Regioselectivity in the Reactions of Methoxydehydrobenzenes with Furans. Part 3.[1] 3-Methoxyfuran and Methoxydehydrobenzenes and the Chemistry of their Adducts

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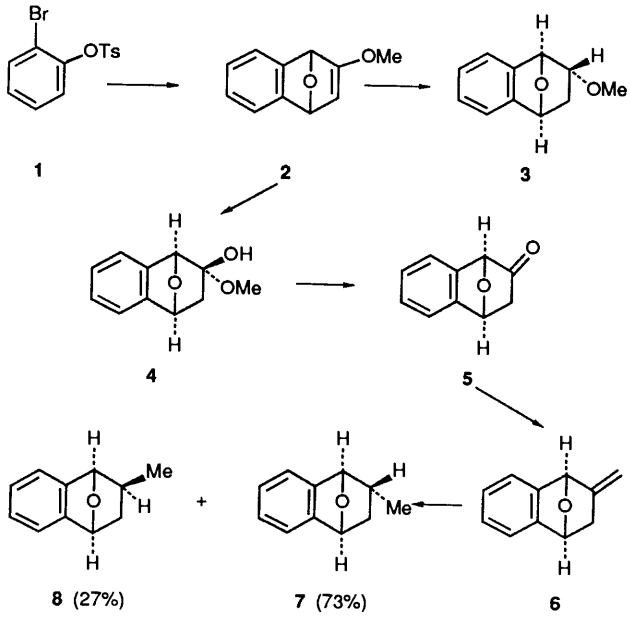
The cycloadditions of methoxydehydrobenzenes containing a 3-methoxy group and 3-methoxyfuran are highly regioselective. The adducts, 1,4-dihydro-2-methoxy-1,4-epoxynaphthalenes, undergo mild acid-catalysed hydrolysis providing, first, an isolable 1,2,3,4-tetrahydro-2-methoxy-1,4-epoxynaphthalen-2-ol, and then a 3,4-dihydro-1,4-epoxynaphthalen-2(1*H*)-one. The chemistry of these ketones is explored. One of them, 3,4-dihydro-5-methoxy-1,4-epoxynaphthalen-2(1*H*)-one, readily undergoes catalytic reduction to yield the hexahydro-1,4-epoxynaphthalene-2,5(1*H*,4a*H*)-dione. The X-ray molecular structure of this dione and of the 2-monobrosyl ester of the derived diol are reported. Treatment of the above adducts with trifluoroacetic acid and acetic anhydride provides a convenient synthesis of 1-acetoxy-2-methoxynaphthalenes.

In Part 2[1] we showed that cycloaddition reactions between dehydrobenzenes with a 3-methoxy substituent and 2-methoxyfuran exhibited a high degree of regioselectivity. We expected a similar degree of regioselectivity in the reactions of 3-methoxyfuran with these intermediates because of the polarization caused by the electron-releasing power of the methoxy group. Indeed, it has been found that 3-methoxyfuran exhibits such regioselectivity, and also enhanced reactivity compared with furan in its cycloadditions with monoactivated ethylenic dienophiles.[2]

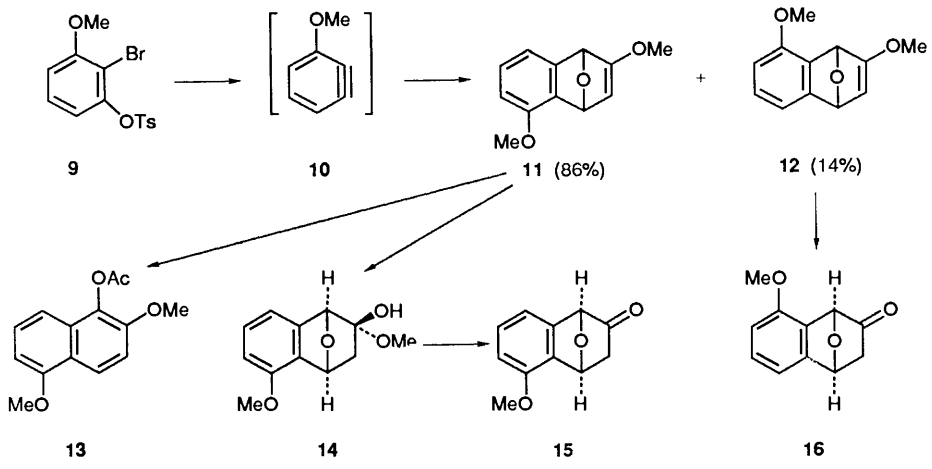
The reactions of dehydrobenzenes with 3-methoxyfuran should yield 1,4-dihydro-2-methoxy-1,4-epoxynaphthalenes which are enol ethers of 3,4-dihydro-1,4-epoxynaphthalen-2(1*H*)-ones. There has been much interest recently in the chemistry of the parent system, 7-oxabicyclo[2.2.1]hept-5-en-2-one,[3] also available in optically active form,[4] which is a valuable intermediate in the synthesis of natural products.[5] The benzannelated analogue, 3,4-dihydro-1,4-epoxynaphthalen-2(1*H*)-one **5** (Scheme 1), has recently been synthesized and attempts to convert it into enol ethers have met with limited success.[6] As a result of our study of the reactions of methoxydehydrobenzenes with 3-methoxyfuran we now describe efficient syntheses of such methoxy-substituted enol ethers, their conversion into substituted 1-acetoxy-2-methoxynaphthalenes and into methoxy-substituted 3,4-dihydro-1,4-epoxynaphthalen-2(1*H*)-ones, and some of the chemistry of these ketones.

The present work commenced with the synthesis of 1,4-dihydro-2-methoxy-1,4-epoxynaphthalene **2** (Scheme 1). For this purpose dehydrobenzene (benzyne) was generated by treatment of 2-bromophenyl toluene-*p*-sulphonate **1** with butyllithium in tetrahydrofuran (THF) at −100 °C in the presence of 3-methoxyfuran, and the solution was then allowed to warm slowly to room temperature. In order to prevent hydrolysis of the enol ether it was necessary to isolate the product by radial chromatography using an eluent that contained some triethylamine. Hydrolysis to the ketone **5** was conveniently carried out by using pyridinium toluene-*p*-sulphonate (PPTS) in aq. THF at room temperature. It was observed that this reaction involved an intermediate and when the reaction was terminated after a short time the intermediate **4** could be isolated by fractional crystallization of the crude product.



Scheme 1

When 3-methoxydehydrobenzene **10** (Scheme 2) was generated from the tosylate **9** in a similar fashion to that mentioned above, and was allowed to react with 3-methoxyfuran, an inseparable mixture of the cycloadducts **11** (86%) and **12** (14%) was obtained in 80% yield. The pure, major isomer **11** was obtained by crystallization of the mixture. Treatment of the adduct **11** with acetic anhydride containing a trace of trifluoroacetic acid (TFA) gave 1-acetoxy-2,5-dimethoxynaphthalene **13**, rather than the isomeric 1-acetoxy-3,8-dimethoxynaphthalene, since the ^{1}H NMR spectrum of the product showed an *ortho*-coupled AB system for the 3- and 4-protons. The direction of ring opening is rationalized by assuming that protonation of the epoxide oxygen is followed by ring cleavage



Scheme 2

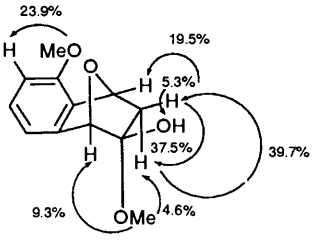


Fig. 1 Nuclear Overhauser effect difference data for the hemiacetal **14**. The tail of the arrow indicates the signal irradiated

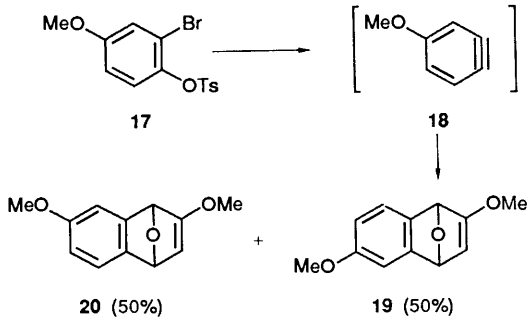
to yield the carbocation at the 4-position which is conjugatively stabilized by the 2-methoxy group. The direction of ring opening of the adducts **27** (Scheme 5), **35** (Scheme 6) and **48** (Scheme 8) can be similarly rationalized.

Hydrolysis of the adduct **11** to the ketone **15** was again achieved by the agency of PPTS in aq. THF and by interrupting the reaction after a short time the intermediate hemiacetal **14** could be isolated by fractional crystallization of the crude product. The structural assignment of the hemiacetal **14** is based on its spectral data. The IR spectrum exhibited a band at 3370 cm^{-1} attributed to an OH stretching frequency. The ^{13}C NMR spectrum revealed a signal for the methoxy group of the hemiacetal at δ_C 50.06, a quaternary carbon atom attributed to C-2 resonating at δ_C 106.39, and the methylene carbon signal at δ_C 43.02 was attributed to C-3. Nuclear Overhauser effect (NOE) difference spectroscopy gave evidence for the stereochemistry and the results are shown in Fig. 1. Significant interactions are those between the *endo*-methoxy group at C-2 and both the bridgehead proton 1-H and 3-H_{endo}, and between 3-H_{exo} and the *exo*-hydroxy group at C-2. Nucleophilic attack by water therefore occurs exclusively from the *exo*-face of the adduct and this mode of attack presumably reflects the unhindered nature of this face of the molecule compared with the *endo*-face. The spectroscopic properties of the hemiacetal **4** derived from the parent adduct **2** are similar to those of the methoxy derivative **14**. In this case the infrared OH stretching band is at 3360 cm^{-1} and in the ^{13}C NMR spectrum the resonance for the methoxy group occurs at δ_C 50.53, that for C-2 at δ_C 106.15, and that for C-3 at δ_C 43.34.

The adduct **2** on catalytic reduction likewise yielded exclusively the *endo*-methoxy compound **3**. In this case the stereochemical assignment is based on the values of the coupling constants of the 2-H_{exo} signal in its ^1H NMR spectrum. This proton exhibits $J_{2\text{-}exo,3\text{-}exo}$ 9.0, $J_{2\text{-}exo,1}$ 4.5, and $J_{2\text{-}exo,3\text{-}endo}$ 2.7 Hz, which are values typical for the similar bicyclo[2.2.1]heptene system.[7] Again addition of hydrogen occurs from the less hindered, *exo*-face of the molecule.

Stable hemiacetals are rare[8] except in carbohydrates, and the formation of compounds **4** and **14** no doubt reflects the relief of strain in the bicyclic compounds **2** and **11** on going from an sp^2-carbon to an sp^3-carbon atom.

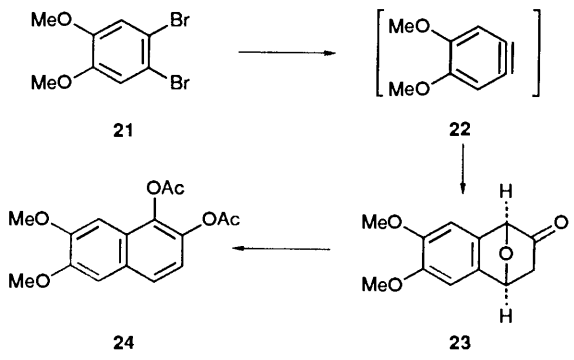
When the mixture of adducts **11**/**12** (Scheme 2) was completely hydrolysed by the above method a separable mixture of the ketones **15** and **16** was obtained. Both ketones exhibited carbonyl bands in their IR spectra at 1765 cm^{-1}, characteristic of strained cyclic five-membered ketones, and their carbonyl carbon atoms resonated near δ_C 207 in their ^{13}C NMR spectra. The structural assignments of these ketones, and hence of their parent adducts **11** and **12**, are based on their ^1H NMR spectra. In the ^1H NMR spectrum of the unsubstituted ketone **5** the bridgehead protons may be differentiated on the grounds of their multiplicities. Thus, 1-H gives a singlet at δ_H 5.00 and 4-H gives a doublet at δ_H 5.69 with $J_{4,3\text{-}exo}$ 5.0 Hz. Similar arguments can be made for the assignment of the bridgehead protons of the symmetrical 3,4-dihydro-6,7-dimethoxy-1,4-epoxynaphthalen-2(1*H*)-one **23** (Scheme 4) (1-H, δ_H 5.29 and 4-H, δ_H 5.88). Therefore the 5-methoxy ketone **15** is that ketone in which 1-H resonates at δ_H 5.01 and 4-H at δ_H 5.89, and the 8-methoxy ketone **16** is the one in which 1-H resonates at δ_H 5.24 and 4-H at δ_H 5.69, in their respective ^1H NMR spectra. Similar assignments allow distinctions to be made between the pairs of ketones **31**/**32** (Scheme 5), **38**/**39** (Scheme 6) and **52**/**53** (Scheme 8).



Scheme 3

The reaction of 4-methoxydehydrobenzene **18** (Scheme 3) with 3-methoxyfuran gave equal amounts of the adducts **19** and **20** which were inseparable by radial chromatography, and were not further investigated.

4,5-Dimethoxydehydrobenzene **22** (Scheme 4) upon reaction



Scheme 4

with 3-methoxyfuran gave an adduct which decomposed to the ketone **23** on radial chromatography with an eluent that did not contain triethylamine. When the ketone **23** was treated at room temperature with acetic anhydride containing a trace of conc. sulphuric acid, 1,2-diacetoxy-6,7-dimethoxynaphthalene **24** was obtained.

3,4-Dimethoxydehydrobenzene **26** (Scheme 5) on reaction with 3-methoxyfuran gave, in 86% yield, a mixture of the adducts **27** (86%) and **28** (14%) from which the pure, major adduct **27** was obtained by crystallization. On treatment with acetic anhydride containing a trace of TFA this adduct **27** yielded 1-acetoxy-2,5,6-trimethoxynaphthalene **29** but with conc. sulphuric acid as catalyst the 1,2-diacetoxynaphthalene **30** resulted. Hydrolysis of the mixture of adducts yielded a mixture of the ketones **31** and **32** from which the major isomer was obtained pure by crystallization.

The results obtained with 3,5-dimethoxydehydrobenzene **34** (Scheme 6) were similar; in this case the ketones **38** and **39** were separated by radial chromatography.

3,4,6-Trimethoxydehydrobenzene **41** (Scheme 7) gave almost equal amounts of the adducts **42** and **43**, which were hydrolysed to an inseparable mixture of the ketones **44** and **45**.

3,4,5-Trimethoxydehydrobenzene **47** (Scheme 8) gave a mixture containing the adducts **48** (77%) and **49** (23%). On hydrolysis the ketones **52** and **53** were obtained, which were separated by radial chromatography. When the mixture of adducts was treated with acetic anhydride containing a trace of TFA, 5-acetoxy-1,2,3,6-tetramethoxynaphthalene **50** was isolated as the major product, but with conc. sulphuric acid as catalyst nuclear acetylation also occurred and the acetonaphthenone **51** was the major product.

3,4,5,6-Tetramethoxydehydrobenzene **55** (Scheme 9) yielded the ketone **56**, which was converted into 5,6-diacetoxy-1,2,3,4-tetramethoxynaphthalene **57** on acetylative ring-cleavage with sulphuric acid as catalyst.

The regioselectivity of the cycloadditions of 3-methoxyfuran, like that of 2-methoxyfuran,[1] with the unsymmetrical dehydrobenzenes containing a 3-methoxy group is very high. There is no regioselectivity in the reactions of 4-methoxy **18** or 3,4,6-trimethoxydehydrobenzene **41**. As in the case of 2-methoxyfuran,[1] the powerful electron-releasing properties of the 3-methoxy group in the furan combines with the inductive polarization induced by the 3-methoxy group in the dehydrobenzene and leads to the high regioselectivity observed.

3,4-Dihydro-1,4-epoxynaphthalen-2(1*H*)-one **5** (Scheme 1) underwent smooth Wittig reaction with methylenetriphenylphosphorane to furnish the exocyclic olefin **6**, which on catalytic reduction yielded a mixture of *endo*-**7** (73%) and *exo*-methyl **8** (27%) compounds. The stereochemistry of these compounds followed from their ^{1}H NMR spectra.

Reduction of the ketone **5** (Scheme 10) and the 5-methoxyketone **15** (Scheme 11) with lithium aluminium hydride yielded the same ratio (86:14) of the *endo*-**58** and **62**, and *exo*-alcohols **59** and **63**; again their structures follow from their ^{1}H NMR spectra. The *exo*-alcohol **59** has previously been obtained by Brown and Vara Prasad by hydroboration of 1,4-dihydro-1,4-epoxynaphthalene.[9] It is of interest to note that 7-oxabicyclo-[2.2.1]heptan-2-one yields exclusively the *endo*-alcohol on reduction with either lithium aluminium hydride[10] or sodium borohydride,[11] whereas the carbocyclic bicyclo[2.2.1]heptan-2-one yields the *endo*- and *exo*-alcohol in the ratio of 9:1.[12]

When the ketones **5** (Scheme 10), **15** (Scheme 11) and **38** (Scheme 12) were allowed to react with methylmagnesium iodide only the *endo*-alcohols **60**, **64** and **69**, respectively, were obtained. The stereochemistry of the alcohol **64** follows from NOE difference spectroscopy and the data are shown in Fig. 2. In particular the C-2 *exo*-methyl group shows strong interactions with both the bridgehead proton at C-1 and 3-H_{exo}.

When the tertiary alcohol **60** was treated with toluene-*p*-sulphonic acid (PTSA) in boiling toluene the known 2-methylnaphthalen-1-ol[13] **61** was secured in high yield. Presumably dehydration of the tertiary alcohol is followed successively by protonation of the epoxide oxygen and ring cleavage to give the more stable carbocation. The tertiary alcohols **64** and **69** similarly afforded the known 2-methylnaphthalen-1-ols **65**[14] and **70**.[15]

The ketone **15** (Scheme 11) underwent ready catalytic hydrogenation at room temperature and pressure. The IR spectrum of the crystalline product showed two carbonyl stretching bands, at 1752 and 1684 cm^{-1}, which were attributed to cyclic five- and six-membered ketones, respectively. The ^{13}C NMR spectrum also showed the presence of two carbonyl groups as well as 4 methylene and 4 methine carbon atoms. The mass spectral and microanalytical data were in agreement with the molecular formula $C_{10}H_{12}O_3$ and the ^{1}H NMR spectrum was in accord with a *cis*-ring junction. Structure **66** thus followed and this was confirmed by an X-ray molecular structure determination (Fig. 3a).

Strained aromatic hydrocarbons are known to undergo catalytic hydrogenation under mild conditions.[16] The ketone **15** is evidently sufficiently strained to undergo reduction. However, the parent ketone **5** was recovered unchanged from these conditions.

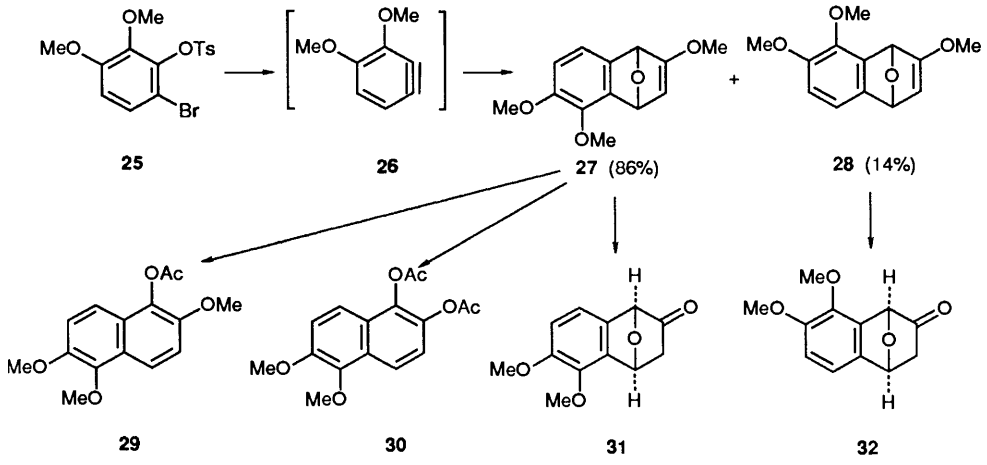
Reduction of the dione **66** with lithium aluminium hydride supplied a gummy diol which was characterized as its monobrosyl ester. Extensive spectroscopic analysis including 2D HETCOR experiments did not lead to unequivocal stereochemical assignment for either of these compounds. An X-ray structural determination on the brosyl ester revealed the structure to be **68** (Fig. 3b) and hence the diol is compound **67**. Reduction of both the keto groups had therefore taken place from the same side of the molecule.

Experimental

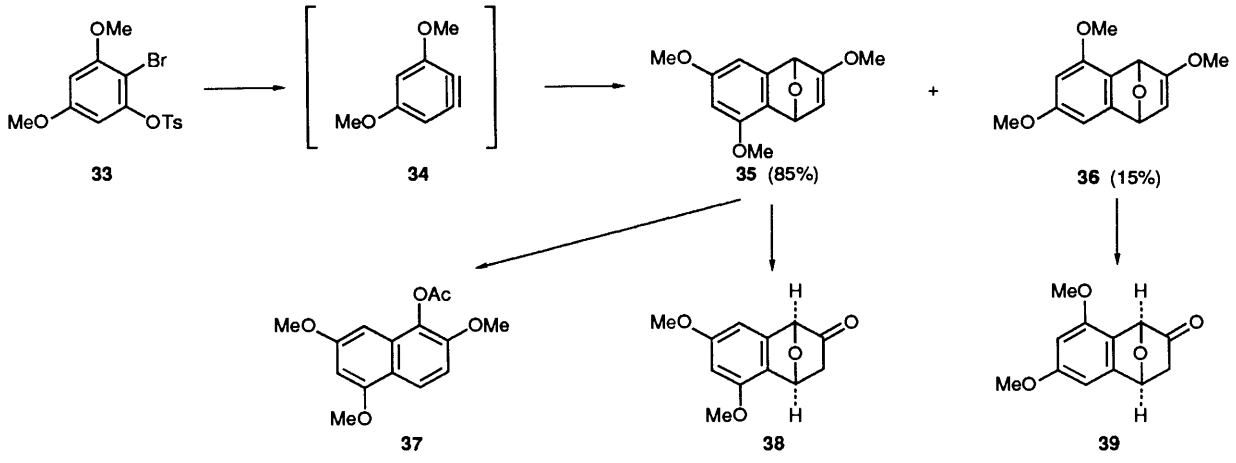
General directions are given in Part 1.[1]

2-Bromophenyl Toluene-p-*sulphonate* **1**.—Toluene-*p*-sulphonyl chloride (10.75 g) was added in portions to a stirred solution of 2-bromophenol (9.8 g) and triethylamine (8.6 g) in anhydrous dichloromethane (150 cm^3) at 0 °C. The solution was stirred at room temperature for 2 h, diluted with dichloromethane and washed in turn with water, aq. sodium hydrogen carbonate and saturated brine. The crude product was crystallized from dichloromethane–hexane as prisms (17.2 g, 93%) of the *tosyl ester* **1**, m.p. 75.5–76.5 °C (Found: C, 47.4; H, 3.1; Br, 24.6; S, 9.6. $C_{13}H_{11}BrO_3S$ requires C, 47.7; H, 3.4; Br, 24.4; S, 9.8%).

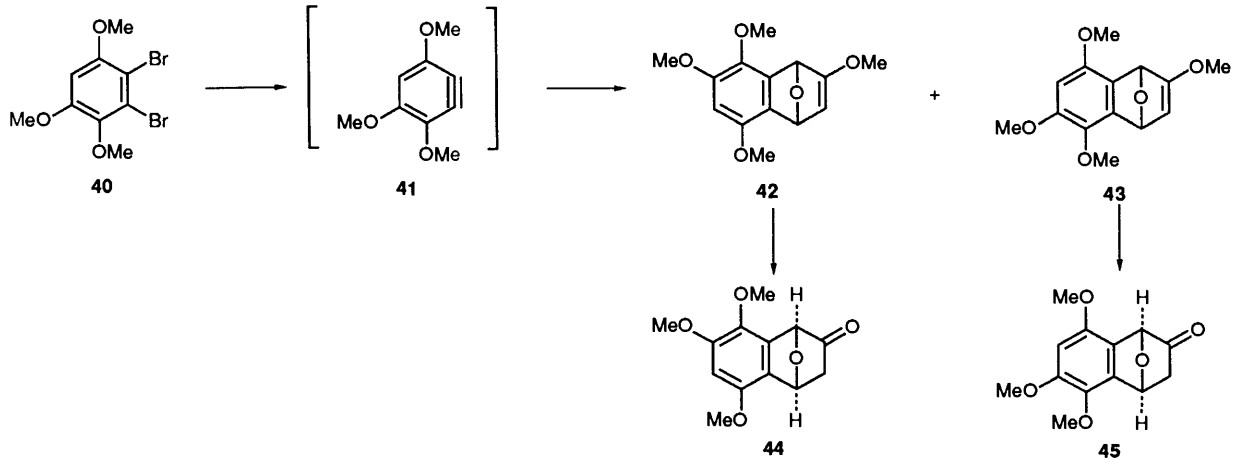
1,4-Dihydro-2-methoxy-1,4-epoxynaphthalene **2**.—A solution



Scheme 5

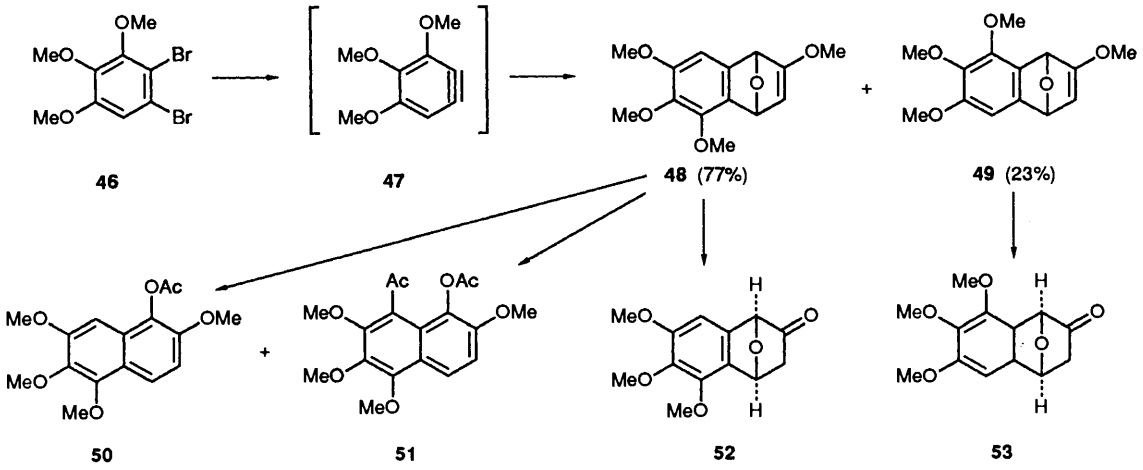


Scheme 6

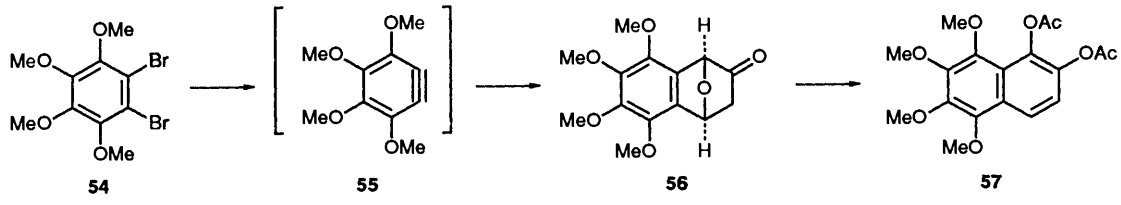


Scheme 7

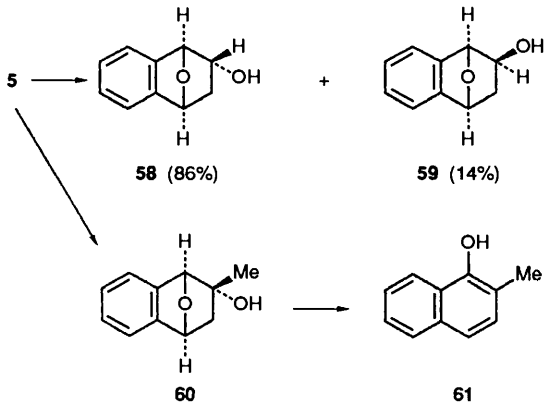
of butyllithium (1.8 mol dm^{-3}) in hexane (3.12 cm^3) was added by syringe to a solution of the tosyl ester **1** (1.7 g) and 3-methoxyfuran (1.3 g, 2.5 mol equiv.) in anhydrous tetrahydrofuran THF (30 cm^3) at −100 °C under argon. After the addition the solution was stirred at −78 °C for 2.5 h, and was then allowed to warm slowly to room temperature. The solution was poured into saturated aq. sodium hydrogen carbonate and extracted with diethyl ether. The crude product was purified by flash chromatography with 20% ethyl acetate–hexane containing 1% triethylamine as eluent, distilled under diminished pressure, b.p. 95 °C at 0.5 mmHg, and finally crystallized from pentane whereupon the *adduct* **2** (578 mg, 64%) formed rods, m.p. 65.5–66 °C (Found: C, 75.3; H, 6.2. $C_{11}H_{10}O_2$ requires C, 75.85; H, 5.8%); δ_H 3.50 (3 H, s, OMe), 5.22 (1 H, br s, 1-H), 5.35 (1 H, $J_{3,4}$ 2.1 $J_{3,1}$ 0.3, 3-H), 5.64 (1 H, narrow m, 4-H), 6.91–7.00 (2 H, m, ArH) and 7.17 and 7.30 (each 1 H, m, ArH); δ_C 57.76 (OMe), 81.54 and 82.87 (C-1 and -4), 102.17 (C-3), 118.49 and 120.20 (C-5 and -8), 124.39 and 125.36 (C-6 and -7), 147.26 and 151.36 (C-4a and -8a) and 176.41 (C-2).



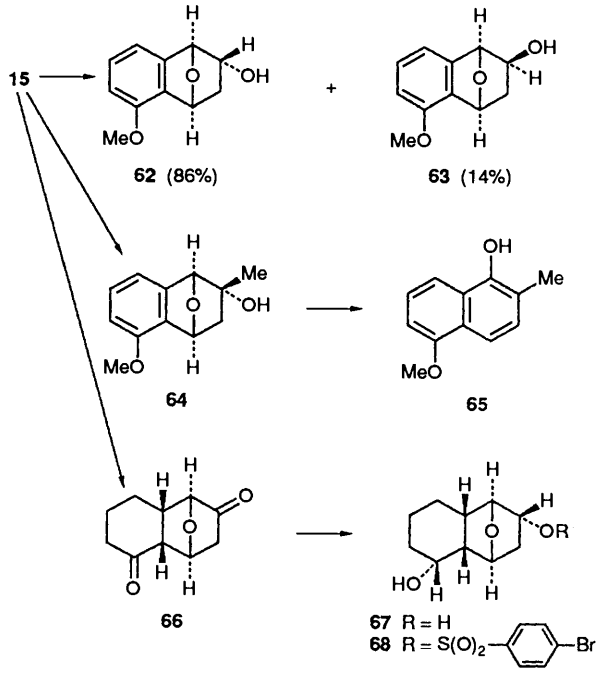
Scheme 8



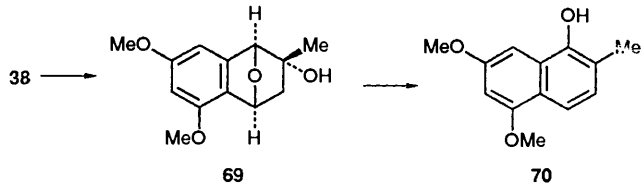
Scheme 9



Scheme 10



Scheme 11



Scheme 12

(1α,4α)-1,2,3,4-*Tetrahydro*-2α-*methoxy*-1,4-*epoxynaphthalen*-2β-*ol* **4**.—A solution of the adduct **2** (322 mg) and PPTS (15 mg) was stirred in aq. THF (10%; 25 cm^3) under argon for 15 min. The solution was diluted with saturated brine and exhaustively extracted with diethyl ether. The crude product was crystallized several times from diethyl ether–hexane which afforded the *hemiacetal* **4** (145 mg, 41%) as needles, m.p. 95–100 °C (Found: C, 69.05; H, 6.2. $C_{11}H_{12}O_3$ requires C, 68.75; H, 6.3%); $\delta_H(C_5D_5N)$ 1.91 (1 H, d, $J_{3\text{-}endo,3\text{-}exo}$ 11.5, 3-H_{endo}), 2.58 (1 H, dd, $J_{3\text{-}exo,3\text{-}endo}$ 11.5, $J_{3\text{-}exo,4}$ 5.4, 3-H_{exo}), 3.41 (3 H, s, OMe), 5.04 (1 H, br, OH), 5.46 (1 H, s, 1-H), 5.54 (1 H, d, $J_{4,3\text{-}exo}$ 5.4, 4-H), 7.20–7.26 (2 H, m, ArH) and 7.31–7.34 and 7.55–7.57 (each 1 H, m, ArH); $\delta_C(C_5D_5N)$ 43.34 (C-3), 50.53 (OMe), 80.06 (C-4), 86.22 (C-1), 106.15 (C-2), 119.15 and 122.12 (C-5 and -8), 126.61 and 127.20 (C-6 and -7) and 144.14 and 147.22 (C-4a and -8a); ν_{max}(KBr)/cm^{-1} 3360s and 1462s.

3,4-*Dihydro*-1,4-*epoxynaphthalen*-2(1H)-*one* **5**.—The adduct **2** (420 mg) and PPTS (20 mg) were stirred with aq. THF (10%; 15 cm^3) under argon for 3 h. The usual work-up gave a crude product, which was purified by radial chromatography and then distillation under diminished pressure which afforded the product **5** as an oil (262 mg, 67%), b.p. 125 °C at 1 mmHg (lit.,[6] 95 °C at 0.5 mmHg) which solidified, m.p. 46–47 °C (lit.,[6] 46–47 °C); δ_H 1.98 (1 H, d, $J_{3\text{-}endo,3\text{-}exo}$ 16.4, 3-H_{endo}), 2.56 (1 H, dd,

$J_{3\text{-}exo,3\text{-}endo}$ 16.4, $J_{3\text{-}exo,4}$ 5.0, 3-H_{exo}), 5.00 (1 H, s, 1-H), 5.69 (1 H, d, $J_{4,3\text{-}exo}$ 5.0, 4-H) and 7.16–7.39 (4 H, m, ArH); δ_C 37.73 (C-3), 79.41 (C-4), 82.76 (C-1), 120.00 and 122.34 (C-5 and -8), 127.74 and 128.63 (C-6 and -7), 137.99 (C-8a), 146.41 (C-4a) and 207.03 (C-2).

(1α,4α)-1,2,3,4-*Tetrahydro*-2α-*methoxy*-1,4-*epoxynaphthalene* **3**.—A solution of the adduct **2** (146 mg) in ethyl acetate (8.0 cm^3) was stirred under hydrogen with palladized strontium carbonate (5%; 40 mg) until absorption ceased. The usual work-up gave the *product* **3** (143 mg, 97%) as an oil, b.p. 70–72 °C at 0.2 mmHg (Found: C, 75.25; H, 7.15. $C_{11}H_{12}O_2$ requires C, 75.0; H, 6.85%); δ_H 1.14 (1 H, dd, $J_{3\text{-}endo,3\text{-}exo}$ 12.0, $J_{3\text{-}endo,2\text{-}exo}$ 2.7, 3-H_{endo}), 2.41 (1 H, ddd, $J_{3\text{-}exo,3\text{-}endo}$ 12.0, $J_{3\text{-}exo,2\text{-}exo}$ 9.0, $J_{3\text{-}exo,4}$ 5.0, 3-H_{exo}), 3.22 (3 H, s, OMe), 4.20 (1 H, ddd, $J_{2\text{-}exo,3\text{-}exo}$ 9.0, $J_{2\text{-}exo,1}$ 4.5, $J_{2\text{-}exo,3\text{-}endo}$ 2.7, 2-H), 5.28 (1 H, d, $J_{4,3\text{-}exo}$ 5.0, 4-H), 5.32 (1 H, d, $J_{1,2\text{-}exo}$ 4.5, 1-H) and 7.15–7.34 (4 H, m, Ar).

Reactions of Methoxydehydrobenzenes with 3-*Methoxyfuran*. —3-*Methoxydehydrobenzene* **10**. A stirred solution of the tosyl ester **9** (2.0 g) and 3-methoxyfuran (820 mg, 1.5 mol equiv.) in anhydrous THF (30 cm^3) was maintained at −100 °C under argon during the slow addition, *via* syringe, of butyllithium (1.78 mol dm^{-3}) in hexane (3.8 cm^3). The solution was stirred at −100 °C for 0.5 h and was then allowed to warm to room temperature, when it was poured into saturated aq. sodium hydrogen carbonate. The crude product, isolated by extraction with ethyl acetate, was purified by radial chromatography with 20% ethyl acetate–hexane, containing 1% triethylamine, as eluent. This afforded a mixture (958 mg, 80%) of 1,4-dihydro-2,5-dimethoxy-1,4-epoxynaphthalene **11** (86%) and 1,4-dihydro-2,8-dimethoxy-1,4-epoxynaphthalene **12** (14%). Crystallization of this mixture from hexane yielded the pure, *major adduct* **11** as prisms, m.p. 81–82 °C (Found: C, 70.65; H, 6.2. $C_{12}H_{12}O_3$ requires C, 70.6; H, 5.9%); δ_H 3.57 (3 H, s, 2-OMe), 3.82 (3 H, s, 5-OMe), 5.24 (1 H, d, $J_{1,4}$ 1.2, 1-H), 5.44 (1 H, d, $J_{3,4}$ 2.1, 3-H), 5.92 (1 H, ddd, $J_{4,3}$ 2.1, $J_{4,1}$ 1.2, $J_{4,8}$ 0.6, 4-H), 6.64 (1 H, dd, $J_{6,7}$ 7.8, $J_{6,8}$ 1.2, 6-H) and 6.95–7.03 (2 H, m, 7- and 8-H); δ_C 55.69 (5-OMe), 57.89 (2-OMe), 80.69 and 82.03 (C-1 and -4), 102.17 (C-3), 110.96 and 113.82 (C-6 and -8), 126.49 (C-7), 137.94 (C-4a), 149.81 and 151.71 (C-5 and -8a) and 176.80 (C-2). The ^1H NMR spectrum of the mother liquors showed signals due to the minor adduct **12**; δ_H 3.59 (3 H, s, 2-OMe), 3.81 (3 H, s, 8-OMe), 5.38 (1 H, d, $J_{3,4}$ 2.1, 3-H), 5.52 (1 H, br s, 1-H) and 5.66 (1 H, dd, $J_{4,3}$ 2.1, $J_{4,1}$ 1.3, 4-H); compound **11**: t_R 6.47 min; *m/z* 205 (16%), 204 (100, M^+), 190 (10), 189 (89), 161 (45), 146 (13), 131 (13), 118 (16), 115 (10) and 102 (14); compound **12**: t_R 8.18 min; *m/z* 205 (13%), 204 (100), 189 (51), 161 (32), 146 (11), 131 (11), 118 (9) and 102 (6).

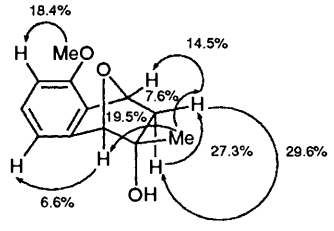


Fig. 2 Nuclear Overhauser effect difference data for the alcohol **64**. The tail of the arrow indicates the signal irradiated

1-*Acetoxy*-2,5-*dimethoxynaphthalene* **13**. The pure adduct **11** (200 mg) was stirred with TFA (5 drops) in acetic anhydride (1 cm^3) for 48 h under argon. The solution was poured into aq. sodium hydrogen carbonate and after the acetic anhydride had been hydrolysed the crude product was isolated by extraction with ethyl acetate and purified by radial chromatography with 20% ethyl acetate–hexane as eluent. The *naphthalene* **13** (195 mg, 81%) was crystallized from diethyl ether–hexane as plates, m.p. 140–141.5 °C (Found: C, 68.35; H, 6.0%; M^+, 204. $C_{14}H_{14}O_4$ requires C, 68.3; H, 5.75%; M, 204); δ_H 2.44 (3 H, s, MeCO), 3.93 and 3.96 (each 3 H, s, OMe), 6.68 (1 H, dd, $J_{6,7}$ 7.0, $J_{6,8}$ 1.6, 6-H), 7.27 (1 H, d, $J_{3,4}$ 9.3, 3-H), 7.33 (1 H, ddd, $J_{8,7}$ 8.5, $J_{8,6}$ 1.6, $J_{8,4}$ 0.4, 8-H), 7.38 (1 H, dd, $J_{7,8}$ 8.5, $J_{7,6}$ 7.0, 7-H) and 8.15 (1 H, dd, $J_{4,3}$ 9.3, $J_{4,8}$ 0.6, 4-H).

(1α,4α)-1,2,3,4-*Tetrahydro*-2α,5-*dimethoxy*-1,4-*epoxynaphthalen*-2β-*ol* **14**. A solution of the pure adduct **11** (150 mg) and PPTS (10 mg) was stirred in aq. THF (10%; 12 cm^3) under

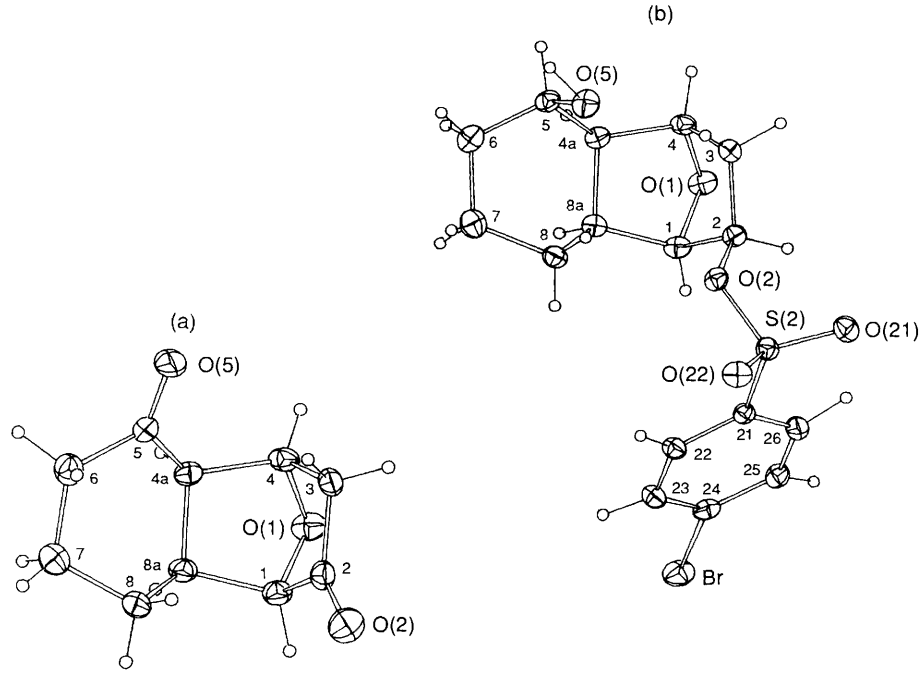


Fig. 3 Projection of the two crystallographically characterized compounds with their fused-ring systems in similar orientation. 20% Thermal ellipsoids are shown for the non-hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å. C-Atoms are denoted by numerals only. (a) Compound **66**. (b) Compound **68**.

argon for 15 min. The solution was diluted with water and extracted exhaustively with diethyl ether. Examination of the ^{1}H NMR spectrum of the crude product showed it to be a mixture of the starting material and the hemiacetal **14** (*ca.* 1:1). On fractional crystallization from diethyl ether–hexane the mixture afforded the hemiacetal **14** (70 mg, 43%) as prisms, m.p. 112–113 °C; $\delta_H(C_5D_5N)$ 2.02 (1 H, d, $J_{3\text{-}endo,3\text{-}exo}$ 11.5, 3-H_{endo}), 2.60 (1 H, dd, $J_{3\text{-}exo,3\text{-}endo}$ 11.5, $J_{3\_exo,4}$ 5.3, 3-H_{exo}), 3.42 (3 H, s, 2-OMe), 3.68 (3 H, s, 5-OMe), 5.49 (1 H, d, $J_{1,4}$ 0.9, 1-H), 5.87 (1 H, dd, $J_{4,3}$ 5.3, $J_{4,1}$ 0.9, 4-H), 6.78 (1 H, X part of ABX, 6-H), 7.23 (2 H, AB part of ABX, 7- and 8-H) and 8.40 (1 H, s, OH); $\delta_C(C_5D_5N)$ 43.02 (C-3), 50.06 (2-OMe), 55.43 (5-OMe), 77.84 (C-4), 88.59 (C-1), 106.39 (C-2), 110.84 (C-8), 114.98 (C-6), 128.51 (C-7), 134.10 (C-4a), 146.38 (C-8a) and 152.53 (C-5); ν_{max}(KBr)/cm^{-1} 3370 (OH); *m/z* 148 (100%), 133 (26), 119 (20), 105 (21), 104 (12), 91 (34) and 89 (11).

3,4-*Dihydro*-5-*methoxy*- **15** *and* 3,4-*Dihydro*-8-*methoxy*-1,4-*epoxynaphthalen*-2(1H)-*one* **16**. A solution of the mixture of adducts **11** and **12** (920 mg) and PPTS (10 mg) in aq. THF (30 cm^3) was stirred at room temperature under argon for 4 h. The usual work-up gave a crude product, which was subjected to radial chromatography with 10% ethyl acetate–hexane as eluent. The first band that was eluted gave the *benzoxatrinorbornenone* **15** (650 mg) as an oil, b.p. 120 °C at 0.2 mmHg (Found: C, 69.2; H, 5.6. $C_{11}H_{10}O_3$ requires C, 69.5; H, 5.3%); δ_H 2.05 (1 H, d, $J_{3\text{-}endo,3\text{-}exo}$ 16.4, 3-H_{endo}), 2.59 (1 H, dd, $J_{3\text{-}exo,3\text{-}endo}$ 16.4, $J_{3\text{-}exo,4}$ 4.9, 3-H_{exo}), 3.84 (3 H, s, OMe), 5.01 (1 H, s, 1-H), 5.89 (1 H, d, $J_{4,3\text{-}exo}$ 4.9, 4-H), 6.81 (1 H, d, $J_{8,7}$ 8.2, 8-H), 7.02 (1 H, d, $J_{6,7}$ 7.3, 6-H) and 7.21 (1 H, dd, $J_{7,6}$ 7.3, $J_{7,8}$ 8.2, 7-H); δ_C 37.27 (C-3), 55.45 (OMe), 77.33 (C-4), 83.13 (C-1), 111.58 (C-8), 114.53 (C-6), 129.71 (C-7), 133.73 (C-4a), 140.00 (C-8a), 152.76 (C-5) and 207.34 (C-2); *m/z* 162 (12%, M − CO), 149 (10), 148 (100), 133 (30), 119 (34), 105 (40), 104 (14), 103 (11), 91 (56), 90 (11) and 89 (23); ν_{max}(film)/cm^{-1} 1765 (C=O). Further elution gave the *benzoxatrinorbornenone* **16** (110 mg) as an oil, b.p. 95 °C at 0.01 mmHg (Found: C, 69.5; H, 5.6%); δ_H 2.02 (1 H, dd, $J_{3\text{-}endo,3\text{-}exo}$ 15.8, $J_{3\text{-}endo,4}$ 0.6, 3-H_{endo}), 2.58 (1 H, ddd, $J_{3\text{-}exo,3\text{-}endo}$ 15.8, $J_{3\text{-}exo,4}$ 5.0, $J_{3\text{-}exo,1}$ 0.3, 3-H_{exo}), 3.85 (3 H, s, OMe), 5.24 (1 H, br s, 1-H), 5.69 (1 H, dd, $J_{4,3\text{-}exo}$ 5.0, $J_{4,3\text{-}endo}$ 0.6, 4-H), 6.76 (1 H, d, $J_{5,6}$ 8.2, 5-H), 6.93 (1 H, d, $J_{7,6}$ 7.2, 7-H) and 7.24 (1 H, dd, $J_{6,5}$ 8.2, $J_{6,7}$ 7.2, 6-H); δ_C37.73 (C-3), 55.75 (OMe), 79.66 (C-4), 80.45 (C-1), 111.22 and 112.54 (C-5 and -7), 124.50 (C-8a), 130.79 (C-6), 148.59 (C-4a), 155.01 (C-8) and 206.43 (C-2); *m/z* 162 (100%, M − CO), 161 (31), 148 (67), 147 (12), 133 (73), 119 (16), 105 (39), 104 (19), 102 (16), 91 (30) and 89 (19); ν_{max}(film)/1765 (C=O).

4-*Methoxydehydrobenzene* **18**. A solution of the tosyl ester[1] **17** (2.0 g) and 3-methoxyfuran (1.1 g) in THF (20 cm^3) was treated with butyllithium in a manner similar to that described above. The crude product was purified by radial chromatography with 20% ethyl acetate–hexane, containing 1% triethylamine, as eluent. This afforded an oily mixture (720 mg, 63%) of 1,4-dihydro-2,7-dimethoxy-1,4-epoxynaphthalene **20** (50%) and 1,4-dihydro-2,6-dimethoxy-1,4-epoxynaphthalene **19** (50%); *m/z* 204 (M$^+$); δ_H compound **20** 3.57 (3 H, s, 2-OMe), 3.77 (3 H, s, 7-OMe), 5.20 (1 H, br s, $W_{\frac{1}{2}}$ 3.5 Hz, 1-H), 5.35 (1 H, dd, $J_{4,3}$ 2.1, $J_{4,8}$ 0.4, 4-H), 5.64 (1 H, m, $W_{\frac{1}{2}}$ 4.5 Hz, 3-H), 6.46 (1 H, dd, $J_{6,5}$ 7.8, $J_{6,8}$ 2.3, 6-H), 6.98 (1 H, dd, $J_{8,6}$ 2.3, $J_{8,4}$ 0.4, 8-H) and 7.06 (1 H, d, $J_{5,6}$ 7.8, 5-H); δ_H compound **19**: 3.57 (3 H, s, 2-OMe), 3.77 (3 H, s, 6-OMe), 5.20 (1 H, br s, $W_{\frac{1}{2}}$ 3.5 Hz, 1-H), 5.40 (1 H, dd, $J_{4,3}$ 2.1, $J_{4,8}$ 0.3, 4-H), 5.64 (1 H, m, $W_{\frac{1}{2}}$ 4.5 Hz, 3-H), 6.42 (1 H, dd, $J_{7,8}$ 7.8, $J_{7,5}$ 2.3, 7-H), 6.84 (1 H, dd, $J_{8,7}$ 7.8, $J_{8,4}$ 0.3, 8-H) and 7.21 (1 H, d, $J_{5,7}$ 2.3, 5-H).

4,5-*Dimethoxydehydrobenzene* **22**. A solution of the dibromo compound[1] **21** (2.0 g) and 3-methoxyfuran (1.7 g, 2.5 mol equiv.) in dry THF (30 cm^3) was treated with butyllithium in a manner similar to that described above. The crude product was purified by radial chromatography with 20% ethyl acetate–hexane as eluent. This gave 3,4-*dihydro*-6,7-*dimethoxy*-1,4-*epoxynaphthalen*-2(1H)-*one* **23** (920 mg, 62%), which was crystallized from diethyl ether–hexane as prisms, m.p. 148–149 °C (Found: C, 65.2; H, 5.9. $C_{12}H_{12}O_4$ requires C, 65.45; H, 5.55%); δ_H 1.99 (1 H, d, $J_{3\text{-}endo,3\text{-}exo}$ 16.1, 3-H_{endo}), 2.58 (1 H, dd, $J_{3\text{-}exo,3\text{-}endo}$ 16.1, $J_{3\text{-}exo,4}$ 4.8, 3-H_{exo}), 3.88 and 3.89 (each 3 H, s, OMe), 4.97 (1 H, s, 1-H), 5.67 (1 H, d, $J_{4,3\text{-}exo}$ 4.8, 4-H) and 6.92 and 6.99 (each 1 H, s, ArH); δ_C 38.00 (C-3), 56.29 (2 × OMe), 79.85 (C-4), 82.86 (C-1), 104.37 and 106.23 (C-5 and -8), 129.75 (C-8a), 139.27 (C-4a),148.87 and 149.77 (C-6 and -7) and 206.95 (C-2); *m/z* 193 (13%), 192 (100, M − CO), 191 (11), 178 (47), 164 (67), 149 (67), 135 (15), 121 (22), 107 (10), 106 (12) and 103 (27); ν_{max}(KBr)/cm^{-1} 1758.

1,2-*Diacetoxy*-6,7-*dimethoxynaphthalene* **24**. The trinorbornenone **23** (150 mg) was dissolved in acetic anhydride (0.5 cm^3), conc. sulphuric acid (1 drop) was added, and the solution was set aside under argon for 18 h. The usual work-up gave a crude product, which was purified by radial chromatography with 20% ethyl acetate–hexane as eluent. The *naphthalene* **24** (90 mg, 55%) was crystallized from diethyl ether–hexane as prisms, m.p. 134.5–136 °C (Found: C, 63.2; H, 5.5%; M$^+$, 304. $C_{16}H_{16}O_6$ requires C, 63.15; H, 5.3%; M, 304); δ_H(80 MHz) 2.32 and 2.45 (each 3 H, s, OAc), 3.98 (6 H, s, 2 × OMe), 7.04 and 7.12 (each 1 H, s, 5- and 8-H) and 7.17 and 7.59 (2 H, AB, $J_{3,4}$ 8.8, 3- and 4-H).

3,4-*Dimethoxydehydrobenzene* **26**. The tosyl ester[1] **25** was allowed to react with 3-methoxyfuran in the presence of butyllithium by the method described above. The crude product was purified by radial chromatography with 25% ethyl acetate–hexane, containing 1% triethylamine, as eluent. This afforded a mixture (86%) of 1,4-*dihydro*-2,5,6-*trimethoxy*-1,4-*epoxynaphthalene* **27** (86%) and 1,4-dihydro-2,7,8-trimethoxy-1,4-epoxynaphthalene **28** (14%). Crystallization of this mixture from diethyl ether–hexane afforded the *major adduct* **27** as prisms, m.p. 112–113.5 °C (Found: C, 66.35; H, 6.05. $C_{13}H_{14}O_4$ requires C, 66.65; H, 6.0%); δ_H 3.60 (3 H, s, 2-OMe), 3.83 and 3.93 (each 3 H, s, OMe), 5.20 (1 H, d, $J_{1,4}$ 1.0, 1-H), 5.39 (1 H, d, $J_{3,4}$ 2.1, 3-H), 6.03 (1 H, ddd, $J_{4,3}$ 2.1, $J_{4,1}$ 1.0, $J_{4,8}$ 0.8, 4-H), 6.44 (1 H, d, $J_{7,8}$ 7.6, 7-H) and 6.96 (1 H, dd, $J_{8,7}$ 7.6, $J_{8,4}$ 0.8, 8-H); δ_C 56.16 (6-OMe), 58.06 (2-OMe), 60.33 (5-OMe), 81.43 and 82.05 (C-1 and -4), 101.53 (C-3), 106.76 and 114.61 (C-7 and -8), 139.44 and 139.55 (C-4a and -8a), 142.47 (C-6), 150.32 (C-5) and 176.52 (C-2); *m/z* 235 (13%), 234 (100, M$^+$), 220 (10), 219 (79), 191 (17), 187 (12), 176 (21), 159 (29) and 131 (29). The ^{1}H NMR spectrum of the mixture showed signals due to the minor adduct **28**: δ_H (*inter alia*) 3.60 (3 H, s, 2-OMe), 3.99 (3 H, s, OMe), 5.61 (1 H, dd, $J_{4,3}$ 2.1, $J_{4,1}$ 1.2, 4-H), 5.65 (1 H, br s, 1-H) and 6.48 and 6.93 (2 H, AB, $J_{5,6}$ 7.5, 6- and 5-H).

1-*Acetoxy*-2,5,6-*trimethoxynaphthalene* **29**. The pure adduct **27** (200 mg) was stirred with acetic anhydride (1 cm^3) and TFA (5 drops) under argon for 18 h. The usual work-up gave a crude product, which was purified by radial chromatography with 20% ethyl acetate–hexane as eluent. The *naphthalene* **29** (168 mg, 71%) was crystallized from diethyl ether–hexane as plates, m.p. 144–145 °C (Found: C, 64.95; H, 5.85. $C_{15}H_{16}O_5$ requires C, 65.2; H, 5.85%); δ_H 2.46 (3 H, s, MeCO), 3.94, 3.97 and 3.99 (each 3 H, s, OMe), 7.30 (1 H, d, $J_{7,8}$ 9.2, 7-H), 7.34 (1 H, d, $J_{3,4}$ 9.3, 3-H), 7.51 (1 H, dd, $J_{8,7}$ 9.2, $J_{8,4}$ 0.75, 8-H) and 8.02 (1 H, dd, $J_{4,3}$ 9.3, $J_{4,8}$ 0.75, 4-H).

1,2-*Diacetoxy*-5,6-*dimethoxynaphthalene* **30**. The pure adduct **27** (300 mg) was stirred with acetic anhydride (0.5 cm^3) and conc. sulphuric acid (1 drop) for 18 h under argon. The usual work-up followed by radial chromatography of the crude product with 25% ethyl acetate–hexane as eluent afforded the *naphthalene* **30** (250 mg, 64%), which was crystallized from diethyl ether–hexane as plates, m.p. 134.5–136 °C (Found: C, 63.3; H, 5.3%; M$^+$, 304. $C_{16}H_{16}O_6$ requires C, 63.15; H, 5.3%; M, 304); δ_H(80 MHz) 2.33 and 2.43 (each 3 H, s, OAc), 3.98 (6

H, s, 2 × OMe), 7.24 (1 H, d, $J_{3,4}$ 9.2, 3-H), 7.32 (1 H, d, $J_{7,8}$ 9.2, 7-H), 7.57 (1 H, dd, $J_{8,7}$ 9.2, $J_{8,4}$ 0.7, 8-H) and 8.04 (1 H, dd, $J_{4,3}$ 9.2, $J_{4,8}$ 0.7, 4-H).

3,4-*Dihydro*-5,6-*dimethoxy*- **31** *and* 3,4-*Dihydro*-7,8-*dimethoxy*-1,4-*epoxynaphthalen*-2(1H)-*one* **32**. The mixture of adducts **27** and **28** was hydrolysed for 3 h and the crude product was purified by radial chromatography with 15% ethyl acetate–hexane as eluent. This afforded a mixture (81%) of the benzoxatrinorbornenones **31** (86%) and **32** (14%) which, after crystallization from diethyl ether–hexane, yielded the *benzoxatrinorbornenone* **31** as prisms, m.p. 94–95 °C (Found: C, 65.35; H, 5.5. $C_{12}H_{12}O_4$ requires C, 65.45; H, 5.5%); δ_H 2.10 (1 H, d, $J_{3\text{-}endo,3\text{-}exo}$ 16.4, 3-H_{endo}), 2.65 (1 H, dd, $J_{3\text{-}exo,4}$ 5.0, $J_{3\text{-}exo,3\text{-}endo}$ 16.4, 3-H_{exo}), 3.87 and 3.93 (each 3 H, s, OMe), 4.97 (1 H, s, 1-H), 6.00 (1 H, d, $J_{4,3\text{-}exo}$ 5.0, 4-H) and 6.74 and 7.06 (2 H, AB, $J_{7,8}$ 7.9, 7- and 8-H); δ_C 38.35 (C-3), 56.28 (6-OMe), 60.60 (5-OMe), 78.11 (C-4), 82.45 (C-1), 111.34 and 117.15 (C-7 and -8), 130.74 (C-8a), 136.48 (C-4a), 142.65 (C-6), 152.47 (C-5) and 206.57 (C-2). The NMR data for the minor ketone **32**, obtained on the mixture, were: δ_H 2.05 (1 H, d, $J_{3\text{-}endo,3\text{-}exo}$ 16.4, 3-H_{endo}), 2.59 (1 H, dd, $J_{3\text{-}exo,3\text{-}endo}$ 16.4, $J_{3\text{-}exo,4}$ 4.9, 3-H_{exo}), 3.84 and 3.99 (each 3 H, s, OMe), 5.39 (1 H, br s, 1-H), 5.63 (1 H, d, $J_{4,3\text{-}exo}$ 4.9, 4-H) and 6.75 and 6.90 (2 H, AB, $J_{5,6}$ 7.8, 6- and 5-H); δ_C 38.64 (C-3), 56.39 (7-OMe), 60.47 (8-OMe), 79.14 (C-4), 81.66 (C-1), 113.69 and 115.70 (C-5 and -6), 129.64 (C-8a), 139.65 (C-4a), 145.23 (C-7), 150.77 (C-8) and 206.22 (C-2); for the mixture: t_R 7.43 min; *m/z* 192 (100%, M − CO), 191 (14), 178 (63), 177 (30), 163 (66), 149 (24), 135 (12), 134 (22), 133 (12), 121 (28), 107 (16), 106 (16), 105 (18), 104 (16) and 103 (12).

3,5-*Dimethoxydehydrobenzene* **34**. Prepared from the tosyl ester[1] **33**, 3-methoxyfuran (1.6 mol equiv.), and butyllithium, the crude product was purified by radial chromatography with 15% ethyl acetate–hexane, containing 1% triethylamine, as eluent. This afforded a mixture (64%) of 1,4-dihydro-2,5,7-trimethoxy-1,4-epoxynaphthalene **35** (85%) and 1,4-dihydro-2,6,8-trimethoxy-1,4-epoxynaphthalene **36** (15%). Crystallization from diethyl ether–hexane afforded the *major adduct* **35** as rosettes of needles, m.p. 109.5–110.5 °C (Found: C, 66.35; H, 5.95. $C_{13}H_{14}O_4$ requires C, 66.65; H, 6.0%); δ_H 3.58 (3 H, s, 2-OMe), 3.78 and 3.82 (each 3 H, s, OMe), 5.20 (1 H, d, $J_{1,4}$ 1.2, 1-H), 5.44 (1 H, d, $J_{3,4}$ 2.1, 3-H), 5.88 (1 H, ddd, $J_{4,3}$ 2.1, $J_{4,1}$ 1.2, $J_{4,8}$ 0.8, 4-H) and 6.16 and 6.68 (2 H, AB, $J_{6,8}$ 1.9, 6- and 8-H); δ_C 55.57 and 55.64 (each OMe), 57.97 (2-OMe), 81.03 and 82.15 (C-1 and -4), 96.37, 101.71 and 102.88 (C-3, -6 and -8), 129.85 (C-4a), 151.12 and 151.99 (C-5 and -8a), 158.99 (C-7) and 176.29 (C-2); *m/z* 235 (15%), 234 (100, M^+), 219 (52), 216 (14), 205 (14), 191 (68), 176 (27), 161 (17), 148 (11) and 133 (11). The ^1H NMR spectrum of the mixture showed signals due to the minor adduct **36**: δ_H 3.59 (3 H, s, 2-OMe), 3.77 and 3.84 (each 3 H, s, OMe), 5.33 (1 H, d, $J_{4,3}$ 2.1, 4-H), 5.48 (1 H, br s, 1-H), 5.59 (1 H, dd, $J_{3,4}$ 2.1, $J_{3,1}$ 0.5, 3-H) and 6.10 and 6.54 (2 H, AB, $J_{5,7}$ 1.8, 7- and 5-H).

1-*Acetoxy*-2,5,7-*trimethoxynaphthalene* **37**. The pure adduct **35** (200 mg) was stirred with acetic anhydride (0.5 cm^3) and conc. sulphuric acid (1 drop) under nitrogen for 18 h. The usual work-up gave a crude product, which was purified by radial chromatography with 20% ethyl acetate–hexane as eluent. The *naphthalene* **37** (134 mg, 57%) was crystallized from diethyl ether–hexane as plates, m.p. 146–147.5 °C (Found: C, 65.45; H, 5.85%; M^+, 276. $C_{15}H_{16}O_5$ requires C, 65.2; H, 5.85%; M, 276); δ_H 2.46 (3 H, s, MeCO), 3.90, 3.93 and 3.95 (each 3 H, s, OMe), 6.36 and 6.58 (2 H, AB, $J_{6,8}$ 2.2, 6- and 8-H), 7.11 (1 H, d, $J_{3,4}$ 9.2, 3-H) and 8.03 (1 H, d, $J_{4,3}$ 9.2, 4-H).

3,4-*Dihydro*-5,7-*dimethoxy*- **38** *and* 3,4-*Dihydro*-6,8-*dimethoxy*-1,4-*epoxynaphthalen*-2(1H)-*one* **39**. The mixture of adducts **35** and **36** (600 mg) was hydrolysed for 4.5 h and the crude product was purified by radial chromatography. The first band that was eluted yielded the *benzoxatrinorbornenone* **38** (300 mg, 53%), which was crystallized from diethyl ether–hexane as prisms, m.p. 110–111 °C (Found: C, 65.65; H, 5.6. $C_{12}H_{12}O_4$ requires C, 65.45; H, 5.5%); δ_H 2.05 (1 H, d, $J_{3\text{-}endo,3\text{-}exo}$ 16.3, 3-H_{endo}) 2.57 (1 H, dd, $J_{3\text{-}exo,3\text{-}endo}$ 16.3, $J_{3\text{-}exo,4}$ 4.7, 3-H_{exo}), 3.80 and 3.83 (each 3 H, s, OMe), 4.96 (1 H, s, 1-H), 5.84 (1 H, d, $J_{4,3\text{-}exo}$ 4.7, 4-H) and 6.36 and 6.59 (2 H, AB, $J_{6,8}$ 1.8, 6- and 8-H); δ_C 37.86 (C-3), 55.52 and 55.76 (each OMe), 77.44 (C-4), 83.40 (C-1), 99.07 and 99.44 (C-6 and -8), 126.45 (C-4a), 141.03 (C-8a), 153.54 (C-5), 161.51 (C-7) and 207.64 (C-2); *m/z* 192 (6%, M − CO), 178 (100), 163 (14), 135 (18), 134 (14), 133 (23), 131 (23), 121 (53) and 105 (11). Further elution supplied the *benzoxatrinorbornenone* **39** (83 mg, 15%) as an oil, b.p. 125 °C at 0.01 mmHg (Found: C, 65.75; H, 5.75%); δ_H 1.99 (1 H, d, $J_{3\text{-}endo,3\text{-}exo}$ 16.4, 3-H_{endo}), 2.55 (1 H, dd, $J_{3\text{-}exo,3\text{-}endo}$ 16.4, $J_{3\text{-}exo,4}$ 5.0, 3-H_{exo}), 3.80 and 3.82 (each 3 H, s, OMe), 5.17 (1 H, s, 1-H), 5.60 (1 H, d, $J_{4,3\text{-}exo}$ 5.0, 4-H) and 6.29 and 6.52 (2 H, AB, $J_{5,7}$ 1.8, 5- and 7-H); δ_C 37.79 (C-3), 55.72 and 55.82 (each OMe), 79.77 and 80.17 (C-1 and -4), 97.95 and 98.62 (C-5 and -7), 116.29 (C-8a), 149.66 (C-4a), 155.81 (C-8), 162.55 (C-6) and 205.95 (C-2); *m/z* 193 (12%), 192 (100, M − CO), 191 (51), 178 (21), 163 (36), 161 (15), 149 (11), 135 (12) and 133 (8).

3,4,6-*Trimethoxydehydrobenzene* **41**. The crude product obtained from the dibromo compound[1] **40** was a mixture of the isomers **42** and **43**, which was hydrolysed to the ketones **44** and **45** which were obtained, after radial chromatography with 20% ethyl acetate–hexane as eluent, as a solid (83%) containing 51 and 49% of the isomers, which could not be separated by radial chromatography: δ_H(major isomer) (*inter alia*) 2.06 (1 H, d, $J_{3\text{-}endo,3\text{-}exo}$ 16.3, 3-H_{endo}), 2.58 (1 H, dd, $J_{3\text{-}exo,3\text{-}endo}$ 16.3, $J_{3\text{-}exo,4}$ 5.0, 3-H_{exo}), 5.19 (1 H, br s, 1-H), 5.88 (1 H, dd, $J_{4,3\text{-}exo}$ 5.0, $J_{4,1}$ 0.8, 4-H) and 6.33 (1 H, s, ArH); δ_H(minor isomer) (*inter alia*) 2.08 (1 H, d, $J_{3\text{-}endo,3\text{-}exo}$ 16.3, 3-H_{endo}), 2.60 (1 H, dd, $J_{3\text{-}exo,3\text{-}endo}$ 16.3, $J_{3\text{-}exo,4}$ 4.8, 3-H_{exo}), 5.28 (1 H, br s, 1-H), 5.83 (1 H, dd, $J_{4,3\text{-}exo}$ 4.8, $J_{4,1}$ 0.8, 4-H) and 6.39 (1 H, s, ArH).

3,4,5-*Trimethoxydehydrobenzene* **47**. Prepared from the dibromo compound[1] **46** the crude product was purified by radial chromatography with 20% ethyl acetate–hexane, containing 1% triethylamine, as eluent which afforded a mixture (74%) of 1,4-dihydro-2,5,6,7-tetramethoxy-1,4-epoxynaphthalene **48** (77%) and 1,4-dihydro-2,6,7,8-tetramethoxy-1,4-epoxynaphthalene **49** (23%) as an oil; δ_H compound **48**: 3.60 (3 H, s, 2-OMe), 3.85, 3.93 and 3.95 (each 3 H, s, OMe), 5.19 (1 H, d, $J_{1,4}$ 1.2, 1-H), 5.44 (1 H, d, $J_{3,4}$ 2.1, 3-H), 6.02 (1 H, ddd, $J_{4,3}$ 2.1, $J_{4,1}$ 1.2, $J_{4,8}$ 0.5, 4-H) and 6.81 (1 H, s, 8-H); δ_H compound **49** 3.62 (3 H, s, 2-OMe), 3.84, 3.89 and 3.90 (each 3 H, s, OMe), 5.37 (1 H, d, $J_{3,4}$ 2.1, 3-H), 5.60 (1 H, dd, $J_{4,3}$ 2.1, $J_{4,1}$ 1.3, 4-H), 5.62 (1 H, br s, 1-H) and 6.72 (1 H, s, 5-H).

5-*Acetoxy*-1,2,3,6-*tetramethoxynaphthalene* **50**. The mixture of adducts **48** and **49** (200 mg) was treated with acetic anhydride and TFA for 48 h. The usual work-up gave a crude product, which was purified by radial chromatography with 20% ethyl acetate–hexane as eluent, and was then crystallized several times from diethyl ether–hexane whereupon the *naphthalene* **50** (120 mg, 52%) formed plates, m.p. 106–107 °C (Found: C, 63.05; H, 6.15%; M^+, 306. $C_{16}H_{18}O_6$ requires C, 62.75; H, 5.9%; M, 306); δ_H(80 MHz) 2.45 (3 H, s, OAc), 3.88 (3 H, s, OMe), 3.92 (6 H, s, 2 × OMe), 3.96 (3 H, s, OMe), 6.79 (1 H, s, 4-H) and 7.17 and 7.94 (2 H, AB, $J_{3,4}$ 9.2, 7- and 8-H).

1-(8-*Acetoxy*-2,3,4,7-*tetramethoxynaphthalen*-1-*yl*)*ethanone* **51**. The mixture of adducts **48** and **49** (300 mg) was treated with acetic anhydride (0.5 cm^3) and conc. sulphuric acid (1 drop) for 18 h. The usual work-up afforded a crude product, which was purified by radial chromatography with 30% ethyl acetate–hexane as eluent and then by several crystallizations from diethyl ether–hexane, when the *ketone* **51** (221 mg, 56%) was obtained as needles, m.p. 108.5–111 °C (Found: C, 62.1; H, 5.95%; M^+, 348. $C_{18}H_{20}O_7$ requires C, 62.05; H, 5.8%; M, 348); δ_H(80 MHz) 2.29 and 2.59 (each 3 H, s, MeCO), 3.90,

3.92, 3.97 and 4.03 (each 3 H, s, OMe) and 7.25 and 8.00 (2 H, AB, $J_{5,6}$ 9.2, 6- and 5-H).

3,4-*Dihydro*-5,6,7-*trimethoxy*- **52** *and* 3,4-*Dihydro*-6,7,8-*trimethoxy*-1,4-*epoxynaphthalen*-2(1H)-*one* **53**. The mixture of adducts **48** and **49** was hydrolysed for 5 h and the crude product was subjected to flash chromatography with 30% ethyl acetate–hexane as eluent. The first band that was eluted provided the *benzoxatrinorbornenone* **52** (322 mg, 60%), which was crystallized from diethyl ether–hexane as rosettes of needles, m.p. 90–92 °C (Found: C, 62.15; H, 5.85. $C_{13}H_{14}O_5$ requires C, 62.4; H, 5.65%); δ_H 2.09 (1 H, d, $J_{3\text{-}endo,3\text{-}exo}$ 16.2, 3-H_{endo}), 2.62 (1 H, dd, $J_{3\text{-}exo,3\text{-}endo}$ 16.2, $J_{3\text{-}exo,4}$ 4.8, 3-H_{exo}), 3.84, 3.86 and 3.96 (each 3 H, s, OMe), 4.95 (1 H, s, 1-H), 5.96 (1 H, d, $J_{4,3\text{-}exo}$ 4.8, 4-H) and 6.76 (1 H, s, 8-H); δ_C 38.33 (C-3), 56.45 (7-OMe), 60.51 and 61.00 (each OMe), 78.45 and 83.02 (C-1 and -4), 101.68 (C-8), 128.87 (C-4a), 133.69 (C-8a), 141.15 (C-6), 147.44 (C-7), 153.91 (C-5) and 206.68 (C-2); t_R 8.17 min; *m/z* 223 (11%), 222 (83, M^+), 209 (13), 208 (100), 194 (17), 193 (47), 179 (62), 165 (11), 164 (13), 151 (20), 150 (11), 149 (15), 148 (13), 136 (13), 135 (22), 134 (10), 121 (15), 104 (15), 93 (14), 91 (16) and 77 (14). Further elution provided the *benzoxatrinorbornenone* **53** (93 mg, 17%), which was crystallized from diisopropyl ether–hexane as rods, m.p. 87–88 °C (Found: C, 62.2; H, 5.4%); δ_H 2.03 (1 H, $J_{3\text{-}endo,3\text{-}exo}$ 16.2, 3-H_{endo}), 2.57 (1 H, dd, $J_{3\text{-}exo,3\text{-}endo}$ 16.2, $J_{3\text{-}exo,4}$ 4.8, 3-H_{exo}), 3.81, 3.94 and 4.00 (each 3 H, s, OMe), 5.34 (1 H, s, 1-H), 5.61 (1 H, d, $J_{4,3\text{-}exo}$ 4.8, 4-H) and 6.70 (1 H, s, 5-H); δ_C 38.01 (C-3), 56.31 (6-OMe), 60.33 and 60.98 (each OMe), 79.62 and 81.56 (C-1 and -4), 99.29 (C-5), 117.65 (C-8a), 137.59 (C-4a), 139.27 (C-7), 149.70 (C-6), 153.40 (C-8) and 206.15 (C-2); t_R 8.23 min; *m/z* 223 (15%), 222 (100, M^+), 208 (17), 207 (24), 193 (16), 179 (37), 165 (9), 149 (12), 135 (22), 121 (12), 104 (16) and 77 (11).

3,4,5,6-*Tetramethoxydehydrobenzene* **55**. The crude product, obtained from the dibromo compound[1] **54**, was purified by radial chromatography with 20% ethyl acetate–hexane as eluent; this afforded 3,4-*dihydro*-5,6,7,8-*tetramethoxy*-1,4-*epoxynaphthalen*-2(1H)-*one* **56** (1.19 g, 76%) as an oil, b.p. 86 °C at 0.5 mmHg (Found: C, 60.2; H, 6.0. $C_{14}H_{16}O_6$ requires C, 60.0; H, 5.75%); δ_H 2.10 (1 H, d, $J_{3\text{-}endo,3\text{-}exo}$ 16.6, 3-H_{endo}), 2.64 (1 H, dd, $J_{3\text{-}exo,3\text{-}endo}$ 16.6, $J_{3\text{-}exo,4}$ 5.0, 3-H_{exo}), 3.87, 3.88, 3.89 and 3.93 (each 3 H, s, OMe), 5.29 (1 H, d, $J_{1,4}$ 0.8, 1-H) and 5.88 (1 H, dd, $J_{4,3\text{-}exo}$ 5.0, $J_{4,1}$ 0.8, 4-H); δ_C 38.21 (C-3), 60.86 and 61.09 (each OMe), 61.29 (2 × OMe), 77.71 (C-4), 81.23 (C-1), 121.70 (C-8a), 132.05 (C-4a), 142.25, 145.10, 145.32 and 146.97 (C-5, -6, -7 and -8) and 206.10 (C-2); *m/z* 253 (15), 252 (100, M − CO), 238 (40), 237 (75), 223 (63), 222 (18), 209 (26), 207 (28), 195 (13), 194 (19), 193 (19), 180 (14), 179 (37), 178 (15), 165 (16), 164 (10), 163 (12), 151 (16), 149 (15), 147 (10), 123 (13), 121 (11) and 119 (15).

5,6-*Diacetoxy*-1,2,3,4-*tetramethoxynaphthalene* **57**. The ketone **56** (150 mg) was stirred with acetic anhydride (0.5 cm^3) and conc. sulphuric acid (1 drop) for 18 h under argon. The usual work-up gave a crude product, which was purified by radial chromatography with 30% ethyl acetate–hexane as eluent. The *naphthalene* **57** (114 mg, 58%) was crystallized from diethyl ether–hexane as prisms, m.p. 85–86 °C (Found: C, 59.3; H, 5.45%; M^+, 364. $C_{18}H_{20}O_8$ requires C, 59.35; H, 5.55%; M, 364); δ_H(80 MHz) 2.34 and 2.38 (each 3 H, s, MeCO), 3.88 (3 H, s, OMe), 3.99 (6 H, s, 2 × OMe), 4.00 (3 H, s, OMe) and 7.20 and 8.00 (2 H, AB, $J_{3,4}$ 9.2, 7- and 8-H).

Reactions of the Ketones **5**, **15** *and* **38**.—1,2,3,4-*Tetrahydro*-2-*methylene*-1,4-*epoxynaphthalene* **6**. A solution of butyllithium (1.79 mol dm^{-3}) in hexane (0.84 cm^3) was added by syringe to a stirred suspension of methyltriphenylphosphonium bromide (570 mg) in anhydrous THF (5 cm^3) at room temperature under argon. The solution was stirred for 20 min and a solution of the ketone **5** (200 mg) in anhydrous THF (5 cm^3) was then added dropwise. The solution was stirred at room temperature for 3 h and was then diluted with water and extracted with ethyl acetate. The crude product was purified by radial chromatography with 5% ethyl acetate–hexane as eluent. The *alkene* **6** (119 mg, 60%) was obtained as an oil, b.p. 58–60 °C at 0.1 mmHg (Found: C, 83.35; H, 6.3. $C_{11}H_{10}O$ requires C, 83.5; H, 6.35%); δ_H 2.04 (1 H, dddd, $J_{3\text{-}endo,3\text{-}exo}$ 14.7, $J_{3\text{-}endo,2}$ 2.0, $J_{3\text{-}endo,2'}$ 2.0, $J_{3\text{-}endo,4}$ 0.5, 3-H_{endo}), 2.72 (1 H, dddd, $J_{3\text{-}exo,3\text{-}endo}$ 14.7, $J_{3\text{-}exo,4}$ 4.9, $J_{3\text{-}exo,2}$ 2.5, $J_{3\text{-}exo,2'}$ 2.0, 3-H_{exo}), 4.87 and 5.19 (each 1 H, narrow m, =CH_2), 5.42 (1 H, br s, 1-H), 5.47 (1 H, br d, $J_{4,3\text{-}exo}$ 4.9, 4-H) and 7.12–7.29 (4 H, m, ArH); t_R 4.55 min; *m/z* 158 (31%, M^+), 130 (25), 129 (98), 127 (29), 118 (100), 115 (30), 102 (14), 90 (25) and 89 (30).

(1α,4α)-1,2,3,4-*Tetrahydro*-2α-*methyl*- **7** *and* (1α,4α)-1,2,3,4-*Tetrahydro*-2β-*methyl*-1,4-*epoxynaphthalene* **8**. A solution of the alkene **6** (65 mg) in ethyl acetate was stirred under hydrogen with palladized charcoal (10%; 10 mg) until absorption ceased. The usual work-up gave a mixture (57 mg, 85%) of the isomers **7** (73%) and **8** (27%) as an oil, b.p. 28–30 °C at 0.01 mmHg (Found: C, 82.7; H, 7.8. Calc. for $C_{11}H_{12}O$: C, 82.45; H, 7.55%); δ_H compound **7**: 0.59 (3 H, d, $J_{Me,2\text{-}endo}$ 6.9, Me), 0.79 (1 H, dd, $J_{3\text{-}endo,3\text{-}exo}$ 11.5, $J_{3\text{-}endo,2\text{-}exo}$ 4.0, 3-H_{endo}), 2.32 (1 H, ddd, $J_{3\text{-}exo,3\text{-}endo}$ 11.5, $J_{3\text{-}exo,2\text{-}exo}$ 10.0, $J_{3\text{-}exo,4}$ 5.2, 3-H_{exo}), 2.84 (1 H, dddq, $J_{2\text{-}exo,3\text{-}exo}$ 10.0, $J_{2\text{-}endo,Me}$ 6.9, $J_{2\text{-}exo,1}$ 4.8, $J_{2\text{-}exo,3\text{-}endo}$ 4.0, 2-H_{exo}), 5.13 (1 H, d, $J_{1,2\text{-}exo}$ 4.8, 1-H), 5.29 (1 H, d, $J_{4,3\text{-}exo}$ 5.2, 4-H) and 7.11–7.24 (4 H, m, ArH); δ_H compound **8**: 1.22 (3 H, d, $J_{Me,2\text{-}endo}$ 6.9, Me), 1.52 (1 H, ddd, $J_{3\text{-}exo,3\text{-}endo}$ 11.5, $J_{3\text{-}exo,4}$ 4.8, $J_{3\text{-}exo,2\text{-}endo}$ 4.0, 3-H_{exo}), 1.64 (1 H, dd, $J_{3\text{-}endo,3\text{-}exo}$ 11.3, $J_{3\text{-}endo,2\text{-}endo}$ 8.0, 3-H_{exo}), 1.80 (1 H, ddq, $J_{2\text{-}endo,3\text{-}endo}$ 8.0, $J_{2\text{-}endo,Me}$ 6.9, $J_{2\text{-}endo,3\text{-}exo}$ 4.0, 2-H_{endo}), 4.91 (1 H, s, 1-H), 5.35 (1 H, d, $J_{4,3\text{-}exo}$ 4.8, 4-H) and 7.11–7.24 (4 H, m, ArH); δ_C compound **7**: 16.58 (Me), 32.35 (C-2), 35.45 (C-3), 79.64 and 82.89 (C-1 and -4), 118.33 and 121.11 (C-5 and -8), 125.95 and 126.67 (C-7 and -6) and 142.38 and 146.28 (C-4a and -8a); δ_C compound **8**: 20.57 (Me), 34.44 (C-2), 36.27 (C-3), 79.61 and 84.71 (C-1 and -4), 118.76 and 118.82 (C-5 and -8), 126.34 (C-6 and -7) and 145.62 and 145.68 (C-4a and -8a); compound **7**: t_R 9.60 min; *m/z* 118 (100%); compound **8**: t_R 9.88 min; *m/z* 118 (100%).

(1α,4α)-1,2,3,4-*Tetrahydro*-1,4-*epoxynaphthalen*-2α- **58** *and* -2β-*ol* **59**. A solution of the ketone **5** (145 mg) in anhydrous diethyl ether (2 cm^3) was added to a stirred solution of lithium aluminium hydride (40 mg) in diethyl ether (10 cm^3) at 0 °C. The mixture was stirred at room temperature for 1 h and was then worked up by the addition of saturated aq. sodium sulphate in the usual way. The crude product was purified by radial chromatography with 50% ethyl acetate–hexane as eluent; this afforded the product as a viscous oil (75 mg, 50%), b.p. 98 °C at 3 mmHg, which was a mixture of the *endo*- **58** (86%) and *exo*-alcohol[9] **59** (14%): δ_H compound **58**: 0.99 (1 H, dd, $J_{3\text{-}endo,3\text{-}exo}$ 12.3, $J_{3\text{-}endo,2\text{-}exo}$ 2.6, 3-H_{endo}), 2.50 (1 H, ddd, $J_{3\text{-}exo,3\text{-}endo}$ 12.3, $J_{3\text{-}exo,2\text{-}exo}$ 8.8, $J_{3\text{-}exo,4}$ 5.2, 3-H_{exo}), 4.56 (1 H, ddd, $J_{2\text{-}exo,3\text{-}exo}$ 8.8, $J_{2\text{-}exo,1}$ 4.8, $J_{2\text{-}exo,3\text{-}endo}$ 2.6, 2-H_{exo}), 5.17 (1 H, d, $J_{1,2\text{-}exo}$ 4.8, 1-H), 5.29 (1 H, d, $J_{4,3\text{-}exo}$ 5.2, 4-H) and 7.14–7.36 (4 H, m, ArH); compound **59** (*inter alia*) 5.10 (1 H, s, 1-H) and 5.35 (1 H, d, $J_{4,3\text{-}exo}$ 5.2, 4-H); δ_C compound **58**: 37.95 (C-3), 69.12 (C-2), 79.89 and 80.94 (C-1 and -4), 118.89 and 122.59 (C-5 and -8), 126.75 and 127.63 (C-6 and -7), 140.32 (C-8a) and 146.52 (C-4a); compound **59**: 39.65 (C-3), 72.46 (C-2), 78.59 (C-4), 86.16 (C-1), 118.89 and 120.56 (C-5 and -8), 126.68 and 127.29 (C-6 and -7), 141.76 (C-8a) and 146.72 (C-4a).

(1α,4α)-1,2,3,4-*Tetrahydro*-5-*methoxy*-1,4-*epoxynaphthalen*-2α- **62** *and* -2β-*ol* **63**. Reduction of the ketone **15** with lithium aluminium hydride in diethyl ether as described for compound **5** gave a mixture (95%) of the *endo*- **62** (86%) and *exo*-alcohol **63** (14%) as a crystalline solid from which the *exo*-alcohol was not removed after several crystallizations from dichloromethane–hexane (Found: C, 68.75; H, 6.3. Calc. For $C_{11}H_{12}O_3$:

C, 68.6; H, 6.45%); δ_H compound **62**: 0.92 (1 H, d, $J_{OH,2\text{-}exo}$ 9.8, D_2O-exchangeable OH), 1.07 (1 H, dd, $J_{3\text{-}endo,3\text{-}exo}$ 12.3, $J_{3\text{-}endo,2\text{-}exo}$ 2.5, 3-H_{endo}), 2.53 (1 H, ddd, $J_{3\text{-}exo,3\text{-}endo}$ 12.3, $J_{3\text{-}exo,2\text{-}exo}$ 8.5, $J_{3\text{-}exo,4}$ 5.1, 3-H_{exo}), 3.83 (3 H, s, OMe), 4.63 (1 H, m, 2-H_{exo}), 5.23 (1 H, d, $J_{1,2\text{-}exo}$ 4.9, 1-H), 5.52 (1 H, d, $J_{4,3\text{-}exo}$ 5.1, 4-H), 6.80 (1 H, d, $J_{6,7}$ 7.2, 6-H), 7.02 (1 H, d, $J_{8,7}$ 7.2, 8-H) and 7.22 (1 H, dd, $J_{7,8} = J_{7,6} = 7.2$, 7-H); compound **63** (*inter alia*) 5.16 (1 H, s, 1-H) and 5.32 (1 H, d, $J_{4,3\text{-}exo}$ 5.0, 4-H); δ_C compound **62**: 37.77 (C-3), 55.51 (OMe), 69.51 (C-2), 77.67 (C-4), 81.28 (C-1), 111.0 and 115.21 (C-6 and -8), 128.63 (C-7), 133.71 (C-4a), 142.38 (C-8a) and 152.21 (C-5).

(1α,4α)-1,2,3,4-*Tetrahydro*-2β-*methyl*-1,4-*epoxynaphthalen*-2α-*ol* **60**. A solution of methylmagnesium iodide (0.5 mol dm^{-3}) in diethyl ether (5 cm^3) was added dropwise to a solution of the ketone **5** (161 mg) in anhydrous diethyl ether (10 cm^3) at 0 °C. The solution was stirred at room temperature for 2 h and was then cooled to 0 °C and an excess of saturated aq. ammonium chloride was added. The usual work-up gave a crude product, which was purified by radial chromatography with 30% ethyl acetate–hexane as eluent and was then distilled under diminished pressure which supplied the *alcohol* **60** (120 mg, 67%) as a viscous oil, b.p. 98–100 °C at 0.5 mmHg (Found: C, 74.5; H, 7.1. $C_{11}H_{12}O_2$ requires C, 75.0; H, 6.85%); δ_H 1.11 (1 H, br OH), 1.29 (1 H, d, $J_{3\text{-}endo,3\text{-}exo}$ 12.2, 3-H_{endo}), 1.59 (3 H, s, Me), 2.19 (1 H, dd, $J_{3\text{-}exo,3\text{-}endo}$ 12.2, $J_{3\text{-}exo,4}$ 5.3, 3-H_{exo}), 4.76 (1 H, s, 1-H), 5.30 (1 H, d, $J_{4,3\text{-}exo}$ 5.3, 4-H) and 7.18–7.38 (4 H, m, ArH); δ_C 27.74 (Me), 45.05 (C-3), 75.82 (C-2), 80.34 (C-4), 86.33 (C-1), 119.04 and 122.59 (C-5 and -8), 126.67 and 127.62 (C-6 and -7), 141.59 (C-8a) and 146.22 (C-4a).

2-*Methylnaphthalen*-1-*ol* **61**. A solution of the alcohol **60** (125 mg) and PTSA (12 mg) in toluene (12 cm^3) was heated under reflux for 5.5 h under argon. The cooled solution was diluted with ethyl acetate and washed successively with saturated aq. sodium hydrogen carbonate and saturated brine. The crude product was filtered through a short column of silica gel with 20% ethyl acetate–hexane. The naphthol **61** (109 mg, 97%) was crystallized from pentane as rosettes of needles, m.p. 60–63 °C (lit.,[13] 64–65 °C); δ_H(80 MHz) 2.41 (3 H, s, Me), 5.09 (1 H, br, D_2O-exchangeable OH) and 7.17–8.19 (6 H, m, ArH).

(1α,4α)-1,2,3,4-*Tetrahydro*-5-*methoxy*-2β-*methyl*-1,4-*epoxynaphthalen*-2α-*ol* **64**. Prepared from the ketone **15** and methylmagnesium iodide, this compound was purified by radial chromatography with 40% ethyl acetate–hexane as eluent and the *alcohol* **64** (276 mg) was crystallized from diethyl ether–hexane as prisms, m.p. 68.5–70 °C (Found: C, 70.0; H, 7.2. $C_{12}H_{14}O_3$ requires C, 69.9; H, 6.85%); δ_H 1.02 (1 H, s, OH), 1.35 (1 H, d, $J_{3\text{-}endo,3\text{-}exo}$ 12.2, 3-H_{endo}), 1.62 (3 H, s, Me), 2.21 (1 H, dd, $J_{3\text{-}exo,3\text{-}endo}$ 12.2, $J_{3\text{-}exo,4}$ 5.1, 3-H_{exo}), 3.84 (3 H, s, OMe), 4.79 (1 H, d, $J_{1,4}$ 0.7, 1-H), 5.52 (1 H, dd, $J_{4,3\text{-}exo}$ 5.1, $J_{4,1}$ 0.7, 4-H), 6.78 (1 H, d, $J_{6,7}$ 7.2, 6-H), 7.02 (1 H, d, $J_{8,7}$ 7.2, 8-H) and 7.21 (1 H, dd, $J_{7,6} = J_{7,8} = 7.2$, 7-H); δ_C 27.67 (Me), 44.61 (C-3), 55.42 (OMe), 76.03 (C-2), 78.05 (C-4), 86.58 (C-1), 110.89 and 115.13 (C-6 and -8), 128.52 (C-7), 133.18 (C-4a), 143.67 (C-8a) and 152.13 (C-5); *m/z* 206 (3%, M^+), 188 (3), 148 (100), 133 (31), 119 (11), 105 (22) and 73 (96).

5-*Methoxy*-2-*methylnaphthalen*-1-*ol* **65**. Treatment of the alcohol **64** (56 mg) with PTSA in boiling toluene supplied the naphthol **65** (47 mg, 92%), which was crystallized from hexane as rosettes of needles, m.p. 107–109 °C (lit.,[14] 107–108 °C); δ_H 2.38 (3 H, s, Me), 3.97 (3 H, s, OMe), 5.11 (1 H, s, OH), 6.77 (1 H, d, $J_{6,7}$ 7.6, 6-H), 7.22 (1 H, d, $J_{3,4}$ 8.5, 3-H), 7.36 (1 H, dd, $J_{7,8}$ 8.5, $J_{7,6}$ 7.6, 7-H), 7.67 (1 H, d, $J_{8,7}$ 8.5, 8-H) and 7.77 (1 H, d, $J_{4,3}$ 8.5, 4-H).

(1α,4α)-1,2,3,4-*Tetrahydro*-5,7-*dimethoxy*-2β-*methyl*-1,4-*epoxynaphthalen*-2α-*ol* **69**. The ketone **38** (210 mg) was treated with methylmagnesium iodide in a manner similar to that described above. Radial chromatography of the crude product with 40% ethyl acetate–hexane as eluent afforded the *alcohol* **69** (150 mg, 67%), which was crystallized from diethyl ether–hexane as prisms, m.p. 125.5–126.5 °C (Found: C, 66.3; H, 7.15. $C_{13}H_{16}O_6$ requires C, 66.1; H, 6.85%); δ_H 1.08 (1 H, br, OH), 1.34 (1 H, d, $J_{3\text{-}endo,3\text{-}exo}$ 12.0, 3-H_{endo}), 1.61 (3 H, s, Me), 2.18 (1 H, dd, $J_{3\text{-}exo,3\text{-}endo}$ 12.0, $J_{3\text{-}exo,4}$ 5.0, 3-H_{exo}), 3.80 and 3.81 (each 3 H, s, OMe), 4.74 (1 H, s, 1-H), 5.45 (1 H, d, $J_{4,3\text{-}exo}$ 5.0, 4-H) and 6.34 and 6.61 (2 H, AB, $J_{6,8}$ 1.8, 6- and 8-H); δ_C 27.68 (Me), 45.08 (C-3), 55.52 and 55.60 (each OMe), 76.22 (C-2), 78.11 (C-4), 86.90 (C-1), 98.14 and 100.60 (C-6 and -8), 125.64 (C-4a), 144.64 (C-8a), 152.61 (C-5) and 160.68 (C-7).

5,7-*Dimethoxy*-2-*methylnaphthalen*-1-*ol* **70**. The alcohol **69** (95 mg) was treated with PTSA in boiling toluene for 1 h, and the crude product was crystallized from diethyl ether–hexane (charcoal) which gave needles (45 mg, 51%) of the naphthol **70**, m.p. 162–165 °C (lit.,[15] 164 °C); δ_H(80 MHz) 2.39 (3 H, s, Me), 3.94 and 3.96 (each 3 H, s, OMe), 4.93 (1 H, s, OH), 6.47 (1 H, d, $J_{6,8}$ 2.2, 6-H), 7.00 (1 H, d, $J_{8,6}$ 2.2, 8-H), 7.08 (1 H, d, $J_{3,4}$ 8.4, 3-H) and 7.67 (1 H, d, $J_{4,3}$ 8.4, 4-H).

(1α,4α,4aβ,8aβ)-3,4,6,7,8,8a-*Hexahydro*-1,4-*epoxynaphthalene*-2,5(1H,4aH)-*dione* **66**. A solution of the ketone **15** (100 mg) in ethyl acetate (10 cm^3) was stirred under hydrogen with palladized charcoal (Englhard, 10%; 30 mg) until absorption ceased. The usual work-up gave the *dione* **66** (98 mg, 94%), which was crystallized from diethyl ether–hexane as prisms, m.p. 103.5–105 °C (Found: C, 66.4; H, 7.05. $C_{10}H_{12}O_3$ requires C, 66.65; H, 6.7%); δ_H 1.04 (1 H, m, 8-H_{ax}), 1.72–1.98 (2 H, m, 7-H_2), 2.04 (1 H, m, 8-H_{eq}), 2.12 (1 H, d, $J_{3\text{-}endo,3\text{-}exo}$ 18.2, 3-H_{endo}), 2.16 (1 H, ddd, $J_{6ax,6eq}$ 18.8, $J_{6ax,7ax}$ 10.5, $J_{6ax,7eq}$ 6.6, 6-H_{ax}), 2.43 (1 H, m, 6-H_{eq}), 2.50 (1 H, ddd, $J_{3\text{-}exo,3\text{-}endo}$ 18.2, $J_{3\text{-}exo,4}$ 5.8, $J_{3\text{-}exo,4a}$ 1.6, 3-H_{exo}), 2.84 (1 H, dddd, $J_{8a,4a} = J_{8a,8ax} = 11.6$, $J_{8a,1} = J_{8a,8eq} = 6.1$, 8a-H), 3.10 (1 H, ddd, $J_{4a,8a}$ 11.6, $J_{4a,4}$ 5.8, $J_{4a,3\text{-}exo}$ 1.6, 4a-H), 4.35 (1 H, d, $J_{1,8a}$ 6.1, 1-H) and 5.11 (1 H, dd, $J_{4,4a} = J_{4,3\text{-}exo} = 5.8$, 4-H); δ_C 21.30 (C-8), 23.66 (C-7), 38.60 (C-8a), 39.75 (C-3), 42.36 (C-6), 51.46 (C-4a), 77.95 (C-4), 83.65 (C-1) and 210.08 and 211.95 (each C=O); ν_{max}(KBr)/cm^{-1} 1752 and 1684; *m/z* 180 (7%, M^+), 152 (18), 124 (69), 123 (39), 110 (11), 97 (18), 96 (20), 95 (100), 83 (12), 82 (20), 81 (35), 80 (19) and 79 (30).

(1α,4α,4aβ,8aβ)-*Decahydro*-1,4-*epoxynaphthalene*-2α,5α-*diol* **67**. A solution of the dione **66** (96 mg) in anhydrous THF (4 cm^3) was added dropwise to a stirred suspension of lithium aluminium hydride (40 mg) in anhydrous THF (2 cm^3). After 3.5 h saturated aq. sodium sulphate was added. The usual work-up gave a crude product, which was purified by flash chromatography with 50% ethyl acetate–hexane as eluent. The diol **67** was obtained as a gum (63 mg, 64%); δ_H 1.25–1.40 (1 H, m, C*H*H), 1.61–1.90 (4 H, m, 2 × CH_2), *ca.* 2.15–2.44 (3 H, m, 4a-, 8a-H and C*H*H), 2.15 (1 H, ddd, $J_{3\text{-}exo,3\text{-}endo}$ 12.9, $J_{3\text{-}exo,2\text{-}exo}$ 12.5, $J_{3\text{-}exo,4}$ 5.0, 3-H_{exo}), 2.38 (1 H, dd, $J_{3\text{-}endo,3\text{-}exo}$ 12.9, $J_{3\text{-}endo,2\text{-}exo}$ 2.7, 3-H_{endo}), 4.29 (1 H, dd, $J_{5,6ax}$ 7.5, $J_{5,4a}$ 4.0, 5-H), 4.33 (1 H, dd, $J_{4,4a} = J_{4,3\text{-}exo} = 5.0$, 4-H), 4.40 (1 H, m, 2-$H_{exo}$) and 4.57 (1 H, dd, $J_{1,8a} = J_{1,2\text{-}exo} = 5.6$, 1-H); δ_C 19.75, 20.22 and 31.44 (each CH_2), 36.47 (C-3), 42.28 (C-8a), 42.96 (C-4a), 67.73 (C-5), 74.82 (C-2), 80.79 (C-4) and 81.50 (C-1); *m/z* 166 (9%, M − 18), 138 (22), 137 (31), 123 (14), 122 (22), 120 (23), 119 (13), 110 (26), 109 (31), 107 (15), 105 (11) and 81 (100).

The diol **67** was treated for 8 days with an excess of *p*-bromobenzenesulphonyl chloride and pyridine. The crude product was purified by flash chromatography with 40% ethyl acetate–light petroleum as eluent. The 2-monobrosylate **68** was crystallized from chloroform–hexane as rosettes, m.p. 133–135 °C (Found: C, 47.3; H, 4.6. $C_{16}H_{19}BrO_5S$ requires C, 47.65; H, 4.75%); δ_H 1.30–1.42 (1 H, m, C*H*H), 1.60–1.70 (2 H, m, CH_2), 1.61–1.72 and 1.78–1.85 (each 1 H, m, C*H*H), 2.07 (1 H, ddd, $J_{3\text{-}exo,3\text{-}endo}$ 13.2, $J_{3\text{-}exo,2\text{-}exo}$ 10.0, $J_{3\text{-}exo,4}$ 5.0, 3-H_{exo}), 2.12–2.40 (3 H, m, 4a-, 8a-H and C*H*H), 2.60 (1 H, dd, $J_{3\text{-}endo,3\text{-}exo}$ 13.2, $J_{3\text{-}endo,2\text{-}exo}$ 5.0, 3-H_{endo}), 4.27 (1 H, dd, $J_{5,4a}$

Table 1 Non-hydrogen atom co-ordinates

	66			**68**		
Atoms	*x*	*y*	*z*	*x*	*y*	*z*
Br				0.564 3(1)	0.5*	0.681 5(1)
C(1)	−0.038 5(5)	0.353 1(2)	0.774 3(2)	0.845 1(9)	0.233 0(3)	0.206 6(7)
O(1)	−0.073 7(3)	0.414 0(2)	0.866 5(2)	0.860 2(7)	0.154 0(2)	0.273 7(5)
C(2)	0.180 7(5)	0.404 5(2)	0.751 0(3)	1.070 3(9)	0.241 5(3)	0.169 1(7)
O(2)	0.227 7(5)	0.412 2(2)	0.659 7(2)	1.112 9(6)	0.309 0(2)	0.055 0(5)
S(2)				1.230 2(2)	0.378 23(9)	0.155 2(2)
O(21)				1.403 5(6)	0.350 9(3)	0.270 1(6)
O(22)				1.255 3(6)	0.430 5(2)	0.005 0(6)
C(21)				1.050 9(8)	0.415 0(3)	0.301 0(7)
C(22)				0.884 4(9)	0.454 5(3)	0.220 2(8)
C(23)				0.738 2(9)	0.481 0(3)	0.332 6(8)
C(24)				0.768 9(9)	0.468 2(3)	0.525 4(8)
C(25)				0.937(1)	0.430 0(4)	0.607 7(8)
C(26)				1.081 0(9)	0.403 6(4)	0.495 5(8)
C(3)	0.323 9(5)	0.442 0(2)	0.865 6(2)	1.112 8(9)	0.167 4(3)	0.067 0(8)
C(4)	0.170 6(5)	0.401 3(2)	0.939 9(2)	0.920(1)	0.121 4(3)	0.095 8(8)
C(4a)	0.189 1(5)	0.285 7(2)	0.951 5(2)	0.733 3(9)	0.143 0(3)	−0.036 1(8)
C(5)	0.442 7(5)	0.244 4(2)	0.996 0(2)	0.726(1)	0.134 7(4)	−0.252 5(8)
O(5)	0.597 3(4)	0.291 7(2)	1.064 4(2)	0.913 5(6)	0.160 7(3)	−0.320 8(5)
C(6)	0.497 7(6)	0.140 7(2)	0.956 5(3)	0.542 (1)	0.177 1(4)	−0.341 2(9)
C(7)	0.309 1(7)	0.097 9(3)	0.856 4(3)	0.535(1)	0.261 6(4)	−0.291(1)
C(8)	0.189 9(7)	0.179 8(2)	0.775 0(3)	0.694 5(9)	0.283 8(3)	−0.126 9(8)
C(8a)	0.045 2(5)	0.250 0(2)	0.831 3(2)	0.693 1(8)	0.225 8(3)	0.031 6(7)

* Defines origin.

Table 2 Non-hydrogen bond lengths (Å)

Bond	**66**	**68**
Br–C(24)		1.901(6)
C(1)–O(1)	1.432(4)	1.461(7)
C(1)–C(2)	1.505(4)	1.531(9)
C(1)–C(8a)	1.539(4)	1.522(7)
O(1)–C(4)	1.446(3)	1.470(7)
C(2)–O(2)	1.211(4)	1.473(7)
C(2)–C(3)	1.498(4)	1.522(8)
O(2)–S(2)		1.568(4)
S(2)–O(21)		1.418(4)
S(2)–O(22)		1.424(5)
S(2)–C(21)		1.759(6)
C(21)–C(22)		1.370(8)
C(21)–C(26)		1.389(8)
C(22)–C(23)		1.383(9)
C(23)–C(24)		1.381(8)
C(24)–C(25)		1.371(8)
C(25)–C(26)		1.372(9)
C(3)–C(4)	1.505(4)	1.528(8)
C(4)–C(4a)	1.528(4)	1.516(8)
C(4a)–C(5)	1.498(4)	1.539(8)
C(4a)–C(8a)	1.546(3)	1.556(8)
C(5)–O(5)	1.210(3)	1.434(8)
C(5)–C(6)	1.505(4)	1.503(9)
C(6)–C(7)	1.502(4)	1.52(1)
C(7)–C(8)	1.498(5)	1.540(9)
C(8)–C(8a)	1.512(5)	1.514(8)

Table 3 Non-hydrogen bond angles (°)

Angle	**66**	**68**
O(1)–C(1)–C(2)	100.7(2)	96.4(4)
O(1)–C(1)–C(8a)	103.4(2)	101.9(4)
C(2)–C(1)–C(8a)	108.0(2)	115.8(4)
C(1)–O(1)–C(4)	96.3(2)	95.9(4)
C(1)–C(2)–O(2)	126.9(3)	114.1(4)
C(1)–C(2)–C(3)	104.2(3)	102.9(4)
O(2)–C(2)–C(3)	128.9(3)	111.6(4)
C(2)–O(2)–S(2)		118.7(3)
O(2)–S(2)–O(21)		109.4(3)
O(2)–S(2)–O(22)		104.0(2)
O(2)–S(2)–C(21)		102.8(2)
O(21)–S(2)–O(22)		120.2(3)
O(21)–S(2)–C(21)		109.2(3)
O(22)–S(2)–C(21)		109.6(3)
S(2)–C(21)–C(22)		119.2(4)
S(2)–C(21)–C(26)		119.4(4)
C(22)–C(21)–C(26)		121.4(5)
C(21)–C(22)–C(23)		119.7(5)
C(22)–C(23)–C(24)		118.1(5)
Br–C(24)–C(23)		119.0(4)
Br–C(24)–C(25)		118.5(4)
C(23)–C(24)–C(25)		122.5(6)
C(24)–C(25)–C(26)		119.1(5)
C(21)–C(26)–C(25)		119.1(5)
C(2)–C(3)–C(4)	100.5(2)	101.1(5)
O(1)–C(4)–C(3)	101.5(2)	101.6(4)
O(1)–C(4)–C(4a)	101.7(2)	99.7(5)
C(3)–C(4)–C(4a)	111.9(2)	114.6(5)
C(4)–C(4a)–C(5)	115.5(2)	122.6(5)
C(4)–C(4a)–C(8a)	102.0(2)	101.0(4)
C(5)–C(4a)–C(8a)	116.6(2)	113.9(5)
C(4a)–C(5)–O(5)	121.0(3)	111.2(5)
C(4a)–C(5)–C(6)	118.2(2)	108.6(5)
O(5)–C(5)–C(6)	120.8(3)	112.4(5)
C(5)–C(6)–C(7)	115.8(3)	115.0(5)
C(6)–C(7)–C(8)	111.5(3)	112.8(5)
C(7)–C(8)–C(8a)	110.2(3)	109.9(5)
C(1)–C(8a)–C(4a)	100.4(2)	102.2(4)
C(1)–C(8a)–C(8)	118.3(3)	120.0(5)
C(4a)–C(8a)–C(8)	113.5(2)	112.4(5)

5.2, $J_{5,6ax}$ 9.9, 5-H), 4.46 (1 H, dd, $J_{1,8a} = J_{1,2\text{-}exo}$ = 5.0, 1-H), 4.55 (1 H, dd, $J_{4,4a} = J_{4,3\text{-}exo}$ = 5.0, 4-H), 4.73 (1 H, ddd, $J_{2\text{-}exo,3\text{-}exo}$ 10.0, $J_{2\text{-}exo,3\text{-}endo} = J_{2\text{-}exo,1}$ 5.0, 2-H_{exo}), and 7.73 (4 H, AA′BB′, ArH); δ_C 19.50, 20.59 and 30.49 (each CH_2), 30.73 (C-3), 39.35 and 44.77 (C-4a and -8a), 67.35 (C-5), 79.25 (C-1), 81.27 (C-4), 81.40 (C-2), 129.06 (CBr), 129.39 and 132.58 (each arom. CH) and 135.13 (CSO_2).

Structure Determinations.—Unique data sets were measured at ~295 K within the limit $2\theta_{max}$ = 50° (ENRAF-Nonius CAD-4 diffractometer, monochromatic Mo-$K\alpha$ radiation source (λ =

Table 4 Fused-ring torsion angles (°). C-Atoms are denoted by number only, O-atoms italicized. Values are for compounds **66**, **68**, respectively.

Angle	Angle	Angle	Angle
1–1–2–3	32.5(3), 45.1(4)	4a–4–*1*–1	−57.2(2), −60.7(5)
1–2–3–4	2.8(3), −10.6(5)	4–*1*–1–8a	56.3(2), 55.9(5)
2–3–4–*1*	−37.1(3), −27.6(5)	4–4a–5–6	−149.2(3), −167.2(5)
3–4–*1*–1	58.3(2), 57.1(5)	4a–5–6–7	13.0(4), 57.5(7)
4–*1*–1–2	−55.3(2), −62.2(4)	5–6–7–8	33.8(5), −11.7(8)
2–1–8a–4a	73.1(3), 73.5(6)	6–7–8–8a	−65.2(4), −45.8(7)
1–8a–4a–4	−2.2(3), −7.3(5)	7–8–8a–4a	48.0(4), 56.9(6)
8a–4a–4–3	−71.3(3), −66.1(6)	8–8a–4a–5	−1.8(4), −10.6(7)
4a–4–3–2	70.6(2), 78.9(6)	8a–4a–5–6	−29.4(4), −45.1(7)
3–2–1–8a	−75.5(3), −61.4(6)	1–8a–8–7	165.2(3), 177.1(5)
1–1–8a–4a	−33.0(3), −29.7(5)	1–8a–4a–5	−129.1(3), −140.7(5)
8a–4a–4–*1*	36.3(3), 41.5(5)	4–4a–8a–8	125.0(3), 122.7(5)
8–8a–1–*1*	−157.0(2), −154.8(5)	*1*–4–4a–5	163.9(2), 169.5(5)
8–8a–1–2	−50.8(3), −51.6(7)	3–4–4a–5	56.3(3), 61.8(7)

0.71073 Å), $2\theta/\theta$ scan mode) yielding N independent reflections, N_0 with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Residuals on $|F|$ at convergence are conventional R, R_w; statistical reflection weights, derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\ \sigma^4(I_{diff})$ were employed. Neutral atom complex scattering factors were used;[17] computation used the XTAL 3.0 program system[18] implemented by S. R. Hall. Pertinent results are given in Fig. 3 and Tables 1–4; material deposited at the Cambridge Crystallographic Data Centre comprises thermal and hydrogen-atom parameters and structure factor amplitudes.*

Crystal Refinement Data.—Compound **66**. $C_{10}H_{12}O_3$, M = 180.2. Monoclinic, space group $P2_1/c$ (C_{2h}^5, No. 14), a = 5.667(4), b = 13.154(2), c = 12.142(6) Å, β = 105.21(5)°, V = 873.4 Å^3. D_c (Z = 4) = 1.37 g cm^{-3}. $F(000)$ = 384. μ_{Mo} = 0.6 cm^{-1} (no correction), specimen 0.22 × 0.25 × 0.35 mm. N = 1533, N_0 = 1134; R = 0.051, R_w = 0.060.

Compound **68**. $C_{16}H_{19}BrO_5S$, M = 403.3. Monoclinic, space group $P2_1$ (C_2^2, No. 4), a = 6.556(7), b = 17.479(14), c = 7.092(3) Å, β = 95.38(7)°, V = 809.0 Å^3. D_c (Z = 2) = 1.66 g cm^{-3}. $F(000)$ = 412. μ_{Mo} = 26.1 cm^{-1}, specimen: 0.43 × 0.30 × 0.25 mm, $A^*_{min,max}$ (gaussian correction) = 1.81, 2.24. N = 1468, N_0 = 1301; R = 0.031, R_w = 0.034 (preferred chirality; both structures are presented in conformity with this. It should be noted that the bulk sample is a racemate.)

Structural Commentary.—The results of the structure determinations are consistent with the above stoichiometry, connectivity and stereochemistry, establishing the latter definitively. In each case, a single molecule comprises the asymmetric unit of the structure. The bromosulphonate, although a racemate, crystallizes in a chiral space group; the absolute configuration of the specimen used for the X-ray work is definitively established, and the results for both compounds are presented in that chirality. Bond lengths and angles are nicely precise and are presented comparatively in the Tables 2 and 3; values are generally as expected and, within the fused-ring systems, show the expected differences concomitant upon change from doubly bonded oxygens at O(2,5) to singly bonded species, most evident in the bonds to either side of the carbonyl group, but with pronounced effects as far away as the O(1) bridgehead. In both compounds, all five-membered rings in the fused system are shown by the table of torsion angles (Table 4) to be clearly 'envelope' in conformation with the bridgehead O(1) deviant; the associated six-membered ring is a 'boat' in both structures. The peripheral ring [C(4a, 8a, 5, 6, 7, 8)] is clearly a boat in the bromosulphonate, but the conformation is markedly different in the precursor with particularly notable changes in the C(5,6,7) string accompanying conversion to a 'half-boat'.

* See under section 5.6.3 of Instructions for Authors, Issue 1.

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