2



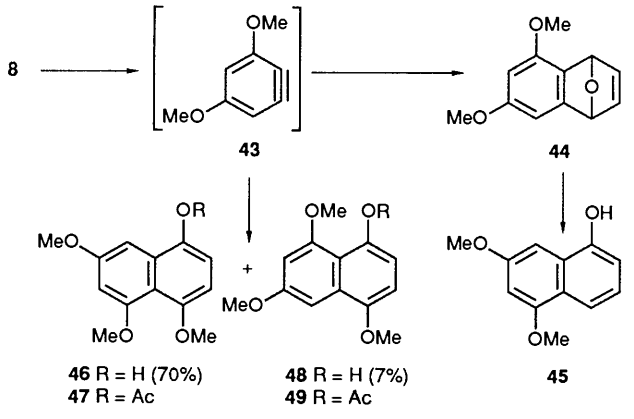

Scheme 3




Scheme 4




Scheme 5




Scheme 6

naphthalenol **53** into its *O*-methyl derivative **54** which, on oxidation with ammonium cerium(IV) nitrate, supplied the *para*-quinone **55** and the *ortho*-quinone **56**. The *para*-quinone **55** had properties in accord with those previously reported.[23]

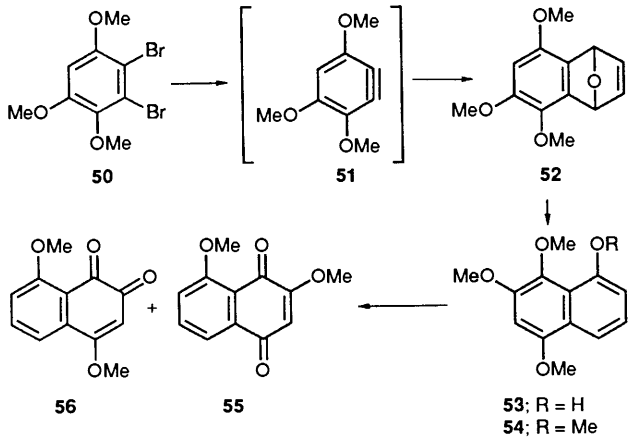
The symmetrical adducts **30**[24] (Scheme 3), **34**[17] (Scheme 4) and **66** (Scheme 9) gave, on ring opening, as expected, the naphthalenols **31**,[25] **35**[26] and **67**.

The cycloadducts of 2-methoxyfuran and the methoxydehydrobenzenes, being strained acetals, defied attempts at isolation,[3] so they were converted directly into naphthalenes by treatment with acid. In the cases of the unsymmetrically substituted dehydrobenzenes two cycloadducts may be formed which would give rise to different naphthalenols. In the case of 3-methoxydehydrobenzene **18** (Scheme 1) the sole product detected was the known naphthalenol **22**.[27] 4-Methoxydehydrobenzene **23** (Scheme 2) gave essentially equal amounts of the acetoxynaphthalenes **26** and **27**, the structures of which followed from their 300 MHz $^1$H NMR spectra. 3,4-Dimethoxydehydrobenzene **37** (Scheme 5) gave predominantly the naphthalenol **41**. The structure of the minor product, the naphthalenol **42**, followed from the presence of a sharp singlet at δ 9.18 in its $^1$H NMR spectrum, which is characteristic of an 8-methoxynaphthalen-1-ol.[28]

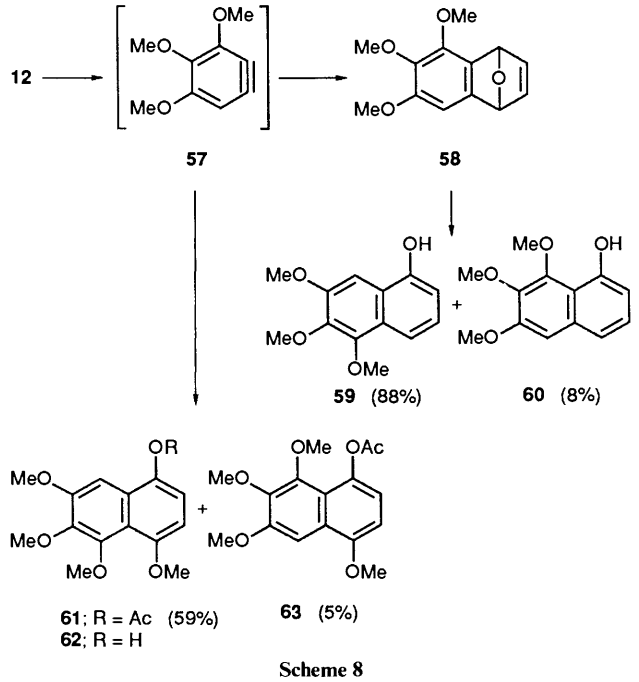
3,5-Dimethoxydehydrobenzene **43** (Scheme 6) gave predominantly the naphthalenol **46**. In this case both of the isomeric acetates **47** and **49** are known compounds.[29] 3,4,5-Trimethoxydehydrobenzene **57** (Scheme 8) gave predominantly the acetate isomer **61**; its structure followed from the presence of a broad signal at δ 6.13, ascribed to a hydroxy group, in the $^1$H NMR spectrum of its $LiAlH_4$ reduction product **62**.

The symmetrically substituted dehydrobenzenes **33** (Scheme 4) and **65** (Scheme 9) gave, on ring opening, as expected, the naphthalenes **36** and **68**.

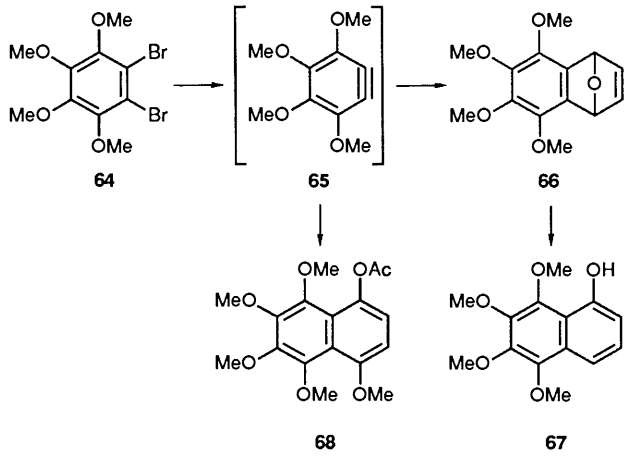
The regioselectivity of the cycloadditions of 2-methoxyfuran with the unsymmetrical dehydrobenzenes containing a 3-methoxy group is very high. There is no regioselectivity in the reaction involving 4-methoxydehydrobenzene **23**. The inductive




Scheme 7




Scheme 8




Scheme 9

polarization induced in a dehydrobenzene by a 3-methoxy group and the powerful electron-releasing properties of the 2-methoxy group in the furan reinforce each other, leading to the high observed regioselectivity. The inductive polarization in 4-methoxydehydrobenzene is much attenuated, consequently leading to loss of regioselectivity.

These reactions therefore provide short and efficient syntheses of specifically oxygenated naphthalenols; many of those which are not new compounds have been obtained previously only by circuitous routes.

## Experimental

General directions are given in Part 1.[1] $^1$H NMR spectra determined at 60 MHz refer to a Hitachi-Perkin Elmer R24B instrument, and those determined at 80 MHz refer to a Bruker WP80 instrument.

*Preparation of Precursors.*—*2-Bromo-4-methoxyphenyl toluene*-p-*sulphonate* **1**. A stirred solution of 2-bromo-4-methoxyphenol[5] (15.8 g) and triethylamine (13.1 cm$^3$) in dichloromethane (100 cm$^3$) was treated dropwise at 0 °C with a solution of toluene-*p*-sulphonyl chloride (17.8 g) in dichloromethane (150 cm$^3$) and was then stirred at room temperature for 2 h. The solution was diluted with dichloromethane, and washed in turn with water, aq. sodium hydrogen carbonate, and saturated brine. The crude product was purified by flash chromatography with 10% ethyl acetate–hexane as eluent which gave the *tosylate* **1** (26.4 g, 95%), which was crystallized from dichloromethane–hexane as prisms, m.p. 73.5–75 °C (Found: Br, 22.5; S, 8.95%; M$^+$, 356/358. $C_{14}H_{13}BrO_4S$ requires Br, 22.35; S, 8.95%; M, 356/358); $\delta_H$(80 MHz) 2.45 (3 H, s, Me), 3.77 (3 H, s, OMe), 6.79 (1 H, dd, $J_{5,6}$ 9.0, $J_{5,3}$ 3.0, 5-H), 7.02 (1 H, d, $J_{3,5}$ 3.0, 3-H), 7.22 (1 H, d, $J_{6,5}$ 9.0, 6-H) and 7.30 and 7.77 (4 H, AA'BB', ArH).

*6-Bromo-2,3-dimethoxyphenyl toluene*-p-*sulphonate* **4**. A stirred solution of 2,3-dimethoxyphenol[6] **2** (12.0 g) and triethylamine (13.1 cm$^3$) in dichloromethane (100 cm$^3$) was treated dropwise at 0 °C with a solution of toluene-*p*-sulphonyl chloride (17.8 g) in dichloromethane (150 cm$^3$) and was then stirred at room temperature for 1 h. The solution was then diluted with dichloromethane and washed in turn with water, aq. sodium hydrogen carbonate and saturated brine. The crude product was purified by flash chromatography over silica gel with 5–15% ethyl acetate–hexane as eluent which gave 2,3-dimethoxyphenyl tosylate **3** (20.6 g, 86%) as an oil.

A stirred solution of this material in chloroform (130 cm$^3$) was treated dropwise with a solution of bromine (10.7 g) in chloroform (50 cm$^3$) at room temperature. The solution was then washed in turn with water, aq. sodium hydrogen carbonate and saturated brine. The crude product crystallized from dichloromethane–hexane as platelets (15.9 g, 61%) of the *tosylate* **4**, m.p. 118.5–119.5 °C (Found: C, 46.9; H, 3.45; Br, 20.55%; M$^+$, 386/388. $C_{15}H_{15}BrO_5S$ requires C, 46.5; H, 3.9; Br, 20.65%; M, 386/388); $\delta_H$(80 MHz) 2.43 (3 H, s, Me), 3.64 and 3.84 (each 3 H, s, OMe), 6.72 and 7.22 (2 H, AB, *J* 9.1, ArH) and 7.87 and 7.97 (4 H, AA'BB', ArH).

*6-Bromo-2,3-dimethoxyphenol* **5**. A solution of tosylate **4** (500 mg) and sodium hydroxide (100 mg) in water (5 cm$^3$)–ethanol (5 cm$^3$) was stirred at 50 °C (bath) under argon for 5 h. The usual work-up gave the phenol **5** (275 mg, 91%) as an oil, b.p. 125 °C at 0.3 mmHg (lit.,[6] 125 °C at 0.3 mmHg), which was identical with an authentic sample.

*3,5-Dimethoxyphenyl toluene*-p-*sulphonate* **7**. Tosylation of 3,5-dimethoxyphenol[8] **6** by a method similar to that described above gave the *tosyl ester* **7** (89%), which was crystallized from dichloromethane–hexane as prisms, m.p. 62–63 °C (Found: C, 58.35; H, 5.4; S, 10.6%; M$^+$, 308. $C_{15}H_{16}O_5S$ requires, C, 58.45; H, 5.25; S, 10.4%; M, 308); $\delta_H$(80 MHz) 2.44 (3 H, s, Me), 3.68 (6 H, s, 2 × OMe), 6.16 (2 H, d, *J* 2.2, 2- and 6-H), 6.33 (1 H, t, *J* 2.2, 4-H) and 7.32 and 7.75 (4 H, AA'BB', ArH).

*2-Bromo-3,5-dimethoxyphenyl toluene-p-sulphonate* **8**. A solution of bromine (14.4 g) in acetic acid (150 $cm^3$) was added dropwise to a stirred solution of the foregoing tosylate **7** (27.8 g) in acetic acid (300 $cm^3$) containing anhydrous sodium acetate (11.0 g). After the addition the solution was stirred at room temperature and was then poured into an excess of aq. sodium hydrogen carbonate. The crude product was isolated by extraction with ethyl acetate and was then crystallized from chloroform, whereupon it formed hexagonal plates of the tosyl ester **8** (32.8 g, 94%), m.p. 112–114 °C (lit.,[11] 111 °C).

*Bromination of 2,6-Dimethoxyphenol* **9** (*with Anthony A. Birkbeck*). (a) *With 1 mol equiv. of bromine*. A solution of bromine (478 mg) in tetrachloromethane (3 $cm^3$) was added slowly, dropwise to a stirred solution of the phenol[10] **9** (460 mg) in tetrachloromethane (10 $cm^3$) at −7 °C. After the addition the solution was diluted with tetrachloromethane and washed successively with water and saturated brine. The crude product was distilled under diminished pressure to afford 3-bromo-2,6-dimethoxyphenol **11** (660 mg, 95%) as an oil, b.p. 120 °C at 4 mmHg (lit.,[13] 185–190 °C at 40 mmHg); $\delta_H$(80 MHz) 3.87 and 3.91 (each 3 H, s, OMe), 5.50 (1 H, br, OH) and 6.54 and 7.01 (2 H, AB, *J* 8.9, ArH).

(b) *With 2 mol equiv. of bromine*. A solution of bromine (1.15 g) in tetrachloromethane (5 $cm^3$) was added dropwise to a stirred solution of the phenol **9** (553 mg) in tetrachloromethane (5 $cm^3$). After 2 h the usual work-up gave a crude product, which was methylated during 5 h with dimethyl sulphate (0.42 $cm^3$) and potassium carbonate (1.0 g) in dimethylformamide (DMF) (10 $cm^3$). The usual work-up gave a crude product, which was flash chromatographed with 5% ethyl acetate–hexane as eluent. The first band that was eluted provided 1,5-dibromo-2,3,4-trimethoxybenzene **13** (520 mg, 45%) as an oil, b.p. 120 °C at 0.5 mmHg (lit.,[12] 118 °C at 0.4 mmHg); $\delta_H$(60 MHz) 3.83 (6 H, s, 2 × OMe), 3.88 (3 H, s, OMe) and 7.40 (1 H, s, ArH). Further elution supplied 1,2-dibromo-3,4,5-trimethoxybenzene **12** (520 mg, 45%) as an oil, b.p. 120 °C at 0.5 mmHg (lit.,[9] 308–313 °C at 748 mmHg); $\delta_H$(60 MHz) 3.78, 3.80 and 3.83 (each 3 H, s, OMe) and 6.88 (1 H, s, ArH).

*1,2-Dibromo-3,4,5-trimethoxybenzene* **12**. Bromination of 1-bromo-3,4,5-trimethoxybenzene **14**[14] by a method similar to that described above supplied the dibromo compound **12** (95%).

*Reactions of Methoxydehydrobenzenes with Furan*.—*1,4-Dihydro-5-methoxy-1,4-epoxynaphthalene* **19**. A solution of *m*-bromoanisole **17** (4.86 g) in anhydrous THF (10 $cm^3$) was added dropwise to a stirred suspension of sodamide (4.0 g) in anhydrous THF (35 $cm^3$)–furan (30 $cm^3$) at 50 °C (bath) under argon. The suspension was stirred at 50 °C (bath) for 1.5 h and was then cooled, poured into water, and extracted with diethyl ether. The crude product was chromatographed over silica gel with 5% ethyl acetate–hexane as eluent. The adduct **19** (2.83 g, 63%) was crystallized from dichloromethane–hexane as prisms, m.p. 63.5–64.5 °C (lit.,[15] 59–60 °C) (Found: C, 76.2; H, 6.05. Calc. for $C_{11}H_{10}O_2$: C, 75.85; H, 5.8%); $\delta_H$(300 MHz) 3.78 (3 H, s, OMe), 5.66 (1 H, dd, $J_{1,2}$ 1.8, $J_{1,4}$ 0.9, 1-H), 5.93 (1 H, ddd, $J_{4,3}$ 1.8, $J_{4,8}$ 1.3, $J_{4,1}$ 0.9, 4-H), 6.56 (1 H, dd, $J_{6,7}$ 7.7, $J_{6,8}$ 1.4, 6-H), 6.87 (1 H, ddd, $J_{8,7}$ 7.0, $J_{8,6}$ 1.4, $J_{8,4}$ 1.3, 8-H), 6.94 (1 H, dd, $J_{7,6}$ 7.7, $J_{7,8}$ 7.0, 7-H), 6.98 (1 H, dd, $J_{2,3}$ 5.5, $J_{2,1}$ 1.8, 2-H) and 7.03 (1 H, dd, $J_{3,2}$ 5.5, $J_{3,4}$ 1.8, 3-H); $\delta_C$ 55.64 (OMe), 80.01 (C-4), 82.48 (C-1), 110.29 and 113.67 (C-6 and -8), 126.91 (C-7), 135.05 (C-4a), 142.87 and 142.97 (C-2 and -3) and 151.55 and 152.89 (C-5 and -8a).

A solution of the adduct **19** (1.95 g) in methanol (40 $cm^3$) was heated under reflux with conc. hydrochloric acid (5 drops) for 1 h under argon. Some of the methanol was evaporated off under reduced pressure and the residue was diluted with water. The crude product was isolated by extraction with ethyl acetate and was then purified by chromatography over silica gel with 5% ethyl acetate–hexane as eluent. 5-Methoxynaphthalen-1-ol **20** (1.90 g, 97%) was crystallized from dichloromethane–hexane as plates, m.p. 137–138 °C (lit.,[16] 140 °C); $\delta_H$(300 MHz) 3.99 (3 H, s, OMe), 5.95 (1 H, br, OH), 6.84 (2 H, br d, $J_{2,3}$ = $J_{6,7}$ = 7.6, 2- and 6-H), 7.29 (1 H, dd, $J_{3,4}$ 8.5, $J_{3,2}$ 7.6, 3-H), 7.39 (1 H, dd, $J_{7,8}$ 8.5, $J_{7,6}$ 7.6, 7-H), 7.74 (1 H, br d, $J_{8,7}$ 8.5, 8-H) and 7.84 (1 H, br d, $J_{4,3}$ 8.5, 4-H). It was converted (acetic anhydride–pyridine) into the acetate, which was crystallized from dichloromethane–hexane as prisms, m.p. 63–66 °C (lit.,[30] 61–63 °C); $\delta_H$(300 MHz) 2.44 (3 H, s, Me), 3.99 (3 H, s, OMe), 6.83 (1 H, m, 3-H), 7.25 (1 H, dd, $J_{6,7}$ 7.5, $J_{6,8}$ 1.1, 6-H), 7.42 (2 H, m, 2- and 4-H), 7.44 (1 H, dd, $J_{7,8}$ 8.5, $J_{7,6}$ 7.5, 7-H) and 8.16 (1 H, dd, $J_{8,7}$ 8.5, $J_{8,6}$ 1.1, 8-H).

*1,4-Dihydro-6-methoxy-1,4-epoxynaphthalene* **24**. A stirred solution of the tosyl ester **1** (2.0 g) in anhydrous THF (25 $cm^3$)–furan (25 $cm^3$) was cooled to −100 °C under argon and a solution of butyllithium (1.25 mol $dm^{-3}$) in hexane (4.48 $cm^3$) was added slowly by syringe. The solution was stirred for 10 min at −100 °C and was then allowed to warm to room temperature during 2 h. The solution was poured into water and was then extracted with ethyl acetate. The crude product was purified by radial chromatography with 10% ethyl acetate–hexane as eluent. The adduct **24** (658 mg, 68%) was crystallized from hexane as needles, m.p. 64–66 °C (lit.,[17] 63–64 °C).

Ring opening of the adduct **24** (658 mg) in a similar manner to that described above gave 7-methoxynaphthalen-1-ol **25** (592 mg, 90%), which was crystallized from dichloromethane–hexane as prisms, m.p. 105–106 °C (lit.,[18] 100–102 °C): $\delta_H$(80 MHz) 3.91 (3 H, s, OMe), 5.52 (1 H, s, OH), 6.76 (1 H, dd, $J_{2,3}$ 7.2, $J_{2,4}$ 1.3, 2-H), 7.04–7.50 (4 H, m, 3-, 4-, 6- and 8-H) and 7.70 (1 H, d, $J_{5,6}$ 7.7, 5-H).

*1,4-Dihydro-5,8-dimethoxy-1,4-epoxynaphthalene* **30**. Prepared from 2-bromo-1,4-dimethoxybenzene **28** by the method of Cragg *et al.*,[24] *via* the intermediate **29**, it formed prisms (from hexane), m.p. 86–87 °C (lit.,[24] 86–87 °C): $\delta_H$(300 MHz) 3.77 (6 H, s, 2 × OMe), 5.92 (2 H, narrow m, 1- and 4-H), 6.53 (2 H, s, ArH) and 7.06 (2 H, narrow m, 2- and 3-H); $\delta_C$ 56.37 (OMe), 80.33 (C-1 and -4), 111.67 (C-6 and -7), 137.46 (C-4a and -8a), 142.90 (C-2 and -3) and 147.90 (C-5 and -8).

Ring-opening of this adduct (500 mg) by a method similar to that described above gave 5,8-dimethoxynaphthalen-1-ol **31** (475 mg, 95%), which was crystallized from diethyl ether–pentane as platelets, m.p. 102–104 °C (lit.,[25] 103–104 °C); $\delta_H$(80 MHz) 3.94 and 4.01 (each 3 H, s, OMe), 6.66 (2 H, s, 6- and 7-H), 6.87 (1 H, dd, $J_{2,3}$ 8.3, $J_{2,4}$ 1.3, 2-H), 7.36 (1 H, dd, $J_{3,2}$ = $J_{3,4}$ = 8.3, 3-H), 7.72 (1 H, dd, $J_{4,3}$ 8.3, $J_{4,2}$ 1.3, 4-H) and 9.44 (1 H, s, OH). The methyl ether formed plates, from dichloromethane–hexane, m.p. 116–120 °C (lit.,[31] 116–118 °C).

*1,4-Dihydro-6,7-dimethoxy-1,4-epoxynaphthalene* **34**. A stirred solution of 1,2-dibromo-4,5-dimethoxybenzene[32] **32** (2.0 g) in anhydrous THF (20 $cm^3$)–furan (20 $cm^3$) was maintained at −78 °C under argon and was treated dropwise with butyllithium (1.29 mol $dm^{-3}$) in hexane (5.3 $cm^3$). The solution was stirred at −78 °C for 0.5 h and was then allowed to warm to room temperature during 2 h. The usual work-up yielded a crude product, which was purified by radial chromatography to afford the adduct **34** (800 mg, 58%), which was crystallized from dichloromethane–hexane as prisms, m.p. 128–130 °C (lit.,[17] 145 °C); $\delta_H$(300 MHz) 3.82 (6 H, s, 2 × OMe), 5.66 (2 H, t, $J_{1,2}$ = $J_{3,4}$ = 1.0, 1- and 4-H), 6.96 (2 H, s, ArH) and 7.02 (2 H, t, $J_{2,1}$ = $J_{2,4}$ = 1.0. 2- and 3-H); $\delta_C$ 56.29 (OMe), 82.38 (C-1 and 4), 106.68 (C-5 and -8), 141.58 (C-4a and -8a), 143.14 (C-2 and -3) and 145.66 (C-6 and -7).

Ring opening of the adduct yielded 6,7-dimethoxynaphthalen-1-ol **35** (91%), which was crystallized from toluene as prisms, m.p. 172–176 °C (lit.,[26] 168–169 °C); $\delta_H$(80 MHz) 4.00 and 4.02 (each 3 H, s, OMe), 6.69 (1 H, dd, $J_{2,3}$ 6.9, $J_{2,4}$ 1.8, 2-H),

7.16–7.37 (2 H, m, 3- and 4-H) and 7.24 and 7.47 (each 1 H, s, 5- and 8-H).

1,4-*Dihydro*-5,6-*dimethoxy*-1,4-*epoxynaphthalene* **38**. Prepared from the tosyl ester **4** (2.0 g) by a method similar to that described above, the *adduct* **38** was crystallized from dichloromethane–hexane as plates (793 mg, 75%), m.p. 93–94 °C (Found: C, 70.85; H, 6.1%; $M^+$, 204. $C_{12}H_{12}O_3$ requires C, 70.6; H, 5.9%; M, 204); $\delta_H$(300 MHz) 3.81 and 3.94 (each 3 H, s, OMe), 5.64 (1 H, narrow m, 1-H), 6.05 (1 H, narrow m, 4-H), 6.42 (1 H, d, $J_{7,8}$ 7.6, 7-H), 6.86 (1 H, d, $J_{8,7}$ 7.6, 8-H) and 7.00 (2 H, narrow m, 2- and 3-H); $\delta_C$ 56.23 (6-OMe), 60.42 (5-OMe), 81.18 and 81.96 (C-1 and -4), 107.30 and 114.40 (C-7 and -8), 136.64 (C-4a), 141.45 and 141.79 (C-6 and -8a), 143.07 and 143.69 (C-2 and -3) and 149.76 (C-5).

Ring opening of the adduct (500 mg) and purification of the crude product by radial chromatography with 5–10% ethyl acetate–hexane as eluent gave, from a band of higher $R_f$, 7,8-dimethoxynaphthalen-1-ol **39** (361 mg, 74%) as an oil;[22] the acetate was crystallized from dichloromethane as prisms, m.p. 92–93 °C (lit.,[22] 91–92 °C); $\delta_H$ 2.36 (3 H, s, Me), 3.88 and 3.93 (each 3 H, s, OMe), 7.05 (1 H, dd, $J_{2,3}$ 7.3, $J_{2,4}$ 1.5, 2-H), 7.27 and 7.60 (2 H, AB, $J_{5,6}$ 9.1, 6- and 5-H), 7.28 (1 H, dd, $J_{3,4}$ 8.0, $J_{3,2}$ 7.3, 3-H) and 7.64 (1 H, dd, $J_{4,3}$ 8.0, $J_{4,2}$ 1.5, 4-H). The band of lower $R_f$ gave 5,6-dimethoxynaphthalen-1-ol **40** (10 mg, 2%) as an oil; the acetate was obtained as an oil; *m/z* 246 ($M^+$, 34%) and 204 (100).

1,4-*Dihydro*-5,7-*dimethoxy*-1,4-*epoxynaphthalene* **44**. This was prepared (80%) by the method of Tochtermann *et al.*,[7] and it was crystallized from dichloromethane–hexane as platelets, m.p. 75–77 °C (lit.,[7] 66–67 °C); $\delta_H$(300 MHz) 3.76 and 3.80 (each 3 H, s, OMe), 5.63 (1 H, dd, $J_{1,2}$ 1.8, $J_{1,4}$ 0.9, 1-H), 5.91 (1 H, ddd, $J_{4,3}$ 1.8, $J_{4,1}$ 0.9, $J_{4,8}$ 0.7, 4-H), 6.09 (1 H, d, $J_{6,8}$ 1.9, 6-H), 6.59 (1 H, br d, $J_{8,6}$ 1.9, 8-H), 6.97 (1 H, dd, $J_{2,3}$ 5.5, $J_{2,1}$ 1.8, 2-H) and 7.05 (1 H, dd, $J_{3,2}$ 5.5, $J_{3,4}$ 1.8, 3-H); $\delta_C$ 55.66 and 55.88 (OMe), 80.13 and 82.63 (C-1 and -4), 95.63 (C-6), 101.80 (C-8), 126.55 (C-4a), 142.05 and 143.49 (C-2 and -3), 152.87 and 153.18 (C-5 and -8a) and 159.45 (C-7).

Ring opening yielded 5,7-dimethoxynaphthalen-1-ol **45** (79%), which was crystallized from dichloromethane–hexane as needles, m.p. 134–135 °C (lit.,[19] 125–127.5 °C); $\delta_H$(300 MHz) 3.93 and 3.95 (each 3 H, s, OMe), 5.34 (1 H, s, OH), 6.52 and 7.05 (2 H, AB, *J* 2.0, 6- and 8-H), 6.82 (1 H, dd, $J_{2,3}$ 7.5, $J_{2,4}$ 1.0, 2-H), 7.14 (1 H, dd, $J_{3,4}$ 8.4, $J_{3,2}$ 7.5, 3-H) and 7.74 (1 H, dd, $J_{4,3}$ 8.4, $J_{4,2}$ 1.0, 4-H). The *acetate* formed needles (from dichloromethane–hexane), m.p. 88–89 °C (Found: C, 68.05; H, 6.05%; $M^+$, 246. $C_{14}H_{14}O_4$ requires C, 68.3; H, 5.75%; M, 246); $\delta_H$(80 MHz) 2.40 (3 H, s, Me), 3.86 and 3.90 (each 3 H, s, OMe), 6.48 and 6.66 (2 H, AB, *J* 2.1, 6- and 8-H), 7.15–7.38 (2 H, m, 2- and 3-H) and 8.03 (1 H, dd, $J_{4,3}$ 6.8, $J_{4,2}$ 2.8, 4-H).

1,4-*Dihydro*-5,6,8-*trimethoxy*-1,4-*epoxynaphthalene* **52** (*with Robert W. and Teresa M. Baker*). Prepared from 2,3-dibromo-1,4,5-trimethoxybenzene[33] **50**, furan and butyllithium (*via* the intermediate **51**) the *adduct* **52** (77%) was crystallized from diethyl ether–hexane as prisms, m.p. 95–97 °C (Found: C, 66.7; H, 5.85%; $M^+$, 234. $C_{13}H_{14}O_4$ requires C, 66.65; H, 6.0%; M, 234); $\delta_H$(300 MHz) 3.80, 3.81 and 3.85 (each 3 H, s, OMe), 5.91 (1 H, dd, $J_{1,2}$ 1.7, $J_{1,4}$ 1.0, 1-H), 5.96 (1 H, dd, $J_{4,3}$ 1.7, $J_{4,1}$ 1.0, 4-H), 6.12 (1 H, s, 7-H) and 7.00 and 7.04 (each 1 H, dd, *J* 5.5, 1.7, 2- and 3-H); $\delta_C$ 56.37 and 56.77 (OMe), 61.25 (5-OMe), 80.15 and 80.70 (C-1 and -4), 96.11 (C-7), 126.06 (C-4a), 136.66 (C-8a), 140.10 (C-5), 141.67 and 143.07 (C-2 and -3), 149.29 and 151.35 (C-6 and -8).

The adduct **52** (200 mg) was stirred in methanol (5 $cm^3$) containing conc. hydrochloric acid (5 drops) for 1 h at room temperature under nitrogen. The usual work-up gave 5,7,8-trimethoxynaphthalen-1-ol **53** (190 mg, 95%), which was crystallized from diethyl ether–hexane as prisms, m.p. 95–95.5 °C (lit.,[20] 133 °C); $\delta_H$(300 MHz) 3.96, 3.98 and 4.01 (each 3 H, s, OMe), 6.59 (1 H, s, 6-H), 6.88 (1 H, dd, $J_{2,3}$ 7.6, $J_{2,4}$ 1.1, 2-H), 7.22 (1 H, dd, $J_{3,4}$ 8.4, $J_{3,2}$ 7.6, 3-H), 7.64 (1 H, dd, $J_{4,3}$ 8.4, $J_{4,2}$ 1.1, 4-H) and 9.71 (1 H, s, OH).

A solution of the naphthol **53** (500 mg) in dichloromethane (5 $cm^3$) containing dimethyl sulphate (0.8 g) and tetrabutylammonium iodide (20 mg) was stirred with a solution of sodium hydroxide (250 mg) in water (5 $cm^3$) for 2 h. The usual work-up gave 1,2,4,8-*tetramethoxynaphthalene* **54** (484 mg, 91%), which was crystallized from diethyl ether–hexane as needles, m.p. 99–99.5 °C (Found: C, 68.0; H, 6.75. $C_{14}H_{16}O_4$ requires C, 67.75; H, 6.5%); $\delta_H$(300 MHz) 3.84, 3.92, 3.94 and 3.96 (each 3 H, s, OMe), 6.65 (1 H, s, 3-H), 6.84 (1 H, dd, $J_{7,6}$ 7.7, $J_{7,5}$ 1.0, 7-H), 7.21 (1 H, dd, $J_{6,7} = J_{5,6}$ = 7.7, 6-H) and 7.78 (1 H, dd, $J_{5,6}$ 7.7, $J_{5,7}$ 1.0, 5-H); $\delta_C$ 55.63, 56.24 and 57.61 (each OMe), 61.67 (1-OMe), 96.65 (C-3), 107.29 (C-7), 114.55 (C-5), 121.52 (C-8a), 123.30 (C-6), 123.55 (C-4a), 136.14 (C-1), 149.64 and 151.99 (C-2 and -4) and 155.55 (C-8).

A solution of the naphthalene **54** (400 mg) in acetonitrile (5 $cm^3$) was added to a stirred solution of ammonium cerium(IV) nitrate (1.3 g) in the minimum volume of water. The solution was stirred for 1 h and was then diluted with water and extracted with dichloromethane. Radial chromatography of the crude product with 40% ethyl acetate–hexane as eluent afforded, from the first band to be eluted, 2,8-dimethoxynaphthalene-1,4-dione **55** (145 mg, 45%), which was crystallized from methanol as yellow laths, m.p. 201–202 °C (lit.,[23] 202–202.5 °C); $\delta_H$ 3.88 and 4.01 (each 3 H, s, OMe), 6.10 (1 H, s, 3-H), 7.27 (1 H, dd, $J_{5,6}$ 8.2, $J_{5,7}$ 1.3, 5-H), 7.68 (1 H, dd, $J_{6,5}$ 8.2, $J_{6,7}$ 7.7, 6-H) and 7.75 (1 H, dd, $J_{7,6}$ 7.7, $J_{7,5}$ 1.3, 7-H). Further elution provided 4,8-*dimethoxynaphthalene*-1,2-*dione* **56** (98 mg, 28%), which was crystallized from methanol as orange spars, m.p. 208–209 °C (Found: C, 65.75; H, 4.55. $C_{12}H_{10}O_4$ requires C, 66.05; H, 4.6%); $\delta_H$ 3.99 and 4.00 (each 3 H, s, OMe), 5.95 (1 H, s, 3-H), 7.17 (1 H, dd, $J_{5,6}$ 8.5, $J_{5,7}$ 1.0, 5-H), 7.52 (1 H, dd, $J_{7,6}$ 7.8, $J_{7,5}$ 1.0, 7-H) and 7.63 (1 H, dd, $J_{6,5}$ 8.5, $J_{6,7}$ 7.8, 6-H).

1,4-*Dihydro*-5,6,7-*trimethoxy*-1,4-*epoxynaphthalene* **58**. Prepared from 1,2-dibromo-3,4,5-trimethoxybenzene **12** (3.0 g), furan, and butyllithium at −100 °C, it was purified by radial chromatography with 15% ethyl acetate–hexane as eluent, distilled under diminished pressure, b.p. 130 °C at 0.05 mmHg, and finally crystallized from dichloromethane–hexane whereupon it was obtained as prisms (1.48 g, 69%) of the *adduct* **58**, m.p. 82–83 °C (Found: C, 66.75; H, 6.15%; $M^+$, 234. $C_{13}H_{14}O_4$ requires C, 66.65; H, 6.0%; M, 234); $\delta_H$(300 MHz) 3.79, 3.82 and 3.95 (each 3 H, s, OMe), 5.63 (1 H, dd, $J_{1,2}$ 1.8, $J_{1,4}$ 0.9, 1-H), 6.04 (1 H, dd, $J_{4,3}$ 1.8, $J_{4,1}$ 0.9, 4-H), 6.72 (1 H, s, 8-H), 7.00 (1 H, dd, $J_{3,2}$ 5.5, $J_{3,4}$ 1.8, 2-H) and 7.05 (1 H, dd, $J_{2,3}$ 5.5, $J_{2,1}$ 1.8, 3-H); $\delta_C$ 56.57 (7-OMe), 60.23 and 60.98 (each OMe), 81.52 and 82.47 (C-1 and -4), 102.02 (C-8), 128.59 (C-4a), 137.57 (C-8a), 142.53 and 143.01 (C-2 and -3), 145.21 and 147.94 (C-6 and -7) and 150.91 (C-5).

Ring opening gave a crude product, which was purified by radial chromatography with 5–20% ethyl acetate–hexane as eluent. The first band yielded 6,7,8-trimethoxynaphthalen-1-ol **60** (8%), which was crystallized from dichloromethane–hexane as plates, m.p. 73–75 °C (lit.,[34] 74–75 °C); $\delta_H$(80 MHz) 3.93 (6 H, s, 2 × OMe), 4.13 (3 H, s, OMe), 6.61–7.36 (3 H, m, 2-, 3- and 4-H), 6.91 (1 H, s, 5-H) and 9.42 (1 H, s, OH). The *acetate* formed prisms (from dichloromethane–hexane), m.p. 106–106.5 °C (Found: C, 65.45; H, 6.05%; $M^+$, 276. $C_{15}H_{16}O_5$ requires C, 65.2; H, 5.85%; M, 276); $\delta_H$(80 MHz) 2.36 (3 H, s, MeCO), 3.92 (9 H, s, 3 × OMe), 6.94 (1 H, dd, $J_{2,3}$ 7.2, $J_{2,4}$ 1.4, 2-H), 6.96 (1 H, s, 5-H), 7.30 (1 H, dd, $J_{3,2}$ 7.2, $J_{3,4}$ 8.2, 3-H) and 7.55 (1 H, dd, $J_{4,3}$ 8.2, $J_{4,2}$ 1.4, 4-H). Further elution gave 5,6,7-trimethoxynaphthalen-1-ol **59** (88%), which was crystallized as prisms from dichloromethane–hexane, m.p. 95–96 °C (lit.,[21] 92–95 °C); $\delta_H$(80 MHz) 3.93, 4.00 and 4.04 (each 3 H, s, OMe), 6.78 (1 H, dd, $J_{2,3}$ 7.4, $J_{2,4}$ 1.1, 2-H), 7.16 (1 H, dd, $J_{3,4}$ 8.3, $J_{3,2}$

7.4, 3-H), 7.37 (1 H, s, 8-H) and 7.62 (1 H, br d, $J_{4,3}$ 8.3, 4-H). The *acetate* was obtained as an oil, b.p. 135 °C at 0.005 mmHg (Found: C, 65.0; H, 5.85; $M^+$, 276. $C_{15}H_{16}O_5$ requires C, 65.2; H, 5.85; M, 276); $\delta_H$(80 MHz) 2.38 (3 H, s, MeCO), 3.97 (6 H, s, 2 × OMe), 4.04 (3 H, s, OMe), 6.89 (1 H, s, 8-H), 7.15 (1 H, dd, $J_{2,3}$ 7.8, $J_{2,4}$ 1.5, 2-H), 7.34 (1 H, dd, $J_{3,2}$ 7.8, $J_{3,4}$ 7.5, 3-H) and 7.95 (1 H, br d, $J_{4,3}$ 7.5, 4-H).

1,4-*Dihydro*-5,6,7,8-*tetramethoxy*-1,4-*epoxynaphthalene* **66**. Prepared from 1,2-dibromo-3,4,5,6-tetramethoxybenzene[35] **64**, the product was crystallized from dichloromethane–hexane as prisms (59%) of the *adduct* **66**, m.p. 81.5–82 °C (Found: C, 63.85; H, 6.4%; $M^+$, 264. $C_{14}H_{16}O_5$ requires C, 63.65; H, 6.1%; M, 264); $\delta_H$(300 MHz) 3.84 and 3.89 (each 6 H, s, 2 × OMe), 5.97 (2 H, t, $J_{1,2} = J_{4,3}$ = 1.0, 1- and 4-H) and 7.02 (2 H, t, $J_{2,1} = J_{3,4}$ = 1.0, 2- and 3-H); $\delta_C$ 60.87 and 61.12 (each 2 × OMe), 80.63 (C-1 and -4), 132.25 (C-4a and -8a), 142.26 (C-2 and -3) and 143.29 and 143.45 (C-5, -6, -7 and -8).

Ring opening provided 5,6,7,8-tetramethoxynaphthalen-1-ol **67** (63%) as an oil; $\delta_H$(80 MHz) 3.96, 3.98, 4.01 and 4.08 (each 3 H, s, OMe), 6.81 (1 H, dd, $J_{2,3}$ 7.5, $J_{2,4}$ 1.3, 2-H), 7.27 (1 H, dd, $J_{3,4}$ 8.4, $J_{3,2}$ 7.5, 3-H), 7.56 (1 H, dd, $J_{4,3}$ 8.4, $J_{4,2}$ 1.3, 4-H) and 9.51 (1 H, s, OH). The *acetate* was obtained as an oil, b.p. 175 °C at 0.005 mmHg (Found: C, 62.85; H, 5.95%; $M^+$, 306. $C_{16}H_{18}O_6$ requires C, 62.75; H, 5.9%; $M^+$, 306); $\delta_H$(80 MHz) 2.36 (3 H, s, MeCO), 3.88, 3.97, 3.98 and 4.00 (each 3 H, s, OMe), 6.95 (1 H, dd, $J_{2,3}$ 7.4, $J_{2,4}$ 1.3, 2-H), 7.35 (1 H, dd, $J_{3,4}$ 8.4, $J_{3,2}$ 7.4, 3-H) and 7.99 (1 H, dd, $J_{4,3}$ 8.4, $J_{4,2}$ 1.3, 4-H).

*Reactions of Methoxydehydrobenzenes with 2-Methoxyfuran.*—3-*Methoxydehydrobenzene* **18** (*with Robert W. and Teresa M. Baker*). A solution of butyllithium (1.78 mol $dm^{-3}$) in hexane (3.8 $cm^3$) was added to a stirred solution of the tosyl ester[1] **21** (2.0 g) and 2-methoxyfuran (1.1 g, 2 mol equiv.) in anhydrous THF (30 $cm^3$) at −100 °C under argon. The solution was stirred at −100 °C for 0.5 h and was then allowed to warm to room temperature. The mixture was acidified by the addition of conc. hydrochloric acid, stirred at room temp. for 15 min, and then poured into water. The crude product was isolated by extraction with ethyl acetate and was then crystallized from chloroform to afford 4,5-dimethoxynaphthalen-1-ol **22** (910 mg, 80%) as needles, m.p. 164.5–166 °C (lit.,[27] 164 °C); $\delta_H$(300 MHz) 3.92 and 3.98 (each 3 H, s, OMe), 5.12 (1 H, s, OH), 6.71 and 6.76 (2 H, AB, $J_{2,3}$ 8.3, 2- and 3-H), 6.91 (1 H, dd, $J_{6,7}$ 7.8, $J_{6,8}$ 1.0, 6-H), 7.41 (1 H, dd, $J_{7,8}$ 8.4, $J_{7,6}$ 7.8, 7-H) and 7.77 (1 H, dd, $J_{8,7}$ 8.4, $J_{8,6}$ 1.0, 8-H); *m/z* 204 ($M^+$, 100%), 133 (12) and 105 (16).

4-*Methoxydehydrobenzene* **23**. The crude product, obtained from the tosyl ester **1**, was acetylated with acetic anhydride and pyridine and was then chromatographed over silica gel with 5% ethyl acetate–hexane as eluent. This afforded a mixture (39%) of 4-acetoxy-1,6-dimethoxynaphthalene **27** (55%), $t_R$ 16.0 min; *m/z* 246 ($M^+$, 22%), 205 (10), 204 (85), 190 (13), 189 (100) and 161 (4); and 1-acetoxy-4,6-dimethoxynaphthalene **26** (45%), $t_R$ 15.9 min; *m/z* 246 ($M^+$, 24%), 205 (13), 204 (100), 189 (65) and 161 (14). In another experiment chromatography of the crude naphthols allowed the enrichment of one isomer, and hence after acetylation and with double irradiation assisted the analysis of the $^1$H NMR spectra of the isomers: $\delta_H$(300 MHz) compound **27**: 2.42 (3 H, s, MeCO), 3.88 and 3.93 (each 3 H, s, OMe), 6.58 and 7.08 (2 H, AB, $J_{3,2}$ 8.3, 3- and 2-H), 7.02 (1 H, d, $J_{5,7}$ 2.5, 5-H), 7.12 (1 H, dd, $J_{7,8}$ 9.2, $J_{7,5}$ 2.5, 7-H) and 8.16 (1 H, dd, $J_{8,7}$ 9.2, $J_{8,5}$ 0.4, 8-H); compound **26**: 2.40 (3 H, s, MeCO), 3.91 and 3.95 (each 3 H, s, OMe), 6.70 and 6.96 (2 H, AB, $J_{2,3}$ 8.3, 3- and 2-H), 7.17 (1 H, dd, $J_{7,8}$ 9.2, $J_{7,5}$ 2.6, 7-H), 7.53 (1 H, d, $J_{5,7}$ 2.6, 5-H) and 7.68 (1 H, dd, $J_{8,7}$ 9.3, $J_{8,5}$ 0.3, 8-H).

4,5-*Dimethoxydehydrobenzene* **33**. Prepared from 1,2-dibromo-4,5-dimethoxybenzene **32**, the crude product was acetylated and chromatographed over silica gel with 20% ethyl acetate–hexane as eluent to afford 1-*acetoxy*-4,6,7-*trimethoxynaphthalene* **36** (21%), which was crystallised from diethyl ether as needles, m.p. 169–170 °C (Found: C, 62.4; H, 5.95%; $M^+$, 276. $C_{15}H_{16}O_5$ requires C, 62.5; H, 5.85%; M, 276); $\delta_H$(80 MHz) 2.43 (3 H, s, MeCO), 3.99 (6 H, s, 2 × OMe), 4.02 (3 H, s, OMe), 6.68 and 7.02 (2 H, AB, *J* 8.4, 3- and 2-H), 7.02 (1 H, s, 5-H) and 7.54 (1 H, s, 8-H).

3,4-*Dimethoxydehydrobenzene* **37**. Prepared from the tosyl ester **4**, the crude product was purified by radial chromatography with 10–15% ethyl acetate–hexane as eluent. The first band afforded 4,7,8-trimethoxynaphthalen-1-ol **42** (8%) as an oil which rapidly became green on storage; *m/z* 235 (14%), 234 ($M^+$, 92%), 219 (100), 204 (17), 201 (13), 186 (14), 176 (36), 175 (16), 161 (22), 160 (10), 158 (12), 132 (10) and 117 (14); $\delta_H$(80 MHz) 3.90, 3.96 and 4.05 (each 3 H, s, OMe), 6.58 and 6.74 (2 H, AB, $J_{2,3}$ 8.4, 2- and 3-H), 7.20 and 7.98 (2 H, AB, $J_{5,6}$ 9.3, 6- and 5-H) and 9.18 (1 H, s, OH). The *acetate* was crystallized from dichloromethane–hexane as prisms, m.p. 136–137 °C (Found: C, 64.9; H, 6.0%; $M^+$, 276. $C_{15}H_{16}O_5$ requires C, 65.2; H, 5.85%; M, 276); $\delta_H$(80 MHz) 2.34 (3 H, s, MeCO), 3.86 (3 H, s, OMe), 3.94 (6 H, s, 2 × OMe), 6.59 and 6.96 (2 H, AB, $J_{2,3}$ 8.3, 3- and 2-H) and 7.25 and 8.05 (2 H, AB, $J_{5,6}$ 9.3, 6- and 5-H). Further elution yielded 4,5,6-trimethoxynaphthalen-1-ol **41** (55%) as a thick oil; *m/z* 235 (15%), 234 ($M^+$, 100), 219 (24), 204 (37), 187 (39), 176 (14), 159 (11), 147 (10), 131 (21), 118 (10) and 102 (14); $\delta_H$(80 MHz) 3.90, 3.92 and 3.98 (each 3 H, s, OMe), 6.59 and 6.68 (2 H, AB, $J_{2,3}$ 8.2, 2- and 3-H) and 7.28 and 7.95 (2 H, AB, $J_{7,8}$ 9.2, 7- and 8-H). The *acetate* was crystallized as needles (from dichloromethane–hexane), m.p. 106–107 °C (Found: C, 65.3; H, 6.2%; $M^+$, 276. $C_{15}H_{16}O_5$ requires C, 65.2; H, 5.85%; M, 276); $\delta_H$(80 MHz) 2.42 (3 H, s, MeCO), 3.88 (3 H, s, OMe), 3.97 (6 H, s, 2 × OMe), 6.77 and 6.99 (2 H, AB, $J_{2,3}$ 8.4, 3-and 2-H) and 7.30 and 7.55 (2 H, AB, $J_{7,8}$ 9.2, 7- and 8-H).

3,5-*Dimethoxydehydrobenzene* **43**. Prepared from the tosyl ester **8**, the crude product was purified by radial chromatography with 10–20% ethyl acetate–hexane as eluent. The first band supplied 4,6,8-trimethoxynaphthalen-1-ol[29] **48** (7%) as a solid which rapidly darkened on exposure to light and air; $\delta_H$(80 MHz) 3.66, 3.90 and 3.97 (each 3 H, s, OMe), 6.48 and 7.13 (2 H, AB, $J_{5,7}$ 2.3, 7- and 5-H), 6.62 and 6.72 (2 H, AB, $J_{2,3}$ 8.4, 2- and 3-H) and 8.72 (1 H, s, OH). The acetate **49** was crystallized from dichloromethane–hexane as prisms, m.p. 145–147 °C (lit.,[29] 145–146 °C) (Found: C, 65.0; H, 6.1%; $M^+$, 276. Calc. for $C_{15}H_{16}O_5$: C, 65.2; H, 5.85%; M, 276); $\delta_H$(80 MHz) 2.32 (3 H, s, MeCO), 3.87, 3.90 and 3.95 (each 3 H, s, OMe), 6.54 and 7.18 (2 H, AB, $J_{5,7}$ 2.3, 7- and 5-H) and 6.74 and 6.82 (2 H, AB, $J_{2,3}$ 8.3, 3- and 2-H). Further elution provided 4,5,7-trimethoxynaphthalene-1-ol **46** (70%) as a solid which rapidly darkened on exposure to light and air; *m/z* 235 (16%), 234 ($M^+$, 100), 233 (13), 219 (10), 218 (10), 191 (24), 176 (16), 161 (11) and 117 (10); $\delta_H$(80 MHz) 3.88, 3.91 and 3.93 (each 3 H, s, OMe), 5.40 (1 H, br, OH), 6.54 and 6.72 (2 H, AB, $J_{2,3}$ 8.4, 2- and 3-H) and 6.56 and 7.10 (2 H, AB, $J_{6,8}$ 2.4, 6- and 8-H). The acetate **47** was crystallized from dichloromethane–hexane as prisms, m.p. 114–115 °C (lit.,[29] 111–112 °C); $\delta_H$(80 MHz) 2.37 (3 H, s, MeCO), 3.84 (3 H, s, OMe), 3.88 (6 H, s, 2 × OMe), 6.52 and 6.65 (2 H, AB, $J_{6,8}$ 2.3, 6- and 8-H) and 6.62 and 7.08 (2 H, AB, $J_{2,3}$ 8.4, 3- and 2-H).

3,4,5-*Trimethoxydehydrobenzene* **57**. Prepared from 1,2-dibromo-3,4,5-trimethoxybenzene **12**, the crude product was acetylated, and purified by flash chromatography with 20% ethyl acetate–hexane as eluent. The first band provided 8-acetoxy-1,2,3,5-tetramethoxynaphthalene **63** (5%) as an oil; *m/z* 307 (5%), 306 ($M^+$, 26), 264 (100), 249 (99), 219 (8), 206 (10) and 188 (14); $\delta_H$(80 MHz) 2.39 (3 H, s, MeCO), 3.95, 3.98, 4.00 and 4.01 (each 3 H, s, OMe), 6.71 and 6.90 (2 H, AB, $J_{6,7}$ 8.1, 6- and 7-H) and 7.45 (1 H, s, 4-H). Further elution gave 5-*acetoxy*-1,2,3,8-*tetramethoxynaphthalene* **61** (59%), which was crystal-

lized from dichloromethane–hexane as prisms, m.p. 101–102 °C (Found: C, 62.6; H, 5.95%; $M^+$, 306. $C_{16}H_{18}O_6$ requires C, 62.75; H, 5.9%; M, 306); $\delta_H$(80 MHz) 2.43 (3 H, s, MeCO), 3.91 (3 H. s, OMe), 3.96 (6 H, s, 2 × OMe), 3.98 (3 H, s, OMe), 6.69 and 7.05 (2 H, AB, $J_{6,7}$ 8.5, 6- and 7-H) and 6.88 (1 H, s, 4-H).

A small sample of this material was reduced, in the usual way, with lithium aluminium hydride in THF. Work-up afforded 4,5,6,7-tetramethoxynaphthalen-1-ol **62** as an oil; *m/z* 265 (15%), 264 ($M^+$, 100), 249 (15), 234 (59), 217 (16) and 206 (15); $\delta_H$(80 MHz) 3.89 (3 H, s, OMe), 3.93 (6 H, s, 2 × OMe), 3.98 (3 H, s, OMe), 6.13 (1 H, br, OH), 6.54 and 6.66 (2 H, AB, $J_{2,3}$ 8.3, 2- and 3-H) and 7.40 (1 H, s, 8-H).

3,4,5,6-*Tetramethoxydehydrobenzene* **65**. Prepared from 1,2-dibromo-3,4,5,6-tetramethoxybenzene **64**, the crude product was acetylated, and then purified by radial chromatography with 15% ethyl acetate–hexane as eluent. This afforded 5-*acetoxy*-1,2,3,4-8-*pentamethoxynaphthalene* **68** (31%), which was crystallized as needles from dichloromethane–hexane, m.p. 75–76 °C (Found: C, 60.85; H, 6.1%; $M^+$, 336. $C_{17}H_{20}O_7$ requires C, 60.7; H, 6.0%; M, 336); $\delta_H$(80 MHz) 2.34 (3 H, s, MeCO), 3.86 (6 H, s, 2 × OMe), 3.94 (3 H, s, OMe), 3.99 (6 H, s, 2 × OMe) and 6.72 and 6.91 (2 H, AB, $J_{6,7}$ 8.4, 7- and 6-H).

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