187. Acid-Catalyzed Cleavage of 1,4-Dimethyl-1,4-dihydronaphthalene 1,4-Endoperoxide. Reactivity of the Resulting Hydroperoxy Carbocation with Nucleophiles[1])

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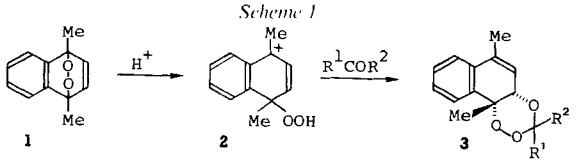
(31.V.85)

In the presence of acids, 1,4-dimethyl-1,4-dihydronaphthalene 1,4-endoperoxide readily reacts with nucleophiles to produce methyl- and ring-substituted naphthalenes in high yields. The regioselectivity observed depends on the nucleophile. The key intermediate is shown to be the corresponding hydroperoxy carbocation which could be intercepted in certain cases prior to aromatization. The hydroperoxide also undergoes *Hock*-type cleavage and dimerization giving 2,3-dihydro-1-benzoxepins, 4-methyl-1-naphthol, and a 1,2,5,6-tetraoxocane as by-products.

Introduction. – Although 1,4-endoperoxides have potential in organic synthesis [2–5], their utility is usually confined to transformations involving rearrangement, cleavage, reduction, or fragmentation of the peroxide function. Apart from the acid-catalyzed rearrangement of certain 1,4-endoperoxides to 1,2-dioxetanes [2], and the cleavage of some anthracene endoperoxides [6], the action of acids on 1,4-endoperoxides has received scant attention [7]. We have recently shown [8] [9] that 1,4-dimethyl-1,4-dihydronaphthalene 1,4-endoperoxide (**1**), commonly used as a reagent for generating singlet oxygen [10], can react with electrophiles such as aldehydes, ketones, and α-keto esters in the presence of acids or trimethylsilyl trifluoromethanesulfonate to give 1,2,4-trioxanes **3**. This reactivity was rationalized in terms of the formation of the hydroperoxy carbocation **2** which adds across the electrophilic carbonyl moiety to form the *cis*-fused six-membered ring *(Scheme 1)*. We now show that acid catalysis is equally effective in enabling **1** to react with certain nucleophiles, thereby providing a preparative route to a range of naphthalene derivatives.

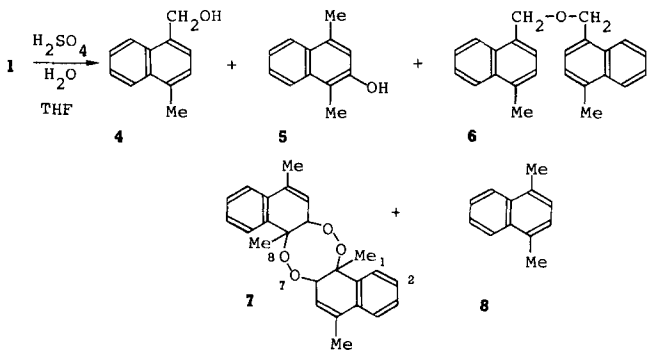
Scheme 1



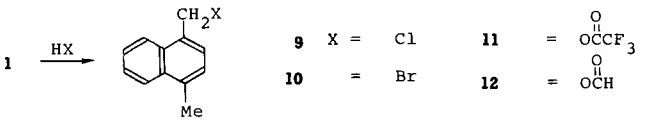
Results. – The hydrolysis of **1** in aqueous 10% H_2SO_4/THF gave two hydroxy compounds **4** and **5** as major products in yields of 38 and 21%, respectively. Minor products were 1,4-dimethylnaphthalene (**8**; 4%) as well as the dimeric ether **6** (2%), and the 1,2,5,6-tetraoxocane **7** (1%, *Scheme 2*). When higher concentrations of **1** were used, ether **6** was formed in higher yield (16%), whereas tetraoxocane **7** was absent. Repetition

[1]) Preliminary communication, see [1].

Scheme 2



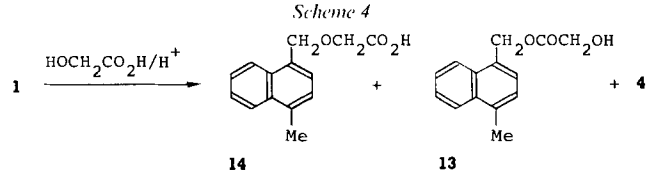
Scheme 3



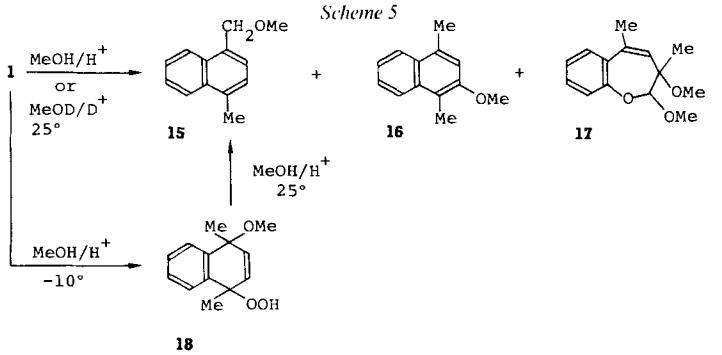
of the experiment in aqueous 5N HCl/THF gave none of these products. Instead, the methyl chloride **9** was produced quantitatively. Similarly, the bromide **10** was the sole product from the reaction of **1** with aqueous 20% HBr/THF being obtained in 77% yield after purification *(Scheme 3)*.

Analogous results were obtained when trifluoroacetic, formic, and glycolic acids were employed in aprotic solvents. The latter two acids, owing to their weakness, required the addition of *Amberlyst-15* to effect cleavage of **1**. In all cases, the appropriate methyl-substituted carboxylates **11**, **12**, and **13** were formed in yields of 52, 76, and 19%, respec-

Scheme 4



Scheme 5



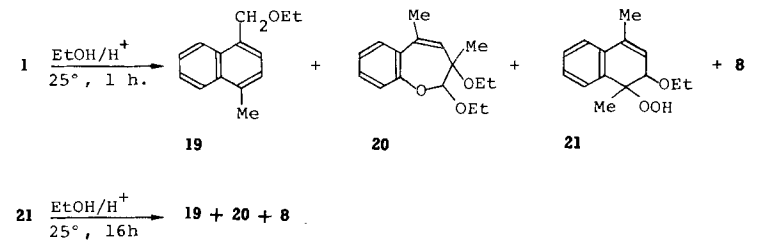
tively. The last reaction also afforded alcohol **4** in 18% yield together with the ether **14** (52%, *Scheme 4*).

Alcohols were also found to be highly reactive towards **1** in the presence of *Amberlyst-15*, but with less regioselectivity. Methanolysis of **1** at room temperature gave the methyl and phenyl ethers **15** and **16** in 36 and 31% yields, respectively, accompanied by the 2,3-dihydro-1-benzoxepin **17** (10%; *Scheme 5*). When CH_3OD and *Amberlyst-15* pretreated with CH_3OD were used, products **15**–**17** were formed in comparable amounts.

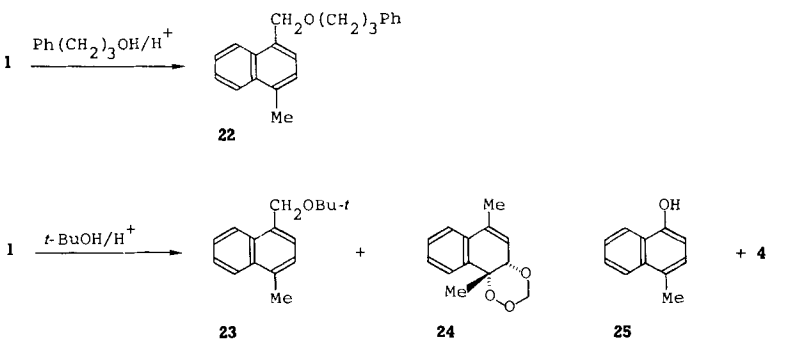
Methanolysis of **1** at −10° gave the epimeric hydroperoxides **18** as sole product in 75% yield after purification *(Scheme 5)*. Further submission of **18** to MeOH at room temperature gave the same products **15**–**17** as before.

Ethanolysis of **1** at room temperature gave the naphthylmethyl ether **19** in 40% yield, accompanied by the benzoxepin **20**, the hydroperoxide **21**, and **8** in yields of 12, 4, and 14%, respectively *(Scheme 6)*. Subsequent treatment of **21** under the same conditions, but for a longer period, gave **19**, **20**, and **8** in yields of 48, 14, and 10%.

Scheme 6



Scheme 7



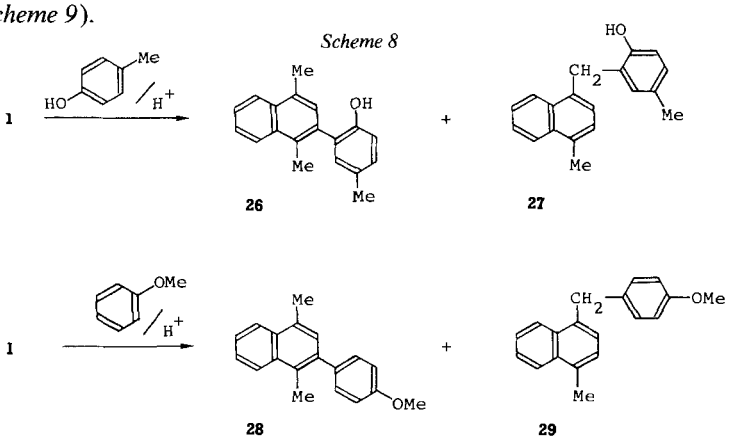
On reaction with **1**, 3-phenyl-1-propanol and *t*-BuOH gave chiefly the naphthylmethyl ethers **22** and **23** (49 and 50% yields, resp.; *Scheme 7*). From the reaction with *t*-BuOH, the alcohol **4**, 1,2,4-trioxane **24**, and naphthol **25** were also isolated in yields of 18, 8, and 8%, respectively. A control experiment revealed that **4**, **5**, **8**, **24**, and **25** were also formed in sizable yields, *viz.* 17, 9, 18, 12, and 9%, when **1** was treated with *Amberlyst-15* alone in CH_2Cl_2.

As a nucleophile, *p*-cresol behaved differently. Condensation with **1** occurred at C(2) on the benzene ring to give the phenol derivatives **26** and **27** in yields of 77 and 10%,

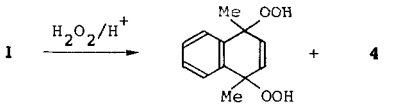
respectively *(Scheme 8)*. Anisole displayed similar regioselectivity giving **28** and **29** in 46 and 22% yields, respectively.

Lastly, the solvolysis of **1** in H_2O_2/Et_2O in the presence of *Amberlyst-15* was studied. The dihydroperoxides **30** were formed as epimers in 53% yield together with the alcohol **4** (10%; *Scheme 9*).

Scheme 8



Scheme 9



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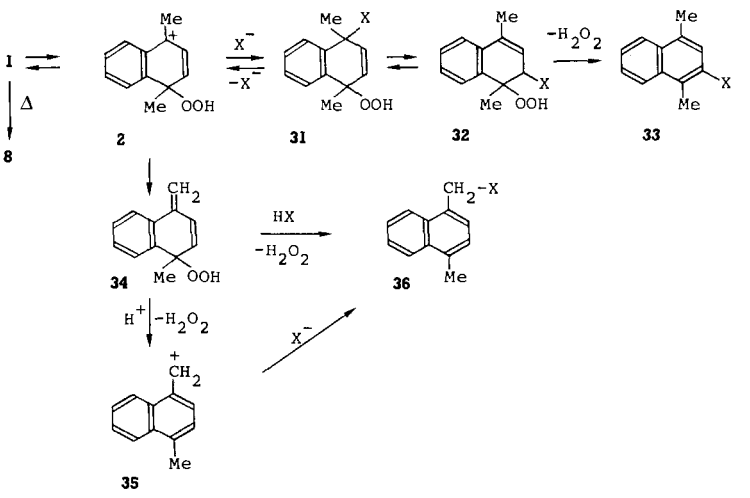
Discussion. – All the foregoing results are most conveniently interpreted in terms of the intermediacy of the hydroperoxy carbocation **2** which is formed as a first event by protonation of the peroxide bridge which subsequently undergoes C,O-bond cleavage. Nucleophiles (*e.g.* X^-) initially attack **2** at C(1) to produce **31**, which appears to be the kinetic product *(Scheme 10)*. Rearrangement then occurs to give the thermodynamically

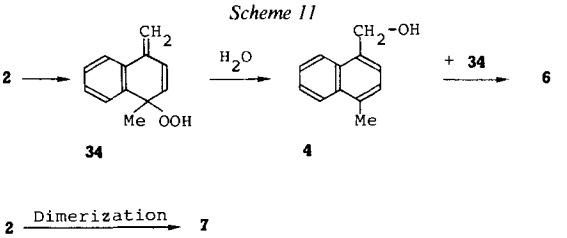
Scheme 10



favored isomer **32** which can aromatize by elimination of hydrogen peroxide to form **33**. Alternatively, **2** may undergo deprotonation to the conjugated diene **34** which may aromatize in two ways, either by a vinylogous S_N2' process in which the nucleophile attacks the methylidene C-atom, thereby expelling hydroperoxide at the same time, or by prior loss of hydroperoxide anion to form the naphthylmethyl cation **35** which later acquires the nucleophile. In either case the end result is the methyl derivative **36**.

Lastly, **2** can dimerize. When the first formed methyl derivative is an alcohol, *e.g.* **4**, then it can react as a nucleophile with **34** or **35** and give the ether **6** *(Scheme 11)*. Simple dimerization of **2** in a head-to-tail sense forms the rare entity, the 1,2,5,6-tetraoxocane **7** [11].

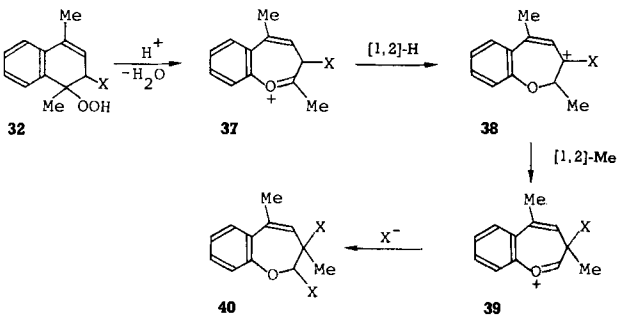
Scheme 11



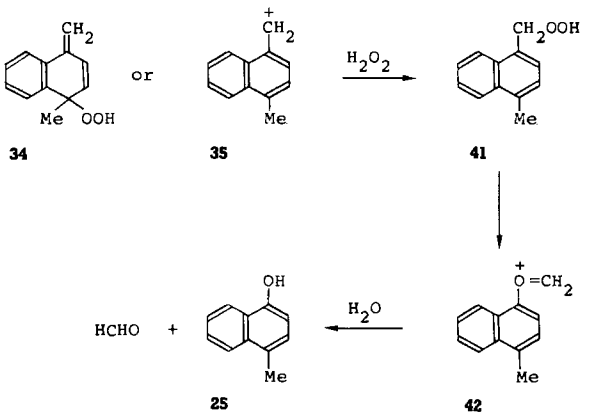
Evidence for the reversible formation of **1**, the cation **2**, and the hydroperoxides **31** and **32** stems from the methanolysis and ethanolysis of the methoxy (**18**) and ethoxy (**21**) hydroperoxides. These experiments led to the same products in similar ratios as those obtained directly from the endoperoxide **1**. Hence, it appears that the hydroperoxy carbocation **2** is the common reactive intermediate. The formation of 1,4-dimethylnaphthalene **8** during the ethanolysis of **21** could be due to the reversion of **21** to **1**, following by its thermal decomposition to **8** and singlet oxygen. When **1** was treated with CH_3OD/D^+ at room temperature, no deuterium was incorporated in the products **15–17**, thereby indicating that the deprotonation of **2** to **34** is irreversible under the reaction conditions.

The 2,3-dihydro-1-benzoxepins **17** and **20** may arise *via* protonation and *Hock*-type cleavage [12] of the thermodynamically more stable hydroperoxide **32** *(Scheme 12)*. Migration of the phenyl group yields the benzohomopyrylium ion **37**, which undergoes successive [1,2]H- and [1,2]-methyl-group shifts (**37**→**38**→**39**). The final cation is trapped by the nucleophile to give the benzoxepin **40**. Benzohomopyrylium cations have been

Scheme 12



Scheme 13



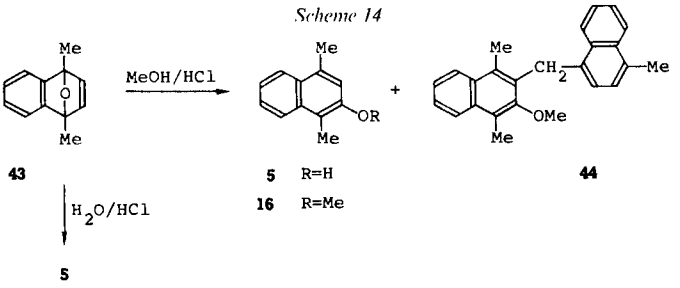
postulated as reactive intermediates in a recent synthesis of 2,3-dihydro-1-benzoxepins from 1,6-dimethyl-5-methylene-3,4-benzo-2-oxabicyclo[4.1.0]hept-3-ene and orthoformates or acetals [13].

Hock-cleavage can also account for the formation of 4-methyl-1-naphthol (**25**). The diene **34** or the naphthylmethyl cation **35** can initially afford the hydroperoxymethyl derivative **41** *(Scheme 13)*. Rearrangement to **42** followed by hydrolysis will give the naphthol **25** by liberating formaldehyde. The latter then reacts with free hydroperoxy carbocation **2**, generating the 1,2,4-trioxane **24** (see *Scheme 1*). Consequently, **24** and **25** are obtained in similar yields.

The regioselectivity observed in the reactions of **1** with nucleophiles may be a function of the size of the nucleophile. Bulky nucleophiles give exclusively methyl-substituted products. *p*-Cresol and anisole are exceptional in giving mainly ring-substituted products. Another remarkable result is the exclusive formation of the chloride **9** and the bromide **10** when **1** was treated with aqueous HCl or HBr solutions. The greater softness of Cl^- and Br^- compared to H_2O may be the cause since the proposed electrophilic intermediates are also soft. Support for this view is provided by the mode of attack of *p*-cresol which occurs at the softer C(2) position rather than on the OH group. The same argument applies to the preferential attack of glycolic acid *via* its OH rather than its COOH function.

Our results find a mechanistic parallel with the acid-catalyzed cleavage of 1,4-epoxy-1,4-dihydro-1,4-dimethylnaphthalene (**43**) [14]. Nonetheless, the latter behaves differently to **1** under similar reaction conditions. In particular, treatment of **43** with dilute HCl

Scheme 14



solution furnishes none of the methyl chloride **9**, but gives instead the naphthol **5** as sole product. When MeOH is added to HCl, the ethers **16** and **44** are formed in addition to **5** *(Scheme 14)*. It is also worth noting that substitution on the side-chain has been observed during the nitration [15] and photooxygenation [16] of 1,4-dimethylnaphthalene.

We will report elsewhere on the preparative use of some of these derivatives as well as on studies dealing with related unsymmetrically substituted endoperoxides.

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Experimental Part

1. *General.* All solvents were redistilled before use. TLC: silica gel *60 F_{254} (Merck)*. Prep. TLC: silica gel *60 F_{254} (Merck;* thickness 2 mm). HPLC: *Waters-M-45* instrument equipped with a *R401* differential refractometer and a *Hewlett-Packard-338OS* integrator, using as eluant MeCN/MeOH/H_2O 4:1:2; retention times (t_R) in sec. GLC: *Hewlett-Packard-5880A* series instrument using a *Hewlett-Packard* high-speed capillary column (0.2 mm × 12.5 mm; liquid phase: cross-linked dimethylsilicone) programmed as follows: injection at 140°; after 2.2 min, the temp. was increased by 10°/min to 160° and 0.3 min later by 30°/min to 210°. Products were identified by comparison of their retention times with those of authentic samples. M.p.: *Reichert*-hot-stage microscope (uncorrected). IR: *Perkin-Elmer-681* spectrometer. ^{1}H- and ^{13}C-NMR: *Bruker-WH-360* and *Varian-XL-100* spectrometers ($CDCl_3$ used as solvent throughout, chemical shifts in ppm relative to internal TMS (= 0 ppm), coupling constants *J* in Hz). MS: *CH-4 MAT* and *Finnigan GC/MS 4023* using the *INCOS* data system. Elemental analyses were determined by Dr. *H. Eder*, Service de Microchimie, Institut de Chimie Pharmaceutique, University of Geneva.

2. *1,4-Epidioxy-1,4-dimethyl-1,4-dihydronaphthalene* (**1**) was prepared by the methylene-blue-sensitized photooxygenation of 1,4-dimethylnaphthalene (**8**) [10].

3. *Hydrolysis of* **1**. 3.1. To a soln. of **1** (846 mg, 4.5 mmol) in THF (10 ml), aq. 10% H_2SO_4 (5 ml) was added with stirring at 25°. After 3 h, H_2O (20 ml) was added followed by extraction with Et_2O (3 × 20 ml). The combined Et_2O extracts were washed with sat. aq. NaCl soln. (1 × 20 ml), dried ($MgSO_4$), and evaporated. A yellow oil (830 mg) was obtained which on chromatography over a silica-gel column using successively CH_2Cl_2/hexane 1:1, CH_2Cl_2, and AcOEt/hexane 1:4 gave **4-8**. *4-Methylnaphthalene-1-methanol* (**4**; 290 mg, 38%): Colorless crystals, m.p. 76–77° (recrystallized from petroleum ether (60–80°)/CH_2Cl_2; [16]: 73–74°; [17]: 77°). R_f 0.22 (CH_2Cl_2). ^{1}H-NMR (360 MHz): 1.80 (br. *s*, 1 H); 2.72 (*s*, 3 H); 5.12 (*s*, 2 H); 7.30 (*d*, *J* = 7, 1 H); 7.41 (*d*, *J* = 7, 1 H); 7.57 (*m* 2 H); 8.06 (*m*, 1 H); 8.17 (*m*, 1 H).

1,4-Dimethyl-2-naphthol (**5**; 165 mg, 21%); Colorless crystals, m.p. 134–135° (recrystallized from petroleum ether (60–80°)/CH_2Cl_2; [14]: 133–133.5°; [18]: 135–136°). R_f 0.31 (CH_2Cl_2). ^{1}H-NMR (100 MHz): 2.53 (*s*, 3 H); 2.65 (*s*, 3 H); 4.84 (br. *s*, 1 H); 6.94 (*s*, 1 H); 7.30–7.70 (*m*, 2 H); 7.80–8.12 (*m*, 2 H).

Bis[(4-methyl-1-naphthyl)methyl] Ether (**6**; 11 mg, 2%); Colorless solid, m.p. 112–114° ([17]: 117°). R_f 0.61 (CH_2Cl_2). ^{1}H-NMR (360 MHz): 2.71 (*s*, 6 H); 5.02 (*s*, 4 H); 7.28 (*m*, 2 H); 7.40–7.60 (*m*, 6 H); 8.03 (*d*, *J* = 8, 2 H); 8.14 (*d*, *J* = 8, 2 H). MS: 326 (13, M^+), 184 (11), 171 (17), 156 (100), 155 (67), 141 (52), 115 (26).

5,8a,13,16a-Tetramethyl-dinaphtho[2,1-c,2',1'-g][1,2,5,6]tetraoxocine (**7**; 8 mg, 1%): Colorless crystals, m.p. 230°. R_f 0.56 (CH_2Cl_2). ^{1}H-NMR (360 MHz): 1.30 (*s*, 3 H); 1.60 (*s*, 3 H); 2.05 (*d*, *J* = 1, 3 H); 2.07 (*d*, *J* = 1, 3 H); 4.01 (*d*, *J* = 6, 1 H); 4.26 (*d*, *J* = 6, 1 H); 5.87 (*dq*, *J* = 6,1H); 5.91 (*dq*, *J* = 6, 1, 1 H); 7.10–7.36 (*m*, 7 H); 7.82 (*d*, *J* = 6, 1 H). ^{13}C-NMR (90.6 MHz): 19.7 (*q*, 2 overlapg. signals); 25.7 (*q*); 26.3 (*q*); 78,5 (*d*); 83.2 (*d*); 84,8 (*s*); 85,7 (*s*); 121,2; 121.4; 123.6; 124.1; 125.0; 125.5; 126.7; 127.1; 128..0; 128.1; 131.1; 132.6; 135.0; 135.7; 137.3; 138.9. MS: no M^+, 344.5 (3, $M^+ - 32$), 327 (4), 257 (6), 242 (5), 227 (8), 198 (4), 183 (6), 172 (38), 159 (93), 158 (84), 157 (73), 146 (46), 129 (100), 128 (77), 115 (43). Anal. calc. for $C_{24}H_{24}O_4$ (376.48): C 76.56, H 6.43; found: C 76.84, H 6.26.

1.4-Dimethylnaphthalene (**8**; 27 mg, 4%): R_f 0.71 (CH_2Cl_2). *Warning.* In all experiments with **1**, H_2O_2 is liberated, thereby creating a risk of explosion. Consequently, all operations should be conducted behind a safety shield. If experiments are repeated on a larger scale than described, then it is advisable *not* to remove all the solvent prior to chromatography.

3.2. A soln. of **1** (200 mg, 1.06 mmol) in THF (0.2 ml) was mixed with a soln. of H_2SO_4 (4 drops of conc. H_2SO_4 and 1 drop of H_2O in 0.2 ml of THF) with stirring at 25°. After 10 min, **1** (200 mg, 1.06 mmol) was added and stirring continued for 2 h. Workup and chromatography were effected as described in *3.1.* Ether **6** was obtained (55 mg, 16%). No **7** was detected.

4. *1-Chloromethyl-4-methylnaphthalene* (**9**). By using *Procedure 3.1,* the reaction of **1** (188 mg, 1 mmol) in THF (3 ml) with aq. 5N HCl (3 ml) gave pure **9** as a pale yellow oil which crystallized on standing (190 mg, 100%). Chromatography over a short *Florisil* column with CH_2Cl_2 furnished **9** as colorless crystals, m.p. 60–61° ([19]: 60–63°). R_f 0.93 (CH_2Cl_2). ^{1}H-NMR (360 MHz): 2.72 (*s*, 3 H); 5.06 (*s*, 2 H); 7.28 (*d*, *J* = 7, 1 H); 7.40 (*d*, *J* = 7, 1 H); 7.58 (*m*, 2 H); 8.05 (*m*, 1 H); 8.16 (*m*, 1 H). MS: 192 (8, M^+ + 2), 190 (24, M^+), 155 (100).

5. *1-Bromomethyl-4-methylnaphthalene* (**10**). Using *Procedure 3.1,* **1** (188 mg, 1 mmol) and aq. 20% HBr (1.5 ml), on reaction for 30 min, afforded a yellow oil (300 mg). Purification by chromatography (short *Florisil* column, CH_2Cl_2) gave **10** (180 mg, 77%) as colorless crystals, m.p. 74–75° ([17]: 85°; [20]: 77°). R_f 0.75 (CH_2Cl_2, partial dec. on silica gel). ^{1}H-NMR (360 MHz): 2.66 (*s*, 3 H); 4.96 (*s*, 2 H); 7.24 (*d*, *J* = 7, 1 H); 7.43 (*d*, *J* = 7, 1 H); 7.60 (*m*, 2 H); 8.02 (*d*, *J* = 8, 1 H); 8.17 (*d*, *J* = 8, 1 H). MS: 236 (5, M^+ + 1), 234 (5, M^+), 155 (100).

6. *(4-Methyl-1-naphthyl)methyl Trifluoroacetate* (**11**). To a soln. of **1** (188 mg, 1 mmol) in CH_2Cl_2 (3 ml) was added CF_3COOH (150 mg, 1.3 mmol) with stirring at 25°. After 10 min, Et_2O (20 ml) was added. The Et_2O soln. was extracted with H_2O (10 ml) and sat. aq. NaCl soln. (10 ml), dried ($MgSO_4$), and evaporated. The resulting brown oil (300 mg) was purified on a *Florisil* column (CH_2Cl_2) to give **11** as colorless oil (140 mg, 52%). R_f 0.66 (CH_2Cl_2). IR (CCl_4): 1784*s* (ester), 1220*s*, 1170*s*, 1134*s*. ^{1}H-NMR (360 MHz): 2.73 (*s*, 3 H); 5.82 (*s*, 2 H); 7.35 (*d*, *J* = 7, 1 H); 7.51 (*d*, *J* = 7, 1 H); 7.63 (*m*, 2 H); 8.02 (*m*, 1 H); 8.08 (*m*, 1 H). MS: 268 (51, M^+), 155 (100). Anal. calc. for $C_{14}H_{11}F_3O_2$ (268.25): C 62.68, H 4.14, F 21.25; found: C 62.92, H 4.30, F 21.06.

7. *(4-Methyl-1-naphthyl)methyl Formate* (**12**). To a soln. of **1** (188 mg, 1 mmol) in THF (2 ml) was added successively HCO_2H (0.2 ml) and *Amberlyst-15* (500 mg) with stirring at 25°. After ½ h, the mixture was filtered over *Celite* and evaporated. The residue was purified by column chromatography over silica gel (CH_2Cl_2) to give **12** as a colorless oil (151 mg, 76%). Treatment with Et_2O/hexane 1:9 afforded colorless crystals, m.p. 34–36°. R_f 0.50 (CH_2Cl_2). IR (CCl_4): 1731*s* (ester), 1160*s*. ^{1}H-NMR (360 MHz): 2.71 (*s*, 3 H); 5.66 (*s*, 2 H); 7.32 (*d*, *J* = 7, 1 H); 7.46 (*d*, *J* = 7, 1 H); 7.58 (*m*, 2 H); 8.05 (*m*, 2 H); 8.17 (*s*, 1 H). MS: 200 (45, M^+), 155 (100). Anal. calc. for $C_{13}H_{12}O_2$ (200.25): C 77.97, H 6.05; found: C 78.06, H 6.28.

8. *Reaction of* **1** *with Glycolic Acid. Procedure 7* was applied to the reaction of **1** (250 mg, 1.33 mmol) in THF (3 ml) with glycolic acid (500 mg, 6.58 mmol, pre-treated with 4-Å molecular sieves in THF) in the presence of *Amberlyst-15* (1 g) for 3 h. Workup and column chromatography (silica gel, AcOEt/hexane 3:7, then AcOEt) gave **14**, **13**, and **4** (41 mg, 18%). [(4-Methyl-1-naphthyl)methoxy]acetic acid (**14**, 160 mg, 52%); Colorless oil which on treatment with toluene produced colorless crystals, m.p. 109–111°. R_f 0.07 (AcOEt/hexane 3:7). IR (CCl_4): 3420*w*, 2850–2950*m*, 1782*s* and 1730*s* (free and H-bonded COOH). ^{1}H-NMR (360 MHz): 2.71 (*s*, 3 H); 4.16 (*s*, 2H); 5.08 (*s*, 2 H); 7.29 (*d*, *J* = 7, 1 H); 7.37 (*d*, *J* = 7, 1 H); 7.58 (*m*, 2 H); 8.05 (*m*, 1 H); 8.20 (*m*, 1 H). MS: 230 (47, M^+), 215 (12), 171 (29), 170 (18), 155 (100), 153 (31), 143 (18), 141 (18), 128 (45), 115 (38). Anal. calc. for $C_{14}H_{14}O_3$ (230.28): C 73.02, H 6.14; found: C 72.89, H 6.29.

(4-Methyl-1-naphthyl)methyl Glycolate (**13**; 57 mg, 19%); Colorless oil. R_f 0.15 (AcOEt/hexane 3:7). IR (CCl_4): 3618*w* and 3550*m* (free and H-bonded OH), 1742*s* (ester). ^{1}H-NMR (360 MHz): 2.38 (br. *t*, *J* = 6, 1 H); 2.72 (*s*, 3 H); 4.18 (*d*, *J* = 6, 2 H); 5.67 (*s*, 2 H); 7.31 (*d*, *J* = 7, 1 H); 7.46 (*d*, *J* = 7, 1 H); 7.58 (*m*, 2 H); 8.01 (*m*, 2 H); 8.06 (*m*, 1 H). MS: 230 (12, M^+), 171 (4), 158 (23), 155 (100), 153 (12), 128 (17), 115 (18). The sample for elemental anal. was obtained by rechromatography (silica-gel column, AcOEt/CH_2Cl_2 15:85). Anal. calc. for $C_{14}H_{14}O_3$ (230.28): C 73.02, H 6.14; found: C 72.90, H 6.26.

9. *Methanolysis of* **1** *at 25°. Procedure 7,* but using **1** (188 mg, 1 mmol) in MeOH (5 ml) and *Amberlyst-15* (280 mg) afforded after 24 h and workup a yellow oil (176 mg). Prep. TLC (CH_2Cl_2) furnished **15**–**17**. *1-Methoxymethyl-4-methylnaphthalene* (**15**; 66 mg, 36%): Colorless oil ([17]: oil. b.p. 160–170°/0.13 Torr). R_f 0.74 (CH_2Cl_2). ^{1}H-NMR (360 MHz): 2.58 (*s*, 3 H); 3.42 (*s*, 3 H); 4.89 (*s*, 2 H); 7.28 (*d*, *J* = 7, 1 H); 7.38 (*d*, *J* = 7, 1 H); 7.55 (*m*, 2 H); 8.03 (*m*, 1 H); 8.14 (*m*, 1 H). MS: 186 (5, M^+), 156 (100), 155 (32), 154 (7), 153 (14), 152 (16), 141 (75).

2-Methoxy-1,4-dimethyl-naphthalene (**16**; 57 mg, 31%): pale yellow crystals, m.p. 66–67° (recrystallized from MeOH; [14]: 68.4–68.8°; [18]: 67–69°). R_f 0,87 (CH_2Cl_2). ^{1}H-NMR (360 MHz): 2.53 (*s*, 3 H); 2.70 (*s*, 3 H); 3.94 (*s*, 3 H); 7.12 (*s*, 1 H); 7.40 (*t*, *J* = 7, 1 H); 7.49 (*t*, *J* = 7, 1 H); 7.96 (*t*, *J* = 7, 2 H). MS: 186 (100, M^+), 171 (15), 156 (6), 153 (4), 143 (14), 141 (10), 128 (17), 115 (7).

2,3-Dihydro-2,3-dimethoxy-3,5-dimethyl-1-benzoxepin (**17**; 24 mg, 10%); pale yellow oil. R_f 0.57 (CH_2Cl_2). IR (CH_2Cl_2): 1078*s* and 1105*s* (C–O). ^{1}H-NMR (360 MHz): 1.38 (*s*, 3 H); 2.04 (*d*, *J* = 1.5, 3 H); 3.46 (*s*, 3 H); 3.55 (*s*, 3 H); 4.22 (*s*, 1 H); 5.47 (*q*, *J* = 1.5, 1 H); 6.80 (*d*, *J* = 7, 1 H); 6.88 (*m*, 1 H); 7.14 (*m*, 2 H). ^{13}C-NMR (90.6 MHz): 18.1 (*q*); 21.9 (*q*); 57.6 (*q*); 57.8 (*q*); 80.0 (*s*, C(3)); 108.8 (*d*, C(2)); 115.7 (*d*, C(4)); 120.6 (*d*); 122.8 (*s*); 123.2

(*d*); 123.3 (*d*); 128.9 (*s* + *d*, 2 overlapg. signals); 152.7 (*s*, C(9a)). MS: 234 (15, M^+), 203 (19), 186 (13), 173 (13), 160 (49), 159 (100), 155 (17), 145 (18). Anal. calc. for $C_{14}H_{18}O_3$ (234.32): C 71.76, H 7.76; found: C 72.04, H 7.94.

Repetition of this experiment with CH_3OD and *Amberlyst-15* pretreated with CH_3OD for 3 h gave **15**–**17** in yields of 42, 25, and 9%, resp.

10. *Methanolysis of* **1** *at* $-10°$. *Procedure 7*, but using **1** (115 mg, 0.6 mmol), MeOH (5 ml), and *Amberlyst-15* (500 mg) at $-10°$ for 3 h, gave, after column chromatography at $-20°$ (silica gel, AcOEt/CH_2Cl_2 1:4) *4-methoxy-1,4-dimethyl-1,4-dihydro-1-naphthyl hydroperoxide* (**18**; 101 mg, 75%) as unstable, colorless oil constiting of 2 epimers in a 3:1 ratio (^{1}H-NMR). R_f 0.47 (AcOEt/CH_2Cl_2 1:4). IR (CCl_4): 3512*m*, 3316*w*. ^{1}H-NMR (360 MHz): major epimer: 1.45 (*s*, 3 H); 1.48 (*s*, 3 H); 2.95 (*s*, 3 H); 5.98 (*d*, *J* = 10, 1 H); 6.17 (*d*, *J* = 10, 1 H); 7.40 (*m*, 2 H); 7.51 (*s*, 1 H); 7.58 (*m*, 2 H); minor epimer: 1.55 (*s*, 3 H); 1.57 (*s*, 3 H); 2.91 (*s*, 3 H); 5.97 (*d*, *J* = 10, 1H); 6.10 (*d*, *J* = 10, 1 H); 7.40 (*m*, 2 H); 7.46 (*s*, 1 H); 7.58 (*m*, 2 H).

11. *Methanolysis of* **18**. A soln. of **18** (10 mg, 0.045 mmol) in MeOH (0.5 ml) was stirred with *Amberlyst-15* (50 mg) for 2 h at 25°. Anal. by GLC revealed that the main products were **15**–**17** formed in 49, 37, and 13% yield, resp.

12. *Ethanolysis of* **1**. A soln. of **1** (940 mg, 5 mmol) in abs. EtOH (15 ml) was treated with *Amberlyst-15* (2 g) for 1 h at 25°. After workup, the resulting yellow oil (1100 mg) on chromatography on silica gel (flash column, CH_2Cl_2) gave **8** (109 mg, 14%) and **19**–**21**. *1-Ethoxymethyl-4-methylnaphthalene* (**19**; 396 mg, 40%): Colorless oil ([17]: oil, b.p. 155–160°/0.11 Torr). R_f 0.63 (CH_2Cl_2). ^{1}H-NMR (360 MHz): 1.26 (*t*, *J* = 7, 3 H); 2.70 (*s*, 3 H); 3.61 (*q*, *J* = 7, 2 H); 4.94 (*s*, 2 H); 7.26 (*d*, *J* = 7, 1 H); 7.38 (*d*, *J* = 7, 1 H); 7.55 (*m*, 2 H); 8.02 (*m*, 1 H); 8.16 (*m*, 1 H). MS: 200 (65, M^+), 185 (22), 156 (55), 155 (100), 143 (23), 141 (25), 128 (27), 115 (16).

2,3-Diethoxy-2,3-dihydro-3,5-dimethyl-benzoxepin (**20**; 49 mg, 4%): Colorless oil. R_f 0.37 (CH_2Cl_2). IR (CCl_4): 1113*s*, 1070*s*. ^{1}H-NMR (360 MHz): 1.08 (*t*, *J* = 7, 3 H); 1.26 (*t*, *J* = 7, 3 H); 1.42 (*s*, 3 H); 2.03 (*d*, *J* = 1, 3 H); 3.52 (*m*, 1 H); 3.65 (*m*, 1 H); 3.75 (*m*, 2 H); 4.36 (*s*, 1 H); 5.51 (*q*, *J* = 1, 1 H); 6.77 (*d*, *J* = 7, 1 H); 6.87 (*t*, *J* = 7, 1 H); 7.13 (*ml*, 2 H). MS: 262 (2, M^+), 244 (3), 173 (4), 168 (4), 159 (58), 145 (4), 143 (8), 133 (13), 132 (8), 103 (100), 86 (11), 84 (20), 75 (53). The sample for elemental anal. was purified by HPLC (t_R 960, *radial pak* 10μ column). Anal. calc. for $C_{16}H_{22}O_3$ (262.38): C 73.24, H 8.47; found: C 73.24, H 8.59.

2-Ethoxy-1,4-dimethyl-1,2-dihydro-1-naphthyl Hydroperoxide (**21**; 142 mg, 12%): Colorless crystals, m.p. 92° (after purification by HPLC (t_R 348, *Nova pak* 5μ column) and recrystallization from pentane/Et_2O 10:1). R_f 0.23 (CH_2Cl_2). IR (CCl_4): 3362*m*, 1085*s*, 1065*s*. ^{1}H-NMR (360 MHz): 1.21 (*t*, *J* = 7, 3 H); 1.42 (*s*, 3 H); 2.15 (*d*, *J* = 1, 3 H); 3.58 (*m*, 1 H); 3.71 (*m*, 1 H); 4.10 (*d*, *J* = 5.5, 1 H); 5.97 (*dq*, *J* = 5.5, 1, 1 H); 7.33 (*m*, 3 H); 7.66 (*d*, *J* = 7, 1 H). MS: no M^+, 216 (7), 201 (10), 188 (7), 187 (6), 173 (14), 172 (12), 159 (100), 156 (83), 155 (25), 146 (37), 145 (70), 144 (33), 141 (81), 129 (26), 128 (28), 115 (51). Anal. calc. for $C_{14}H_{18}O_3$ (234.32): C 71.76, H 7.76; found: C 71.80, H 7.81.

13. *Ethanolysis of* **21**. A soln. of **21** (7 mg, 0.03 mmol) in abs. EtOH (0.1 ml) was stirred with *Amberlyst-15* (100 mg) for 16 h at 25°. GLC showed that the chief products were **19**, **20**, and **8** formed in 48, 14, and 10% yields, resp.

14. *4-Methyl-1-(3'-phenylpropoxy)naphthalene* (**22**). To a soln. of **1** (500 mg, 2.65 mmol) in 3-phenylpropanol (7 ml), *Amberlyst-15* (1 g) was added with stirring at 25°. After 5 h, the mixture was passed through a silica-gel column (hexane/CH_2Cl_2 1:1, then CH_2Cl_2) to give a pale yellow oil (630 mg). Column chromatography (silica gel, CH_2Cl_2) gave **22** (379 mg, 49%) as a colorless oil. R_f 0.55 (CH_2Cl_2). ^{1}H-NMR (360 MHz): 1.97 (*m*, 2 H); 2.73 (*s* + *t*, 5 H); 3.57 (*t*, *J* = 6, 2 H); 4.96 (*s*, 2 H); 7.14–7.33 (*m*, 6 H); 7.39 (*d*, *J* = 7, 1 H); 7.58 (*m*, 2 H); 8.05 (*m*, 1 H); 8.20 (*m*, 1 H). MS: 290 (27, M^+), 155 (100), 141 (19), 128 (22), 115 (20), 91 (70), 77 (13). Anal. calc. for $C_{21}H_{22}O$ (290.43): C 86.84, H 7.65; found: C 86.80, H 7.85.

15. *Reaction of* **1** *with* t-*BuOH*. A soln. of **1** (500 mg, 2.66 mmol) in *t*-BuOH (5 ml) and *Amberlyst-15* (1 g) were stirred for 16 h at 25°. Filtration through *Celite* and evaporation of *t*-BuOH at 0.05 Torr gave a residue which on chromatography (flash column, silica gel, CH_2Cl_2) afforded **4** (83 mg, 18%) and **23**–**25**. *1-(*tert*-Butoxy)methyl-4-methylnaphthalene* (**23**; 305 mg, 50%): Colorless crystals, m.p. 54–55° (after purification by HPLC, t_R 952, *Nova pak* 5μ column). R_f 0.62 (CH_2Cl_2). IR (CCl_4): 1196*s*. ^{1}H-NMR (360 MHz): 1.37 (*s*, 9 H); 2.67 (*s*, 3 H); 4.86 (*s*, 2 H); 7.28 (*d*, *J* = 7.5, 1 H); 7.53 (*m*, 2 H); 8.02 (*m*, 1 H); 8.11 (*m*, 1 H). MS: 228 (43, M^+), 172 (32), 155 (86), 143 (100), 128 (27), 115 (19). Anal. calc. for $C_{16}H_{20}O$ (228.36): C 83.15, H 8.85; found: C 84.31, H 8.82.

*6,10b-Dimethyl-4a,10b-dihydro-3*H*-naphtho[2,1-*e*][1,2,4]trioxine* (**24**; 45 mg, 8%): Colorless solid, m.p. 48–49°. R_f 0.49 (CH_2Cl_2). ^{1}H-NMR (360 MHz): 1.28 (*s*, 3 H); 2.16 (*d*, *J* = 1.5, 3 H); 4.06 (*d*, *J* = 7, 1 H); 5.12 (*d*, *J* = 8, 1 H); 5.51 (*d*, *J* = 8, 1 H); 5.93 (*dq*, *J* = 7, 1.5, 1 H); 7.23–7.50 (*m*, 3 H); 7.96 (*d*, *J* = 7, 1 H). ^{13}C-NMR (90.6 MHz); 19.4 (*q*); 23.8 (*q*); 72.6 (*d*); 82.3 (*s*); 95.7 (*t*); 119.7 (*d*); 134.3; 125.0; 127.6; 128.8; 133.1; 137.9; 138.3. MS: no M^+, 172 (65), 159 (100), 157 (21), 145 (12), 141 (26), 115 (31). Anal. calc. for $C_{13}H_{14}O_3$ (218.27): C 71.53, H 6.48; found: C 71.84, H 6.72.

4-Methyl-1-naphthol (**25**; 34 mg, 8%): Colorless crystals, m.p. 80–81° ([14]: 82–83°). R_f 0.31 (CH_2Cl_2). IR (CCl_4): 3608*s* (OH). ^{1}H-NMR (360 MHz): 2.63 (*s*, 3 H); 5.26 (br. *s*, 1 H); 6.73 (*d*, *J* = 8, 1 H); 7.15 (*d*, *J* = 8, 1 H); 7.53 (*m*, 2 H); 7.96 (*m*, 1 H); 8.22 (*m*, 1 H). MS: 158 (100, M^+), 129 (37), 128 (42), 115 (23).

16. *Control Experiment.* A soln. of **1** (50 mg, 0.27 mmol) in CH_2Cl_2 (2 ml) was stirred with *Amberlyst-15* (200 mg) for 2 h at 25°. The presence of **8**, **4**, **5**, **24**, and **25** in yields of 18, 17, 7, 12, and 9%, resp., was revealed by GLC and ^{1}H-NMR (360 MHz).

17. *Reaction of* **1** *with* p-*Cresol.* To a soln. of **1** (300 mg, 1.6 mmol) in CH_2Cl_2 (1 ml), *p*-cresol (2 g) and *Amberlyst-15* (1 g) were added. Stirring at 25° for 16 h followed by filtration through *Celite* and evaporation gave a soln. containing *p*-cresol. The latter was removed by column chromatography (silica gel, CH_2Cl_2; R_f 0.25). Further chromatographic purification (flash column, silica gel, CH_2Cl_2/hexane 1:1) furnished **26** and **27**. *2-(1,4-Dimethyl-2-naphthyl)-4-methylphenol* (**26**; 320 mg, 77%): Colorless oil. R_f 0.53 (CH_2Cl_2). IR (CCl_4): 3560*s* (OH). ^{1}H-NMR (360 MHz): 2.35 (*s*, 3 H); 2.52 (*s*, 3 H); 2.71 (*s*, 3 H); 4.66 (*s*, 1 H); 6.92 (*d*, *J* = 8, 1 H); 7.00 (*d*, *J* = 2, 1 H); 7.13 (*dd*, *J* = 8, 2, 1 H); 7.21 (*s*, 1 H); 7.61 (*m*, 2 H); 8.06 (*m*, 1 H); 8.14 (*m*, 1 H). MS: 262 (100, M^+), 247 (54), 232 (25), 215 (12), 202 (16), 131 (16), 123 (15), 114 (18), 107 (22), 101 (19), 95 (11). Anal. calc. for $C_{19}H_{18}O$ (262.37): C 86.97, H 6.93; found: C 86.71, H 7.23.

4-Methyl-2-(4-methyl-1-naphthyl)methyl-phenol (**27**; 43 mg, 10%): Colorless oil. R_f 0.41 (CH_2Cl_2). IR (CCl_4): 3620*s* and 3400–3550*s* (free and H-bonded OH). ^{1}H-NMR (360 MHz): 2.19 (*s*, 3 H); 2.70 (*s*, 3 H); 4.38 (*s*, 2 H); 4.70 (*s*, 1 H); 6.73 (*d*, *J* = 8, 1 H); 6.82 (br. *s*, 1 H); 6.91 (br. *d*, *J* = 8, 1 H); 7.14 (*d*, *J* = 7, 1 H); 7.25 (*d*, *J* = 7, 1 H); 7.53 (*m*, 2 H); 8.07 (*m*, 2 H). MS: 262 (17, M^+), 142 (100), 115 (6). Anal. calc. for $C_{19}H_{18}O$ (262.37): C 86.97, H 6.93; found: C 86.69, H 6.84.

18. *Reaction of* **1** *with Anisole. Procedure 17* was followed using a soln. of **1** (300 mg, 1.6 mmol) and anisole (5 ml). Excess anisole was removed at 60°/0.01 Torr. Chromatography (flash column, silica gel, CH_2Cl_2/hexane 1:3) gave **28** and **29**. *2-(4'-Methoxyphenyl-1,4-dimethyl-naphthalene* (**28**; 192 mg, 46%): colorless crystals, m.p. 77–78°. R_f 0.24 (CH_2Cl_2/hexane 1:3). IR (CCl_4): 1515*s*, 1247*s*. ^{1}H-NMR (360 MHz): 2.60 (*s*, 3 H); 2.72 (*s*, 3 H); 3.90 (*s*, 3 H); 7.01 (*d*, *J* = 8.5, 2 H); 7.26 (*s*, 1 H); 7.32 (*d*, *J* = 8.5, 2 H); 7.57 (*m*, 2 H); 8.04 (*m*, 1 H); 8.12 (*m*, 1 H). MS: 262 (100, M^+), 247 (21), 231 (13), 215 (19), 203 (22), 202 (22), 189 (11), 131 (10), 107 (11), 101 (11). Anal. calc. for $C_{19}H_{18}O$ (262.37): C 86.97, H 6.93; found: C 87.21, H 7.22.

1-[(4'-Methoxyphenyl)methyl]-4-methylnaphthalene (**29**; 91 mg, 22%): Colorless crystals, m.p. 80–82°. R_f 0.19 (CH_2Cl_2/hexane 1:3). IR (CCl_4): 1510*s*, 1247*s*. ^{1}H-NMR (360 MHz): 2.70 (*s*, 3 H); 3.77 (*s*, 3 H); 4.38 (*s*, 2 H); 6.81 (*d*, *J* = 8.5, 2 H); 7.11 (*d*, *J* = 8.5, 2 H); 7.17 (*d*, *J* = 7, 1 H); 7.26 (*d*, *J* = 7, 1 H); 7.48 (*m*, 2 H); 8.01 (*m*, 2 H). MS: 262 (100, M^+), 247 (83), 231 (22), 215 (32), 203 (19), 202 (23), 189 (10), 155 (12), 154 (11), 153 (10), 152 (8), 121 (18), 115 (15), 101 (10). Anal. calc. for $C_{19}H_{18}O$ (262.37): C 86.97, H 6.93; found: C 87.13, H 7.09.

19. *Perhydrolysis of* **1**. To a soln. of **1** (1.128 g, 6 mmol) in 1.5N H_2O_2/Et_2O (30 ml), *Amberlyst-15* (1.2 g) was added. After stirring at 25° for 4 h, the mixture was filtered through *Celite*. Et_2O (20 ml) was added, the resulting soln. was washed with H_2O (3 × 50 ml) and sat. aq. NaCl soln. (1 × 10 ml), dried ($MgSO_4$), and evaporated to give a yellow oil (1.180 g) containing mainly *1,4-dihydroperoxy-1,4-dimethyl-1,4-dihydronaphthalene* (**30**) as a 1:1 mixture of epimers (^{1}H-NMR (360 MHz)). Crystallization from $CHCl_3$ gave **30** (700 mg, 53%) as colorless crystals, m.p. 128–130°. One of the epimers crystallized selectively by repeated solution in $CHCl_3$ and cooling, m.p. 138–142°. ^{1}H-NMR (360 MHz): 1.47 (*s*, 6 H); 6.20 (*s*, 2 H); 7.45 (*m*, 4 H; 2 H after D_2O exchange); 7.63 (*m*, 2 H). MS: 222 (trace, M^+), 189 (14), 172 (100), 157 (43), 156 (55), 144 (19), 141 (28), 129 (51), 128 (41), 115 (20). Anal. calc. for $C_{12}H_{14}O_4$ (222.26): C 64.84, H 6.36; found: C 64.55, H 6.62.

The other epimer was unstable. ^{1}H-NMR (360 MHz; characteristic signals): 1.55 (*s*, 6 H); 6.16 (*s*, 2 H). Alcohol **4** (103 mg, 10%) was obtained by column chromatography (silica gel, CH_2Cl_2) of the remaining mixture.

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