Regioselectivity in the Reactions of Methoxydehydrobenzenes with Furans. Part 1. Reactions of 3-Methoxydehydrobenzene and 3-(Methoxycarbonyl)-dehydrobenzene with 2-Substituted Furans

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The isomer ratios for the cycloadducts obtained for the reaction of 3-methoxydehydrobenzene, generated from 2-amino-6-methoxybenzoic acid by aprotic diazotization, or from 2-bromo-3-methoxyphenyl toluene-*p*-sulphonate by treatment with butyllithium, and for the reaction of 3-(methoxycarbonyl)dehydrobenzene, generated from 2-amino-6-(methoxycarbonyl)benzoic acid by aprotic diazotization, with seven 2-substituted furans are recorded. These results are discussed in terms of an asynchronous, concerted, biradicaloid reaction pathway.

In connection with other work a need arose to synthesize certain specifically substituted naphthalenols. An attractive method would be the acid-induced ring opening of adducts of dehydrobenzenes with substituted furans. The ring-opening reaction for the parent system, 1,4-dihydro-1,4-epoxynaphthalene which gives naphthalen-1-ol, was originally described by Wittig and Pohmer.[1] It has since been used to synthesize a number of t-butylnaphthalenols.[2,3]

The regioselectivity of the reactions of substituted dehydrobenzenes with substituted furans has not been extensively explored. Franck and co-workers have examined the reactions of 3,5-di-t-butyldehydrobenzene with 2-t-butylfuran,[3] 2-benzylfuran [3] and 2,3-di-t-butylfuran.[2] In the two last mentioned cases the more sterically hindered adducts predominated. Newman and Kannan[4] found that 3-methyldehydrobenzene, generated by a variety of methods, exhibited little regioselectivity in its reactions with a variety of 2-substituted furans and remarked that the regioselectivity of these cycloadditions was little influenced by polar or steric effects. Pollart and Rickborn,[5] whilst concurring with the views of Newman and Kannan, were perplexed to explain even the low degree of selectivity observed. They proposed that the regioselectivity of similar cycloadditions might depend more on the dehydrobenzene structure rather than on that of the furan. This view appears to be vindicated by the work of Rogers and Averill[6] on the reactions of 3-substituted dehydrobenzenes with 1,8-disubstituted anthracenes, and by that of Gribble *et al.*[7,8] on the reactions of 3-fluorodehydrobenzene with 2-alkylfurans.

For our synthetic purposes we were interested in the cycloadditions of methoxy-substituted dehydrobenzenes with substituted furans. It appeared appropriate to commence our studies with 3-methoxydehydrobenzene and 2-substituted furans. The 2-substituted furans are readily accessible[9] and it appeared likely that the methoxy group would polarize the triple bond much more than would a 3-alkyl group. The addition of nucleophiles to the triple bond of 3-methoxydehydrobenzene exhibits a much higher preference for the 1-position than does the similar addition to 3-methyldehydrobenzene,[10] owing to the greater inductive effect of the methoxy group. Recent results by Razzuk and Biehl[11] have extended the range of methoxy-substituted dehydrobenzenes studied, and they found that nucleophiles add exclusively to the 1-position of both 3,5-dimethoxy- and 3,4,5-trimethoxydehydrobenzene.

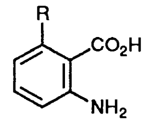
In simplistic mechanistic terms these nucleophilic additions may be rationalized by assuming that the π-bond involved in the reaction is that which is orthogonal to the dehydrobenzene ring. The important electronic interaction is therefore that which is transmitted through the σ-framework by the inductive effect. The methoxy group at the 3-position, being inductively electron withdrawing, will hence polarize the 3-position in a partial positive sense, the 2-position in a partial negative sense, and therefore the 1-position in a partial positive sense, which will thus be the site of nucleophilic attack. The inductive electron-releasing ability of an alkyl group is only feeble, but its effect is opposite to that of a methoxy group. It was therefore of inherent interest to investigate the reactions of 3-methoxydehydrobenzene with 2-substituted furans since the results might throw light on the polar and steric demands of such reactions, and indeed since they are unsymmetrical, on the extent of synchroneity in their transition states. Since a methoxycarbonyl group is also inductively electron withdrawing but would exert different steric demands to a methoxy group the investigation was also extended to the reactions of 3-(methoxycarbonyl)dehydrobenzene with 2-substituted furans.

So far as we are aware, there is only one example of a reaction between 3-methoxydehydrobenzene and a 2-substituted furan recorded in the literature: that involving 2-acetoxyfuran; neither the yield nor the ratio of adducts was recorded.[12]

3-Methoxydehydrobenzene has been generated by aprotic diazotization [12,13] of 2-amino-6-methoxybenzoic acid [14] **1**, and by treatment of 3-bromoanisole with butyllithium.[15] Whilst the former method was deemed suitable for reactions with those 2-substituted furans containing a substituent labile to butyllithium we sought a less ambiguous organometallic method than that dependent on 3-bromoanisole.

3-Methoxyphenol **3** was therefore converted by a standard method into its tetrahydropyranyl ether **4**. This compound was then treated with butyllithium and the resultant lithium–hydrogen-exchange product was then allowed to react with 1,2-dibromoethane.[16] Acidic work-up of the product of this reaction supplied a moderate yield of 2-bromo-3-methoxyphenol **5**, which was converted into its tosyl ester **6**. This compound proved to be an excellent precursor to 3-methoxydehydrobenzene since on treatment with butyllithium a lithium–bromine-exchange ensued, followed by the elimination of toluene-*p*-sulphonate.

3-Methoxydehydrobenzene was generated by treatment of the tosylate **6** with butyllithium at −100 °C in tetrahydrofuran (THF) in the presence of 2-methylfuran **7a**, 2-isopropylfuran **7b**, 2-t-butylfuran **7c**, and the dioxolane **7g**. The cycloadducts, so formed, were not separable by radial chromatography and the ratios recorded in Table 1 were obtained by integration of the



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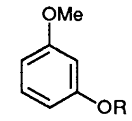
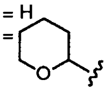
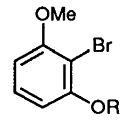
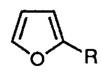
2 R = CO_2Me



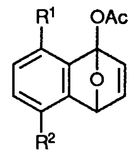
3 R = H
4 R = 



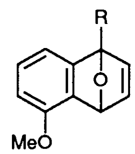
5 R = H
6 R = Ts

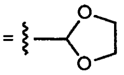


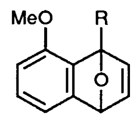
7a–g
See Table

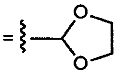


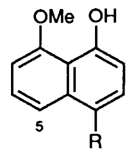
8 R^1 = OMe, R^2 = H
9 R^1 = H, R^2 = OMe
10 R^1 = CO_2Me, R^2 = H
11 R^1 = H, R^2 = CO_2Me



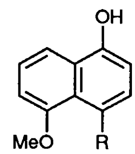
12 R = Me
14 R = Pr^i
16 R = Bu^t
18 R = Br
20 R = CO_2Me
22 R = 



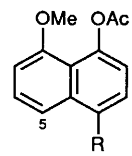
13 R = Me
15 R = Pr^i
17 R = Bu^t
19 R = Br
21 R = CO_2Me
23 R = 



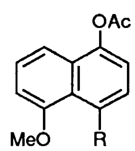
24 R = Me
26 R = Pr^i



25 R = Me
27 R = Pr^i
28 R = Bu^t



29 R = Bu^t
30 R = Br



31 R = Bu^t
32 R = Br

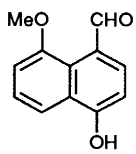


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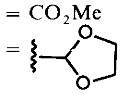
Table 1 Isomer ratios in reactions of 2-substituted furans with 3-substituted dehydrobenzenes

Furan	*syn*:*anti* Ratio for dehydrobenzene			
	3-Methoxy	3-Fluoro[a]	3-Methyl[b]	3-Methoxy-carbonyl
7a R = Me	70:30	64:36	42:58	43:57
7b R = Pr^i	74:26	89:11		30:70
7c R = Bu^t	85:15	90:10	37:63	23:77
7d R = OAc	75:25			38:62
7e R = Br	63:37			17:83
7f R = CO_2Me	56:44		43:57	33:67
7g R = 	49:51		39:61	27:73

[a] Ref. 8. [b] Ref. 4.

300 MHz ^1H NMR spectra of the mixtures or by GLC. In the case of 2-t-butylfuran a sample of the pure, major, *syn*-adduct **17** was secured by repeated crystallization of the mixture of adducts. It is now well established that the method of generation of the dehydrobenzene has no effect on the ratio of adducts obtained in unsymmetrical cycloaddition reactions.[4,8,17] The same is true of the addition of nucleophiles.[18] It was therefore not thought necessary to repeat extensively such tests in the present case. A check was carried out in one case, however. The same ratio of adducts was obtained for 2-methylfuran when the intermediate 3-methoxydehydrobenzene was generated by aprotic diazotization of 2-amino-6-methoxybenzoic acid **1** in 1,4-dioxane at 70 °C and by treatment of the tosylate **6** with butyllithium in THF at −100 °C.

3-Methoxydehydrobenzene generated from the anthranilic acid **1** was allowed to react with 2-acetoxyfuran **7d**, 2-bromofuran **7e** and methyl furan-2-carboxylate **7f**; the ratios of cycloadducts, obtained in a similar way, are also recorded in Table 1. In the case of 2-acetoxyfuran **7d** the adducts were separated by radial chromatography and their spectroscopic properties were in agreement with those recorded by Warrener and co-workers.[12] In particular the ^1H NMR signal of the bridgehead proton occurs at higher field in the *syn*-adduct **8** (δ 5.66) than in the *anti*-adduct **9** (δ 5.91). This is true for all the adducts prepared in this work, and has also been noted by Gribble *et al.*[8]

In order to provide further evidence for the structural assignment of the cycloadducts several of the adduct mixtures were subjected to acid-induced ring opening. A solution of the adduct **12**/**13**, from 2-methylfuran, in a mixture of methanol and THF was treated with a trace of conc. hydrochloric acid at room temperature and the naphthalenols, so obtained, were separated by radical chromatography. The known naphthalenol[19] **24** derived from the minor, *anti*-adduct **12** was eluted first on account of the intramolecular hydrogen bond between the 8-methoxy and 1-hydroxy groups which also gave rise to a characteristic ^{1}H NMR signal at δ 9.31.[20] The major, *syn*-adduct **13** yielded the naphthalenol **25**, which was converted into its known *O*-methyl derivative.[21]

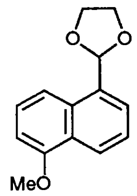
Since naphthalenes containing isopropyl[22] and t-butyl substituents[2,3] in a *peri*-relationship to another substituent are prone to undergo ready protodealkylation, milder conditions were adopted for the ring opening of the adduct mixtures **14**/**15** and **16**/**17**. Therefore, treatment of the adduct mixture **14**/**15** with acetic anhydride containing a trace of trifluoroacetic acid (TFA) gave a mixture of acetates, which on treatment with lithium aluminium hydride provided the new naphthalenols **26** and **27**. The chromatographically more mobile isomer **26** again displayed a characteristic low-field, intramolecularly hydrogen-bonded proton signal at δ 9.40 in its ^{1}H NMR spectrum. The adduct mixture **16**/**17** on acetylative ring opening supplied the acetates **29** and **31**. The naphthalenol **28** derived from the acetate **31** underwent rapid decomposition on exposure to light and air. Such decomposition has been noted for a similar compound and it has been attributed to endoperoxide formation.[2]

It is interesting to note the effect of increasing the steric compression of the 5-proton by the *peri*-substituent in compounds **24**, **26** and **29**. In the methyl compound **24** the 5-proton resonates at δ 7.54 in its ^{1}H NMR spectrum, in the isopropyl compound **26** and the t-butyl compound **29** the similar proton resonates at δ 7.70 and δ 8.06. In the bromo compound **30** the 5-proton resonates at δ 7.78.

The adduct mixture **18**/**19** was also subjected to acetylative ring-opening and this provided the acetates **30** and **32**. When the adduct mixture **22**/**23** was treated with a trace of conc. hydrochloric acid in methanol–THF at 50 °C one of the adducts underwent acetal hydrolysis and ring cleavage and the other was recovered unchanged. It was the sterically hindered *syn*-adduct **23** which underwent cleavage since the known aldehyde[23] **33** was obtained.

Deoxygenation of the mixture of adducts **22** and **23** by the method of Wege and co-workers,[24] which involves treatment of the epoxynaphthalenes with enneacarbonyldiiron in hot benzene, gave a separable mixture of the naphthalenes **34** and **35**, which were converted by hydrolysis into the known aldehydes **36**[25] and **37**.[26]

3-(Methoxycarbonyl)dehydrobenzene was generated by aprotic diazotization of 2-amino-6-(methoxycarbonyl)benzoic acid **2**[6] and was allowed to react in turn with each of the 2-substituted furans **7a**–**7g**. The ratios of the cycloadducts obtained are shown in Table 1. Although the adducts **38** and **39** obtained from 2-methylfuran **7a** could not be separated by chromatography their structures followed from the characteristic resonance of the 4-protons in their ^{1}H NMR spectra, that in the *anti*-adduct **38** occurring at δ 6.28 and that in the *syn*-adduct **39** occurring at δ 5.62. These structural assignments were confirmed by deoxygenation of the mixture of epoxynaphthalenes, when the major *anti*-adduct **38** gave methyl 5-methylnaphthalene-1-carboxylate **50**[27] and the *syn*-adduct **39** gave methyl 8-methylnaphthalene-1-carboxylate **51**.[28] In the case of 2-isopropylfuran **7b** and 2-t-butylfuran **7c** the major, *anti*-adducts **40** and **42** were separated from the mixtures by radial chromatography. Deoxygenation of the mixture of isopropyl adducts **40** and **41** gave the separable naphthalenes **52** and **53**, and deoxygenation of the pure t-butyl adduct **42** gave the naphthalene **54**.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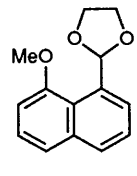
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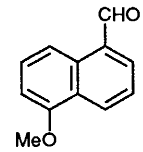
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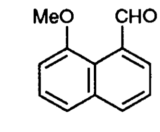
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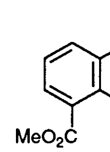
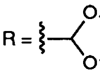
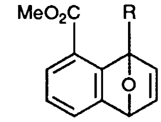
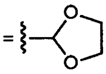
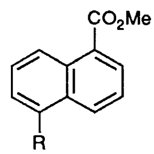
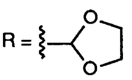


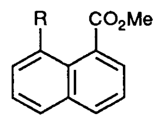
38 R = Me
40 R = Pr^i
42 R = Bu^t
44 R = Br
46 R = CO_2Me
48 R = 



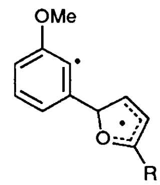
39 R = Me
41 R = Pr^i
43 R = Bu^t
45 R = Br
47 R = CO_2Me
49 R = 



50 R = Me
52 R = Pr^i
54 R = Bu^t
56 R = 



51 R = Me
53 R = Pr^i
55 R = CO_2Me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2-Acetoxyfuran **7d**, 2-bromofuran **7e**, methyl furan-2-carboxylate **7f** and 2-(1,3-dioxolan-2-yl)furan **7g** gave separable mixtures of the adducts **10**/**11**, **44**/**45**, **46**/**47** and **48**/**49**, respectively. Deoxygenation of the adduct **47** gave the known naphthalene **55**,[29] and deoxygenation of the adduct **48** gave the naphthalene **56**.

Three mechanisms may be envisaged for (4 + 2) cycloaddition reactions.[30] The extreme cases are, on the one hand, a synchronous, concerted process in which the two new bonds are formed to the same extent in the transition state which is therefore aromatic in character, and on the other hand, a two-step process in which each new bond is formed in a kinetically different step and a discrete ionic or biradical intermediate is involved. The third mechanism is an asynchronous, concerted process with unsymmetrical bond formation in the transition state which is 'biradicaloid' in character. The energy difference between a biradicaloid transition state and a true biradical is thought to be small.[30] Predictions of regiochemistry made for unsymmetrical cycloaddition reactions on the basis of this interpetation, which is simpler than frontier orbital theory, are claimed to be accurate. These predictions also work well for the more highly polarized 3-methoxy- and 3-fluoro-dehydrobenzene since, as expected for reactions involving a biradicaloid transition state, any conjugating substituent R (see structure **57**) is able to stabilize the furanoid radical, so that the sterically hindered *syn*-adduct predominates. The difference in the proportions of the *syn*- and *anti*-adducts is small so that the difference in energy between the transition states leading to the *syn*- and *anti*-adducts must also be very small.

The results obtained for 3-methyldehydrobenzene, which is less polarized than either 3-methoxy- or 3-fluoro-dehydrobenzene, reflect the small energy difference between the two pathways since here the less hindered *anti*-adducts, as predicted by the inductive polarization of the dehydrobenzene, assume a slight preponderance, except for the case of 2-t-butylfuran.

The inductively induced substituent polarization as measured by σ_I-values for a methoxy group (0.27) and a methoxycarbonyl group (0.30) [31] are very similar so that on electronic grounds the ratios of *syn* and *anti* adducts obtained for 3-(methoxycarbonyl)-dehydrobenzene would be expected to be similar to those obtained for 3-methoxydehydrobenzene. It is seen from Table 1 that this is not the case. In particular the results obtained for the reactions of alkylfurans with 3-(methoxycarbonyl)dehydrobenzene are the reverse of those obtained with 3-fluoro- and 3-methoxy-dehydrobenzene. Since the methoxycarbonyl group has greater steric bulk than the methoxy group it appears that this effect is sufficient to outweigh the electronic effect.

In Parts 2 and 3 we shall show that by the use of 2- and 3-methoxyfuran in cycloadditions with 3-methoxydehydrobenzenes the regioselectivity may be enhanced and that advantage may be taken of this in the regioselective synthesis of naphthalenols.

Experimental

M.p.s were determined with a Kofler hot-stage apparatus and are uncorrected. Distillations were carried out with a Büchi GKR-50 Kugelrohr apparatus and the quoted b.p.s refer to the oven temperature. All organic extracts were washed with saturated brine, and were then dried with anhydrous sodium sulphate prior to evaporation under diminished pressure. Radial chromatography was carried out with a Harrison Research Chromatotron with plates coated with Merck Kieselgel $60PF_{254}$. Silica gel for column chromatography was BDH 60–120 mesh. Gas chromatographic retention times refer to a cross-linked methylsilicone gum capillary column (25 m) maintained at a temperature of 80 °C for 1 min then programmed to rise to 240 °C at 20 °C min^{-1} with an injector temperature of 250 °C with hydrogen as carrier gas at a flow rate of 6.5 cm^3 min^{-1}. ^{1}H NMR spectra were recorded at 300 MHz and ^{13}C NMR spectra were recorded at 75.5 MHz with deuteriochloroform as solvent on a Bruker AM-300 instrument. *J*-Values are given in Hz. The assignment of the former was assisted by double-resonance experiments, and of the latter by the DEPT technique. Mass spectra (35 eV) were recorded with a Hewlett Packard 5986 instrument.

2-(3-*Methoxyphenoxy*)*tetrahydropyran* **4** (*with Robert W. and Teresa M. Baker*).—Dihydropyran (10 cm^3) was added to a stirred solution of anhydrous toluene-*p*-sulphonic acid (100 mg) in dry THF (10 cm^3) at 0 °C under argon. After 10 min, 3-methoxyphenol **3** (22.0 g) and dihydropyran (30 cm^3) were added simultaneously, dropwise. The solution was then stirred at 0 °C for 15 min and next diluted with diethyl ether and washed in turn with dil. sodium hydroxide, water, and finally with saturated brine. The crude product was distilled under diminished pressure to yield the *pyran* **4** (36.3 g, 98%) as an oil, b.p. 150 °C at 0.05 mmHg (Found: C, 68.85; H, 7.95. $C_{12}H_{16}O_3$ requires C, 69.2; H, 7.75%).

2-*Bromo*-3-*methoxyphenol* **5** (*with Robert W. and Teresa M. Baker*).—Butyllithium (1.78 mol dm^{-3}) in hexane (29.7 cm^3) was added dropwise at room temperature to a solution of the pyran **4** (10.0 g) in dry THF (100 cm^3) under argon. The solution was stirred at room temperature for 3 h and then 1,2-dibromoethane (10.0 g) was added dropwise to the mixture at 0 °C. The solution was stirred at room temperature for 1 h, sufficient dil. hydrochloric acid was added to render the mixture acidic, and the mixture was stirred for a further 30 min. The solution was extracted with diethyl ether and the phenolic material was separated by extraction into aq. sodium hydroxide in the usual way. The crude product was chromatographed over silica gel with 5% ethyl acetate–hexane as eluent. The more mobile material from the column was distilled under reduced pressure to give the *phenol* **5** (4.9 g, 50%), b.p. 90 °C at 0.05 mmHg, which was crystallized from hexane as prisms, m.p. 78.5–79 °C (Found: C, 41.65; H, 3.45; Br, 39.25. $C_7H_7BrO_2$ requires C, 41.4; H, 3.45; Br, 39.35%).

2-*Bromo*-3-*methoxyphenyl Toluene*-p-*sulphonate* **6** (*with Robert W. and Teresa M. Baker*).—Toluene-*p*-sulphonyl chloride (3.76 g) was added in portions to a stirred solution of the phenol **5** (4.0 g) and triethylamine (3.0 g) in dichloromethane (100 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 finally with saturated brine. The crude product was chromatographed over silica gel with 20% ethyl acetate–hexane as eluent. The *tosyl ester* **6** (6.47 g, 92%) was crystallized from dichloromethane–hexane as prisms, m.p. 104–105 °C (Found: C, 46.95; H, 3.6; Br, 22.2; S, 8.7. $C_{14}H_{13}BrO_4S$ requires C, 47.05; H, 3.65; Br, 22.35; S, 8.95%); δ_H 2.44 (3 H, s, Me), 3.87 (3 H, s, OMe), 6.79 (1 H, dd, $J_{4,5}$ 8.4, $J_{4,6}$ 1.2, 4-H), 6.98 (1 H, dd, $J_{6,5}$ 8.4, $J_{6,4}$ 1.2, 6-H), 7.25 (1 H, dd, $J_{5,4} = J_{5,6} = 8.4$, 5-H) and 7.32 and 7.80 (4 H, AA′BB′, ArH).

General Methods for Reactions of Furans with 3-*Methoxydehydrobenzene*.—(a) *From* 2-*bromo*-3-*methoxyphenyl toluene*-p-*sulphonate* **6**. A stirred solution of the furan (8.5 mmol) and the tosyl ester **6** (2.0 g, 5.6 mmol) in anhydrous THF (30 cm^3) was cooled to −100 °C and butyllithium (1.79 mol dm^{-3}; 6.8 mmol) in hexane (3.8 cm^3) was added *via* syringe under argon. The solution was stirred at −100 °C for 30 min and then allowed to warm slowly to room temperature. The solution was then poured into saturated aq. sodium hydrogen carbonate and extracted with diethyl ether. The extract was washed with water and saturated brine.

(b) *From* 2-*amino*-6-*methoxybenzoic acid* **1**. A stirred solution of the furan (3.0 mmol) in anhydrous 1,4-dioxane (1 cm^3) was heated under dry nitrogen to 70 °C and treated by the dropwise simultaneous addition of solutions of the anthranilic acid [14] **1** (500 mg, 3 mmol) and isoamyl (3-methylbutyl) nitrite (0.5 cm^3) and each in 1,4-dioxane (1 cm^3). After the addition the solution was poured into aq. sodium hydrogen carbonate (5%; 10 cm^3) and extracted with hexane. The extract was washed successively with water and saturated brine.

2-*Methylfuran* **7a**. (*a*) Radial chromatography of the crude product obtained by method (a) with 10% ethyl acetate–hexane, containing 1% triethylamine, as eluent afforded a mixture (56%) containing 1,4-dihydro-8-methoxy-1-methyl-1,4-epoxynaphthalene **13** (71%) and 1,4-dihydro-5-methoxy-1-methyl-1,4-epoxynaphthalene **12** (29%) as a crystalline solid; δ_H compound **13**: 2.04 (3 H, s, Me), 3.77 (3 H, s, OMe), 5.56 (1 H, d, $J_{4,3}$ 1.9, 4-H), 6.58 (1 H, dd, $J_{5,6}$ 8.2, $J_{5,7}$ 0.8, 5-H) and 6.99 (1 H, ddd, $J_{3,2}$ 5.4, $J_{3,4}$ 1.9, $J_{3,Me}$ 0.4, 3-H); compound **12**: 1.90 (3 H, s, Me), 3.80 (3 H, s, OMe), 5.86 (1 H, br d, $J_{4,3}$ 1.9, 4-H), 6.57 (1 H, br d, $J_{8,7}$ 8.1, 8-H), 6.76 (1 H, d, $J_{2,3}$ 5.4, 2-H) and 7.05 (1 H, ddd, $J_{3,2}$ 5.4, $J_{3,4}$ 1.9, $J_{3,Me}$ 0.4, 3-H); the signals for the remaining protons occurred at δ 6.61–6.98; δ_C compound **13**: 17.05 (Me), 55.35 (OMe), 81.79 (C-4), 90.06 (C-1), 110.16 and 113.23 (C-5 and -7), 126.90 (C-6), 136.37 (C-8a), 144.00 and 146.07 (C-2 and -3) and 153.51 and 153.61 (C-4a and -8); compound **12**: 15.22 (Me), 55.67 (OMe), 79.39 (C-4), 89.50 (C-1), 110.16 and 112.22 (C-6 and -8), 126.80 (C-7), 136.42 (C-4a), 144.21 and 145.45 (C-2 and -3) and 152.49 and 153.80 (C-5 and -8a); compound **13**: t_R 8.13 min; m/z 189 (16%), 188 (100, M^+), 186 (27), 173 (71), 172 (10), 171 (57), 145 (22), 129 (11), 128 (41), 127 (25), 116 (11) and 115 (52); compound **12**: t_R 8.25 min; m/z 189 (16%), 188 (100, M^+), 186 (14), 174 (10), 173 (64), 172 (10), 160 (30), 159 (12), 146 (10), 145 (53), 129 (18), 128 (30), 127 (33), 117 (11), 116 (13) and 115 (73).

A solution of the mixture (462 mg) in THF (20 cm^3)–methanol (5 cm^3) was stirred at room temperature temperature with conc. hydrochloric acid (3 drops) for 2 h. The usual work-up and radial chromatography with 5% ethyl acetate–hexane as eluent gave, first, 8-methoxy-4-methylnaphthalen-1-ol **24** (131 mg, 30%), which was crystallized as laths (from methanol), m.p. 71–72 °C (lit.,[19] 75–76 °C); δ_H 2.55 (3 H, d, $J_{Me,3}$ 0.6, Me), 4.07 (3 H, s, OMe), 6.79 (1 H, d, $J_{2,3}$ 7.8, 2-H), 6.83 (1 H, br d, $J_{7,6}$ 7.7, 7-H), 7.20 (1 H, br d, $J_{3,2}$ 7.8, 3-H), 7.37 (1 H, dd, $J_{6,5}$ 8.6, $J_{6,7}$ 7.7, 6-H), 7.54 (1 H, dd, $J_{5,6}$ 8.6, $J_{5,7}$ 0.9, 5-H) and 9.31 (1 H, s, OH). Further elution gave *5-methoxy-4-methylnaphthalen-1-ol* **25** (292 mg, 69%), which was crystallized from dichloromethane–hexane as needles, m.p. 138–140 °C (Found: C, 76.25; H, 6.65%; M^+, 188. $C_{12}H_{12}O_2$ requires C, 76.55; H, 6.45%; M, 188); δ_H 2.80 (3 H, d, $J_{Me,3}$ 0.8, Me), 3.91 (3 H, s, OMe), 5.23 (1 H, br, OH), 6.69 (1 H, d, $J_{2,3}$ 7.7, 2-H), 6.84 (1 H, br d, $J_{6,7}$ 7.7, 6-H), 7.00 (1 H, br d, $J_{3,2}$ 7.7, 3-H), 7.36 (1 H, dd, $J_{7,8}$ 8.4, $J_{7,6}$ 7.7, 7-H) and 7.77 (1 H, dd, $J_{8,7}$ 8.4, $J_{8,6}$ 1.1, 8-H). The methyl ether was crystallized from ethanol as glistening leaflets, m.p. 106 °C (lit.,[21] 105 °C); δ_H 2.80 (3 H, d, $J_{Me,3}$ 0.9, Me), 3.90 and 3.95 (each 3 H, s, OMe), 6.70 (1 H, d, $J_{2,3}$ 7.9, 2-H), 6.84 (1 H, br d, $J_{6,7}$ 7.7, 6-H), 7.08 (1 H, br d, $J_{3,2}$ 7.9, 3-H), 7.33 (1 H, dd, $J_{7,8}$ 8.4, $J_{7,6}$ 7.7, 7-H) and 7.87 (1 H, dd, $J_{8,7}$ 8.4, $J_{8,6}$ 1.1, 8-H).

(*b*) Radial chromatography of the crude product obtained by method (b) gave a mixture (26%) of compounds **13** (69%) and **12** (31%).

2-*Isopropylfuran* **7b**. Radial chromatography of the crude product obtained by method (a) yielded (71%) a mixture of 1,4-dihydro-1-isopropyl-8-methoxy-1,4-epoxynaphthalene **15** (74%) and 1,4-dihydro-1-isopropyl-5-methoxy-1,4-epoxynaphthalene **14** (26%) as an oil; δ_H compound **15**: 1.16 (6 H, d, Me_2), 2.97 (1 H, septet, C*H*Me_2), 3.79 (3 H, s, OMe), 5.63 (1 H, d, $J_{4,3}$ 1.8, 4-H) and 6.58 (1 H, dd, $J_{5,6}$ 8.2, $J_{5,7}$ 0.8, 5-H); compound **14**: 1.13 (6 H, d, Me_2), 2.66 (1 H, septet, C*H*Me_2), 3.80 (3 H, s, OMe), 5.90 (1 H, d, $J_{4,3}$ 1.8, 4-H), 6.56 (1 H, dd, $J_{8,7}$ 8.1, $J_{8,6}$ 0.7, 8-H) and 7.05 (1 H, dd, $J_{3,2}$ 5.5, $J_{3,4}$ 1.8, 3-H); the signals for the remaining protons occurred at δ 6.94–6.98; δ_C compound **15**: 16.16 (Me_2), 28.07 (Me_2CH), 55.18 (OMe), 81.56 (C-4), 98.23 (C-1), 110.00 and 113.27 (C-5 and -7), 126.90 (C-6), 135.45 (C-8a), 143.84 and 144.94 (C-2 and -3) and 153.12 and 154.13 (C-4a and -8); δ_C compound **14**: 16.07 (Me_2), 27.65 (Me_2CH), 55.59 (OMe), 79.08 (C-4), 109.79 and 113.60 (C-6 and 8), 137.00 (C-4a), 143.75 and 144.21 (C-2 and -3) and 152.35 and 152.54 (C-5 and -8a).

A solution of this mixture (720 mg) in acetic anhydride (3 cm^3) was stirred at room temperature for 5 h under argon. The usual work-up gave a crude product, which was dissolved in dry diethyl ether (5 cm^3) and added dropwise to a stirred solution of lithium aluminium hydride (165 mg) in diethyl ether (15 cm^3). After 1 h the usual work-up with saturated aq. sodium sulphate gave a crude product, which was purified by radial chromatography with 5% ethyl acetate–hexane as eluent. The first band to be eluted yielded 4-isopropyl-8-methoxynaphthalen-1-ol **26** (89 mg, 12%) as an oil; δ_H 1.34 (6 H, d, Me_2), 3.56 (1 H, septet, C*H*Me_2), 4.04 (3 H, s, OMe), 6.79 (1 H, br d, $J_{7,6}$ 7.8, 7-H), 6.87 (1 H, d, $J_{2,3}$ 8.3, 2-H), 7.27 (1 H, d, $J_{3,2}$ 8.3, 3-H), 7.35 (1 H, dd, $J_{6,5}$ 8.9, $J_{6,7}$ 7.8, 6-H), 7.70 (1 H, br d, $J_{5,6}$ 8.9, 5-H) and 9.40 (1 H, s, D_2O-exchangeable OH); m/z 216 (M^+, 34%). Further elution yielded 4-isopropyl-5-methoxynaphthalen-1-ol **27** (344 mg, 50%) as an oil which decomposed on attempted distillation under diminished pressure; δ_H 1.29 (6 H, d, Me_2), 3.94 (3 H, s, OMe), 4.39 (1 H, septet, C*H*Me_2), 5.70 (1 H, br, OH), 6.77 (1 H, br d, $J_{6,7}$ 7.9, 6-H), 6.88 (1 H, d, $J_{2,3}$ 7.7, 2-H), 7.24 (1 H, d, $J_{3,2}$ 7.7, 3-H), 7.36 (1 H, dd, $J_{7,8}$ 8.4, $J_{7,6}$ 7.9, 7-H) and 7.83 (1 H, dd, $J_{8,7}$ 8.4, $J_{8,6}$ 1.1, 8-H); m/z 216 (M^+, 72%).

2-*t-Butylfuran* **7c**. Radial chromatography of the crude product obtained by method (b) gave a mixture (34%) containing 1-t-butyl-1,4-dihydro-5-methoxy-1,4-epoxynaphthalene **16** (15%) and 1-t-butyl-1,4-dihydro-8-methoxy-1,4-epoxynaphthalene **17** (85%). Crystallization of the mixture from hexane afforded the *adduct* **17** as prisms, m.p. 110–111 °C (Found: C, 78.75; H, 8.05. $C_{15}H_{18}O_2$ requires C, 78.25; H, 7.9%); δ_H 1.274 (9 H, s, Bu^t), 3.82 (3 H, s, OMe), 5.60 (1 H, apparent narrow t, 4-H), 6.62 (1 H, dd, $J_{5,6}$ 8.3, $J_{5,7}$ 0.9, 5-H), 6.87 (1 H, dd, $J_{7,6}$ 7.0, $J_{7,5}$ 0.9, 7-H), 6.96 (2 H, apparent narrow d, 2- and 3-H) and 6.97 (1 H, dd, $J_{6,7}$ 8.3, $J_{6,5}$ 7.0, 6-H); δ_C 26.76 (Me), 32.28 (*C*Me_3), 54.84 (OMe), 81.41 (C-4), 102.36 (C-1), 110.24 and 113.19 (C-5 and -7), 126.98 (C-6), 135.21 (C-8a), 143.29 and 143.78 (C-2 and -3) and 152.46 and 154.90 (C-4a and -8); t_R 16.73 min; m/z 230 (M^+, 16%), 215 (34), 189 (12), 174 (28), 146 (16), 131 (13), 115 (21) and 57 (100). The minor adduct **16** obtained in admixture with its isomer **17** had the following spectral properties: δ_H (*inter alia*) 1.266 (9 H, s, Bu^t), 3.80 (3 H, s, OMe) and 5.88 (1 H, d, *J* 1.8, 4-H); δ_C 26.54 (Me), 32.44 (*C*Me_3), 55.51 (OMe), 78.79 (C-4), 99.95 (C-1), 109.41 and 115.19 (C-6 and -8), 139.00 (C-4a), 142.83 and 144.30 (C-2 and -3) and 151.87 and 154.86 (C-5 and -8a); t_R 17.22 min; m/z 230 (M^+, 31%), 215 (63), 189 (24), 187 (18), 186 (13), 175 (12), 174 (72), 172 (15), 171 (10), 159 (17), 146 (48), 145 (11), 131 (22), 128 (14), 115 (34) and 57 (100).

The mixture of adducts (210 mg) was stirred with a solution of TFA (5 drops) in acetic anhydride (1 cm^3) for 8 h under argon. The usual work-up gave a crude product, which was purified by radial chromatography with 10% ethyl acetate–hexane as eluent. The first band that was eluted afforded *1-acetoxy-4-t-butyl-5-methoxynaphthalene* **31** (180 mg, 85%) as an oil, b.p. 115 °C at 0.01 mmHg (Found: C, 74.5; H, 7.55%; M^+, 272. $C_{17}H_{20}O_3$ requires C, 74.95; H, 7.4%; M, 272); δ_H 1.56 (9 H, s, Bu^t), 2.41 (3 H, s, MeCO), 3.89 (3 H, s, OMe), 6.88 (1 H, dd, $J_{6,7}$ 7.7, $J_{6,8}$ 1.2, 6-H), 7.10 (1 H, d, $J_{2,3}$ 8.3, 2-H), 7.38 (1 H, dd, $J_{7,8}$ 8.4, $J_{7,6}$ 7.7, 7-H), 7.52 (1 H, dd, $J_{8,7}$ 8.4, $J_{8,6}$ 1.2, 8-H) and 7.59 (1 H, d, $J_{3,2}$ 8.3, 3-H).

A solution of this material (114 mg) in dry diethyl ether (3 cm^3) was added dropwise to stirred lithium aluminium hydride (24 mg) in diethyl ether (5 cm^3). After 1 h, work-up with saturated aq. sodium sulphate in the usual way afforded 4-t-butyl-5-methoxynaphthalen-1-ol **28** (90 mg) as an oil which quickly decomposed on storage; δ_H 1.53 (9 H, s, Bu^t), 3.93 (3 H, s, OMe), 5.69 (1 H, br, OH), 6.71 (1 H, d, $J_{2,3}$ 8.2, 2-H), 6.92 (1 H, dd, $J_{6,7}$ 7.7, $J_{6,8}$ 1.2, 6-H), 7.39 (1 H, dd, $J_{7,8}$ 8.3, $J_{7,6}$ 7.7, 7-H), 7.42 (1 H, d, $J_{2,3}$ 8.2, 3-H) and 7.92 (1 H, dd, $J_{8,7}$ 8.3, $J_{8,6}$ 1.2, 8-H). Further elution provided *1-acetoxy-4-t-butyl-8-methoxynaphthalene** **29** (31.7 mg, 15%), b.p. 115 °C at 0.01 mmHg (Found: C, 74.7; H, 7.55%; M^+, 272. $C_{17}H_{20}O_3$ requires C, 74.95; H, 7.4%; M, 272); δ_H 1.60 (9 H, s, Bu^t), 2.36 (3 H, s, MeCO), 3.91 (3 H, s, OMe), 6.84 (1 H, br d, $J_{7,6}$ 7.5, 7-H), 6.98 (1 H, d, $J_{2,3}$ 8.2, 2-H), 7.38 (1 H, dd, $J_{6,5}$ 8.9, $J_{6,7}$ 7.5, 6-H), 7.47 (1 H, d, $J_{3,2}$ 8.2, 3-H) and 8.06 (1 H, dd, $J_{5,6}$ 8.9, $J_{5,7}$ 0.7, 5-H).

2-*Acetoxyfuran* **7d**. The crude product obtained by method (b) was purified by radial chromatography with 10% ethyl acetate–hexane containing 1% triethylamine as eluent. The first

* *Systematic name:* 4-acetoxy-1-t-butyl-5-methoxynaphthalene.

band to be eluted provided 1-acetoxy-1,4-dihydro-5-methoxy-1,4-epoxynaphthalene **9** (31.4 mg, 4.8%) as an oil (lit.,[12] b.p. 145 °C at 0.02 mmHg); δ_H 2.31 (3 H, s, Me), 3.82 (3 H, s, OMe), 5.91 (1 H, br d, $J_{4,3}$ 1.9, 4-H), 6.63 (1 H, br d, $J_{8,7}$ 8.2, 8-H), 6.94 (1 H, br d, $J_{6,7}$ 7.1, 6-H), 7.02 (1 H, dd, $J_{7,8}$ 8.2, $J_{7,6}$ 7.1, 7-H), 7.06 (1 H, d, $J_{2,3}$ 5.5, 2-H) and 7.09 (1 H, dd, $J_{3,2}$ 5.5, $J_{3,4}$ 1.9, 3-H); δ_C 21.30 (Me), 55.65 (OMe), 76.56 (C-4), 110.67 (C-6 or -8), 111.50 (C-1), 113.14 (C-8 or -6), 127.25 (C-7), 135.41 (C-4a), 141.05 and 143.30 (C-2 and -3), 148.13 and 152.56 (C-5 and -8a) and 166.50 (C=O). Further elution supplied 1-acetoxy-1,4-dihydro-8-methoxy-1,4-epoxynaphthalene **8** (91.9 mg, 14.2%) as an oil (lit.,[12] b.p. 150 °C at 0.02 mmHg); δ_H 2.27 (3 H, s, Me), 3.79 (3 H, s, OMe), 5.66 (1 H, dd, $J_{4,3}$ 1.7, $J_{4,2}$ 0.7, 4-H), 6.62 (1 H, dd, $J_{5,6}$ 8.3, $J_{5,7}$ 0.6, 5-H), 6.88 (1 H, dd, $J_{7,6}$ 7.1, $J_{7,5}$ 0.6, 7-H), 7.00 (1 H, dd, $J_{6,5}$ 8.3, $J_{6,7}$ 7.1, 6-H), 7.05 (1 H, dd, $J_{3,2}$ 5.6, $J_{3,4}$ 1.7, 3-H) and 7.08 (1 H, dd, $J_{2,3}$ 5.6, $J_{2,4}$ 0.7, 2-H); δ_C 21.24 (Me), 55.63 (OMe), 79.16 (C-4), 110.61 and 113.66 (C-5 and -7), 110.75 (C-1), 127.83 (C-6), 131.01 (C-8a), 141.64 and 144.03 (C-2 and -3), 151.30 and 152.92 (C-4a and -8) and 166.02 (C=O).

2-Bromofuran **7e**. The crude product obtained by method (b) was subjected to radial chromatography with 10% ethyl acetate–hexane, containing 1% triethylamine, as eluent. This afforded a mixture (19%) of 1-bromo-1,4-dihydro-8-methoxy-1,4-epoxynaphthalene **19** (63%) and 1-bromo-1,4-dihydro-5-methoxy-1,4-epoxynaphthalene **18** (37%) as a crystalline solid; δ_H (**19**) (*inter alia*) 3.81 (3 H, s, OMe), 5.61 (1 H, d, $J_{4,3}$ 1.8, 4-H), 6.63 (1 H, dd, $J_{7,6}$ 7.5, $J_{7,5}$ 1.1, 7-H), 6.94 (1 H, d, $J_{2,3}$ 5.4, 2-H) and 7.05 (1 H, dd, $J_{3,2}$ 5.4, $J_{3,4}$ 1.8, 3-H); compound **18** (*inter alia*) 3.84 (3 H, s, OMe), 5.90 (1 H, d, $J_{4,3}$ 1.8, 4-H), 6.66 (1 H, br, d, $J_{6,7}$ 7.8, 6-H), 6.93 (1 H, dd, $J_{3,2}$ 5.4, $J_{3,4}$ 1.8, 3-H) and 7.03 (1 H, d, $J_{2,3}$ 5.4, 2-H); δ_C compound **19** (*inter alia*) 55.91 (OMe), 66.26 (C-1), 111.61 and 113.23 (C-5 and -7), 133.67 (C-8a) and 143.82 and 146.37 (C-2 and -3); compound **15:** (*inter alia*) 55.73 (OMe), 62.73 (C-1), 110.98 and 113.75 (C-6 and -8), 133.78 (C-4a) and 144.14 and 145.94 (C-2 and -3); the remaining carbons resonated at δ_C 79.81 and 81.96 (C-4), 127.51 and 128.22 (C-6 **19** and -7 **18**) and 150.66, 151.27, 152.43 and 153.69 (C-4a and -8 **19** and C-8a and -5 **18**).

A solution of this mixture (128 mg) in acetic anhydride (1.0 cm^3) was treated with TFA (3 drops) and set aside at room temperature under argon for 62 h. The usual work-up gave a crude product, which was purified by radial chromatography with 5% ethyl acetate–hexane as eluent. After some starting material was eluted the next band afforded *1-acetoxy-4-bromo-5-methoxynaphthalene* **32** (45 mg, 30%), which was crystallized from hexane as cubes, m.p. 105–106 °C (Found: C, 52.75; H, 3.7%; M$^+$, 294/296. $C_{13}H_{11}BrO_3$ requires C, 52.9; H, 3.75%; M, 294/296); δ_H 2.44 (3 H, s, Me), 3.95 (3 H, s, OMe), 6.95 (1 H, dd, $J_{6,7}$ 7.2, $J_{6,8}$ 1.6, 6-H), 7.04 (1 H, d, $J_{2,3}$ 8.2, 2-H), 7.43 (1 H, dd, $J_{7,8}$ 8.5, $J_{7,6}$ 7.2, 7-H), 7.48 (1 H, dd, $J_{8,7}$ 8.5, $J_{8,6}$ 1.6, 8-H) and 7.75 (1 H, d, $J_{3,2}$ 8.2, 3-H). Further elution provided *1-acetoxy-4-bromo-8-methoxynaphthalene** **30** (36 mg, 24%), which was crystallized from hexane as prisms, m.p. 91–91.5 °C (Found: C, 53.15; H, 3.65%; M$^+$, 294/296); δ_H 2.37 (3 H, s, Me), 3.93 (3 H, s, OMe), 6.92 (1 H, br d, $J_{7,6}$ 7.3, 7-H), 6.93 (1 H, d, $J_{2,8}$ 8.1, 2-H), 7.50 (1 H, dd, $J_{6,5}$ 8.6, $J_{6,7}$ 7.3, 6-H), 7.75 (1 H, d, $J_{3,2}$ 8.1, 3-H) and 7.88 (1 H, dd, $J_{5,6}$ 8.6, $J_{5,7}$ 0.9, 5-H). There were some mixed fractions.

Methyl furan-2-carboxylate **7f**. Radial chromatography of the product obtained by method (b) afforded a mixture (12%) of methyl 1,4-dihydro-8-methoxy-1,4-epoxynaphthalene-1-carboxylate **21** (56%) and methyl 1,4-dihydro-5-methoxy-1,4-epoxynaphthalene-1-carboxylate **20** (44%) as an oil; δ_H compound **21:** (*inter alia*) 3.77 and 3.94 (each 3 H, s, OMe), 5.77 (1 H, d, $J_{4,3}$ 1.9, 4-H), 7.05 (1 H, dd, $J_{3,2}$ 5.4, $J_{3,4}$ 1.9, 3-H) and 7.24 (1 H, d, $J_{2,3}$ 5.4, 2-H); compound **20**: (*inter alia*) 3.82 and 3.97 (each 3 H, s, OMe), 6.03 (1 H, br d, $J_{4,3}$ 1.7, 4-H), 7.07 (1 H, d, $J_{2,3}$ 5.4, $J_{2,4}$ 0.4, 2-H) and 7.10 (1 H, dd, $J_{3,2}$ 5.4, $J_{3,4}$ 1.7, 3-H); the signals for the remaining protons occurred at δ 6.91–7.07; δ_C compound **21**: (*inter alia*) 52.62 (CO_2Me), 83.21 (C-4), 89.42 (C-1), 110.28 and 113.86 (C-5 and -7), 127.85 (C-6), 134.39 (C-8a), 141.44 and 143.27 (C-2 and -3), 150.80 and 152.75 (C-4a and -8) and 168.15 (C=O); compound **20**: (*inter alia*) 52.68 (CO_2Me), 80.11 (C-4), 90.51 (C-1), 110.76 and 113.11 (C-6 and -8), 127.12 (C-7), 133.87 (C-4a), 142.21 and 143.54 (C-2 and -3), 149.53 and 152.98 (C-5 and -8a) and 168.21 (C=O); the remaining carbons occurred at δ_C 55.63 and 55.78 (OMe).

2-(1,3-Dioxolan-2-yl)furan† **7g**. Radial chromatography of the crude product obtained by method (a), with 10% ethyl acetate–hexane, containing 1% triethylamine as eluent gave a mixture (59%) of 1-(1,3-dioxolan-2-yl)-1,4-dihydro-5-methoxy-1,4-epoxynaphthalene [2-(1,4-dihydro-5-methoxy-1,4-epoxynaphthalen-1-yl)-1,3-dioxolane] **22** (41%) and 1-(1,3-dioxolan-2-yl)-1,4-dihydro-8-methoxy-1,4-epoxynaphthalene [2-(1,4-dihydro-8-methoxy-1,4-epoxynaphthalen-1-yl)-1,3-dioxolane] **23** (59%) as a crystalline solid; δ_H compound **23**: 3.83 (3 H, s, OMe), 4.02–4.21 (4 H, m, CH_2CH_2), 5.73 (1 H, d, $J_{4,3}$ 1.7, 4-H), 6.24 (1 H, s, acetal CH), 6.64 (1 H, br d, $J_{5,6}$ 8.6, 5-H) and 6.88–7.07 (4 H, m, 2-, 3-, 5- and 6-H); δ_C 55.75 (OMe), 65.84 (2 × CH_2), 82.42 (C-4), 94.05 (C-1), 100.80 (acetal CH), 110.46 and 113.60 (C-5 and -7), 127.43 (C-6), 133.41 (C-8a), 142.06 and 143.66 (C-2 and -3) and 152.36 and 152.96 (C-4a and -8); t_R compound **22**: 9.88 min (51.4%) and compound **23**: 10.69 min (48.6%).

Acid Treatment of the Adducts **22** *and* **23**.—A solution of the adducts **22** and **23** (350 mg) in THF (15 cm^3)–methanol (20 cm^3) containing conc. hydrochloric acid (3 drops) was heated under nitrogen at 50 °C (bath) for 14 h. The usual work-up gave a crude product, which was purified by radial chromatography with 20% ethyl acetate–hexane as eluent. The first band that was eluted provided *1-(1,3-dioxolan-2-yl)-1,4-dihydro-5-methoxy-1,4-epoxynaphthalene* **22** (125 mg, 87%), which was crystallized from ethyl acetate–hexane as prisms, m.p. 77–77.5 °C (Found: C, 68.25; H, 5.8. $C_{14}H_{14}O_4$ requires C, 68.3; H, 5.75%); δ_H 3.80 (3 H, s, OMe), 4.01–4.22 (4 H, m, CH_2CH_2), 5.65 (1 H, br s, acetal CH), 5.98 (1 H, d, $J_{4,3}$ 1.8, 4-H), 6.59 (1 H, dd, $J_{6,7}$ 8.1, $J_{6,8}$ 0.9, 6-H), 6.92 (1 H, d, $J_{2,3}$ 5.4, 2-H), 6.97 (1 H, dd, $J_{7,8}$ 8.0, $J_{7,6}$ 8.1, 7-H), 7.03 (1 H, br d, $J_{8,7}$ 8.0, 8-H) and 7.10 (1 H, ddd, $J_{3,2}$ 5.4, $J_{3,4}$ 1.8, $J_{3,acetal}$ 0.5, 3-H); δ_C 55.66 (OMe), 65.73 and 65.92 (each CH_2), 80.28 (C-4), 93.02 (C-1), 101.22 (acetal CH), 110.40 and 113.88 (C-6 and -8), 127.01 (C-7), 136.16 (C-4a), 141.02 and 144.30 (C-2 and -3), 150.03 (C-8a) and 152.68 (C-5); *m/z* 246 (M$^+$, 6%) 174 (11), 115 (18) and 73 (100). This was followed by 4-hydroxy-8-methoxynaphthalene-1-carbaldehyde **33** (101 mg, 60%), which was crystallized from methanol as beige prisms, m.p. 223–224 °C (decomp.) [lit.,[23] 221–221.5 °C (decomp.)]; δ_H[300 MHz; $CDCl_3$ + $(CD_3)_2SO$] 4.01 (3 H, s, OMe), 6.98 (1 H, dd, $J_{3,2}$ 8.1, $J_{3,CHO}$ 0.8, 3-H), 7.24 (1 H, dd, $J_{7,6}$ 7.8, $J_{7,5}$ 1.0, 7-H), 7.41 (1 H, dd, $J_{6,5}$ 8.4, $J_{6,7}$ 7.8, 6-H), 7.97 (1 H, dd, $J_{5,6}$ 8.4, $J_{5,7}$ 1.0, 5-H), 8.02 (1 H, d, $J_{2,3}$ 8.1, 2-H), 10.35 (1 H, br, OH) and 11.05 (1 H, d, $J_{CHO,3}$ 0.8, CHO).

Deoxygenation of the Adducts **22** *and* **23**.—A solution of the adducts **22** and **23** (622 mg) in anhydrous benzene (20 cm^3) was stirred and treated with enneacarbonyldiiron (1.105 g) at 50–60 °C (bath) under nitrogen. After 40 min, when the carbonyl had dissolved, the solution was heated under reflux for 20 h. The solution was cooled, then filtered through Celite, and the pad was washed with dichloromethane. The residue left on removal of the solvent was passed through a short column of silica gel

Systematic name: * 4-acetoxy-1-bromo-5-methoxynaphthalene. † 2-(2-furyl)-1,3-dioxolane.

with 10% ethyl acetate–hexane as eluent and was next purified by radial chromatography with the same eluent. The first band to be eluted afforded 2-(5-methoxynaphthalen-1-yl)-1,3-dioxolane **34** (169 mg), which was crystallized from hexane as cubes, m.p. 83–85 °C. On treatment of a solution of this material in THF with a few drops of conc. hydrochloric acid during 2 h it afforded 5-methoxynaphthalene-1-carbaldehyde **36** (94%), which was crystallized from hexane as pale yellow plates, m.p. 52 °C (lit.,[25] 66 °C); δ_H 3.98 (3 H, s, OMe), 6.88 (1 H, dd, $J_{6,7}$ 7.8, $J_{6,8}$ 0.8, 6-H), 7.56 (each 1 H, superimposed dds, 3- and 7-H), 7.95 (1 H, dd, $J_{2,3}$ 7.1, $J_{2,4}$ 1.4, 2-H), 8.56 (1 H, ddd, $J_{4,3}$ 8.4, $J_{4,2}$ 1.4, $J_{4,8}$ 0.9, 4-H), 8.77 (1 H, ddd, $J_{8,7}$ 8.7, $J_{8,4}$ 0.9, $J_{8,6}$ 0.8, 8-H) and 10.37 (1 H, s, CHO). Further elution provided 2-(8-methoxynaphthalen-1-yl)-1,3-dioxolane **35**, which was crystallized from hexane as cubes, m.p. 52–53 °C. On deprotection this substance afforded 8-methoxynaphthalene-1-carbaldehyde **37**, which was crystallized from methanol as prisms, m.p. 88–89 °C (lit.,[26] 88–90 °C); δ_H 4.00 (3 H, s, OMe), 6.99 (1 H, dd, $J_{7,6}$ 7.4, $J_{7,5}$ 1.4, 7-H), 7.26–7.55 (3 H, m, 3-, 5- and 6-H), 7.93 (1 H, dd, $J_{2,3}$ 7.2, $J_{2,4}$ 1.4, 2-H), 7.97 (1 H, dd, $J_{4,3}$ 8.1, $J_{4,2}$ 1.4, 4-H) and 11.09 (1 H, d, J 0.5, CHO).

General Method for Reactions of Furans with 3-(*Methoxycarbonyl*)*dehydrobenzene*.—A solution of 2-amino-6-(methoxycarbonyl)benzoic acid **2**[6] (1.17 g, 6 mmol) in anhydrous 1,2-dimethoxyethane (DME) (5 cm^3) was added dropwise during 20 min to a stirred solution of the furan (3 mmol) and isoamyl nitrite (0.78 cm^3) in anhydrous DME (3 cm^3) at 82–85 °C (bath) under dry nitrogen. After the addition the solution was heated under reflux for 20 min, and then further isoamyl nitrite (0.78 cm^3) was added, followed by the dropwise addition, during 20 min, of a further solution of 2-amino-6-(methoxycarbonyl)benzoic acid **2** (1.17 g) in anhydrous DME (5 cm^3). The solution was then heated under reflux for 40 min, allowed to cool, and was then poured into aq. sodium hydrogen carbonate (5%, 25 cm^3). The crude product was isolated by extraction with diethyl ether and was then purified by radial chromatography.

2-*Methylfuran* **7a**. Radial chromatography of the crude product with 10% ethyl acetate–hexane, containing 1% triethylamine, as eluent afforded an oily mixture (52%) of methyl 1,4-dihydro-1-methyl-1,4-epoxynaphthalene-8-carboxylate* **39** (43%) and methyl 1,4-dihydro-1-methyl-1,4-epoxynaphthalene-5-carboxylate† **38** (57%); δ_H compound **39**: 2.00 (3 H, s, Me), 3.89 (3 H, s, OMe), 5.62 (1 H, d, $J_{4,3}$ 1.9, 4-H), 6.89 (1 H, d, $J_{2,3}$ 5.4, 2-H), 7.00 (1 H, dd, $J_{6,7}$ 8.0, $J_{6,5}$ 7.0, 6-H), 7.06 (1 H, dd, $J_{3,2}$ 5.4, $J_{3,4}$ 1.9, 3-H), 7.30 (1 H, dd, $J_{5,6}$ 7.0, $J_{5,7}$ 1.0, 5-H) and 7.39 (1 H, dd, $J_{7,6}$ 8.0, $J_{7,5}$ 1.0, 5-H); compound **38**: 1.93 (3 H, s, Me), 3.91 (3 H, s, OMe), 6.28 (1 H, d, $J_{4,3}$ 1.9, 4-H), 6.79 (1 H, d, $J_{2,3}$ 5.4, 2-H), 7.05 (1 H, dd, $J_{7,6}$ 8.0, $J_{7,8}$ 7.0, 7-H), 7.08 (1 H, dd, $J_{3,2}$ 5.4, $J_{3,4}$ 1.9, 3-H), 7.29 (1 H br d, $J_{8,7}$ 7.0, 8-H) and 7.54 (1 H, dd, $J_{6,7}$ 8.0, $J_{6,8}$ 0.9, 6-H); δ_C compound **39**: (*inter alia*) 17.12 (Me), 51.67 (OMe), 88.70 (C-1), 143.70 and 144.77 (C-2 and -3), 151.65 and 152.62 (C-4a and -8a) and 166.91 (C=O); compound **38**: (*inter alia*) 14.93 (Me), 51.67 (OMe), 81.99 (C-4), 91.49 (C-1), 144.96 and 146.07 (C-2 and -3), 152.36 and 153.71 (C-4a and -8a) and 166.31 (C=O); compound **39**: t_R 10.55 min; m/z 216 (M^+, 4%), 185 (18), 175 (31), 174 (100), 143 (15), 142 (37), 130 (10), 129 (29), 128 (28), 127 (21), 115 (47) and 114 (18); compound **38**: t_R 10.77 min; m/z 216 (9), 190 (45), 188 (11), 185 (23), 175 (41), 174 (100), 159 (11), 157 (11), 156 (21), 143 (16), 142 (35), 132 (16), 130 (11), 129 (59), 128 (67), 127 (35), 115 (51), 114 (25) and 102 (15).

The mixture of epoxynaphthalenes (142 mg) was deoxygenated with enneacarbonyldiiron in a manner similar to that described above. Radial chromatography of the crude product with 2.5% ethyl acetate–hexane as eluent gave, first, methyl 5-methylnaphthalene-1-carboxylate **50** (23.1 mg), which was crystallized from aq. methanol as needles, m.p. 38 °C (lit.,[29] 39 °C); δ_H 2.73 (3 H, s, Me), 4.00 (3 H, s, OMe), 7.37 (1 H, br, d, $J_{6,7}$ 6.9, 6-H), 7.49 (1 H, dd, $J_{7,8}$ 8.7, $J_{7,6}$ 6.9, 7-H), 7.52 (1 H, dd, $J_{3,4}$ 8.5, $J_{3,2}$ 7.2, 3-H), 8.14 (1 H, dd, $J_{2,3}$ 7.2, $J_{2,4}$ 1.2, 2-H), 8.21 (1 H, br d, $J_{4,3}$ 8.5, 4-H) and 8.72 (1 H, br d, $J_{8,7}$ 8.7, 8-H). Further elution gave methyl 8-methylnaphthalene-1-carboxylate **51** as an oil (14.5 mg) (lit.,[28] b.p. 170–171 °C at 15 mmHg); δ_H 2.60 (3 H, s, Me), 3.99 (3 H, s, OMe), 7.38–7.47 (3 H, m, 3-, 6- and 7-H), 7.57 (1 H, dd, $J_{2,3}$ 7.0, $J_{2,4}$ 1.4, 2-H), 7.74 (1 H, br dd, $J_{5,6}$ 7.9, $J_{5,7}$ 1.7, 5-H) and 7.91 (1 H, dd, $J_{4,3}$ 8.3, $J_{4,2}$ 1.4, 4-H).

2-*Isopropylfuran* **7b**. Radial chromatography of the crude product afforded an oily mixture (44%) of methyl 1,4-dihydro-1-isopropyl-1,4-epoxynaphthalene-8-carboxylate‡ **41** (30%) and methyl 1,4-dihydro-1-isopropyl-1,4-epoxynaphthalene-5-carboxylate¶ **40** (70%). Repeated radial chromatography of the mixture with 2.5% ethyl acetate–hexane, containing 1% triethylamine, as eluent allowed the isolation of the *adduct* **40** as an oil, b.p. 80–82 °C at 0.005 mmHg (Found: C, 73.65; H, 6.8. $C_{15}H_{16}O_3$ requires C, 73.75; H, 6.6%); δ_H 1.17 and 1.25 (each 3 H, d, Me), 2.69 (1 H, septet, CH), 3.91 (3 H, s, OMe), 6.32 (1 H, d, $J_{4,3}$ 1.9, 4-H), 6.87 (1 H, d, $J_{2,3}$ 5.5, 2-H), 7.04 (1 H, dd, $J_{7,6}$ 8.0, $J_{7,8}$ 7.1, 7-H), 7.07 (1 H, dd, $J_{3,2}$ 5.5, $J_{3,4}$ 1.9, 3-H), 7.34 (1 H, br d, $J_{8,7}$ 7.1, 8-H) and 7.53 (1 H, dd, $J_{6,7}$ 8.0, $J_{6,8}$ 0.9, 6-H); δ_C 17.98 and 18.21 (each Me), 27.41 (CH), 51.93 (OMe), 81.77 (C-4), 96.07 (C-1), 123.22 (C-5), 123.44 (C-7), 124.84 (C-6), 124.91 (C-8), 143.74 and 144.45 (C-2 and 3), 150.98 and 154.82 (C-4a and -8a) and 166.45 (C=O); t_R 12.08 min; m/z 244 (M^+, 2%), 218 (13), 203 (31), 171 (21), 169 (10), 142 (20), 141 (14), 115 (40), 114 (12) and 71 (100); δ_H compound **41**: 0.96 and 1.12 (each 3 H, d, Me), 3.24 (1 H, septet, CH), 3.89 (3 H, s, OMe), 5.67 (1 H, d, $J_{4,3}$ 1.7, 4-H), 6.86 (1 H, d, $J_{2,3}$ 5.5, 2-H), 6.98 (1 H, dd, $J_{6,7}$ 8.0, $J_{6,5}$ 7.1, 6-H), 6.99 (1 H, dd, $J_{3,2}$ 5.5, $J_{3,4}$ 1.7, 3-H), 7.29 (1 H, dd, $J_{5,6}$ 7.1, $J_{5,7}$ 1.0, 5-H) and 7.35 (1 H, dd, $J_{7,6}$ 8.0, $J_{7,5}$ 1.0, 7-H); δ_C compound **41**: 18.04 and 18.49 (each Me), 26.71 (CH), 52.12 (OMe), 80.53 (C-4), 99.29 (C-1), 122.46 (C-6), 124.69 (C-7), 125.35 (C-5), 126.04 (C-8), 144.25 and 144.60 (C-2 and -3), 151.42 and 152.73 (C-4a and -8a) and 167.51 (C=O); t_R 11.27 min; m/z 244 (M^+, 0.5%), 203 (11), 115 (34), 114 (11), 71 (93) and 43 (100).

Deoxygenation of a mixture of the adducts (156 mg) gave, after radial chromatography with 5% ethyl acetate–hexane as eluent, from a faster band, *methyl* 5-*isopropylnaphthalene*-1-*carboxylate* **52** (66 mg) as an oil, b.p. 98 °C at 0.01 mmHg (Found: C, 78.65; H, 7.25%; M^+, 228. $C_{15}H_{16}O_2$ requires C, 78.9; H, 7.05%; M, 228); δ_H 1.39 (6 H, d, Me_2), 3.75 (1 H, septet, CH), 3.99 (3 H, s, OMe), 7.46–7.59 (3 H, m, 3-, 6- and 7-H), 8.11 (1 H, dd, $J_{2,3}$ 7.2, $J_{2,4}$ 1.2, 2-H), 8.34 (1 H, br d, $J_{4,3}$ 8.8, 4-H) and 8.70 (1 H, br d, $J_{8,7}$ 8.6, 8-H). Further elution supplied *methyl* 8-*isopropylnaphthalene*-1-*carboxylate* **53** (57 mg) as an oil, b.p. 88 °C at 0.01 mmHg (Found: C, 78.75; H, 7.25%; M^+, 228); δ_H 1.32 (6 H, d, Me_2), 3.30 (1 H, septet, CH), 3.93 (3 H, s, OMe), 7.41 (1 H, dd, $J_{3,4}$ 8.1, $J_{3,2}$ 7.0, 3-H), 7.51 (1 H, dd, $J_{6,5}$ 7.8, $J_{6,7}$ 7.0, 6-H), 7.56 (1 H, dd, $J_{2,3}$ 7.0, $J_{2,4}$ 1.4, 2-H), 7.59 (1 H, dd, $J_{7,6}$ 7.0, $J_{7,5}$ 1.4, 7-H), 7.71 (1 H, dd, $J_{5,6}$ 7.8, $J_{5,7}$ 1.4, 5-H) and 7.91 (1 H, dd, $J_{4,3}$ 8.1, $J_{4,2}$ 1.4, 4-H).

2-*t-Butylfuran* **7c**. Radial chromatography of the crude product afforded an oily mixture (50%) of methyl 2-t-butyl-1,4-dihydro-1,4-epoxynaphthalene-8-carboxylate§ **43** (23%) and methyl 2-t-butyl-1,4-dihydro-1,4-epoxynaphthalene-5-

Systematic names: * compound **39**: methyl 5,8-epoxy-5,8-dihydro-8-methylnaphthalene-1-carboxylate; † compound **38**: methyl 5,8-epoxy-5,8-dihydro-5-methylnaphthalene-1-carboxylate; ‡ compound **41**: Methyl 5,8-epoxy-5,8-dihydro-8-isopropylnaphthalene-1-carboxylate; ¶ compound **40**: methyl 5,8-epoxy-5,8-dihydro-5-isopropylnaphthalene-1-carboxylate; § compound **43**: methyl 8-t-butyl-5,8-epoxy-5,8-dihydronaphthalene-1-carboxylate.

carboxylate* **42** (77%). Repeated radial chromatography of the mixture allowed the isolation of the *adduct* **42** as an oil, b.p. 90–91 °C at 0.005 mmHg (Found: C, 74.65; H, 7.2. $C_{16}H_{18}O_3$ requires C, 74.4; H, 7.0%); δ_H 1.28 (9 H, s, Bu^t), 3.91 (3 H, s, OMe), 6.33 (1 H, d, $J_{4,3}$ 1.9, 4-H), 6.98 (1 H, d, $J_{2,3}$ 5.5, 2-H), 7.01 (1 H, dd, $J_{7,6}$ = $J_{7,8}$ = 7.3, 7-H), 7.07 (1 H, dd, $J_{3,2}$ 5.5, $J_{3,4}$ 1.9, 3-H) and 7.52 (2 H, superimposed ds, $J_{6,7}$ = $J_{8,7}$ = 7.2, 6- and 8-H); δ_C 26.48 (Me), 32.32 (*C*Me$_3$), 51.91 (OMe), 81.57 (C-4), 98.95 (C-1), 123.10 (C-5), 124.54 (C-7), 124.73 (C-6), 124.92 (C-8), 143.43 and 143.80 (C-2 and -3), 150.35 and 155.55 (C-4a and -8a) and 166.46 (C=O); t_R 12.33 min; *m/z* 174 (9%), 115 (14) and 57 (100); δ_H compound **43**: 1.21 (9 H, s, Bu^t), 3.87 (3 H, s, OMe), 5.62 (1 H, d, $J_{4,3}$ 1.6, 4-H), 6.91–6.99 (4 H, m, 2-, 3-, 5- and 6-H) and 7.23 (1 H, dd, $J_{7,8}$ 6.8, $J_{7,5}$ 1.4, 7-H); δ_C 27.15 (Me), 32.72 (*C*Me$_3$), 52.39 (OMe), 80.68 (C-4), 102.43 (C-1), 120.70 (C-6), 123.76 (C-7), 124.64 (C-5), 128.43 (C-8), 142.16 and 144.59 (C-2 and -3), 146.56 and 152.97 (C-4a and -8a) and 170.86 (C=O); t_R 12.77 min; *m/z* 217 (18%), 174 (15), 115 (13) and 57 (100).

Deoxygenation of the adduct **42** (179 mg) afforded *methyl 5-t-butylnaphthalene-1-carboxylate* **54** (158 mg, 74%) as an oil, b.p. 94 °C at 0.05 mmHg (Found: C, 79.5; H, 7.7; M$^+$, 242. $C_{16}H_{18}O_2$ requires C, 79.3; H, 7.5%; M, 242); δ_H 1.62 (9 H, s, Bu^t), 3.99 (3 H, s, OMe), 7.45–7.58 (3 H, m, 3-, 6- and 7-H), 8.04 (1 H, dd, $J_{2,3}$ 7.1, $J_{2,4}$ 1.0, 2-H) and 8.67 (2 H, superimposed broad d, $J_{8,7}$ = $J_{4,3}$ = 8.7, 4- and 8-H).

2-Acetoxyfuran **7d**. Radial chromatography of the product with 10% ethyl acetate–hexane, containing 1% triethylamine, as eluent gave, from the faster band, *methyl 1-acetoxy-1,4-dihydro-1,4-epoxynaphthalene-5-carboxylate*† **11** (18%), as an oil, b.p. 122–124 °C at 0.05 mmHg (Found: C, 64.5; H, 4.75. $C_{14}H_{12}O_5$ requires C, 64.6; H, 4.65%); δ_H 2.33 (3 H, s, Me), 3.94 (3 H, s, OMe), 6.33 (1 H, br d, $J_{4,3}$ 2.0, 4-H), 7.09 (1 H, d, $J_{2,3}$ 5.5, 2-H), 7.11 (1 H, dd, $J_{7,6}$ 8.0, $J_{7,8}$ 7.2, 7-H), 7.13 (1 H, dd, $J_{3,2}$ 5.5, $J_{3,4}$ 2.0, 3-H), 7.42 (1 H, br d, $J_{8,7}$ 7.2, 8-H) and 7.61 (1 H, dd, $J_{6,7}$ 8.0, $J_{6,8}$ 0.9, 6-H); δ_C 21.29 (Me), 52.17 (OMe), 79.30 (C-4), 111.06 (C-1), 123.45 (C-5), 123.57 (C-7), 125.62 (C-6), 126.15 (C-8), 141.75 and 142.91 (C-2 and -3), 147.05 and 152.17 (C-4a and -8a) and 166.10 and 166.59 (each C=O); t_R 7.03 min; *m/z* 260 (M$^+$, 5%), 218 (18), 187 (24), 186 (100), 185 (28), 158 (23), 130 (21), 129 (11), 102 (17) and 101 (11). Further elution supplied methyl 1-acetoxy-1,4-dihydro-1,4-epoxynaphthalene-8-carboxylate‡ **10** (11%), which was crystallized from ethyl acetate–hexane as cubes, m.p. 145–147 °C; δ_H 2.26 (3 H, s, Me), 3.87 (3 H, s, OMe), 5.72 (1 H, d, $J_{4,3}$ 1.9, 4-H), 7.04 (1 H, d, $J_{2,3}$ 5.2, 2-H), 7.08 (1 H, dd, $J_{6,5}$ 7.2, $J_{6,7}$ 8.0, 6-H), 7.10 (1 H, dd, $J_{3,2}$ 5.2, $J_{3,4}$ 1.9, 3-H), 7.35 (1 H, br d, $J_{5,6}$ 7.2, $J_{5,7}$ 0.9, 5-H) and 7.54 (1 H, dd, $J_{7,6}$ 8.0, $J_{7,5}$ 0.9, 7-H); δ_C 21.19 (Me), 52.15 (OMe), 78.33 (C-4), 111.31 (C-1), 123.56 (C-6), 125.38 (C-8), 125.76 (C-7), 126.36 (C-5), 141.16 and 145.03 (C-2 and -3), 147.60 and 149.94 (C-4a and -8a) and 165.96 and 166.26 (C=O); t_R 7.05 min; *m/z* 260 (M$^+$, 5%), 218 (17), 187 (24), 186 (100), 185 (30), 158 (22), 130 (15) and 102 (12).

2-Bromofuran **7e**. Radial chromatography of the crude product with 5% ethyl acetate–hexane, containing 1% triethylamine, as eluent gave, from a faster band, *methyl 1-bromo-1,4-epoxynaphthalene-5-carboxylate*¶ **44** (33%) as an oil, b.p. 134 °C at 0.01 mmHg (Found: C, 51.05; H, 3.1; Br, 28.4. $C_{12}H_9BrO_3$ requires C, 51.25; H, 3.25; Br, 28.4%); δ_H 3.94 (3 H, s, OMe), 6.33 (1 H, d, $J_{4,3}$ 2.1, 4-H), 6.98 (1 H, d, $J_{2,3}$ 5.3, 2-H), 7.10 (1 H, dd, $J_{3,2}$ 5.3, $J_{3,4}$ 2.1, 3-H), 7.16 (1 H, dd, $J_{7,6}$ 8.0, $J_{7,8}$ 7.1, 7-H), 7.50 (1 H, br d, $J_{8,7}$ 7.1, 8-H) and 7.62 (1 H, dd, $J_{6,7}$ 8.0, $J_{6,8}$ 0.9, 6-H); δ_C 52.25 (OMe), 82.56 (C-4), 91.62 (C-1), 123.48 (C-5), 124.01 (C-7), 125.94 (C-6), 126.41 (C-8), 143.71 and 146.67 (C-2 and -3), 150.18 and 150.73 (C-4a and -8a) and 165.88 (C=O); t_R 6.53 min; *m/z* 282 (M$^+$, 4%), 280 (M$^+$, 4), 256 (8), 254 (10), 201 (20), 173 (100), 143 (76), 142 (22), 130 (11), 129 (14), 116 (19), 115 (94), 114 (77), 113 (51) and 102 (19). Further elution supplied *methyl 1-bromo-1,4-dihydro-1,4-epoxynaphthalene-8-carboxylate*§ **45** (7%) as an oil, b.p. 122 °C at 0.05 mmHg (Found: C, 51.55; H, 3.1%); δ_H 3.94 (3 H, s, OMe), 5.70 (1 H, d, $J_{4,3}$ 1.9, 4-H), 7.05 (1 H, dd, $J_{3,2}$ 5.5, $J_{3,4}$ 1.9, 3-H), 7.08 (1 H, d, $J_{2,3}$ 5.5, 2-H), 7.09 (1 H, dd, $J_{6,7}$ = $J_{6,5}$ = 7.0, 6-H) and 7.35 (2 H, superimposed ds, $J_{7,6}$ = $J_{5,6}$ = 7.0, 5- and 7-H); δ_C 55.22 (OMe), 81.16 (C-4), 91.79 (C-1), 122.41 (C-6), 125.80 (C-7), 126.15 (C-5), 126.45 (C-8), 144.77 and 144.91 (C-2 and -3), 148.77 and 149.27 (C-4a and -8a) and 166.76 (C=O); t_R 6.72 min; *m/z* 282 (M$^+$, 1%), 280 (M$^+$, 1), 256 (6), 254 (6), 174 (14), 173 (100), 143 (73), 142 (11), 130 (10), 116 (13), 115 (85), 114 (62), 113 (32) and 102 (16).

Methyl furan-2-carboxylate **7f**. Radial chromatography of the crude product with 5% ethyl acetate–hexane, containing 1% triethylamine, as eluent gave from a faster band, dimethyl 1,4-dihydro-1,4-epoxynaphthalene-1,5-dicarboxylate **46** (21%) as an oil, b.p. 94 °C at 0.005 mmHg; δ_H 3.94 and 4.00 (each 3 H, s, OMe), 6.47 (1 H, d, $J_{4,3}$ 1.9, 4-H), 7.10 (1 H, dd, $J_{7,6}$ 8.0, $J_{7,8}$ 7.0, 7-H), 7.11 (1 H, d, $J_{2,3}$ 5.4, 2-H), 7.15 (1 H, dd, $J_{3,2}$ 5.4, $J_{3,4}$ 1.9, 3-H), 7.53 (1 H, br d, $J_{8,7}$ 7.0, 8-H) and 7.61 (1 H, dd, $J_{6,7}$ 8.0, $J_{6,8}$ 0.9, 6-H); δ_C 52.09 and 52.64 (each OMe), 82.77 (C-4), 89.72 (C-1), 123.42 (C-7), 124.00 (C-5), 125.43 (C-6), 126.05 (C-8), 143.12 and 143.16 (C-2 and -3), 143.16 and 148.23 (C-4a and -8a) and 165.94 and 167.90 (each C=O); t_R 7.18 min; *m/z* 260 (M$^+$, 10%), 234 (37), 229 (19), 203 (13), 201 (32), 200 (92), 191 (31), 176 (12), 173 (48), 171 (10), 170 (11), 169 (24), 157 (16), 156 (10), 149 (20), 144 (12), 143 (59), 142 (22), 130 (17), 129 (67), 128 (33), 127 (13), 116 (19), 115 (100), 114 (62), 113 (33) and 102 (20). Further elution supplied dimethyl 1,4-dihydro-1,4-epoxynaphthalene-1,8-dicarboxylate **47** (10%), which was crystallized from ethyl acetate–hexane as cubes, m.p. 157–159 °C; δ_H 3.86 and 3.90 (each 3 H, s, OMe), 5.84 (1 H, d, $J_{4,3}$ 1.8, 4-H), 7.11 (1 H, dd, $J_{6,7}$ 8.0, $J_{6,5}$ 7.1, 6-H), 7.12 (1 H, dd, $J_{3,2}$ 5.5, $J_{3,4}$ 1.8, 3-H), 7.28 (1 H, d, $J_{2,3}$ 5.5, 2-H), 7.43 (1 H, dd, $J_{5,6}$ 7.1, $J_{5,7}$ 0.9, 5-H) and 7.58 (1 H, dd, $J_{7,6}$ 8.0, $J_{7,5}$ 0.9, 7-H); δ_C 51.91 and 52.64 (each OMe), 82.60 (C-4), 92.52 (C-2), 124.87 (C-6), 125.87 (C-7), 125.98 (C-5), 140.59 and 144.86 (C-2 and -3), 150.07 and 150.48 (C-4a and -8a) and 165.86 and 167.16 (each C=O); t_R 7.08 min; *m/z* 260 (M$^+$, 10%), 234 (10), 229 (31), 203 (15), 201 (45), 200 (60), 185 (11), 174 (14), 173 (100), 170 (12), 169 (15), 163 (15), 157 (15), 143 (63), 142 (14), 130 (12), 129 (41), 128 (19), 116 (11), 115 (72), 114 (40), 113 (18) and 102(16).

Deoxygenation of this compound yielded dimethylnaphthalene-1,8-dicarboxylate **55** (79%), which was crystallized from methanol as needles, m.p. 102–103 °C (lit.,[29] 102–103 °C); δ_H 3.92 (6 H, s, 2 × OMe), 7.54 (2 H, dd, J_o = $J_{o'}$ = 8.2, 3- and 6-H) and 8.00 and 8.01 (each 2 H, dd, J_o = $J_{o'}$ = 8.2, J_m 1.2, 2-, 4-, 5- and 7-H); δ_C 52.07 (OMe), 125.26 (C-3 and -6), 127.32 (C-1 and -8), 129.65 (C-8a), 130.20 (C-2 and -7), 132.42 (C-4 and -5), 134.20 (C-4a) and 169.22 (C=O).

2-(1,3-Dioxolan-2-yl)furan **7g**. Radial chromatography of the crude product with 10% ethyl acetate–hexane, containing 1% triethylamine, as eluent gave, from a faster band, *methyl 1-(1,3-dioxolan-2-yl)-1,4-dihydro-1,4-epoxynaphthalene-5-carboxylate*‖ **48** (34%) as an oil, b.p. 132 °C at 0.01 mmHg (Found: C, 65.5; H, 5.25. $C_{15}H_{14}O_5$ requires C, 65.7; H, 5.15%); δ_H 3.93 (3 H, s, OMe), 4.04–4.25 (4 H, m, 2 × CH$_2$), 5.65 (1 H, s, CH), 6.41 (1 H, d, $J_{4,3}$ 1.9, 4-H), 6.99 (1 H, d, $J_{2,3}$ 5.5, 2-H), 7.07 (1 H, dd,

Systematic names: * compound **42**: methyl 5-t-butyl-5,8-epoxy-5,8-dihydronaphthalene-1-carboxylate; † compound **11**: methyl 5-acetoxy-5,8-epoxy-5,8-dihydronaphthalene-1-carboxylate; ‡ compound **10**: methyl 8-acetoxy-5,8-epoxy-5,8-eihydronaphthalene-1-carboxylate; ¶ compound **44**: methyl 5-bromo-5,8-epoxy-5,8-dihydronaphthalene-1-carboxylate; § compound **45**: methyl 8-bromo-5,8-epoxy-5,8- dihydronaphthalene-1-carboxylate; ‖ compound **48**: methyl 5-(1,3-dioxolan-2-yl)-5,8-epoxy-5,8-dihydronaphthalene-1-carboxylate.

$J_{7,6}$ 8.0, $J_{7,8}$ 7.1, 7-H), 7.13 (1 H, dd, $J_{3,2}$ 5.5, $J_{3,4}$ 1.9, 3-H), 7.52 (1 H, br d, $J_{8,7}$ 7.1, 8-H) and 7.57 (1 H, dd, $J_{6,7}$ 8.0, $J_{6,8}$ 0.9, 6-H); δ_C 52.08 (OMe), 65.77 and 66.00 (each CH_2), 83.02 (C-4), 92.32 (C-1), 101.15 (CH), 123.50 (C-5), 124.14 (C-7), 125.31 (C-6), 125.56 (C-8), 141.85 and 143.89 (C-2 and -3), 148.84 and 153.34 (C-4a and -8a) and 166.33 (C=O); t_R 8.27 min; m/z 274 (M^+, 1%), 115 (15) and 73 (100). Further elution furnished *methyl* 1-(1,3-*dioxolan*-2-*yl*)-1,4-*dihydro*-1,4-*epoxynaphthalene*-8-*carboxylate* * **49** (12%), which was crystallized from ethyl acetate–hexane as prisms, m.p. 126–127 °C (Found: C, 65.55; H, 5.1%); δ_H 3.90–4.13 (4 H, m, 2 × CH_2), 3.91 (3 H, s, OMe), 5.78 (1 H, d, $J_{4,3}$ 1.8, 4-H), 6.43 (1 H, s, CH), 7.04 (1 H, dd, $J_{6,7}$ 8.0, $J_{6,5}$ 7.1, 6-H), 7.05 (1 H, d, $J_{2,3}$ 5.5, 2-H), 7.12 (1 H, dd, $J_{3,2}$ 5.5, $J_{3,4}$ 1.8, 3-H), 7.35 (1 H, dd, $J_{5,6}$ 7.1, $J_{5,7}$ 0.9, 5-H) and 7.44 (1 H, dd, $J_{7,6}$ 8.0, $J_{7,5}$ 0.9, 7-H); δ_C 52.23 (OMe), 65.92 and 65.95 (each CH_2), 81.48 (C-4), 95.63 (C-1), 100.65 (CH), 123.07 (C-6), 125.28 (C-7), 125.73 (C-5), 125.78 (C-8), 141.37 and 144.91 (C-2 and -3), 149.48 and 151.07 (C-4a and -8a) and 167.25 (C=O); t_R 7.75 min; m/z 274 (M^+, 0.5%), 115 (11) and 73 (100).

Deoxygenation of compound **48** yielded *methyl* 5-(1,3-*dioxolan*-2-*yl*)*naphthalene*-1-*carboxylate* **56** (75%), which was crystallized from hexane as cubes, m.p. 72–73 °C (Found: C, 69.45; H, 5.55%; M^+, 258. $C_{15}H_{14}O_4$ requires C, 69.75; H, 5.45%; M, 258); δ_H 3.99 (3 H, s, OMe), 4.10–4.21 (4 H, m, 2 × CH_2), 6.45 (1 H, s, CH) 7.55 (1 H, dd, $J_{7,8}$ 8.6, $J_{7,6}$ 7.8, 7-H), 7.60 (1 H, dd, $J_{3,4}$ 8.7, $J_{3,2}$ 7.6, 3-H), 7.82 (1 H, br d, $J_{2,3}$ 7.6, 2-H), 8.16 (1 H, dd, $J_{6,7}$ 7.8, $J_{6,8}$ 1.3, 6-H), 8.43 (1 H, br d, $J_{8,7}$ 8.6, 8-H) and 8.92 (1 H, br d, $J_{4,3}$ 8.7, 4-H).

Systematic names: * compound **49**: methyl 8-(1,3-dioxolan-2-yl)-5,8-epoxy-5,8-dihydronaphthalene-1-carboxylate.

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