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Naphthopyrans and their C4 Alcohols by Cyclization of Substituted Naphthalenes using Potassium *t*-Butoxide in Dimethylformamide. Generality and Stereochemical, including Conformational, Effects

Robin G. F. Giles,[A,C] *Ivan R. Green,*[B,C] *Wendell P. Swigelaar,*[B] *and C. Peter Taylor*[C]

[A]Department of Chemistry, Murdoch University, Murdoch WA 6150, Australia.
[B]Department of Chemistry, University of the Western Cape, Bellville, 7530, South Africa.
[C]Corresponding authors. Email: r.giles@murdoch.edu.au; igreen@uwc.ac.za

The generality of the high-yielding, stereoselective cyclization of 2-allyl-3-(1′-hydroxyethyl)-1,4-dimethoxynaphthalene **1** to afford *trans*-3,4-dihydro-5,10-dimethoxy-1,3-dimethylnaphtho[2,3-*c*]pyran **2** is investigated by replacing each of the methoxy groups in the substrate by an ethyl substituent and subjecting these to cyclization reaction conditions identical to those originally reported. For shorter reaction times with potassium *tert*-butoxide in dimethylformamide under nitrogen, the derived 1-ethyl-, 4-ethyl-, and 1,4-diethylnaphthalenes all cyclize to the *trans*-1,3-dimethyl compounds, whereas longer times yield increasing proportions of the corresponding *cis*-isomers. Under air, the epimeric C4 alcohols *rel*-(1*R*,3*R*,4*S*)-3,4-dihydro-5-ethyl-4-hydroxy-10-methoxy-1,3-dimethylnaphtho[2,3-*c*]pyran **50** and its *rel*-(1*R*,3*R*,4*R*) isomer **51** are also isolated from 2-allyl-1-ethyl-3-(1′-hydroxyethyl)-4-methoxynaphthalene **11**. The half-chair conformation of pyran **50** is inverted relative to that of its C4 epimer **51**.

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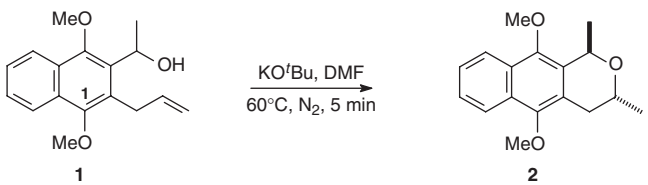
Introduction

We have previously reported the base-induced cyclization of 2-allyl-3-(1′-hydroxyethyl)-1,4-dimethoxynaphthalenes to afford naphthopyrans in reactions that are unusual in that they proceed rapidly in high yield and with complete stereoselectivity and also, prima facie, involve the intramolecular nucleophilic addition of alkoxide to a double bond. Thus, under nitrogen at 60°C, the substrate **1** affords solely the *trans*-1,3-dimethylnaphthopyran **2** in 5 min in virtually quantitative yield under the influence of potassium *t*-butoxide in dimethylformamide (Scheme 1).[1] Prolonging the reaction time produces an increasing proportion of the corresponding *cis*-isomer. There is little stereoselectivity in the analogous Lewis acid-catalyzed reactions.[2,3] As a consequence, these base-promoted cyclizations have found use in the stereoselective synthesis of natural products,[4] their derivatives,[5] and analogues.[6–10]

We have also identified[11] the structural features in the corresponding benzenoid analogues required for these remarkably smooth transformations. In the series of *ortho*-pentenylbenzyl alcohols **3**–**6** only the dimethoxy compound **3** cyclized smoothly (in a yield of 85%) to afford benzopyran **7** using butoxide as described above. The *ortho*-methoxybenzyl alcohol **4**, in which there is only one flanking methoxy group, provided a mixture from which the product **8** was formed in a yield of only 29% whereas neither **5**, the regioisomer of **4**, nor the analogue **6** without any methoxy substituent, cyclized at all under the standard conditions. This suggested that the ring-closure was facilitated through steric compression forcing the reacting centres together, although the involvement of electronic factors arising from the methoxy substituents at C1 and C4 could not be excluded. Literature precedents[12–14] exist for the formation of ethers, under basic conditions, from the reaction of an alcohol function with an unactivated double bond when the two are held in close proximity.



1 **2**

Scheme 1.

The present paper describes efforts to establish or exclude, in these cyclizations, any involvement of electronic factors arising from the two methoxy groups through replacing either one or both of these with an ethyl substituent, as such substitution would minimize spatial changes in the substrates. The three compounds **9**–**11**, analogues of the dimethyl ether **1**, were therefore synthesized and their reactions with butoxide in dimethylformamide at 60°C were investigated with respect to both substrate cyclization and product stereochemistry. Three additional substrates for ring closure, **12**–**14**, were also assembled. The first two of these were the hydroxymethyl analogues of **9** and **10** in which the replacement of the benzylic methyl with hydrogen might be expected

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to reduce crowding. The less sterically congested compound **14** lacking the ethyl substituent in **12** was also made.

Results and Discussion

Syntheses of the Substrates ***9–14***

A convenient synthesis of naphthalene **9** was achieved starting with naphthalene **15** obtained[15] from propiophenone using a Stobbe reaction. Selective hydrolysis of the acetate ester and allylation of the intermediate naphthol **16** afforded the ether **17**. Claisen rearrangement of this ether gave the tetrasubstituted naphthol **21** as shown by the upfield shift of the allyl methylene protons in the ^{1}H NMR spectrum, as well as the absence of the aromatic singlet present in its precursors **15**–**17**. This unstable naphthol **21** was *O*-methylated immediately to form the ether **22** and the ester function was reduced to give the alcohol **12**. Manganese dioxide oxidation of this alcohol provided the required aldehyde **23** in a yield of 63% and with an infrared carbonyl absorption of 1694 cm^{-1}. Treatment of the aldehyde **23** with methylmagnesium iodide gave the required alcohol **9**. Its overall yield from the Stobbe product **15** was 27% in seven steps.

The manganese dioxide oxidation of the alcohol **12** also produced a minor by-product that showed an infrared carbonyl absorption at 1746 cm^{-1} and, aside from the expected ethyl and methoxy resonances in the ^{1}H NMR spectrum, the only non-aromatic proton absorption was a sharp two-proton singlet at δ 5.38 with a corresponding signal at δ 68.5 in the ^{13}C NMR spectrum. This led to its formulation as either the γ-lactone **27** or its regioisomer in which the ethyl and methoxy substituents were reversed, and this was obtained in a yield of 17%.

The tetrasubstituted naphthol **21** was also used for the assembly of the required diethyl target **10**. Freshly prepared material obtained through pyrolysis of the allyl ether **17** was converted into the triflate **24** and this was followed by a smooth Stille reaction[16] with tetraethyltin in the presence of bistriphenylphosphinedichloropalladium(II) that provided the diethylnaphthyl ester derivative **25** in a yield of 96%. This ester was reduced to provide the alcohol **13**, which was in turn converted using manganese dioxide into the aldehyde **26** and the γ-lactone **28** in yields of 65 and 18%, respectively. The aldehyde **26** was transformed into the required alcohol **10** using methylmagnesium iodide in a reaction that also provided the vinylisonaphthofuran **29**, in yields of 63 and 20%, respectively. Furan **29** could arise (Scheme 2) through the abstraction of an allylic methylene proton from **26** by the Grignard reagent to give the highly resonance-stabilized enolate anion **30** that cyclized to the naphthofuran anion **31**. The alcohol **10** was formed in an overall yield of 22% in five steps from the allyl ether **17**, or in 17% in seven steps from the Stobbe product **15**.

For the γ-lactone **28**, only one structure is possible in view of the symmetry present through both substituents at C4 and C9 being ethyl groups, whereas for its analogue **27** described above such symmetry is absent, leading, therefore, to two possible regioisomers. In the formation of these γ-lactones from their precursor alcohols **12** and **13**, either one or other of the adjacent hydroxymethyl or allyl substituents on the naphthalene ring might undergo oxidation of the respective benzylic groups, the former to a carboxyl or the latter to an acrylyl (prop-2-enoyl) group, from which the observed γ-lactones would arise. Although it would be premature to hypothesize on a mechanism for the subsequent cyclization of any derived *ortho*-allylnaphthoic acid intermediate, it could be speculated that one possible mechanism involved the cyclization of the alternative *ortho*-acrylyl and hydroxymethyl groups, which would lead to the isomeric hemiacetal that would then undergo further oxidative loss of two carbons to yield the observed γ-lactones. Although this mechanism would lead to **28** and the regioisomer of **27**, the almost identical carbonyl absorptions for the two analogous γ-lactones suggest virtually no difference in conjugation with the carbonyl and, therefore, that ethyl is *peri*- to each carbonyl, as in the lactones **27** and **28**. Thus, on the available evidence, a choice between **27** and its regioisomer was not made. As this compound was an unwanted minor by-product, it was not investigated further.

The starting material chosen for the target alcohol **11** was the known[17] allyl ether **32**. Claisen rearrangement formed the intermediate tetrasubstituted naphthol **33** that was transformed smoothly into the triflate **34**. A Stille coupling was performed on this compound using tetraethyltin in the presence of bistriphenylphosphinedichloropalladium(II) whereupon the ethylated product **35** was obtained in a yield of 75%. Reduction of the ketone group with lithium aluminium hydride afforded the required alcohol **11** in high yield. The overall yield of this alcohol in the five steps from the allyl ether **32** was 57%.

The alcohol **14** was obtained from the benzaldehyde-derived Stobbe product **18**. This was readily transformed through the sequence **19**,[18] **20**, **36**, **37**, and **14** as for the conversion of the Stobbe-derived naphthalene **15** into **12**.

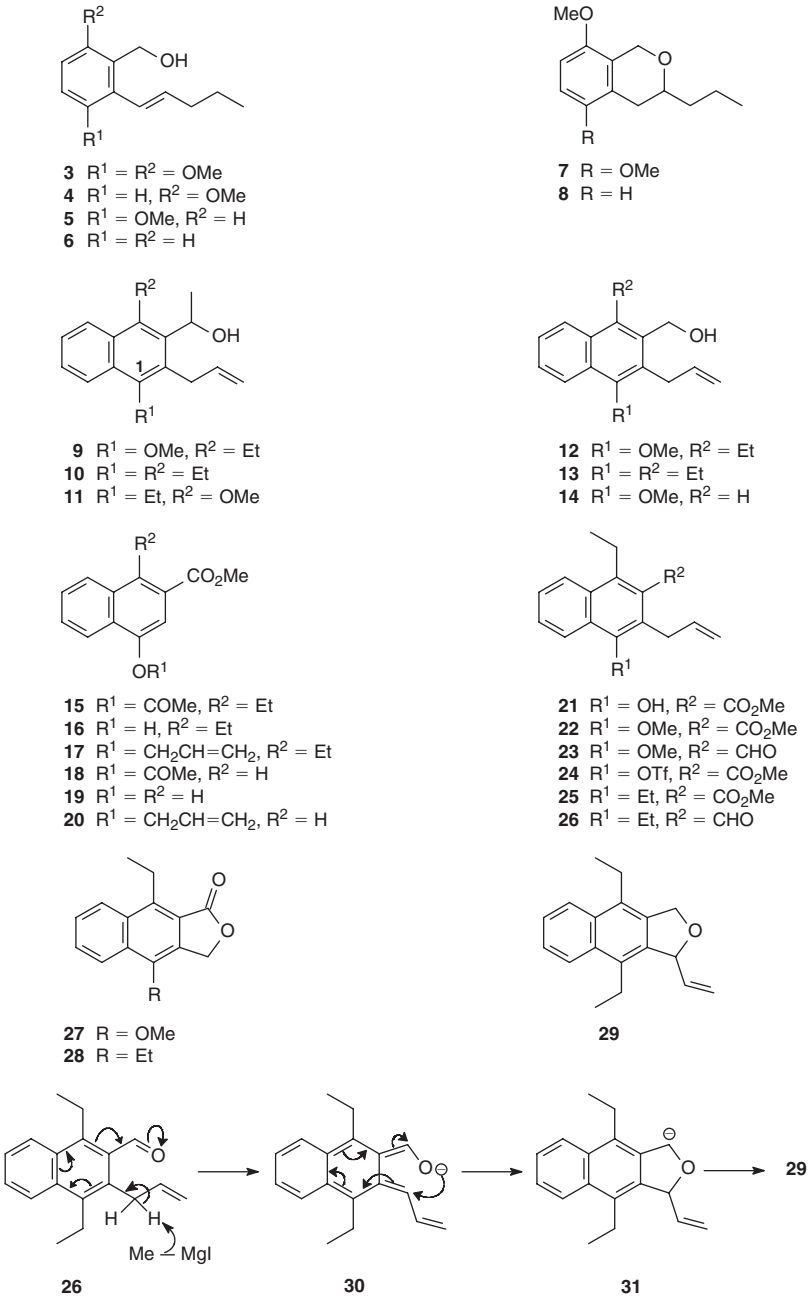
Cyclizations of the Substrates ***9–14***

The alcohol **9** was treated under nitrogen with potassium *tert*-butoxide (4 equivalents) in dry dimethylformamide at 60°C for 30 min, whereupon the *trans*-1,3-dimethylnaphthopyran **38** was obtained as a single product in a yield of 69%. Longer reaction times produced increasing quantities of the *cis*-isomer **41**, as can be seen from the data provided in Table 1 (entries 1–4). The two isomers were readily distinguished by the chemical shifts of their protons H3 as it is known[1] that for such benzo- and naphthopyrans, the values for the *trans*-isomers are at lower field (normally δ 3.9–4.3) than for the corresponding *cis*-isomers (normally δ 3.5–3.8). For the compounds **38** and **41**, these values were δ 4.26 and 3.65, respectively.

When the diethyl alcohol **10** was treated with *t*-butoxide in dimethylformamide at 60°C for 30 min (entry 5), the *trans*- and *cis*-naphthopyrans **39** and **42** were isolated in yields of 43 and 11%, and ^{1}H NMR spectroscopic H3 resonances appeared at δ 4.35 and 3.70, respectively. In addition, under these conditions, the double bond-conjugated alcohol **45** was isolated in 37% yield, as an inseparable 1:1 mixture of geometric *Z*- and *E*-isomers, as well as the phenanthrene **46** in a yield of 6%. Aside from that seen in the ^{1}H NMR spectrum, additional evidence for **45** as a pair of geometric isomers was observed in the ^{13}C NMR spectrum in which all seven sp^3-hybridized carbon atoms appeared as pairs of signals. The related spectrum for phenanthrene **46** showed only five sp^3 carbons.

The observation of the mixture of geometric isomers **45** suggested their intermediacy in the conversion of compound **10** into the naphthopyrans **39** and thence **42**. This was supported by repeating the experiment for 45 min (entry 6) when none of the conjugated compound **45** was obtained and the yields of the *trans*- and *cis*-naphthopyrans **39** and **42** were increased to 55 and 23%, respectively. In this case, the phenanthrene yield was also increased to 15%.

When the reaction temperature was reduced to 45°C and the time to 20 min (entry 7), the pyrans were not observed whereas



Scheme 2.

the mixture of conjugated alcohols **45** and the phenanthrene **46** were isolated in 60 and 5% yields, respectively, together with starting material (~10%) as estimated from the ^{1}H NMR spectrum because it could not be separated from the conjugated isomer **45**.

The conjugation of the allyl group in **10** to give the mixture **45** occurs through a base-induced proton migration (prototropic rearrangement) and a more extensive variant provides a plausible mechanism for the formation of phenanthrene **46** (Scheme 3). Two proton migrations, one in compound **10** and the other in intermediate **47**, would provide the hexatriene **48** that would undergo an electrocyclization to form **49** from which two molecules of hydrogen could be lost (or, alternatively, one hydrogen molecule could be lost earlier, from, e.g. **48**, and then follow a related route) to give **46**. This tentative mechanism would explain why such phenanthrenes were not observed for either of the *ortho*-methoxy allylnaphthalenes **1** or **9**, neither of which possessed an ethyl group at C1.

When the alcohol **11** was cyclized at 60°C for 40 min under nitrogen, the sole product, isolated in 70% yield, was the *trans*-naphthopyran **40** (entry 8). When the time was extended to 2 h (entry 9), the *trans*- and *cis*-products **40** and **43** were isolated in respective yields of 58 and 16%. When the same reaction was performed without the exclusion of air (entry 10), these *trans*- and *cis*-products were isolated in yields of 23 and 17%, respectively, together with an inseparable mixture of C4 epimeric alcohols **50** and **51** in a combined yield of 31% and in a respective ratio of 3:1. Such oxidation has been observed previously in the cyclization of naphthalene **1** to naphthopyran **2** in air, and also on treatment of the naphthopyran **2** with *t*-butoxide

Table 1. Reactions of alcohols 9–14 with potassium *t*-butoxide in dry dimethylformamide

Entry	Substrate	Conditions[A] (T [°C], t [min], atmosphere)	Naphthopyran product(s) (total yield %)	Naphthopyrans (individual yields %)	Naphthopyran ratio	Other products %
1[B]	**9**	60, 30, N_2	**38** (69)	**38** (69)	**38** (100):**41** (0)	–
2[C]	**9**	60, 45, N_2	**38** + **41** (68)	**38** (56) + **41** (12)	**38** (83):**41** (17)[C]	–
3[C]	**9**	60, 60, N_2	**38** + **41** (68)	**38** (50) + **41** (18)	**38** (73):**41** (27)[C]	–
4[B]	**9**	60, 120, N_2	**38** + **41** (69)	**38** (43) + **41** (26)	**38** (62):**41** (38)	–
5[B]	**10**	60, 30, N_2	**39** + **42** (54)	**39** (43) + **42** (11)	**39** (80):**42** (20)	**45** (37) + **46** (6)
6[B]	**10**	60, 45, N_2	**39** + **42** (78)	**39** (55) + **42** (23)	**39** (70):**42** (30)	**45** (0) + **46** (15)
7[B]	**10**	45, 20, N_2	**39** + **42** (0)	–	–	**45** (60) + **46** (5)
8[B]	**11**	60, 40, N_2	**40** (70)	**40** (70)	**40** (100):**43** (0)	–
9[B]	**11**	60, 120, N_2	**40** + **43** (74)	**40** (58) + **43** (16)	**40** (78):**43** (22)	–
10[B]	**11**	60, 120, air	**40** + **43** (40)	**40** (23) + **43** (17)	**40** (58):**43** (42)	**50** (23) + **51** (8)
11[B]	**12**	60, 120, N_2	**57** (69)	–	–	–
12[B]	**13**	60, 60, N_2	**58** (72)	–	–	–
13[B]	**14**	60, 7200 (120 h), air				**59** (25)

[A] In DMF, KO^{t}Bu (4 equiv.).
[B] Isolated yield of individual products.
[C] Yields determined by ^{1}H NMR analysis.

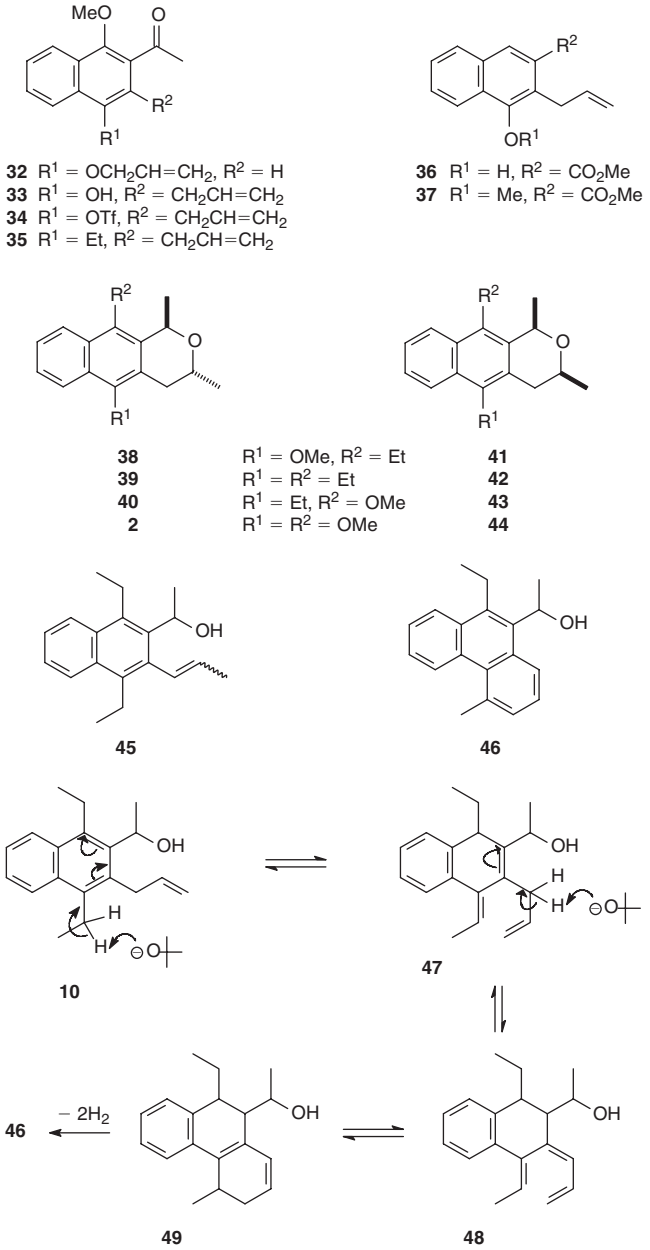
in dimethylformamide in air, when the alcohols **52** and **53** were obtained in a ratio of 1:4 in a yield of 35%.[1] The isolation of the alcohols **50** and **51** in yields comparable with those obtained in the related aerobic reactions of naphthalene **1** and naphthopyran **2** shows that an oxygen substituent at C5 of the naphthopyran is not required for the oxidative step.

In the ^{1}H NMR spectrum of the mixture of compounds **50** and **51**, both the major and minor diastereoisomers showed signals attributable to the same structural entities for two C4 epimeric alcohols, including, about the pyran rings, two methyl substituents and three one-proton heterocyclic protons. There were two anomalies, however, the first in that *both* products showed the small H3/H4 coupling constants of 2.6 and 1.3 Hz for the major and minor diastereoisomers respectively, both being consistent with small dihedral angles between these protons. In all other related 5,10-dimethoxynaphthopyrans formed in this manner,[1,4,5] the pseudoaxial alcohol (e.g. **52**) showed a small coupling constant of ∼2 Hz,[19] whereas in the corresponding pseudoequatorial alcohol (e.g. its epimer **53**), the related coupling constant was ∼7–8 Hz,[19] reflecting the large dihedral angle between the axial proton H3 and the pseudoaxial proton H4. Closer inspection revealed a second anomaly in that the chemical shift, δ 1.18, of the 3-CH_3 protons of the major diastereoisomer **50** was at significantly higher field than that normally shown,[4,5] e.g. at δ 1.43 for the C4 pseudoequatorial alcohol **53** (Table 2).

Individual assignments for the alcohols **50** and **51** were made through comparison of their ^{1}H NMR spectra with those of related compounds (Table 2). The minor diastereoisomer was assigned structure **51** as its resonances compared closely with those of the known[19] 5,10-dimethoxy analogue **52** (for which the only structural difference was the C5 substituent), particularly for those signals attributable to protons further from the respective C5 substituents (Table 2). The major diastereoisomer was assigned structure **50** in which the half-chair conformation of the dihydropyran ring was inverted relative to that in structure **53**,[19] for which the conformations are depicted in the respective part-structures **55** and **56**, respectively. This stereochemical assignment is supported through the comparison of the ^{1}H NMR spectra of compounds **50** and **54**, the latter being the only 2-benzopyran-4-ol hitherto known[20,21] to have this unusual inverted conformation for the pyran ring. In particular, there is close agreement between the chemical shifts for the 3-CH_3 doublets and the H3/H4 coupling constants, viz. δ 1.18 and 2.6 Hz for compound **50** and δ 1.21 and 2.2 Hz for compound **54**.

We have recently shown[20–22] that, for 2-benzopyrans such as **54**, the relative intensities of the 1,8- and 4,5-*peri*-interactions determine the conformation adopted by the dihydropyran half-chair. In the 5,10-dimethoxynaphthopyran case **53**, the C3 methyl prefers to adopt the equatorial orientation always hitherto found[23–25] for such 5,10-dioxygenated naphthopyrans, whereas the C1 methyl is pseudoaxial to minimize 1,10-*peri*-interactions and the C4 hydroxy group is pseudoequatorial, possibly aided to a minor degree through hydrogen bonding to the C5 oxygen. (That this hydrogen bonding is not strong is suggested by the chemical shift of the hydroxyl proton at $\delta \sim 4$). Replacement of the C5 oxygen steric requirement in **53** by that of the larger methylene group in analogue **50** is sufficient to require the inversion of the half-chair conformation, thereby allowing the C4 hydroxy group to adopt the pseudoaxial conformation to minimize this increased 4,5-*peri*-interaction at the expense of both the C3 methyl becoming axial and the C1 methyl pseudoequatorial, despite of the latter increasing the 1,10-*peri*-interaction. This is the first example of a dihydronaphthopyran adopting the inverted conformation of the half-chair. Furthermore, it is the first example, to our knowledge, of a dihydropyran in which the C1 methyl with a neighbouring *peri*-methoxy group adopts a pseudoequatorial orientation. In the three previous cases in which this inversion was observed in isolated products,[20–22] the *peri*-substituent was a hydrogen atom. We have also proposed[20,26] a transition state involving such a conformational inversion leading to the synthesis of a natural product derivative.

Two further observations are also noteworthy, first that the 1,3-*trans*, 3,4-*trans* (*trans*/*trans*) alcohol **50** predominated over the *trans*/*cis* epimer **51** in this oxidation process, as found[1,4,5] for all the pairs of C4 epimeric alcohols produced under the aerobic conditions of this reaction, in spite of the alternative conformation found in the product **50**. Second, a comparison



Scheme 3.

of the ratio of products obtained on reaction of naphthalene **11** under anaerobic and aerobic conditions while other conditions remained constant (Table 1, entries 9 and 10) shows that the yield of the *cis*-dimethylnaphthopyran **43** remains approximately constant, while that of the *trans* epimer **40** is reduced by 35% in the aerobic reaction and the combined yield of the C4 epimeric alcohols **50** and **51** rises by 31%. This observation strongly suggests that these alcohols are formed from the *trans*-pyran **40** once this is formed in solution, a view also supported by the fact that the only alcohols observed have the *trans*-1,3-dimethyl stereochemistry. This is consistent with the previously reported[1] conversion of pyran **2** into epimeric alcohols **52** and **53**, while **44**, the C1 epimer of **2**, was found not to react.[1]

Cyclization of alcohol **12** with *t*-butoxide under nitrogen for 2 h afforded the naphthopyran **57** as the sole product in a yield of 69% (entry 11). Likewise the alcohol **13** when treated under

Table 2. Chemical shifts (δ), coupling constants (J Hz), and instrument operating frequencies (MHz) for naphthopyrans 50–53 and benzopyran 54 determined in $CDCl_3$

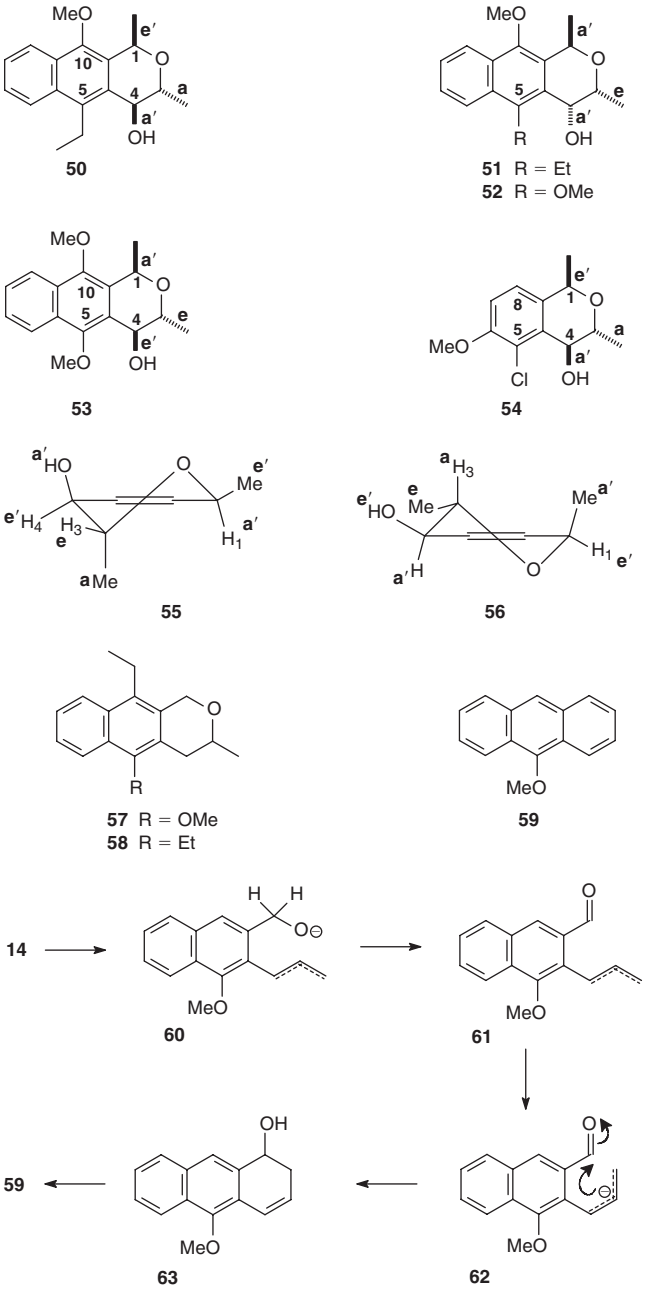
	50	51	52	53	54
MHz	200	200	100	100	300
3-CH_3	1.18	1.46	1.44	1.43	1.21
1-CH_3	1.68	1.63	1.61	1.70	1.53
10-OCH_3	3.87	3.89	3.90	3.90	–
H3	4.34	4.19	4.14	3.9–4.3	4.32
H4	4.68	4.60	4.78	4.81	4.63
H1	5.22	5.35	5.35	5.26	4.85
J H3/H4	2.6	1.3	2	7	2.2

the same conditions for 1 h (entry 12) gave the naphthopyran **58** in a yield of 72%.

By contrast, the less crowded analogue **14** did not react under the standard conditions with *t*-butoxide under nitrogen. In the presence of air, however, reaction did occur slowly (over 120 h) and 9-methoxyanthracene[27] **59** was isolated in 25% yield, for which the ^{1}H NMR spectrum showed only aromatic and methoxy protons in a ratio of 3:1. A possible mechanism (Scheme 4) involving an oxidation process would be the slow conversion of the alcohol **14** into the corresponding aldehyde **61** under the reaction conditions, presumably via the conjugated alkoxide anion **60**. Subsequent proton abstraction from the allyl substituent of **61** would lead to the cyclization of anion **62** and dehydration of the derived alcohol **63** to give the observed product **59**. Simpler mechanisms not involving an oxidative step would not explain the necessity for air.

Conclusions

The generality of the cyclizations of 2-allyl-3-(1′-hydroxyethyl)-1,4-dimethoxynaphthalenes with *tert*-butoxide in dimethylformamide to afford naphtho[2,3-*c*]pyrans has been extended through replacement of either or both of the methoxy groups with ethyl substituents. To make valid comparisons, the conditions used in the present study were identical to those originally reported for the cyclization of **1** to **2**.[1] Each of the naphthalenes **9**–**11** fully substituted in one ring cyclized, as did the corresponding hydroxymethyl derivatives **12** and **13**, whereas the trisubstituted analogue **14** failed to provide a naphthopyran. For the naphthalenes **9**–**11**, the product naphthopyrans were 1,3-disubstituted and the first-formed kinetic products were 1,3-*trans* while more prolonged treatment yielded increasing quantities of the corresponding thermodynamically favoured 1,3-*cis*-isomers, as was established for the conversion of the 1,4-dimethoxy compounds such as **1** into the 1,3-dimethylnaphthopyrans **2**.[1] The yields of the naphthopyrans obtained through cyclizations for the ethylated compounds **9**–**13** were of the order of 70% compared with generally higher yields (87% to virtually quantitative) for the various 1,4-dimethoxy substrates investigated.[1,4,5] The yields for the cyclizations of the 1-hydroxyethyl derivatives **9**–**11** and their hydroxymethyl analogues **12** and **13** were similar, suggesting that the extra methyl in the former group did not play a significant role in these reactions. The isolation of the two naphthopyran-4-ols **50** and **51** under aerobic conditions confirmed that a C5 oxygen was not required for their formation, a process that has previously been shown to occur through oxidation of the 1,3-*trans*-dimethylnaphthopyrans.[1,4] The conformation of the



Scheme 4.

Fig. 1.

dihydropyran ring in pyranol **50** is inverted relative to that in its C4 epimer **51**.

It appears that steric compression is essential for cyclizations to occur in good yields, for the limited number of substrates investigated, but that the involvement of as yet undefined electronic factors may be necessary to achieve the excellent yields observed for the formation of **2**[1] and related examples.[4–10] Further support for this conjecture is the recently reported[28] cyclization of the dimethoxy-substituted benzenoid system **64**, a regioisomeric analogue of **3**, to give solely the *trans*-1,3-dimethyl-2-benzopyran **65** (Fig. 1) in 96% yield at a somewhat increased temperature (80°C).

The Stille coupling reactions for the conversions of **24** into **25** and **34** into **35** occurred remarkably smoothly in spite of significant steric congestion.

Experimental

General

All ^{1}H and ^{13}C NMR spectra were measured on either a Varian 60, 80, XL 100, Gemini 200 MHz or a Bruker Advance DPX 300 MHz spectrometer for solutions in deuterochloroform as solvent using $CHCl_3$ as internal standard. Coupling constants J are quoted in Hz. Unless otherwise stated, IR spectra were measured for Nujol mulls on a Perkin-Elmer FTIR Paragon 2000 spectrometer. Mass spectra were recorded on a VG Micromass 16F mass spectrometer. Solvents of recrystallization are given in parentheses after melting points. Preparative layer chromatography (PLC) was performed on glass plates coated with Merck Kieselgel $60F_{254}$, whereas column chromatography refers to dry-packed columns using the same gel (70–230 mesh). Hexane refers to that fraction of bp 60–75°C and ether to diethyl ether. The phrase 'residue obtained on workup' refers to the residue obtained when the organic layer was separated, dried ($MgSO_4$), and the solvent evaporated under reduced pressure. In NMR spectra, assignments with the same superscript may be interchanged.

Methyl 4-Ethyl-1-hydroxy-3-naphthoate ***16***

The acetate **15**[15] (2.37 g, 8.71 mmol) was dissolved in a sodium hydroxide solution (0.75%) in methanol (150 mL) and subsequently stirred at 25°C for 30 min and then acidified with hydrochloric acid (0.5 M). After removal of the methanol under reduced pressure, the thick mobile residue was diluted with water (150 mL) and exhaustively extracted with ethyl acetate. The residue obtained on workup was chromatographed (30% ethyl acetate/hexane) to give *naphthoate* **16** (2.00 g, 100%) as white crystals, mp 143–144.5°C (isopropyl alcohol) (Found: C 73.1, H 6.2. $C_{14}H_{14}O_3$ requires C 73.1, H 6.2%). ν_{max}/cm^{-1} 3320, 1725. δ_H (100 MHz) 1.35 (3H, t, J 7.8, CH_2CH_3), 3.31 (2H, q, J 7.8, CH_2CH_3), 3.95 (3H, s, OCH_3), 6.01 (1H, s, 1-OH), 7.23 (1H, s, H2), 7.60 (2H, m, H6, H7), 8.18 (1H, m, H5) and 8.28 (1H, m, H8). δ_C 15.9 (CH_2CH_3), 22.5 (CH_2CH_3), 52.3 (OCH_3), 108.5 (C2), 122.5 (C6)[a], 125.4 (C7)[a], 126.67 (C3)[b], 126.73 (C5)[c], 126.9 (C4)[b], 127.1 (C8)[c], 133.1 (C4a)[d], 135.8 (C8a)[d], 149.8 (C1) and 169.2 (C=O). m/z 230 (M^+, 93%), 215 (100), 171 (34), 170 (26), 141 (25), 115 (36).

Methyl 1-Allyloxy-4-ethyl-3-naphthoate ***17***

Naphthoate **16** (2.0 g, 8.7 mmol) dissolved in acetone (150 mL) was treated with anhydrous potassium carbonate (3.60 g, 26.0 mmol) and allyl bromide (2.24 mL, 3.13 g, 25.9 mmol) and the resulting mixture was stirred vigorously and heated under reflux for 14 h. The cooled solution was filtered and the acetone was removed under reduced pressure. The residue was dissolved in ether (200 mL) and washed with water, after which the residue obtained on workup was chromatographed (5% ethyl acetate/hexane) to yield the *naphthoate* **17** (1.83 g, 78%) as white plates, mp 59–60°C (hexane) (Found: C 75.7, H 6.8. $C_{17}H_{18}O_3$ requires C 75.6, H 6.7%). ν_{max}/cm^{-1} 1723. δ_H (100 MHz) 1.37

(3H, t, *J* 7.2, CH_2CH_3), 3.32 (2H, q, *J* 7.2, CH_2CH_3), 3.97 (3H, s, OCH_3), 4.74 (2H, dm, *J* 5.2, $CH_2CH{=}CH_2$), 5.35 (1H, dm, *J* 10.6, *cis* $CH{=}CH_2$), 5.54 (1H, dm, *J* 17.2, *trans* $CH{=}CH_2$), 6.40 (1H, m, $CH_2CH{=}CH_2$), 7.15 (1H, s, H2), 7.60 (2H, m, H6 and H7), 8.18 (1H, m, H5), 8.38 (1H, m, H8). δ_C 15.9 (CH_2CH_3), 22.5 (CH_2CH_3), 52.2 (OCH_3), 69.1 (OCH_2), 105.1 (C2), 117.6 ($CH{=}CH_2$), 122.7 (C6)[a], 125.2 (C7)[a], 126.7 (C5)[a], 127.0 (C3)[b], 127.1 (C8)[a], 127.8 (C4)[b], 132.9 (C4a)[c], 133.2 ($CH{=}CH_2$), 135.7 (C8a)[c], 152.5 (C1) and 169.2 (C=O). *m/z* 270 (M^+, 86%), 229 (69), 197 (100), 169 (68), 141 (46).

Methyl 2-Allyl-4-ethyl-1-hydroxy-3-naphthoate ***21***

Allyloxy ester **17** (786 mg, 2.91 mmol) was pyrolyzed at 180–190°C as a neat oil under nitrogen in an oil bath for 1 h. The darkened residue was chromatographed (15% ethyl acetate/hexane) to yield the *naphthol* **21** (673 mg, 86%) as an unstable oil (darkened on standing; both ^{1}H NMR spectra and TLC of this naphthol showed changes after standing at 25°C for 24 h) (Found: C 75.5, H 6.8. $C_{17}H_{18}O_3$ requires C 75.6, H 6.7%). ν_{max}/cm^{-1} 3490, 1732. δ_H (100 MHz) 1.31 (3H, t, *J* 7.4, CH_2CH_3), 2.95 (2H, q, *J* 7.4, CH_2CH_3), 3.46 (2H, dm, *J* 6.2, $ArCH_2$), 3.95 (3H, s, OCH_3), 5.24 (1H, dq, *J* 19.0 and 2.1, *trans* $CH{=}CH_2$), 5.28 (1H, dq, *J* 11.2 and 2.1, *cis* $CH{=}CH_2$), 5.62 (1H, s, 1-OH), 6.06 (1H, m, $CH{=}CH_2$), 7.54 (2H, m, H6 and H7), 8.01 (1H, m, H5) and 8.25 (1H, m, H8). δ_C 15.9 (CH_2CH_3), 23.8 (CH_2CH_3), 33.3 ($CH_2CH{=}CH_2$), 52.1 (OCH_3), 117.1 ($CH{=}CH_2$), 122.3 (C6)[a], 124.4 (C7)[a], 125.8 (C2)[b], 126.0 (C4)[b], 126.5 (C5)[a], 126.6 (C8)[a], 129.8 (C3)[b], 131.3 (C4a)[c], 132.2 (C8a)[c], 135.7 ($CH{=}CH_2$), 148.8 (C1) and 170.8 (C=O). *m/z* 270 (M^+, 100%), 255 (89), 239 (15), 223 (26).

Methyl 2-Allyl-4-ethyl-1-methoxy-3-naphthoate ***22***

To freshly prepared naphthol **21** (563 mg, 2.09 mmol) dissolved in acetone (100 mL) was added potassium carbonate (863 mg, 6.25 mmol) and dimethyl sulfate (0.61 mL, 813 mg, 6.26 mmol) and the mixture was heated under reflux with vigorous stirring under nitrogen for 2 h. The cooled mixture was filtered, the acetone removed under reduced pressure, and the residue taken up in ether. The organic extract was washed successively with ammonia (25%), water, hydrochloric acid (1 M), and finally water. The residue obtained on workup was chromatographed (5% ethyl acetate/hexane) to yield the *naphthoate* **22** as a light yellow oil (516 mg, 87%) (Found: C 76.1, H 7.1. $C_{18}H_{20}O_3$ requires C 76.1, H 7.1%). ν_{max}/cm^{-1} 1726. δ_H (100 MHz) 1.32 (3H, t, *J* 7.8, CH_2CH_3), 2.98 (2H, q, *J* 7.8, CH_2CH_3), 3.60 (2H, dm, *J* 6.2, $ArCH_2$), 3.92 (6H, s, 2 × OCH_3), 5.04 (1H, dq, *J* 16.8 and 2.0, *trans* $CH{=}CH_2$), 5.05 (1H, dq, *J* 11.4 and 2.0, *cis* $CH{=}CH_2$), 5.96 (1H, m, $CH{=}CH_2$), 7.54 (2H, m, H6 and H7) and 8.10 (2H, m, H5 and H8). δ_C 15.8 (CH_2CH_3), 23.9 (CH_2CH_3), 32.0 ($ArCH_2$), 51.9 ($ArOCH_3$), 62.5 (CO_2CH_3), 115.7 ($CH{=}CH_2$), 122.9 (C6)[a], 124.6 (C2)[b], 124.9 (C7)[a], 126.3 (C5)[a], 126.6 (C8)[a], 128.8 (C4)[b], 131.7 (C4a)[c], 132.7 (C3)[b], 133.7 (C8a)[c], 136.7 ($CH{=}CH_2$), 152.7 (C1), 170.4 (C=O). *m/z* 284 (M^+, 100%), 269 (36), 237 (36).

2-Allyl-4-ethyl-3-hydroxymethyl-1-methoxynaphthalene ***12***

A solution of the ester **22** (1.63 g, 5.74 mmol) in ether (100 mL) was added dropwise to a stirred slurry of lithium aluminium hydride (436 mg, 11.5 mmol) in ether (50 mL) over 15 min at 25°C. Stirring was continued for a further 5 h and then the mixture was heated under reflux for an additional 1.5 h, after which sufficient saturated ammonium chloride solution was slowly added to the cooled mixture to destroy the excess of reagent. The residue obtained on workup was chromatographed (30% ethyl acetate/hexane) to yield the *naphthyl alcohol* **12** (1.27 g, 86%) as white crystals, mp 85–86.5°C (hexane) (Found: C 79.6, H 8.0. $C_{17}H_{20}O_2$ requires C 79.7, H 7.9%). ν_{max}/cm^{-1} 3360. δ_H (100 MHz) 1.33 (3H, t, *J* 7.8, CH_2CH_3), 2.05 (1H, s, 1-OH), 3.23 (2H, q, *J* 7.8, CH_2CH_3), 3.80 (2H, dm, *J* 5.4, $ArCH_2$), 3.90 (3H, s, OCH_3), 4.85 (2H, s, $ArCH_2OH$), 4.90 (1H, dq, *J* 18.0 and 2.1, *trans* $CH{=}CH_2$), 5.09 (1H, dq, *J* 10.2 and 2.1, *cis* $CH{=}CH_2$), 6.10 (1H, m, $CH{=}CH_2$), 7.50 (2H, m, H6 and H7) and 8.15 (2H, m, H5 and H8). δ_C 16.3 (CH_2CH_3), 21.7 (CH_2CH_3), 30.7 ($CH_2CH{=}CH_2$), 59.4 (OCH_3), 62.4 ($ArCH_2OH$), 115.5 ($CH{=}CH_2$), 122.8 (C6)[a], 124.8 (C7)[a], 125.9 (C5)[a], 126.0 (C8)[a], 127.3 (C2)[b], 128.2 (C3)[b], 132.4 (C4)[b], 134.4 (C4a)[c], 136.8 (C8a)[c], 139.1 ($CH{=}CH_2$) and 152.8 (C1). *m/z* 256 (M^+, 42%), 235 (100), 234 (87), 223 (48).

2-Allyl-4-ethyl-1-methoxynaphthalene-3-carbaldehyde ***23*** *and Either 9-Ethyl-4-methoxy-1,3-dihydronaphtho[2,3-c]furan-1(3H)-3-one* ***27*** *or its Regioisomer 4-Ethyl-9-methoxy-1,3-dihydronaphtho[2,3-c]furan-1(3H)-3-one*

To a solution of alcohol **12** (500 mg, 1.95 mmol) in benzene (200 mL) was added activated manganese dioxide (4.0 g, 4.6 mmol) and the resultant mixture was heated under reflux with vigorous stirring for 5 h. The cooled mixture was filtered and the residue obtained on workup was chromatographed (10% ethyl acetate/hexane) to afford the *aldehyde* **23** (310 mg, 63%) as orange crystals, mp 127–128°C (hexane) (Found: C 80.5, H 7.3. $C_{17}H_{18}O_2$ requires C 80.3, H 7.1%). ν_{max}/cm^{-1} 1694. δ_H (200 MHz) 1.37 (3H, t, *J* 7.2, CH_2CH_3), 3.34 (2H, q, *J* 7.2, CH_2CH_3), 3.91 (5H, sharp m, OCH_3 and $CH_2CH{=}CH_2$), 4.90 (1H, dq, *J* 17.2 and 2.2, *trans* $CH{=}CH_2$), 5.09 (1H, dq, *J* 10.2 and 2.2, *cis* $CH{=}CH_2$), 6.10 (1H, m, $CH{=}CH_2$), 7.60 (2H, m, H6 and H7), 8.19 (2H, m, H5 and H8) and 10.63 (1H, s, CHO). δ_C 16.4 (CH_2CH_3), 21.3 (CH_2CH_3), 29.7 ($CH_2CH{=}CH_2$), 62.5 (OCH_3), 116.0 ($CH{=}CH_2$), 123.1 (C6)[a], 125.4 (C7)[a], 126.7 (C5)[a], 127.0 (C2)[b], 128.1 (C8)[a], 130.3 (C4)[b], 131.8 (C3)[b], 132.9 (C4a)[c], 137.7 ($CH{=}CH_2$), 140.8 (C8a)[c], 152.9 (C1) and 195.0 (C=O). *m/z* 254 (M^+, 20%), 253 (100), 223 (80), 225 (43), 213 (80). Further elution afforded the *γ-lactone* **27** (80 mg, 17%) as light red crystals, mp 148–149°C (hexane) (Found: C 74.5, H 5.9; M^+ 242.0938. $C_{15}H_{14}O_3$ requires C 74.4, H 5.9%; M 242.0943). ν_{max}/cm^{-1} 1746. δ_H (200 MHz) 1.30 (3H, t, *J* 7.4, CH_2CH_3), 2.96 (2H, q, *J* 7.4, CH_2CH_3), 4.33 (3H, s, OCH_3), 5.38 (2H, s, $ArCH_2O$), 7.57 (1H, tm, *J* 8.4, 6H), 7.70 (1H, tm, *J* 8.4, H7), 8.04 (1H, dm, *J* 8.4, H5), 8.43 (1H, dm, *J* 8.4, H8). δ_C 14.4 (CH_2CH_3), 21.6 (CH_2CH_3), 63.8 (OCH_3), 68.5 ($ArCH_2O$), 110.6 (C3a)[a], 123.5 (C6)[b], 124.9 (C7)[b], 125.9 (C5)[b], 128.2 (C9a)[a], 128.6 (C9)[a], 129.4 (C8)[b], 135.9 (C4a)[c], 138.4 (C8a)[c], 156.3 (C4), 169.2 (C=O).

2-Allyl-4-ethyl-3-(1′-hydroxyethyl)-1-methoxynaphthalene ***9***

Into a freshly prepared solution of methyl magnesium iodide (from magnesium (85 mg, 3.54 mmol) and methyl iodide (500 mg, 3.54 mmol)) in ether (25 mL) was dripped aldehyde **23** (300 mg, 1.18 mmol) in ether (25 mL) over 15 min under nitrogen with stirring at 25°C. After an additional stirring period of 1 h, the reaction mixture was treated with sufficient saturated aqueous ammonium chloride to destroy the excess of reagent and water (100 mL) was added and the aqueous solution then extracted with

ether. The residue obtained on workup was chromatographed (30% ethyl acetate/hexane) to afford the *naphthyl alcohol* **9** as a thick oil (270 mg, 85%) (Found: C 80.0, H 8.1. $C_{18}H_{22}O_2$ requires C 80.0, H 8.2%). ν_{max}/cm^{-1} 3420. δ_H (200 MHz) 1.35 (3H, t, *J* 7.4, CH_2CH_3), 1.64 (3H, d, *J* 7.0, [CH(OH)CH_3]), 1.94 (1H, s, [CH(O*H*)CH_3]), 3.37 (2H, q, *J* 7.4, CH_2CH_3), 3.80 (2H, m, ArCH_2CH=CH_2), 3.89 (3H, s, OCH_3), 4.87 (1H, dq, *J* 17.2 and 2.2, *trans* CH=CH_2), 5.07 (1H, dq, *J* 10.2 and 2.2, *cis* CH=CH_2), 5.53 (1H, q, *J* 7.0, [C*H*(OH)CH_3]), 6.09 (1H, m, C*H*=CH_2), 7.49 (2H, m, H6 and H7), 8.09 (2H, m, H5 and H8). δ_C 16.4 (CH_2CH_3), 21.7 [CH(OH)*C*H_3], 23.5 (CH_2CH_3), 31.0 (CH_2CH=CH_2), 62.2 (OCH_3), 68.0 [*C*H(OH)CH_3], 115.2 (CH=CH_2), 122.8 (C6)[a], 124.8 (C7)[a], 125.5 (C5)[a], 125.8 (C8)[a], 126.4 (C2)[b], 127.6 (C3)[b], 132.9 (C4)[b], 135.2 (C4a)[c], 138.8 (*C*H=CH_2), 139.1 (C8a)[c], 153.1 (C1). *m/z* 270 (M^+, 29%), 252 (100), 225 (63), 223 (36), 221 (52), 211 (60).

Methyl 2-Allyl-4-ethyl-1-trifluoromethanesufonyloxy-3-naphthoate ***24***

Allyloxy ester **17** (2.8 g, 10.4 mmol) was pyrolyzed at 180–200°C under nitrogen with stirring for 1 h, after which the cooled darkened material was dissolved in pyridine (16 mL) and stirred under nitrogen at this temperature. Trifluoromenthanesulfonic anhydride (3.5 g, 12.4 mmol) was then dripped into the solution and stirring maintained for a further 15 min and then allowed to reach 25°C at which temperature stirring was continued for 12 h. The residue obtained on workup as described earlier was chromatographed (10% ethyl acetate/hexane) and this afforded the *naphthyl triflate* **24** as a pale yellow oil (3.33 g, 80%) (Found: C 53.8, H 4.1. $C_{18}H_{17}F_3O_5S$ requires C 53.7, H 4.3%). ν_{max}/cm^{-1} 1727. δ_H (200 MHz) 1.35 (3H, t, *J* 7.2, CH_2CH_3), 3.02 (2H, q, *J* 7.2, CH_2CH_3), 3.70 (2H, dm, *J* 6.2, ArCH_2), 3.72 (3H, s, OCH_3), 5.09 (1H, dq, *J* 16.2 and 2.2, *trans* CH=CH_2), 5.10 (1H, dq, *J* 11.0 and 2.2, *cis* CH=CH_2), 5.90 (1H, m, C*H*=CH_2) 7.64 (2H, m, H6 and H7), 8.12 (2H, m, H5 and H8). δ_C 15.5 (CH_2CH_3), 24.1 (CH_2CH_3), 32.6 (CH_2CH=CH_2), 52.2 (OCH_3), 117.0 (CH=*C*H_2), 122.3 (q, *J* 318.0, CF_3), 124.8 (C6)[a], 127.2 (C2)[b], 127.3 (C3)[b], 127.5 (C7)[a], 127.7 (C4)[b], 128.3 (C5)[a], 131.6 (C4a)[c], 132.5 (C8a)[c], 134.2 (C8)[a], 138.8 (*C*H=CH_2), 141.4 (C1), 169.0 (C=O). *m/z* 403 ($M^+ + 1$, 27%), 402 (M^+, 23), 269 (100), 238 (70), 210 (60).

Methyl 2-Allyl-1,4-diethyl-3-naphthoate ***25***

To a solution of triflate **24** (2.13 g, 5.3 mmol) in dry dimethylformamide (80 mL) containing bis(triphenylphosphine)dichloropalladium(II) (60 mg, 0.09 mmol), lithium chloride (1.0 g, 23.8 mmol), and 2,6-di-*t*-butyl-4-methylphenol (50 mg, 0.23 mmo1) was added tetraethyltin (5.13 g, 21.9 mmol) and the resulting solution was stirred and heated at 85°C under nitrogen for 96 h and then worked up as described before to afford the *diethylnaphthalene* **25** as a light yellow oil (1.43 g, 96%) (Found: C 80.7, H 7.7. $C_{19}H_{22}O_2$ requires C 80.8, H 7.9%). ν_{max}/cm^{-1} 1731. δ_H (200 MHz) 1.32 (6H, m, CH_2CH_3), 3.05 (4H, m, CH_2CH_3), 3.53 (2H, dm, *J* 5.8, CH_2CH=CH_2), 3.95 (3H, s, OCH_3), 5.00 (1H, dq, *J* 17.0 and 2.1, *trans* CH=CH_2), 5.06 (1H, dq, *J* 10.0 and 2.1, *cis* CH=CH_2), 6.00 (1H, m, C*H*=CH_2), 7.53 (2H, m, H6 and H7) and 8.08 (2H, m, H5 and H8). δ_C 15.0 and 15.6 (CH_2CH_3), 21.4 and 24.1 (CH_2CH_3), 35.3 (CH_2CH=CH_2), 51.8 (OCH_3), 115.5 (CH=*C*H_2), 124.7 (C6)[a], 124.9 (C7)[a], 125.4 (C5)[a], 126.3 (C8)[a], 126.5 (C1)[b], 129.4 (C2)[b], 130.4 (C4)[b], 132.5 (C3)[b], 135.0 (C4a)[c], 136.6 (*C*H=CH_2), 137.3 (C8a)[c], 171.4 (C=O). *m/z* 282 (M^+, 24%), 251 (100), 223 (60), 182 (48).

2-Allyl-1,4-diethyl-3-hydroxymethylnaphthalene ***13***

To a slurry of lithium aluminium hydride (900 mg, 23.7 mmol) in ether (100 mL) was added dropwise with stirring a solution of ester **25** (4.18 g, 14.82 mmol) in ether (100 mL) over 20 min after which the mixture was stirred and heated under reflux for 18 h. Workup as described earlier afforded the *naphthyl alcohol* **13** (2.63 g, 70%) as white cubes, mp 121–122°C (hexane) (Found: C 84.7, H 8.5; M^+ 254.1675. $C_{18}H_{22}O$ requires C 85.0, H 8.7%; M 254.1671). ν_{max}/cm^{-1} 3335. δ_H 1.32 (6H, m, CH_2CH_3), 1.56 (1H, s, CH_2O*H*), 3.07 (2H, q, *J* 7.2, CH_2CH_3), 3.26 (2H, q, *J* 7.0, CH_2CH_3), 3.78 (2H, m, CH_2CH=CH_2), 4.82 (1H, dq, *J* 17.2 and 2.2, *trans* CH=CH_2), 4.88 (2H, s, CH_2OH), 5.80 (1H, dq, *J* 10.2 and 2.2, *cis* CH=CH_2), 6.20 (1H, m, C*H*=CH_2), 7.51 (2H, m, H6 and H7), 8.10 (2H, m, H5 and H8). δ_C 15.3 and 16.3 (CH_2CH_3), 22.0 and 22.1 (CH_2CH_3), 33.5 (CH_2CH=CH_2), 59.9 (ArCH_2OH), 115.7 (CH=*C*H_2), 124.8 (C6)[a], 125.1 (C7)[a], 125.2 (C8)[a], 125.9 (C5)[a], 131.4 (C1)[b], 132.3 (C2)[b], 133.1 (C3)[b], 134.3 (C4)[b], 137.2 (C4a)[c], 138.3 (*C*H=CH_2), 138.5 (C8a)[c].

2-Allyl-1,4-diethylnaphthalene-3-carbaldehyde ***26*** *and 4,9-Diethyl-1,3-dihydronaphtho[2,3-c]furan-3-one* ***28***

To a solution of alcohol **13** (420 mg, 1.65 mmol) in benzene (120 mL) was added activated manganese dioxide (3.0 g, 3.5 mmol) and the mixture was stirred and heated under reflux for 4 h and worked up as described above to yield *aldehyde* **26** as a thick orange oil (270 mg, 65%) (Found: C 85.5, H 7.7. $C_{18}H_{20}O$ requires C 85.7, H 8.0%). ν_{max}/cm^{-1} 1695. δ_H (200 MHz) 1.34 (6H, m, CH_2CH_3), 3.10 (2H, q, *J* 7.8, CH_2CH_3), 3.28 (2H, t, *J* 7.8, CH_2CH_3), 3.78 (2H, m, CH_2CH=CH_2), 4.86 (1H, dq, *J* 17.2 and 2.1, *trans* CH=CH_2), 5.10 (1H, dq, *J* 10.2 and 2.1, *cis* CH=CH_2), 6.10 (1H, m, C*H*=CH_2), 7.58 (2H, m, H6 and H7), 8.12 (1H, dm, *J* 8.2, H5), 8.22 (1H, dm, *J* 8.2, H8), 10.63 (1H, s, CHO). δ_C 15.1 and 16.3 (CH_2CH_3), 21.4 and 21.7 (CH_2CH_3), 33.1 (CH_2CH=CH_2), 116.2 (CH=*C*H_2), 124.9 (C6)[a], 125.5 (C7)[a], 125.8 (C5)[a], 127.7 (C8)[a], 131.4 (C1)[b], 131.9 (C2)[b], 132.8 (C3)[b], 133.9 (C4)[b], 137.0 (*C*H=CH_2), 137.6 (C4a)[c], 141.3 (C8a)[c], and 196.0 (C=O). *m/z* 252 (M^+, 90%), 251 (100), 223 (64), 211 (36). Further elution afforded the *γ-lactone* **28** (73 mg, 18%) as olive-green needles, mp 150–151°C (hexane) (Found: C 79.9, H 6.5; $[M]^+$ 240.1130. $C_{16}H_{16}O_2$ requires C 80.0, H 6.7%; M 240.1150). ν_{max}/cm^{-1} 1745. δ_H (200 MHz) 1.33 (6H, m, CH_2CH_3), 3.02 (2H, q, *J* 7.2, CH_2CH_3), 3.69 (2H, q, *J* 7.6, CH_2CH_3), 5.38 (2H, s, ArCH_2O), 7.66 (2H, m, H6 and H7), 8.14 (1H, dm, *J* 8.0, H5), 8.32 (1H, dm, *J* 8.1, H8). δ_C 14.5 and 15.8 (CH_2CH_3), 19.4 and 22.0 (CH_2CH_3), 67.9 (ArCH_2O), 119.0 (C3a)[a], 124.3 (C6)[b], 126.2 (C7)[b], 126.3 (C5)[b], 128.4 (C8)[b], 131.6 (C9a)[a], 132.5 (C4)[a], 134.5 (C9)[a], 137.8 (C4a)[c], 143.7 (C8a)[c], 171.5 (C=O).

4,9-Diethyl-1-vinyl-1,3-dihydronaphtho[2,3-c]furan ***29*** *and 2-Allyl-1,4-diethyl-3-(1′-hydroxyethyl)naphthalene* ***10***

Into a freshly prepared solution of methyl magnesium iodide (from Mg (43 mg, 1.77 mmol) and methyl iodide (254 mg, 1.79 mmol)) in ether (30 mL) was added aldehyde **26** (150 mg, 0.59 mmol) as described before and the residue obtained on workup was chromatographed (10% ethyl acetate/hexane) to afford the *naphthofuran* **29** as a thick oil (30 mg, 20%) (Found: M^+ 252.1519. $C_{18}H_{20}O$ requires M 252.1514). ν_{max}/cm^{-1} 1245. δ_H (200 MHz) 1.28 (6H, m, CH_2CH_3), 2.99 (4H, m, CH_2CH_3),

5.21 (1H, d, *J* 12.6, pseudoaxial H3), 5.27 (1H, dm, *J* 10.1, *cis* CH=C*H*$_2$), 5.33 (1H, *J* 12.6, pseudoequatorial H3), 5.47 (1H, dm, *J* 17.0, *trans* CH=C*H*$_2$), 5.82 (1H, dm, *J* 7.8, H1), 6.04 (1H, m, C*H*=CH$_2$), 7.50 (2H, m, H6 and H7) and 8.06 (2H, m, H5 and H8). δ_C 14.6 and 14.9 (CH$_2$*C*H$_3$), 22.2 and 23.2 (*C*H$_2$CH$_3$), 71.6 (C3), 85.2 (C1), 116.9 (CH=*C*H$_2$), 124.7 (C6)[a], 124.5 (C7)[a], 125.1 (C8)[a], 125.3 (C5)[a], 130.8 (C4)[b], 132.1 (C9)[b], 132.2 (C3a)[b], 132.3 (C9a)[b], 135.5 (C4a)[c], 136.2 (C9a)[c], 137.6 (*C*H=CH$_2$). Further elution (30% ethyl acetate/hexane) gave the *naphthyl alcohol* **10** as a thick viscous oil (100 mg, 63%) (Found: C 84.9, H 8.7. $C_{19}H_{24}O$ requires C 85.0, H 9.0%). ν_{max}/cm^{-1} 3320. δ_H 1.32 (200 MHz) (6H, m, CH$_2$C*H*$_3$), 1.67 (3H, d, *J* 6.8, CH(OH)C*H*$_3$), 1.84 (1H, s, [CH(O*H*)CH$_3$]), 3.06 (2H, q, *J* 7.8, C*H*$_2$CH$_3$), 3.38 (2H, ill-defined q, C*H*$_2$CH$_3$), 3.78 (2H, m, C*H*$_2$CH=CH$_2$), 4.80 (1H, dq, *J* 17.2 and 2.1, *trans* CH=C*H*$_2$), 5.09 (1H, dq, *J* 10.2 and 2.1, *cis* CH=C*H*$_2$), 5.59 (1H, q, *J* 6.8, C*H*(OH)CH$_3$), 6.18 (1H, m, C*H*=CH$_2$), 7.49 (2H, m, H6 and H7), 8.14 (2H, m, H5 and H8). δ_C 15.3 and 16.3 (CH$_2$*C*H$_3$), 21.9 and 22.0 (*C*H$_2$CH$_3$), 23.4 [CH(OH)*C*H$_3$], 33.8 (*C*H$_2$CH=CH$_2$), 68.3 [*C*H(OH)CH$_3$], 115.6 (CH=*C*H$_2$), 124.7 (C6)[a], 125.0 (C7)[a], 125.1 (C5)[a], 125.4 (C8)[a], 131.7 (C1)[b], 131.8 (C2)[b], 131.9 (C3)[b], 136.7 (C4)[b], 137.8 (C4a)[c], 138.4 (C8a)[c], 138.6 (*C*H=CH$_2$). *m*/*z* 268 (M$^+$, 19%), 250 (100), 223 (46), 221 (33), 209 (32).

3-Acetyl-2-allyl-4-methoxy-1-trifluoromethanesulfonyloxynaphthalene ***34***

2-Acetyl-4-allyloxy-1-methoxynaphthalene **32**[17] (588 mg, 2.29 mmol) was pyrolyzed at 175°C in an oil bath under nitrogen for 7 h to afford the intermediate naphthol **33**. The cooled residue was dissolved in dry pyridine (2.5 mL) and further cooled to 0°C at which time trifluoromethanesulfonic anhydride (676 mg, 2.40 mmol) was added dropwise under nitrogen and the resulting solution was stirred for an additional 5 min. This was allowed to warm to 25°C and then stirred for a further 18 h after which it was quenched with water (100 mL) and the aqueous mixture was extracted with ether. The ether extracts were washed consecutively with water, hydrochloric acid (1 M, thrice), water, and brine. The residue obtained on workup was chromatographed (10% ethyl acetate/hexane) to afford the *naphthyl triflate* **34** as a light yellow oil (703 mg, 83%) (Found: C 52.8, H 4.1. $C_{17}H_{15}F_3O_5S$ requires C 52.6, H 3.9%). ν_{max}/cm^{-1} 1703. δ_H (300 MHz) 2.62 (3H, s, COCH$_3$), 3.67 (2H, dt, *J* 6.1 and 1.6, ArCH$_2$), 3.92 (3H, s, OCH$_3$), 4.99 (1H, dq, *J* 17.1 and 1.6, *trans* CH=C*H*$_2$), 5.11 (1H, dq, *J* 10.2 and 1.6, *cis* CH=C*H*$_2$), 5.85 (1H, ddt, *J* 17.1, 10.2 and 6.1, C*H*=CH$_2$), 7.66 (2H, m, H6 and H7), 8.12 (2H, m, H5 and H8). δ_C 31.1 (CO*C*H$_3$)[a], 33.0 (ArCH$_2$)[a], 64.0 (OCH$_3$), 117.8 (CH=*C*H$_2$), 118.7 (q, *J* 320.3, CF$_3$), 122.1 (C6)[b], 122.6 (C7)[b], 127.5 (C5)[b], 127.8 (C2)[c], 128.0 (C3)[c], 128.5 (C4a)[d], 129.0 (C8)[b], 132.7 (C8a)[d], 134.3 (*C*H=CH$_2$), 139.0 (C4), 153.1 (C1), 203.7 (C=O). *m*/*z* 388 (M$^+$, 7%), 256 (50), 241 (100), 226 (22).

3-Acetyl-2-allyl-1-ethyl-4-methoxynaphthalene ***35***

To a solution of triflate **34** (1.04 g, 2.68 mmol) in dry dimethylformamide (20 mL) containing bis(triphenylphosphine)dichloropalladium(II) (20 mg, 0.03 mmol), lithium chloride (0.34 g, 8.02 mmol), and 2,6-di-*t*-butyl-4-methylphenol (30 mg, 13.6 mmol) was added tetraethyltin (2.60 g, 11.07 mmol) and the resulting solution was stirred under nitrogen at 85°C for 96 h. The cooled reaction mixture was dissolved in ether (150 mL) and washed with aqueous (10%) ammonium fluoride (100 mL), then water (100 mL), followed by 25% aqueous ammonia (100 mL), water, and hydrochloric acid (0.1 M, 100 mL), and finally water. The residue obtained on workup was chromatographed (10% ethyl acetate/hexane) to give *naphthalene* **35** as a yellow oil (540 mg, 75%) (Found: C 80.4, H 7.6. $C_{18}H_{20}O_2$ requires C 80.6, H 7.5%). ν_{max}/cm^{-1} 1703. δ_H (200 MHz) 1.28 (3H, t, *J* 7.4, CH$_2$C*H*$_3$), 2.61 (3H, s, COCH$_3$), 3.07 (2H, q, *J* 7.4, C*H*$_2$CH$_3$), 3.53 (2H, dt, *J* 5.4 and 1.8, ArC*H*$_2$CH=CH$_2$), 3.89 (3H, s, OCH$_3$), 4.90 (1H, dq, *J* 17.2 and 1.8, *trans* CH=C*H*$_2$), 5.07 (1H, dq, *J* 10.2 and 1.8, *cis* CH=C*H*$_2$), 5.98 (1H, m, C*H*=CH$_2$), 7.54 (2H, m, H6 and H7), 8.10 (2H, m, H5 and H8). δ_C 15.2 (CH$_2$*C*H$_3$), 21.4 (CO*C*H$_3$), 33.1 (*C*H$_2$CH=CH$_2$)[a], 33.6 (*C*H$_2$CH$_3$)[a], 63.6 (OCH$_3$), 116.2 (CH=*C*H$_2$), 122.7 (C6)[b], 124.6 (C7)[b], 125.6 (C5)[b], 126.9 (C2)[c], 127.1 (C8)[b], 129.9 (C3)[c], 133.4 (C4a)[d], 133.6 (C8a)[d], 135.6(C4)[c], 136.8 (*C*H=CH$_2$), 151.1 (C1), 206.8 (C=O). *m*/*z* 268 (M$^+$, 70%), 253 (100), 239 (30), 237 (18), 227 (47), 225 (50).

2-Allyl-1-ethyl-3-(1′-hydroxyethyl)-4-methoxynaphthalene ***11***

Using the method described for the reduction of ester **22**, ketone **35** (580 mg, 2.16 mmol) was reduced with lithium aluminium hydride to afford the alcohol **11** as an oil (560 mg, 96%) (Found: C 79.9, H 8.4. $C_{18}H_{22}O_2$ requires C 80.0, H 8.2%). ν_{max}/cm^{-1} 3412, 1634. δ_H (200 MHz) 1.28 (3H, t, *J* 7.6, CH$_2$C*H*$_3$), 1.66 (3H, d, *J* 6.8, CH(OH)*CH*$_3$), 3.04 (2H, dq, *J* 7.6 and 2.2, C*H*$_2$CH$_3$), 3.63 (2H, m, C*H*$_2$CH=CH$_2$), 4.06 (3H, s, OCH$_3$), 4.22 (1H, d, *J* 7.8, CH(O*H*)CH$_3$), 4.84 (1H, dq, *J* 17.2 and 2.2, *trans* CH=C*H*$_2$), 5.10 (1H, dq, *J* 10.2 and 2.2, *cis* CH=C*H*$_2$), 5.27 (1H, q, *J* 6.8, C*H*(OH)CH$_3$), 6.10 (1H, m, C*H*=CH$_2$), 7.50 (2H, m, H6 and H7), 8.05 (2H, m, H5 and H8). δ_C 15.3 (CH$_2$*C*H$_3$), 21.8 [CH(OH)*C*H$_3$], 25.1 (*C*H$_2$CH$_3$), 33.1 (*C*H$_2$CH=CH$_3$), 63.5 (OCH$_3$), 67.5 [*C*H(OH)CH$_3$], 116.1 (CH=*C*H$_2$), 122.5 (C6)[a], 124.6 (C7)[a], 125.1 (C5)[a], 126.0 (C8)[a], 127.2 (C2)[b], 132.0 (C4a)[b], 132.6 (C8a)[b], 133.2 (C4)[b], 135.4 (C3)[b], 136.9 (*C*H=CH$_2$), 152.8 (C1). *m*/*z* 270 (M$^+$, 22%), 252 (100), 239 (10), 223 (46), 221 (60), 211 (36).

Methyl 1-Allyloxy-3-naphthoate ***20***

Ester **19**[18] (1.03 g, 5.1 mmol) in dry acetone (90 mL) was treated with potassium carbonate (2.11 g, 15 mmol) and allyl bromide (1.29 mL, 1.80 g, 15 mmol) and the resultant mixture was rapidly stirred and heated under reflux for 4 h. The cooled solution was filtered and worked up as described for **17** to yield after chromatography the *naphthoate* **20** (1.23 g, 100%) as an oil (Found: C 74.5, H 5.9. $C_{15}H_{14}O_3$ requires C 74.4, H 5.8%). ν_{max}/cm^{-1} (film) 1715 cm. δ_H (100 MHz) 3.96 (3H, s, OCH$_3$), 4.76 (2H, m, ArOCH$_2$), 5.46 (2H, m, CH=C*H*$_2$), 6.20 (1H, m, C*H*=CH$_2$), 7.39 (1H, d, *J* 2, H2), 7.58 (2H, m, H6 and H7), 7.89 (1H, m, H5), 8.21 (1H, d, *J* 2, H4), 8.33 (1H, m, H8). *m*/*z* 242 (M$^+$, 87%), 202 (17), 201 (100), 143 (53).

Methyl 2-Allyl-1-hydroxy-3-naphthoate ***36***

Allyloxy ester **20** (697 mg, 2.88 mmol) was heated neat under nitrogen for 1.5 h in an oil bath at 180°C. The darkened oil was chromatographed (3% ethyl acetate/hexane) to afford *naphthol* **36** (645 mg, 94%) as white needles, mp 62.5–63.5°C (hexane) (Found: C 74.4, H 6.0. $C_{15}H_{14}O_3$ requires C 74.4, H 5.9%). ν_{max}/cm^{-1} 3460, 1689. δ_H (100 MHz) 1.30 (1H, s, 1-OH), 3.89 (2H, m, ArCH$_2$), 3.91 (3H, s, OCH$_3$), 5.17 (2H, m, CH=C*H*$_2$), 6.10 (1H, m, C*H*=CH$_2$), 7.54 (2H, m, H6 and H7), 7.82 (1H, m,

H5), 8.03 (1H, s, H4), 8.18 (1H, m, H8). *m/z* 242 (M^+, 100%), 227 (17), 183 (26), 182 (42), 181 (48).

Methyl 2-Allyl-1-methoxy-3-naphthoate ***37***

Naphthol **36** (694 mg, 2.87 mmol) dissolved in acetone (60 mL) was treated with potassium carbonate (1.19 g, 8.6 mmol) and dimethyl sulfate (0.78 mL, 1.04 g, 8.6 mmol) and the mixture was rapidly stirred and heated under reflux under nitrogen for 1.5 h. The cooled mixture was filtered and the acetone was removed under reduced pressure to produce an oil, which was taken up in ether (150 mL) and washed successively with ammonia (25%), water, hydrochloric acid (0.5 M), and water. The residue obtained on workup was chromatographed (15% ethyl acetate/hexane) to yield the oily *naphthoate* **37** (691 mg, 94%) (Found: C 75.1, H 6.3. $C_{16}H_{16}O_3$ requires C 75.0, H 6.3%). ν_{max}/cm^{-1} 1729. δ_H (100 MHz) 3.91 (6H, s, 2 × OCH_3), 3.92 (2H, m, $ArCH_2$), 4.63 (2H, m, $CH{=}CH_2$), 6.06 (1H, m, $CH{=}CH_2$), 7.57 (2H, m, H6 and H7), 7.88 (1H, m, H5), 8.10 (1H, m, H8), 8.20 (1H, s, H4). *m/z* 256 (M^+, 100%), 241 (24), 209 (58), 182 (31), 181 (43).

2-Allyl-3-hydroxymethyl-1-methoxynaphthalene ***14***

To a stirred suspension of lithium aluminium hydride (87 mg, 2.28 mmol) in ether (20 mL) was added dropwise a solution of ester **37** (157 mg, 0.61 mmol) under nitrogen over 10 min at 25°C. After an additional 10 min stirring, sufficient saturated aqueous ammonium chloride was added to destroy the excess of reagent. The residue obtained on workup was chromatographed (30% ethyl acetate/hexane) to give the *title compound* **14** as a thick oil (130 mg, 93%) (Found: C 79.0, H 6.9. $C_{15}H_{16}O_2$ requires C 78.9, H 7.1%). ν_{max}/cm^{-1} 3330. δ_H (100 MHz) 1.97 (1H, br s, CH_2OH), 3.68 (2H, m, $ArCH_2CH{=}CH_2$), 3.92 (3H, s, OCH_3), 4.80 (2H, s, $ArCH_2OH$), 4.96 (2H, m, $CH{=}CH_2$), 6.08 (1H, m, $CH{=}CH_2$), 7.50 (2H, m, H6 and H7), 7.77 (1H, s, H4), 7.81 (1H, m, H5), 8.07 (1H, m, H8). *m/z* 228 (M^+, 100%), 210 (16), 195 (75), 179 (26), 165 (55).

Base-Induced Cyclization Reactions

cis-*10-Ethyl-3,4-dihydro-5-methoxy-1,3-dimethyl-1*H-*naphtho[2,3-c]pyran* ***41*** *and* trans-*10-Ethyl-3,4-dihydro-5-methoxy-1,3-dimethyl-1*H-*naphtho[2,3-c]pyran* ***38***

Potassium *t*-butoxide (87 mg, 0.78 mmol) was added in one portion to alcohol **9** (53 mg, 0.196 mmol) in dimethylformamide (18 mL) at 60°C under nitrogen and the resulting solution was stirred vigorously for 2 h. The cooled mixture was poured into water (100 mL) and the organic material exhaustively extracted with ether. The residue obtained on workup was chromatographed (10% ethyl acetate/hexane) to afford *naphthopyran* **41** as a thick oil (14 mg, 26%) (Found: C 79.9, H 8.0. $C_{18}H_{22}O_2$ requires C 80.0, H 8.2%). ν_{max}/cm^{-1} 1258. δ_H (200 MHz) 1.30 (3H, t, *J* 7.5, CH_2CH_3), 1.41 (3H, d, *J* 6.2, 3-CH_3), 1.53 (3H, d, *J* 6.2, 1-CH_3), 2.60 (1H, dd, *J* 15.6 and 10.6, pseudoaxial H4), 3.02 (2H, q, *J* 7.5, CH_2CH_3), 3.16 (1H, dd, *J* 15.6 and 1.6, pseudoequatorial H4), 3.65 (1H, ddq, *J* 10.6, 6.2 and 1.6, H3), 3.92 (3H, s, OCH_3), 5.41 (1H, q, *J* 6.2, H1), 7.48 (2H, m, H7 and H8), 8.02 (1H, m, H9), 8.14 (1H, m, H6). δ_C 15.6 (CH_2CH_3), 20.7 (3-CH_3), 22.4 (1-CH_3), 25.8 (CH_2CH_3), 32.1 (C4), 61.6 (OCH_3), 69.4 (C3)[a], 71.5 (C1)[a], 122.4 (C7)[b], 124.3 (C8)[b], 124.5 (C4a)[c], 125.2 (C9)[b], 125.6 (C6)[b], 126.9 (C10a)[c], 131.6 (C10)[c], 131.9 (C5a)[c], 135.6 (C9a)[c], 151.0 (C5). *m/z* 270 (M^+, 55%), 269 (100), 267 (29), 255 (70), 239 (19). Further elution with the same solvent yielded *naphthopyran* **38** (23 mg, 43%) as colourless plates, mp 106–107°C (hexane) (Found: M^+ 270.1615. $C_{18}H_{22}O_2$ requires M 270.1620). ν_{max}/cm^{-1} 1260. δ_H (200 MHz) 1.28 (3H, t, *J* 7.6, CH_2CH_3), 1.39 (3H, d, *J* 5.8, 3-CH_3), 1.61 (3H, d, *J* 6.6, 1-CH_3), 2.64 (1H, dd, *J* 17.0 and 11.0, pseudoaxial H4), 3.00 (2H, dq, *J* 7.6 and 4.0, CH_2CH_3), 3.17 (1H, dd, *J* 17.0 and 3.6, pseudoequatorial H4), 3.89 (3H, s, OCH_3), 4.26 (1H, m, H3), 5.37 (1H, q, *J* 6.6, H1), 7.46 (2H, m, H7 and H8) and 8.05 (2H, m, H6 and H9). δ_C 15.4 (CH_2CH_3), 20.5 (3-CH_3), 21.8 (1-CH_3), 22.5 (CH_2CH_3), 30.9 (C4), 60.8 (OCH_3), 62.3 (C3)[a], 70.1 (C1)[a], 122.3 (C7)[b], 122.5 (C4a)[c], 124.4 (C8)[b], 125.1 (C9)[b], 125.6 (C6)[b], 127.0 (C10a)[c], 130.7 (C10)[c], 131.5 (C5a)[c], 135.0 (C9a)[c], 151.6 (C5).

Repeating the reaction on alcohol **9** (58 mg, 0.21 mmol) and using potassium *t*-butoxide (96 mg, 0.86 mmol) under the same conditions but for 30 min afforded *naphthopyran* **38** (40 mg, 69%) as the sole product. The ratios of *naphthopyrans* **41** and **38** estimated from NMR integrations after 45 min were 17:83 and after 60 min were 27:73.

cis-*5,10-Diethyl-3,4-dihydro-1,3-dimethyl-1*H-*naphtho[2,3-c]pyran* ***42***, trans-*5,10-Diethyl-3,4-dihydro-1,3-dimethyl-1*H-*naphtho[2,3-c]pyran* ***39***, *(*Z*)- and (*E*)-1,4-Diethyl-3-(1′-hydroxyethyl)-2-(prop-1′-enyl)naphthalene* ***45***, *and 9-Ethyl-10-(1′-hydroxethyl)-4-methylphenanthrene* ***46***

To a solution of alcohol **10** (80 mg, 0.30 mmol) in dimethylformamide (12 mL) under nitrogen in an oil bath at 60°C was added at once potassium *t*-butoxide (135 mg, 1.20 mmol) and the resulting solution, which turned from colourless to orange brown, was stirred for 45 min and then worked up as described before to afford *naphthopyran* **42** as a colourless oil (18 mg, 23%) (Found: M^+ 268.1830. $C_{19}H_{24}O$ requires M 268.1827). ν_{max}/cm^{-1} 1264. δ_H (200 MHz) 1.26 (3H, t, *J* 7.6, CH_2CH_3), 1.32 (3H, t, d, *J* 7.2, CH_2CH_3), 1.42 (3H, d, *J* 6.2, 3-CH_3), 1.49 (3H, d, *J* 6.6, 1-CH_3), 2.73 (1H, dd, *J* 15.8 and 10.6, pseudoaxial H4), 2.95 (1H, dd, *J* 15.8 and 2.4, pseudoequatorial H4), 3.07 (4H, m, CH_2CH_3), 3.70 (1H, ddq, *J* 10.6, 6.2, and 2.4, H3), 5.48 (1H, q, *J* 6.6, H1), 7.47 (2H, m, H7 and H8), 8.06 (2H, m, H6 and H9). δ_C 11.1 (CH_2CH_3), 14.8 (CH_2CH_3)[a], 15.5 (3-CH_3)[a], 20.8 (1-CH_3)[a], 21.2 and 25.9 (CH_2CH_3), 33.1 (C4), 72.1 (C3)[b], 73.1 (C1)[b], 124.5 (C7)[c], 124.7 (C8)[c], 125.2 (C6)[c], 125.4 (C9)[c], 129.2 (C5)[d], 131.0 (C4a)[d], 131.1 (C10a)[d], 133.5 (C10)[d], 134.2 (C5a)[d], 135.1 (C9a)[d]. Further elution afforded the *naphthopyran* **39** as a colourless oil (44 mg, 55%) (Found: M^+ 268.1832. $C_{19}H_{24}O$ requires M 268.1827). ν_{max}/cm^{-1} 1265. δ_H (200 MHz) 1.29 (6H, m, CH_2CH_3), 1.41 (3H, d, *J* 6.0, 3-CH_3), 1.64 (3H, d, *J* 6.6, 1-CH_3), 2.70 (1H, dd, *J* 16.8 and 11.0, pseudoaxial H4), 3.06 (5H, m, CH_2CH_3 and pseudoequatorial H4), 4.35 (1H, m, H3), 5.42 (1H, q, *J* 6.6, H1), 7.47 (2H, m, H7 and H8) and 8.07 (2H, m, H6 and H9). δ_C 10.5 (CH_2CH_3), 14.4 (CH_2CH_3)[a], 15.4 (1-CH_3)[a], 20.6 (3-CH_3), 21.5 and 21.9 (CH_2CH_3), 32.2 (C4), 67.3 (C3)[b], 70.8 (C1)[b], 124.4 (C7)[c], 124.6 (C8)[c], 125.2 (C6)[c], 125.3 (C9)[c], 126.7 (C5)[d], 130.7 (C4a)[d], 131.2 (C10a)[d], 132.8 (C10)[d], 133.7 (C5a)[d], 136.1 (C9a)[d]. The final compound to elute was *phenanthrene* **46** (12 mg, 15%) as light yellow crystals, mp 146–147°C (hexane) (Found: M^+ 264.1509. $C_{19}H_{20}O$ requires M 264.1514). ν_{max}/cm^{-1} 3320. δ_H (200 MHz) 1.37 (3H, t, *J* 7.2, CH_2CH_3), 1.86 (3H, d, *J* 7.0, $CH(OH)CH_3$), 2.58 (3H, s, 4-CH_3), 3.24 (2H, m, CH_2CH_3), 5.95 (1H, q, *J* 7.0, $CH(OH)CH_3$), 7.42 (1H, dd, *J* 8.4 and 1.6, H3), 7.61 (2H, m, H6 and H7), 8.15 (1H, m, H2), and 8.64 (3H, m, H5, H8, and H1). δ_C 15.5 (CH_2CH_3), 22.08 (4-CH_3)[a], 22.13 (10-$CHCH_3$)[a], 23.2

(CH_2CH_3), 68.3 (10-$CHCH_3$), 122.9 (C1)[b], 123.0 (C2)[b], 125.0 (C3)[b], 126.2 (C5)[b], 126.4 (C6)[b], 126.6 (C7)[b], 127.4 (C8)[b], 128.4 (C4)[c], 129.8 (C4a)[c], 130.4 (C4b)[c], 130.8 (C8a)[c], 134.5 (C9)[c], 135.5 (C10)[c], 135.7 (C10a)[c].

Repeating the reaction on the alcohol **10** (68 mg, 0.22 mmol) and stopping the reaction after 30 min afforded the following products in order of elution: (i) *naphthopyran* **42** (7.5 mg; 11%); (ii) *naphthopyran* **39** (29 mg; 43%); (iii) a (1:1) mixture of the (*E*)/(*Z*) conjugated *naphthyl alcohols* **45** (25 mg; 37%); and (iv) *phenanthrene* **46** (4 mg; 6%). Spectroscopic data for alcohol **45**: thick oil (Found: M^+ 268.1820. $C_{19}H_{24}O$ requires M 268.1827). ν_{max}/cm^{-1} 3366. δ_H (300 MHz) 1.17 (3H, t, *J* 7.6, CH_2CH_3), 1.36 (3H, t, *J* 7.4, CH_2CH_3), 1.47 and 1.51 (3H, each dd, *J* 6.6 and 1.4, CH=CHCH_3), 1.57 and 1.59 (3H, each d, *J* 7.0, CH(OH)CH_3), 3.04 (2H, q, *J* 7.6, CH_2CH_3), 3.36 (2H, q, *J* 7.4, CH_2CH_3), 5.53 and 5.58 (1H, each q, *J* 7.0, $CH(OH)CH_3$), 5.96 and 6.03 (1H, each dq, *J* ~11.0 and 6.6, CH=$CHCH_3$), 6.73 and 6.77 (1H, each an ill-defined dm, *J* ~11, CH=$CHCH_3$), 7.49 (2H, m, H6 and H7), 8.11 (2H, m, H5 and H8). δ_C 14.59, 14.65, 15.00, and 15.06 (CH_2CH_3), 16.11 and 16.31 [$CH(OH)CH_3$], 21.66 and 21.85 (CH=CHCH_3), 22.6, 22.73, 23.52, and 23.64 (CH_2CH_3), 69.04 and 69.40 [$CH(OH)CH_3$], 124.95 (C6)[a], 125.01 (C7)[a], 125.31 (C5)[a], 125.36 (C8)[a], 127.5 (C4)[b], 129.1 (C3)[b], 130.2 (C2)[b], 130.3 (C1)[b], 131.3 (CH=$CHCH_3$)[c], 136.1 (C4a)[d], 136.4 (C8a)[d], 138.0 (CH=$CHCH_3$)[c].

cis-*5-Ethyl-3,4-dihydro-10-methoxy-1,3-dimethyl-1*H-*naphtho[2,3-c]pyran* ***43*** *and* trans-*5-Ethyl-3,4-dihydro-10-methoxy-1*H-*1,3-dimethylnaphtho[2,3-c]pyran* ***40***

To the alcohol **11** (80 mg, 0.30 mmol) dissolved in degassed dimethylformamide (10 mL) as described before was added potassium *t*-butoxide (134 mg, 1.20 mmol) at 60°C and stirring was continued for 120 min after which time the reaction mixture was worked up as described before to yield first *naphthopyran* **43** (13 mg, 16%) as colourless cubes, mp 108–110°C (hexane) (Found: C 79.8, H 8.1; M^+ 270.1622. $C_{18}H_{22}O_2$ requires C 80.0, H 8.2%; M 270.1620). ν_{max}/cm^{-1} 1260. δ_H (200 MHz) 1.24 (3H, t, *J* 7.8, CH_2CH_3), 1.43 (3H, d, *J* 6.0, 3-CH_3), 1.66 (3H, d, *J* 6.2, 1-CH_3), 2.72 (1H, dd, *J* 15.8 and 10.6, pseudoaxial H4), 2.90 (1H, dd, *J* 15.8 and 2.8, pseudoequatorial H4), 3.04 (2H, dq, *J* 7.8 and 2.8, CH_2CH_3), 3.74 (1H, ddq, *J* 10.6, 6.0, and 2.8, H3), 3.88 (3H, s, OCH_3), 5.29 (1H, q, *J* 6.2, H1), 7.47 (2H, m, H7 and H8), 8.10 (2H, m, H6 and H9). δ_C 14.5 (CH_2CH_3), 21.0 (3-CH_3), 22.1 (1-CH_3), 22.8 (CH_2CH_3), 35.2 (C4), 61.1 (OCH_3), 69.9 (C1)[a], 71.6 (C3)[a], 122.5 (C7)[b], 124.0 (C8)[b], 124.9 (C6)[b], 125.8 (C9)[b], 127.0 (C4a)[c], 128.8 (C5)[c], 131.4 (C9a)[c], 131.7 (C5a)[c], 133.0 (C10a)[c], 150.7 (C10). Further elution with the same eluent afforded *naphthopyran* **40** (46 mg, 58%) as colourless plates, mp 113–114°C (hexane) (Found: C 80.1, H 8.0; M^+ 270.1623. $C_{18}H_{22}O_2$ requires C 80.0, H 8.2%; M 270.1620). ν_{max}/cm^{-1} 1258. δ_H (200 MHz) 1.24 (3H, t, *J* 7.8, CH_2CH_3), 1.41 (3H, d, *J* 6.2, 3-CH_3), 1.65 (3H, d, *J* 6.4, 1-CH_3), 2.65 (1H, dd, *J* 16.8 and 10.8, pseudoaxial H4), 2.95 (1H, dd, *J* 16.8 and 3.6, pseudoequatorial H4), 3.03 (2H, dq, *J* 7.4 and 1.4, CH_2CH_3), 3.90 (3H, s, OCH_3), 4.20 (1H, m, H4), 5.36 (1H, q, *J* 6.4, H1), 7.49 (2H, m, H7 and H8), 8.05 (2H, m, H6 and H9). δ_C 14.3 (CH_2CH_3), 20.78 (3-CH_3)[a], 20.80 (1-CH_3)[a], 22.3 (CH_2CH_3), 34.0 (C4), 61.4 (OCH_3), 62.9 (C1)[b], 69.1 (C3)[b], 122.5 (C7)[c], 124.1 (C8)[c], 124.9 (C6)[c], 125.7 (C9)[c], 126.4 (C4a)[d], 128.5 (C5a)[d], 129.4 (C9a)[d], 132.0 (C10a)[d], 133.5 (C5)[d], 149.7 (C10). Repeating the reaction on a separate sample and stopping the reaction after 40 min afforded *naphthopyran* **40** as the sole product (70%).

cis-*5-Ethyl-3,4-dihydro-10-methoxy-1,3-dimethyl-1*H-*naphtho[2,3-c]pyran* ***43***, trans-*5-Ethyl-3,4-dihydro-10-methoxy-1*H-*1,3-dimethylnaphtho[2,3-c]pyran* ***40***, rac-(*1*R,*3*R,*4*S)-*5-Ethyl-4-hydroxy-3,4-dihydro-10-methoxy-1,3-dimethyl-1*H-*naphtho[2,3-c]pyran* ***50***, *and* rac-(*1*R,*3*R,*4*R)-*5-Ethyl-4-hydroxy-3,4-dihydro-10-methoxy-1,3-dimethyl-1*H-*naphtho[2,3-c]pyran* ***51***

Potassium *t*-butoxide (116 mg, 1.04 mmol) was added in one portion to alcohol **11** (70 mg, 0.26 mmol) in dimethylformamide (6 mL) in an oil bath at 60°C and the resulting mixture was stirred for 2 h in the presence of air. It was then worked up as described earlier to afford after chromatography *naphthopyran* **43** (12 mg, 17%) followed by *naphthopyran* **40** (16 mg, 23%), both having spectroscopic properties identical to those reported above. Further elution yielded an inseparable mixture of the *4-hydroxynaphthopyrans* **50** and **51** in a ratio of 3:1 as a thick oil (25 mg, 34%) (Found: C 75.4, H 7.8; M^+ 286.1566. $C_{18}H_{22}O_3$ requires C 75.5, H 7.7%; M 286.1569). ν_{max}/cm^{-1} 3450. δ_H (major diastereoisomer) (200 MHz) 1.18 (3H, d, *J* 6.6, 3-CH_3), 1.36 (3H, t, *J* 7.4, CH_2CH_3), 1.58 (1H, s, 4-OH), 1.68 (3H, d, *J* 6.4, 1-CH_3), 3.24 (2H, q, *J* 7.4, CH_2CH_3), 3.87 (3H, s, OCH_3), 4.34 (1H, dq, *J* 2.6 and 6.6, H3), 4.68 (1H, br s, H4), 5.22 (1H, q, *J* 6.4, H1), 7.51 (2H, m, H7 and H8), 8.10 (2H, m, H6 and H9). δ_H (minor diastereoisomer) 1.46 (3H, d, *J* 6.6, 3-CH_3), 1.28 (3H, t, *J* 6.2, CH_2CH_3), 1.58 (1H, s, 4-OH), 1.63 (3H, d, *J* 6.4, 1-CH_3), 3.20 (2H, q, *J* 6.2, CH_2CH_3), 3.89 (3H, s, OCH_3), 4.19 (1H, dq, *J* 1.3 and 6.6, H3), 4.60 (1H, br s, H4), 5.35 (1H, q, *J* 6.4, H1), 7.51 (2H, m, H7 and H8), 8.10 (2H, m, H6 and H9).

*10-Ethyl-3,4-dihydro-5-methoxy-3-methyl-1*H-*naphtho[2,3-c]pyran* ***57***

Alcohol **12** (224 mg, 0.82 mmol) was dissolved in dimethylformamide (10 mL) that had been flushed with nitrogen for 10 min after which potassium *t*-butoxide (369 mg, 3.29 mmol) was added in one portion and the reaction mixture was then stirred and heated at 60°C under nitrogen for 2 h. The residue obtained on workup as described earlier was chromatographed (15% ethyl acetate/hexane) to afford the *naphthopyran* **57** (155 mg, 69%), as white cubes, mp 81–82.5°C (aqueous methanol) (Found: C 79.7, H 7.8. $C_{17}H_{20}O_2$ requires C 79.7, H 7.9%). ν_{max}/cm^{-1} 1258. δ_H (100 MHz) 1.20 (3H, t, *J* 8.0, CH_2CH_3), 1.42 (3H, d, *J* 7.0, 3-CH_3), 2.70 (3H, m, CH_2CH_3 and pseudoaxial H4), 3.12 (1H, dd, *J* 17.0 and 3.5, pseudoequatorial H4), 3.85 (3H, s, OCH_3), 3.87 (1H, m, 3-H), 4.89 (1H, d, *J* 17.0, pseudoaxial H1), 5.18 (1H, d, *J* 17.0, pseudoequatorial H1), 7.50 (2H, m, H7 and H8), 8.08 (2H, m, H6 and H9). *m/z* 256 (M^+, 100%), 227 (24), 225 (24), 213 (17), 212 (86), 197 (67).

*5,10-Diethyl-3,4-dihydro-3-methyl-1*H-*naphtho[2,3-c]pyran* ***58***

Alcohol **13** (100 mg, 0.39 mmol) was dissolved in dimethylformamide (12 mL) that had been flushed with nitrogen for 10 min and stirred under nitrogen at 60°C at which time potassium *t*-butoxide (176 mg, 1.57 mmol) was added at once and stirring was continued for 1 h. The solution was then worked up as described before to yield the *naphthopyran* **58** (72 mg, 72%) as white cubes, mp 89–90°C (hexane) (Found: C 85.2, H 8.6. $C_{18}H_{22}O$ requires C 85.0, H 8.7%). ν_{max}/cm^{-1} 1260. δ_H (200 MHz) 1.27 (6H, t, *J* 7.8, CH_2CH_3), 1.47 (3H, d, *J* 6.2, 3-CH_3), 2.94 (6H, m, CH_2CH_3 and H4), 3.88 (1H, m, H3), 4.98 (1H, d, *J* 15.0, pseudoaxial H1), 5.20 (1H, d, *J* 15.0, pseudoequatorial H1), 7.48 (2H, m, H7 and H8), 8.08 (2H, m, H6 and

H9). δ_C 14.18 and 14.24 (CH_2CH_3), 20.1 (3-CH_3), 20.7 and 21.9 (CH_2CH_3), 34.4 (C4), 67.6 (C3), 70.7 (C1), 123.8 (C7)[a], 124.2 (C8)[a], 124.87 (C9)[a], 124.92 (C6)[a], 128.9 (C5)[b], 129.5 (C10)[b], 130.3 (C4a)[b], 130.8 (C10a)[b], 132.4 (C5a)[c], 135.4 (C9a)[c]. *m*/*z* 254 (M^+, 100%), 225 (26), 211 (25), 210 (74).

9-Methoxyanthracene ***59***

Alcohol **14** (93 mg, 0.41 mmol) was dissolved in dimethylformamide (10 mL) and stirred 60°C at which time potassium *t*-butoxide (184 mg, 1.64 mmol) was added at once and the resulting mixture was stirred at the same temperature for 120 h. The cooled mixture was poured into water (100 mL) and the organic material exhaustively extracted with ether. The residue obtained on workup was chromatographed (5% ethyl acetate/hexane) to yield the known anthracene **59** (21 mg, 25%) as white needles, mp 92°C (hexane; lit.[27] 94°C).

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