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Chemical syntheses of *syn*- and *anti*-1,2;3,4-diepoxides derived from 1,4-dimethyl- and 1,2,3,4-tetramethylanthracenes and naphthalenes

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Summary — Chemical isomerization of 1,4-endoperoxides **1a,b,n** derived from *meso*-unsubstituted 1,4-dimethyl- or 1,2,3,4-tetramethylanthracenes (and naphthalenes) to *syn*-1,2;3,4-diepoxides **2a,b,n** has been achieved by treatment at room temperature with $FeSO_4$ in CH_3CN containing pyridine. With analogous 9,10-diphenyl derivatives **1c,d**, heating appears necessary and the same isomerization is then superseded by another type of rearrangement leading to dihydronaphthoxanthenols **4c,d**. An electron-exchange mechanism may explain the difference between both series. In contrast, the isomeric *anti*-1,2;3,4-diepoxides **19b,c,d,n** have been prepared by direct epoxidation of the hydrocarbons **18a-d,n** with dimethyldioxirane generated in situ. In this case, the reaction is more efficient for 9,10-diphenyl derivatives **18c,d** than for meso-unsubstituted ones **18a,b** as the latter can undergo competitive oxidations at *meso*-positions leading to 10-hydroxy-9-anthrones **22a,b** at the same time as anthraquinones **23a,b**.

1,4-endoperoxide rearrangement / dihydronaphthoxanthenol / dimethyldioxirane epoxidation / 10-hydroxy-9-anthrone

Résumé — **Synthèses chimiques d'1,2;3,4-diépoxydes *syn* et *anti* dérivés de 1,4-diméthyl- et de 1,2,3,4-tétraméthyl-anthracènes et naphtalènes.** *L'isomérisation chimique des 1,4-endoperoxydes* **1a,b,n** *dérivés des 1,4-diméthyl- ou 1,2,3,4-tétraméthyl-anthracènes (non substitués en* méso*) ou- naphtalènes, en* syn*-1,2;3,4-diépoxydes* **2a,b,n** *a été avantageusement réalisée par traitement à température ambiante par $FeSO_4$ dans CH_3CN en présence de pyridine. Avec les dérivés analogues diphénylés en* méso **1c,d** *il paraît nécessaire d'opérer à chaud mais l'isomérisation est alors supplantée par un autre type de réarrangement qui conduit aux dihydronaphtoxanthénols* **4c,d**. *La différence observée entre les deux séries peut être expliquée sur la base d'un mécanisme par échange d'électrons. D'autre part, les* anti*-1,2;3,4-diépoxydes isomères* **19b,c,d,n** *ont été préparés par époxydation directe des hydrocarbures correspondants* **18a-d,n** *par le diméthyldioxirane préparé* in situ. *Dans ce cas, la réaction est plus efficace avec les dérivés 9,10-diphénylés* **18c,d** *qu'avec ceux qui n'ont pas de substituants en* méso **18a,b** *car ces derniers peuvent subir des oxydations concurrentes en* méso *conduisant aux 10-hydroxy-9-anthrones* **22a,b** *en même temps qu'aux anthraquinones* **23a,b**.

réarrangement des endoperoxydes 1,4-dihydroanthracéniques / dihydronaphtoxanthénol / époxydation par le diméthyldioxirane / 10-hydroxy-9-anthrone

Introduction

As shown earlier [1, 2], *syn*-1,2;3,4-diepoxides **2** derived from 1,4-dimethyl- or 1,2,3,4-tetramethylanthracenes and naphthalenes can be obtained by irradiating the corresponding 1,4-endoperoxides **1** at long wavelengths. Competing photoisomerization to β,γ-epoxyketones in some cases, such as those of the 1,2,3,4-tetramethyl derivatives [2], or more generally, the propensity of these diepoxides to undergo further photochemical changes, may cut down the yields, particularly in large-scale preparations. Consequently, it seemed appropriate to investigate the possibility of carrying out the same isomerization by chemical means.

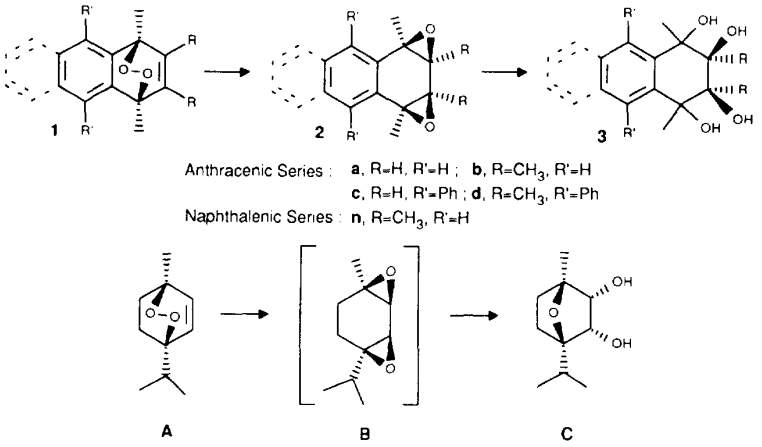
On the other hand, these diepoxides are also prone to undergo a great variety of isomerizations in the presence of protic or Lewis acids. Although some of these rearrangements have already been reported [1, 2], new observations allow a more complete overview which will be presented later. Therefore, it appeared desirable to extend the studies to the *anti* isomers **19** of the preceding diepoxides.

We present, herein, the results obtained in the chemical syntheses of both types of compounds.

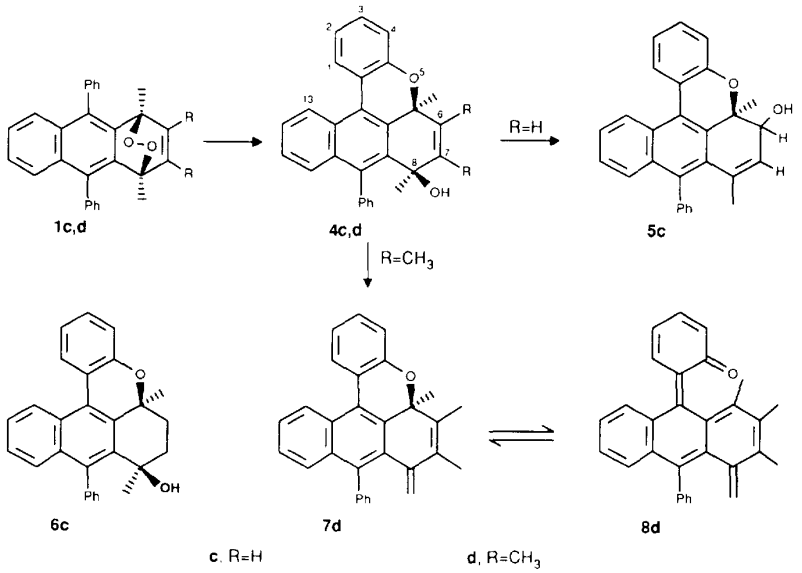
Syntheses of *syn*-diepoxides. Isomerizations of 1,4-anthracenic endoperoxides by ferrous ion

Cobalt(II) *meso*-tetraphenylporphine (CoTPP) being the best reported catalyst for promoting the chemical rearrangement of 1,4-endoperoxides to *syn*-diepoxides

* Correspondence and reprints



Scheme 1



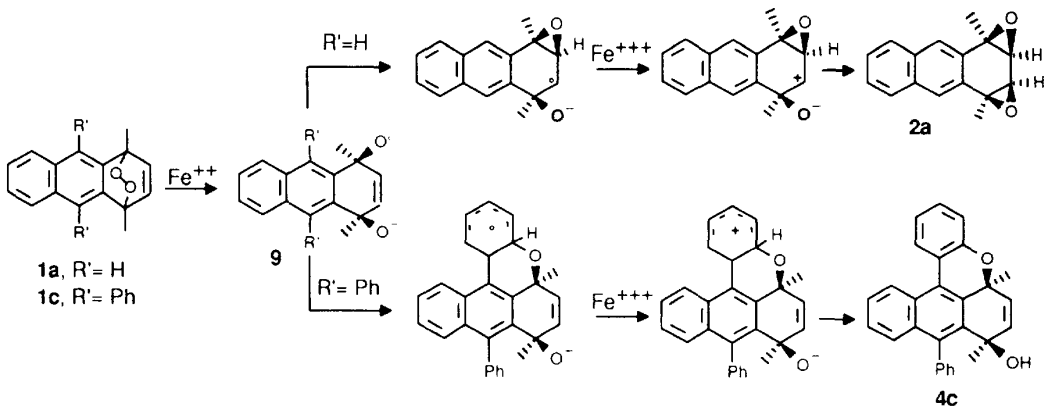
Scheme 2

in alicyclic series, we applied the literature procedure [3, 4] to the anthracenic endoperoxides **1a,b**. These latter compounds appeared to be totally inert whatever the reaction conditions; they were recovered unchanged after a number of two-day treatments with CoTPP in methylene chloride, ether or acetone, from 25 to 60 °C. The reason for this inertness is not clear although one may a priori suspect endoperoxides such as **1a,b**, which are richer in electrons than their alicyclic counterparts, to be less reactive towards reductants [see 3].

We then considered using ferrous ion catalysis and found that the treatment of endoperoxide **1b** by $FeSO_4$ in acetonitrile/water (1:1), at room temperature, led in high yield to the tetrol **3b**, previously obtained by acid-catalyzed hydrolysis of diepoxide **2b** [2]. Therefore, a transient formation of the diepoxide during the reaction seemed to be very likely as has been suggested for the related rearrangement of ascaridole **A** to ascaridole-glycol **C** under the same conditions [5] (scheme 1). In both cases, subsequent hydrolytic opening of the diepoxide was probably due to the acidity of the medium, caused in particular by the ferric ion formed. As expected, when treated by $FeSO_4$ in anhydrous acetonitrile with added pyridine at room temperature, endoperoxides **1a,b,n** led within a few hours to diepoxides **2a,b,n**, in high yields (80–90%); the concurrent formation of β,γ-epoxyketones was not observed.

The same procedure however was not successful with the *meso*-diphenyl series. At room temperature, endoperoxides **1c,d** appeared to be unreactive, whereas under heating, isomerization to diepoxides was largely superseded by another type of rearrangement. By extended heating at 70–80 °C in pyridine containing $FeSO_4$, **1c,d** led essentially to dihydronaphthoxanthenols **4c,d**, which could be isolated in yields of 60–70% (scheme 2).

In pure acetonitrile, dihydronaphthoxanthenols **4c,d** rearranged easily when treated at room temperature by $Fe_2(SO_4)_3$; **4c** gave its allylic isomer **5c**, whereas



Scheme 3

4d underwent essentially a dehydration to **7d**, a light-sensitive hydrocarbon. These last transformations explain the obtention of more or less complex reaction mixtures by extended heating of endoperoxides **1c,d** in acetonitrile, in the presence of $FeSO_4$ but without pyridine. Endoperoxide **1c** afforded principally **5c**, while with **1d** only a small proportion of **7d** was isolated, by TLC, beside a major product (50%) which appeared, from spectrographic data, to be **20d** (see scheme 5). In the latter case, it is probable that a partial isomerization of **1d** to diepoxide **2d** occurred, followed by an acid-catalyzed rearrangement of **2d**. *Syn*-diepoxide **2d** being unobtainable via photoisomerization of endoperoxide **1d** [2], it has been checked that **20d** forms easily by acid treatment of the isomeric *anti*-diepoxide **19d**. Rearrangement of **2d**, or its *anti*-isomer **19d**, to **20d** could logically be interpreted as involving a simple opening of one of the epoxide groups to an allylic alcohol, as was observed with **2b** and **2n** under acidic conditions [2], while the other group would undergo a pinacolic-type ring contraction.

Structural assignments of the new naphthoxanthenic compounds are based on spectral data, and particularly on ^1H NMR spectra which show low-field multiplets corresponding to the aromatic protons located at positions 1 and 13 (bay region). In addition, dihydronaphthoxanthenol **4c** has been hydrogenated to the previously known tetrahydro-derivative **6c** [6b], on Pt at room temperature.

Methylidenedihydronaphthoxanthene **7d**, which absorbs longer-wavelength radiation than the alcohols **4c,d**, also differs from the latter by a special sensitivity to normal daylight which may affect its recovery from reaction mixtures. A yellow coloration develops rather quickly in the solutions or in adsorbed bands of **7d** on drying SiO_2 chromatographic plates; this coloration disappears more or less completely in the dark. Such behavior is characteristic of photochromic tautomerism and should very probably be assigned to the 2*H*-chromene moiety present in **7d** (scheme 2). Valence tautomerization should lead to the colored dienone **8d** [7] and, as in many other cases, **8d** may also suffer irreversible side reactions, particularly in the presence of oxygen. For the moment, we restricted ourselves to checking that the yellow color of the solutions is immediately discharged by addition of tetracyanoethylene, as predicted by the dienic character of **8d**.

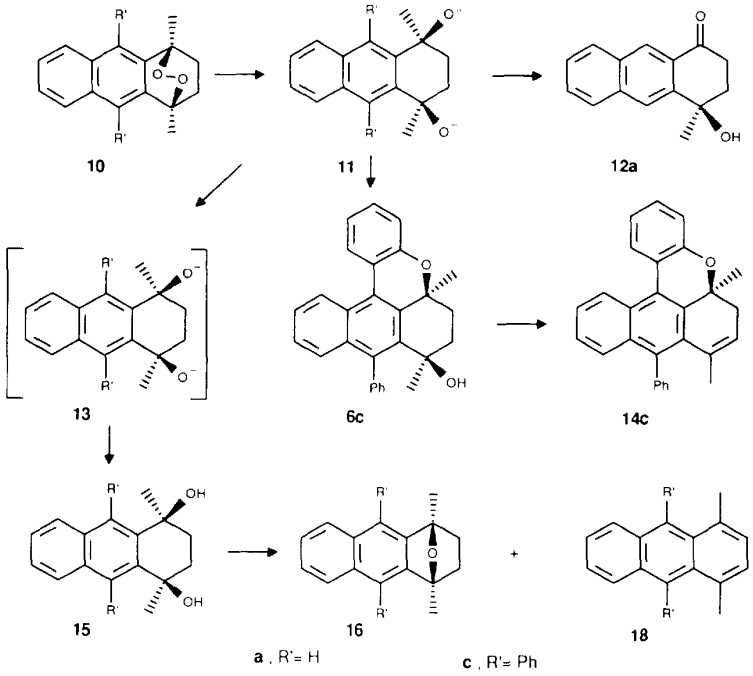
Returning to the various catalyzed isomerizations of endoperoxides **1**, the electron exchange mechanism exemplified in scheme 3 for **1a,c**, similar to that proposed [5] but subsequently questioned [3] for the case of ascaridole, explains the observed transformations fairly well. In particular, in the *meso*-diphenyl radical-anion **9c** one expects that radical attack of the neighboring phenyl group, leading ultimately to **4c**, should compete with addition to the double bond leading to diepoxide **2c**.

It is noteworthy that the same difference in behavior occurs in the tetrahydro series between *meso*-unsubstituted and *meso*-diphenyl derivatives. When treated with ferrous sulfate, 1,4-dimethyl-endoperoxides **10a,c** simultaneously underwent one- and two-electron reductions (scheme 4).

With endoperoxide **10a**, one-electron reduction led to hydroxyanthracenone **12a** in moderate yields, arising from β-scission of the radical moiety of **11a**, while with **10c** we obtained higher yields of tetrahydronaphthoxanthenol **6c** (in pyridine) or (in acetonitrile) its dehydration product dihydronaphthoxanthene **14c**. In the intermediate radical-anion **11c**, radical attack of the phenyl group thus appears to be at least as efficient as in the dihydro series.

The competitive two-electron reduction led in both cases as expected, through dianions **13a,c**, to *cis*-diols **15a,c** or to their dehydration derivatives: transannular epoxides **16a,c** and hydrocarbons **18a,c**.

The above results for the stepwise reduction of endoperoxides **10a,c** by the ferrous ion differ from those previously observed in the thermolysis and photolysis of these compounds [6a,b], even if limited formation of the same compounds can occur in these processes, in particular with **10c** [6b]. Under the latter reaction conditions, the likely intermediates are the diradicals formed by homolysis of the peroxidic bond; competing with other attacks, these diradicals are able to add to the naphthalene nucleus itself, leading to unstable diepoxides which can rearrange further. Obviously no comparable process operates here, with radical-anions **11a,c**.



Scheme 4

Syntheses of *anti*-diepoxides: direct epoxidation of anthracenic and naphthalenic hydrocarbons

According to the reported behavior of naphthalene, direct diepoxidation of the corresponding hydrocarbons seemed to be the most attractive route to test. As a matter of fact, the *anti*-1,2;3,4-diepoxide has been directly obtained from naphthalene by several methods, though most frequently in low yields. For instance, this was the case with epoxidations by *m*-chloroperbenzoic acid (*m*-CPBA) in the presence of sodium bicarbonate [8] or by sodium hypochlorite with phase-transfer catalysts [9], which resulted in yields of 15–20%. If use of dimethyldioxirane [10] led to an even lower yield (5%), that of the more potent methyl(trifluoromethyl)-dioxirane [11] appeared finally to be the more satisfying since it led to a 90% yield of isolated diepoxide.

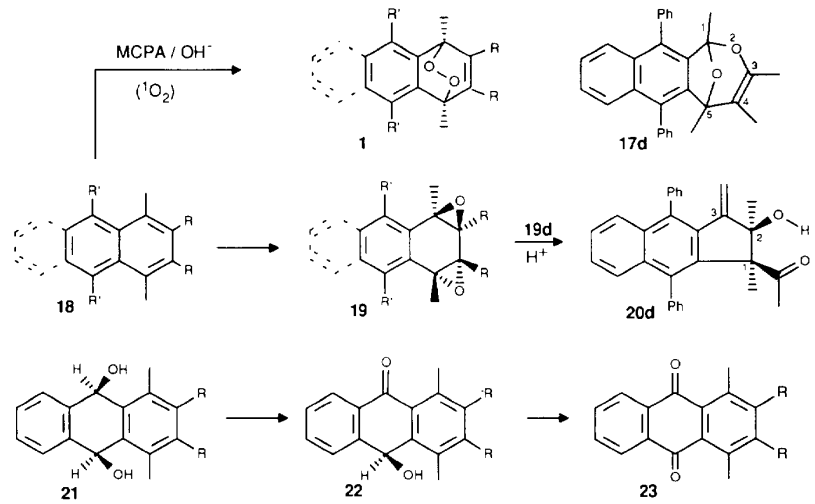
On the other hand, anthracene itself is reported to afford 9,10-anthraquinone in high yields by all the preceding methods, but an *anti*-1,2;3,4-diepoxide has apparently been obtained, in limited yield (16%), from 9,10-diphenylanthracene treated as before by *m*-CPBA [8]. Since we expected an activating effect of the methyl substituents, we first applied this simple procedure to anthracenic hydrocarbons **18a–d**, ie, we stirred a solution of the hydrocarbon in methylene chloride containing an excess of *m*-CPBA with an aqueous saturated sodium bicarbonate solution.

In the 1,4-dimethyl series, the result with **18a** was a complex mixture of products containing essentially 1,4-dimethylanthraquinone **23a**, whereas with the 9,10-diphenyl derivative **18c**, an appreciable fraction (35–40%) of the *anti*-diepoxide **19c** could be isolated from the reaction mixture.

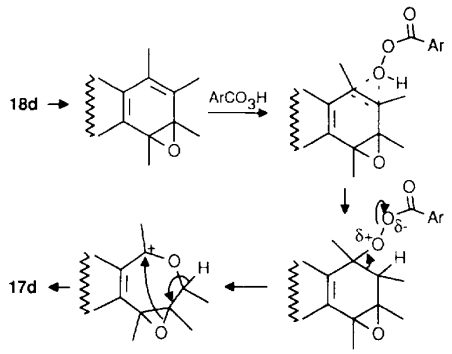
In the 1,2;3,4-tetramethyl series, *anti*-diepoxides **19b** and **19d** were also obtained, but, in both cases, in limited yields. Thus with **18b**, less than 20% of **19b** was separated with difficulty by TLC from the complex reaction mixture and, unexpectedly, a small fraction of endoperoxide **1b** was also isolated. As formation of **1b** is also observed when working in the dark, it is very likely that it comes from the trapping of singlet oxygen released by the dismutation of *m*-CPBA. It is known that dismutation of peracids in slightly alkaline medium can liberate $^1O_2$, even up to 95% [12]. Moreover, a partial endoperoxidation of 9-methyl-10-phenylanthracene, in similar conditions, has been formerly observed by McKeown and Waters [13]. The high reactivity of the tetramethyl hydrocarbon **18b** towards $^1O_2$-addition would explain why this side reaction occurred with this substrate.

With **18d**, the reaction mixture appeared to be less complex than the one mentioned above, but *anti*-diepoxide **19d**, separated by TLC, was also accompanied by a side product formed in the same proportion (around 20%). Oddly enough, this latter compound is neither the corresponding endoperoxide **1d** nor one of its derivatives since it is the only product isolated after treatment of **18d** by *m*-CPBA *in the absence of base*. According to a thorough NMR analysis (see the *Experimental section*), it appears to be the bicyclic ketal **17d**. This unusual side product may possibly derive from the intermediate monoepoxide via a rearrangement accompanying further epoxidation as shown in scheme 6.

Returning to the epoxidation of hydrocarbons, it seemed appropriate to test the applicability of dimethyldioxirane. We used an in situ method of epoxidation with oxone in a mixture of acetone/methylene chloride as described by Jeyaraman and Murray [10]. Very satisfactory results were obtained with the 9,10-diphenylanthracenes **18c** and **18d** and with tetramethylnaphthalene **18n**; after clean and rather rapid reactions,



Scheme 5



Scheme 6

the *anti*-diepoxides **19c,d,n** were directly separated, as crystalline crops, in quasi-quantitative yields for **19d** and **19n** and over 70% yield for **19c**.

Possible oxidations at the *meso*-positions were a complicating factor with the *meso*-unsubstituted anthracenes **18a** and **18b**. With the more reactive **18b**, column chromatography allowed the recovery of a significant fraction of diepoxide **19b** (50–55%) beside the oxidation products, whereas with **18a** no diepoxide **19a** could be separated. Concerning the oxidation products, it is noteworthy that in both cases the corresponding 10-hydroxy-9-anthrone was the most abundant, complete oxidation to anthraquinone remaining limited. With **18a**, up to 45–50% of **22a** was recovered beside 10% of anthraquinone **23a**. With **18b**, the hitherto unknown **22b** (around 20%) was accompanied by a small fraction of **23b** and a slightly larger amount of a unique quinol (12%). This quinol has been identified with the minor isomer formed in the hydride reduction of anthraquinone **23b**. According to previous studies on the stereochemistry of the hydride reduction of anthraquinones [14a,b], it may tentatively be assigned the *cis* configuration **21b**, the main reduction product being the *trans*-isomer.

The above behavior of methylated anthracenes **18a** and **18b**, in contrast to that of anthracene itself, which gives only anthraquinone when treated by dimethyldioxirane, shows that this *meso*-oxidation may be considered a stepwise process, the methyl substituents in the present case confering increased stability to the intermediates.

To conclude, it can be added that no *syn*-diepoxides **2** were detected in the preceding reactions. Dimethyldioxirane, which is much more convenient to use than peracids and sufficiently reactive towards activated substrates such as **18b–n**, also has the advantage of being totally stereospecific. Unfortunately, the intrinsic tendency of *meso*-unsubstituted anthracenes to undergo oxidation limits its use in this series.

Experimental section

^1H and ^{13}C NMR spectra were recorded, unless otherwise specified, in $CDCl_3$ with TMS as internal standard ($\delta = 0$) on Varian EM 390 or Bruker AM 250 and AC 300 spectrometers, UV on Uvikon 810 and IR on Perkin-Elmer 298 apparatus. Thin-layer chromatographic separations were run on Merck 60 silica gel (230–400 mesh). Melting points were taken on Kofler or Maquenne blocks and are uncorrected.

General procedure for isomerization of endoperoxides **1a,b** *and* **n**

$FeSO_4 \cdot 7\ H_2O$ (3 equiv) was added to a solution of endoperoxide **1a,b** or **n** (0.2 g) in acetonitrile (10 mL)/pyridine (0.3 mL) and the mixture was stirred for 24 h at room temperature. It was then poured into water and extracted with ether. After washing it with water and drying once ($MgSO_4$), the ether layer afforded, on evaporation, a crystalline crop of crude diepoxide **2**, which was washed with ether to completely remove the pyridine. (If more pyridine

is added, washing with aqueous 0.5 N HCl may be necessary).

Diepoxides **2a** [1], **2b** and **2n** [2] were obtained in yields of 80–90%. They were identified with authentic samples produced by photoisomerization.

• *Obtention of tetrol* **3b**

The same procedure applied to 120 mg of endoperoxide **1b** in a mixture of acetonitrile/water (1:1) afforded 95 mg (70%) of tetrol **3b** [2].

General procedure for rearrangement of endoperoxides **1c,d**

$FeSO_4 \cdot 7\ H_2O$ (3 equiv) was added to a solution of endoperoxide **1c,d** (0.2 g) in pyridine (10 mL) or acetonitrile (10 mL) and the mixture was maintained at 80 °C, under stirring, for 24–48 h. After treatment with water and extraction with ether or ethyl acetate, the organic layer was washed with aqueous HCl 1 N to remove the remaining pyridine if necessary, then with water, and finally dried. The residue of the evaporated solution was purified by TLC on silica gel.

Rearrangements of endoperoxide **1c**

• *In pyridine*

After reaction and work-up, separation by TLC (eluent: CH_2Cl_2/cyclohexane, 80:20) afforded, in the order of elution: a few mg of 1,4-dimethyl-9,10-diphenylanthracene **18c**, a small fraction of unreacted endoperoxide **1c**, and a major fraction of dihydronaphthoxanthenol **4c** (recovered in yields of 70–85%).

• *In acetonitrile*

The same procedure, followed by TLC (eluent: cyclohexane/AcOEt, 70:30), afforded in the order of elution, the same side products and a major fraction of **5c** (recovered in yields of 65–70%).

Isomerization of **4c** *to* **5c**

Compound **4c** (47 mg) was stirred with 20 mg $Fe_2(SO_4)_3$ in acetonitrile (15 mL) for 12 h. Usual work-up followed by TLC on silica gel afforded 41 mg (87%) of **5c**.

• *5a,8-Dimethyl-9-phenyl-5a,8-dihydronaphtho-[3,2,1-kl]xanthen-8-ol,* **4c**

Colorless crystals, mp 240 °C (ethanol).

IR (KBr): 3 590, 3 450 cm^{-1}.

UV (ether), λ_{max} nm (log ε): 347 (4.07), 331 (4.13), 305 (3.82), 295 (3.60), 249 (4.51).

^1H NMR (300 MHz, $CDCl_3$) δ: 1.35 (s, 3H, CH_3-5a), 1.58 (s, 3H, CH_3-8), 2.28 (s, 1H, OH), 5.91 (d, 1H) and 6.25 (d,1H) J = 10.1 Hz (H-6,7), 7.11–7.50 (m, 11H), 8.02 (d, 1H) and 8.55 (d, 1H) J = 8.6 Hz (H-1,13).

^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 24.7 (CH_3), 31.5 (CH_3), 70.6 and 74.1 (*C*-5a,8), 118.6 to 135.4 (13 Ar*C*H and *C*-6,7), 124.1 to 139.6 (8 Ar*C*), 154.2 (*C*-4a).

EIMS (70 eV, m/z, rel intensity): 390 (M^+, 32), 375 (77), 372 (50), 357 (100).

Anal calc for $C_{28}H_{22}O_2$: C, 86.12; H, 5.68. Found: C, 85.84; H, 5.80.

Catalytic hydrogenation: 72 mg of **4c** in THF stirred under H_2 with Pt (from PtO_2) afforded 68 mg (94%) of crystals identified with **6c** [6b].

• *5a,8-Dimethyl-9-phenyl-5a,6-dihydronaphtho-[3,2,1-kl]xanthen-6-ol,* **5c**

Colorless crystals, mp 223–224 °C (ethanol).

IR (KBr): 3 560, 3 420 cm^{-1}.

UV (ether), λ_{max} nm (log ε): 338 (4.19), 275 (4.44), 250 (4.35), 221 (4.55).

^1H NMR (300 MHz, $CDCl_3$) δ: 1.32 (s, 3H, CH_3-5a), 1.35 (d, 3H, J = 1 Hz, CH_3-8), 2.69 (s large, 1H, OH), 4.25 (d, 1H, $J_{6,7}$ = 7 Hz, H-6), 6.06 (dq, 1H, $J_{6,7}$ = 7 Hz, J = 1 Hz , H-7), 7.10–7.44 (m, 11H), 7.98 (d, 1H) and 8.54 (d, 1H), J = 8.5 Hz, (H-1,13).

^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 19.0 (CH_3), 23.8 (CH_3), 69.4 and 81.5 (*C*-5a,6), 118.8 to 131.5 (13 Ar*C*H and C-7), 123.7–140.4 (9 Ar*C*), 153.2 (*C*-4a).

EIMS (70 eV, m/z, rel intensity): 390 (M^+, 32), 375 (50), 374 (100), 372 (35).

HRMS: calc for $C_{28}H_{22}O_2$ 390.1619; found 390.1614.

Rearrangement of endoperoxide **1d**

• *In pyridine*

After heating (30–48 h) and usual work-up, TLC on silica gel (eluent: ether/cyclohexane, 60:40) afforded in the order of elution: a few mg of methylenedihydronaphthoxanthene **7d**, a large fraction of dihydronaphthoxanthenol **4d** (recovered in yields from 55–60%), and a fraction of unidentified products.

• *In acetonitrile*

A mixture of **1d** (60 mg), $FeSO_4 \cdot 7\ H_2O$ (3 equiv) in acetonitrile (20 mL) was stirred at 70 °C for 3 days. After usual work-up, TLC of the residue on silica gel (eluent: CH_2Cl_2/AcOEt, 95:5) afforded in the order of elution: a few mg of methylenedihydronaphthoxanthene **7d**, a large fraction of **20d** (30 mg, 50%), and a fraction of unidentified products.

20d was also obtained by acid hydrolysis of the *anti*-diepoxide **19d** (vide infra).

• *5a,6,7,8-Tetramethyl-9-phenyl-5a,8-dihydronaphtho[3,2,1-kl]xanthen-8-ol,* **4d**

Colorless crystals, mp 152–155 °C (decomp).

IR (Nujol): 3 500 cm^{-1}.

UV (ether), λ_{max} nm (log ε): 344 (4.09), 332 (4.16), 244 (4.55), No absorption above 375 nm.

^1H NMR (300 MHz, $CDCl_3$) δ: 1.32 (s, 3H, CH_3-5a), 1.56 (s, 3H, CH_3-8), 1.86 (d, 3H, J = 0,5 Hz, CH_3-7), 2.03 (s, 1H, OH), 2.09 (d, 3H, J = 0,5 Hz, CH_3-6), 7.10–7.53 (m, 11H), 8.02 (d, 1H) and 8.55 (d, 1H), J = 8,5 Hz (H-1,13).

Attributions of signals were based upon positive NOE: from 1.86 (CH_3-7) to 1.56 (CH_3-8) and 2.09 (CH_3-6) and from 2.09 (CH_3-6) to 1.32 (CH_3-5a) and 1.86 (CH_3-7).

^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 14.0 (2 CH_3), 23.4 (CH_3), 30.4 (CH_3), 73.4 and 76.6 (*C*-5a,8), 119.3 to 133.3 (13 Ar*C*H), 124.4 to 140.5 (8 Ar*C* and *C*-6,7), 154.3 (*C*-4a).

EIMS (70 eV, m/z, rel intensity): 418 (M^+, 13), 403 (71), 388 (100).

HRMS: calc for $C_{30}H_{26}O_2$ 418.1933; found 418.1932.

• *5a,6,7-Trimethyl-8-methylidene-5a,8-dihydronaphtho[3,2,1-kl]xanthene,* **7d**

Colorless crystals, mp 205–206 °C.

UV (ether), λ_{max} nm (log ε): 340 (4.15), 336 (4.17), 248 (4.59). Absorption extends up to 395 nm.

^1H NMR (300 MHz, $CDCl_3$) δ: 1.29 (s, 3H, CH_3-5a), 1.98 (s, 3H, CH_3-7), 2.11 (s, 3H, CH_3-6), 4.67 (s, 1H, CH_2), 5.15 (s, 1H, CH_2), 7.12–7.52 (m, 11H), 8.04 (d, 1H) and 8.61 (d, 1H), J = 8,5 Hz (H-1,13).

Attributions of signals were based upon positive NOE: from 1.29 (CH_3-5a) to 2.11 (CH_3-6) and from 1.98 (CH_3-7) to 2.11 (CH_3-6) and 5.15 (H-CH_2).

The isomeric structure with the alternative linkage, 5a,7,8-trimethyl-6-methylidene-5a,6-dihydronaphtho-[3,2,1-*kl*]xanthene, has been ruled out by the fact that no NOE can be observed between aliphatic CH_3 at 1.29 ppm and any of the methylidenic protons.

^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 12.8 (CH_3), 16.0 (CH_3), 20.9 (CH_3), 78.0 (*C*-5a), 115.4 (CH_2), 119.0 to 131.6 (13 Ar*C*H), 124.1 to 141.4 (8 Ar*C* and *C*-6,7,8), 154.1 (*C*-4a).

EIMS (70 eV, m/z, rel intensity): 400 (M^+, 18), 385 (100), 369 (28).

HRMS: calc for $C_{30}H_{24}O$ 400.1827, found 400.1828.

• *Photochemical instability*

A solution of **7d** in CH_2Cl_2 turned yellow in normal daylight in a few minutes. TLC of the solution on silica gel (eluent: CH_2Cl_2) showed two bands; the more eluted one, which was initially colorless, quickly turned yellow during the drying process, while the less eluted one, which was initially yellow, turned colorless when maintained in darkness.

Dehydration of **4d** *to* **7d**

$Fe_2(SO_4)_3$ (400 mg) was added to a stirred solution of **4d** (92 mg) in acetonitrile (13 mL) and stirring was continued at room temperature for 3 h. After work-up, the residue was purified by TLC on silica gel (eluent CH_2Cl_2). Quick extraction of the more eluted fraction, followed by washing with hexane, gave colorless crystals of **7d** (71 mg, 78%).

Reaction of $FeSO_4$ with endoperoxide **10a**

• *In pyridine*

Endoperoxide **10a** (214 mg) and $FeSO_4 \cdot 7\ H_2O$ (2 equiv) in pyridine (10 mL) were stirred at 80 °C for 2 h. After work-up, separation by TLC on silica gel (eluent: cyclohexane/AcOEt, 90:10) afforded in the order of elution: 2 mg of epoxide **16a**, 8 mg of unreacted peroxide **10a**, 82 mg of hydroxyanthracenone **12a** (38%), and 38 mg of *cis*-diol **15a** (17%).

• *In acetonitrile*

10a (40 mg) and $FeSO_4 \cdot 7\ H_2O$ (2 equiv) in acetonitrile (20 mL) were stirred at 80 °C for 12 h. After work-up, separation by TLC on silica gel (eluent CH_2Cl_2) afforded in the order of elution: 17 mg of 1,4-dimethylanthracene **18a** (50%), 5 mg of epoxide **16a** (13%), 4 mg of hydroxyanthracenone **12a** (11%), 6 mg of *cis*-diol **15a** (15%).

• cis-*Diol* **15a**

This was identified with an authentic sample [6a]. Treated in acetonitrile by $Fe_2(SO_4)_3$, it leads to epoxide **16a** and to hydrocarbon **18a**.

• *1,4-Epoxy-1,4-dimethyl-1,2,3,4-tetrahydroanthracene,* **16a**

Colorless crystals, mp 80–81 °C (ethanol).

UV (ether), λ_{max} nm (log ε): 315 (2.85), 303 (2.82), 281 (3.54), 271 (3.72), 262 (3.67), 254 (3.56);

^{1}H NMR (90 Mz, $CDCl_3$) δ: 1.90 (6H, CH_3), 1.50–2.10 (m, 4H, H-2,3), 7.53 (s, 2H, H-9,10), 7.30–7.90 (m, 4H, AA'BB', H-5 to H-8).

^{13}C NMR (20 MHz, $CDCl_3$) δ: 17.8 (CH_3), 36.1 (CH_2-2,3), 84.7 (*C*-1,4), 115.4 (*C*-9,10), 125.5 and 128.1 (Ar*C*H-5 to 8), 132.8 and 147.2 (*C*-4a and 9a).

EIMS (70 eV, m/z, rel intensity): 224 (M^+,13), 196 (100), 181 (11).

Anal calc for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found C, 85.63; H, 7.21.

• *4-Hydroxy-4-methyl-1,2,3,4-tetrahydroanthracen-1-one,* **12a**

Colorless crystals, mp 85 °C (benzene).

IR (KBr): 3 300 (OH) and 1 680 cm^{-1} (CO).

UV (ether), λ_{max} nm (log ε): 350 (3.18), 337 (3.18), 301 (3.79), 289 (3.88), 279 (3.73), 251 (4.73).

^{1}H NMR (90 Mz, $CDCl_3$) δ: 1.71 (s, 3H, CH_3-4), 2.06–2.43 (m, 2H, H-3), 2.70–3.00 (m, 2H, H-2), 7.43–8.10 (m, 4H, H-5 to H-8), 8.13 (s, 1H, H-10), 8.56 (s, 1H, H-9).

Attributions of signals were based upon Eu(fod)$_3$-induced chemical shift differences. $\Delta^{0,1}$Eu(fod)$_3$ observed were: 73.8 Hz for δ 2.06–2.43, 115.2 Hz for δ 2.70–3.00, 60.3 Hz for δ 8.13, and 108.0 Hz for δ 8.56.

^{13}C NMR (20 MHz, $CDCl_3$) δ: 29.4 (CH_3), 35.9 (*C*-2), 37.9 (*C*-3), 70.3 (*C*-4), 124.0 to 129.9 (Ar*C*H), 128.8 to 144.7 (Ar*C*), 197.8 (*C*-1, CO).

EIMS (70 eV, m/z, rel intensity): 226 (M^+, 61), 211 (100), 198 (18).

HRMS: calc for $C_{15}H_{14}O_2$ 226.0994, found 226.0992.

Anal calc for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found C, 79.64; H, 6.21.

Reaction of $FeSO_4$ with endoperoxide **10c**

• *In pyridine*

Endoperoxide **10c** (53 mg) and $FeSO_4 \cdot 7\ H_2O$ (0.5 equiv) in pyridine (5 mL) were stirred at 80 °C for 2 h. Usual work-up and separation by TLC on silica gel (eluent: CH_2Cl_2/cyclohexane, 75:25) gave: 39 mg of unreacted endoperoxide **10c** (74%) and 12 mg of tetrahydronaphthoxanthenol **6c** (23%), which was identified with an authentic sample obtained according to [6b].

When heating was continued for 3 days, the yield of **6c** was raised to 35%, and no other products apart from unreacted endoperoxide **10c** were detected.

• *In acetonitrile*

Endoperoxide **10c** (52 mg) and $FeSO_4 \cdot 7\ H_2O$ (0.5 equiv) in acetonitrile (5 mL) were stirred under reflux for 2.3 h. Usual work-up and separation by TLC on silica gel (eluent: CH_2Cl_2/cyclohexane, 75:25) gave: 27 mg of dihydronaphthoxanthene **14c** (55%), 8 mg of epoxide **16c** (16%), and 15 mg of unreacted endoperoxide **10c** (29%).

Dihydronaphthoxanthene **14c** and epoxide **16c** were identified with authentic samples obtained according to [6b]. Treated with $FeSO_4 \cdot 7\ H_2O$ in acetonitrile at room temperature, tetrahydronaphthoxanthenol **6c** was entirely dehydrated to **14c**.

General procedure for epoxidation of hydrocarbons **18** *with* m-*CPBA*

A solution of hydrocarbon **18** (200 mg) in methylene chloride (20 mL) containing *m*-CPBA (2.5 equiv, 250 mg) was stirred with saturated sodium bicarbonate (20 mL) for a few hours at room temperature. It was then washed twice with aqueous sodium thiosulfate and finally with water. The organic phase was dried over anhydrous sodium sulfate and concentrated.

The residue was either crystallized directly or separated by TLC on silica gel (eluent: CH_2Cl_2/cyclohexane, 90:10).

• *Partial epoxidation of* **18b**

After 2 h of stirring and treament, difficult separation of the residue by TLC afforded in the order of elution: 30 mg of endoperoxide **1b** (15%) and 36 mg of *anti*-diepoxide **19b** (18%).

• *Partial epoxidation of* **18c**

After 18 h of stirring, treatment led to a partly crystalline residue which was washed several times with a mixture of ether/pentane (50:50). The *anti*-diepoxide **19c** (84 mg; 39%) was obtained.

• *Partial epoxidation of* **18d**

After 1.5 h of stirring followed by treatment, separation of the residue by TLC afforded in the order of elution: a few mg of unreacted **18d**, 43 mg of ketal **17d** (22%), and 38 mg of *anti*-diepoxide **19d** (19%).

General procedure for epoxidation of hydrocarbons **18** *with dimethyldioxirane*

The procedure was that described in ref [10] but applied to smaller amounts.

In a typical reaction a mixture of acetone (50 mL), phosphate buffer (15 mL), methylene chloride (20 mL), tetra-*n*-butyl ammonium hydrogen sulfate (100 mg) and hydrocarbon **18d** (200 mg) was stirred vigorously at room temperature while a solution of potassium peroxymonosulfate (*Oxone*, $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, 6 g in 30 mL of water) was added dropwise over a period of 1–1.5 h. The pH was maintained between 7.5 and 8.5 by monitoring with a pH electrode and dropwise addition of an aqueous solution of KOH 1 N. The end of the reaction was indicated by the decolorization of the solution.

The reaction mixture was then poured onto ice-cold water and extracted with methylene chloride. The organic phase was washed three times with water, dried (K_2CO_3) and concentrated. The residue was either crystallized directly or separated by TLC on silica gel.

• *Oxidation of* **18a**

After a reaction on 200 mg of **18a**, the partly crystalline residue afforded, after washing with a mixture CH_2Cl_2/hexane (50:50), a first crop of **22a**. Separation of the mother liquors by TLC on silica gel (eluent: CH_2Cl_2) led in the order of elution to 1,4-dimethylanthraquinone **23a** (22 mg, 8%) and to a second crop of **22a**.

Altogether 102 mg (45%) of 10-hydroxy-1,4-dimethyl-9-anthrone **22a** was recovered. **22a** was identified with an authentic sample prepared according to [15]. No diepoxide **19a** could be identified.

• *Epoxidation and oxidation of* **18b**

After a reaction on 500 mg of **18b**, the residue was separated by column chromatography on Kieselgel 100 (Merck). Elution carried out with mixtures of hexane/ethyl acetate (95:5, then 90:10 and finally 50:50) led, in order, to: 37 mg of anthraquinone **23b** (6.5%), 306 mg of *anti*-diepoxide **19b** (54%), 115 mg of 10-hydroxy-9-anthrone **22b** (20%), and 71 mg of a 9,10-dihydroxy-9,10-dihydroanthracene, considered to be **21b** (12%).

• *Epoxidations of* **18c**, **18d** *and* **18n**

In every case, a reaction on 200 mg as described above led to a crystalline residue which was washed several times with hexane or ether. Approximately 70% of the corresponding *anti*-diepoxide was isolated in the process, although more diepoxide was present in the mother liquors which indicates a quasi-integral transformation. No *syn*-diepoxide could be detected.

• anti-*1,2;3,4-Diepoxy-1,2,3,4-tetramethyl-1,2,3,4-tetrahydroanthracene,* **19b**

Colorless crystals, mp 190–191 °C (benzene).

^{1}H NMR (300 Mz, $CDCl_3$) δ 1.73 (s, 6H, CH_3-2,3), 1.87 (s, 6H, CH_3-1,4), 7.45–7.51 and 7.79–7.88 (m, 4H, AA′BB′, H-5 to H-8), 8.13 (m, 2H, H-9,10).

^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 14.9 (*C*H_3), 17.5 (*C*H_3), 60.8, 67.2 (*C*-1 to *C*-4), 126.9, 127.6, 128.8 (Ar*C*H), 132.2, 132.9 (Ar*C*).

EIMS (70 eV, *m/z* rel intensity): 266 (M^+, 6), 223 (100).

Anal calc for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.18; H, 6.83.

• anti-*1,2;3,4-Diepoxy-1,4-dimethyl-9,10-diphenyl-1,2,3,4-tetrahydroanthracene,* **19c**

Colorless crystals; mp 246–248 °C (benzene/ethanol).

^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.85 (s, 6H, CH_3-1,4), 3.44 (s, 2H, H-2,3), 7.40–7.44 and 7.79–7.82 (m, 4H, AA′BB′, H-5 to H-8), 7.52–7.66 (m, 10H, H-Ph).

^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 24.1 (*C*H_3), 55.7, 61.1 (*C*-1 to *C*-4), 126.4 to 132.6 (Ar*C*H), 130.4, 132.5, 139.6, 141.7 (Ar*C*).

EIMS (70 eV, *m/z*, rel intensity): 390 (M^+, 5), 358 (100).

Anal calc for $C_{28}H_{22}O_2$: C, 86.12; H, 5.68. Found: C, 86.20; H, 5.67.

• anti-*1,2;3,4-Diepoxy-1,2,3,4-tetramethyl-9,10-diphenyl-1,2,3,4-tetrahydroanthracene,* **19d**

Colorless crystals, mp 276–277 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.88 (s, 6H, CH_3-1,4), 1.57 (s, 6H, CH_3-2,3), 7.42–7.47 and 7.89–7.93 (m, 4H, AA′BB′, H-5 to H-8), 7.49–7.71 (m, 10H, H-Ph).

^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 14.9 (*C*H_3), 19.8 (*C*H_3), 60.5, 64.0 (*C*-1 to *C*-4), 126.2–133.2 (7 Ar*C*H), 132.5, 132.6, 139.6, 141.1 (Ar*C*).

EIMS (70 eV, *m/z*, rel intensity): 418 (M^+, 20), 375 (100).

HRMS: calc for $C_{30}H_{26}O_2$: 418.19328, found 418.19318.

• anti-*1,2;3,4-Diepoxy-1,2,3,4-tetramethyl-1,2,3,4-tetrahydronaphthalene,* **19n**

Colorless crystals, mp 128–130 °C (CH_2Cl_2/hexane).

^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.68 (s, 6H, CH_3), 1.72 (s, 6H, CH_3), 7.29–7.35 and 7.63–7.69 (m, 4H, AA′BB′, H-5 to H-8).

^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 14.7 (*C*H_3), 17.1 (*C*H_3), 60.3, 66.9 (*C*-1 to *C*-4), 128.6, 128.7 (Ar*C*H), 134.8 (Ar*C*).

EIMS (70 eV, *m/z*, rel intensity): 216 (M^+, 0.02) 173 (100).

Anal calc for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.70; H, 7.54.

• *1,5-Epoxy-1,3,4,5-tetramethyl-6,11-diphenyl-1,5-dihydronaphtho[2,3-c]oxepine,* **17d**

Colorless crystals, mp 264–266 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.21 (s, 3H, CH_3-5), 1.28 (q, 3H, J = 1 Hz, CH_3-4), 1.68 (s, 3H, CH_3-1), 1.98 (q, 3H, J = 1 Hz, CH_3-3), 7.20–7.77 (m, 14H, H-Ar).

Attributions of signals were based upon positive NOE: from 1.21 (CH_3-5) to 1.68 (CH_3-1) and 7.5 (H-Ph), from 1.28 (CH_3-4) to 1.98 (CH_3-3), from 1.68 (CH_3-1) to 1.21 (CH_3-5) and 1.98 (CH_3-3), from 1.98 (CH_3-3) to 1.28 (CH_3-4) and 1.68 (CH_3-1).

^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 18.2, 18.9, 19.0, 19.6 (CH_3), 64.4 (C-5), 93.4 (C-1), 119.4 (C-4, C=C), 125.4–132.4 (14 ArCH), 132.2–141.0 (8 ArC), 149.9 (C-3, C=C).

Attributions of signals were deduced from decouplings observed on the coupled ^{13}C spectrum by selective irradiation of various protons:

– irradiation at 1.98 ppm (CH_3-3) suppresses a coupling: at 18.2 ppm (C-CH_3-3), 149.9 ppm (J = 6.8 Hz) (C-3) and 119.4 ppm (J = 4 Hz) (C-4). These coupling constants are typical for a double bond polarized by one O atom [16].

– irradiation at 1.68 ppm (CH_3-1) suppresses a coupling: at 18.9 ppm (C-CH_3-1), 93.4 ppm (C-1) and 64.4 ppm (J = 2.8 Hz) (C-5).

EIMS (70 eV, m/z, rel intensity): 418 (M^+, 8), 375 (100).

HRMS: calc for $C_{30}H_{26}O_2$ 418.19328, found 418.19318.

• *Partial reduction of 1,2,3,4-tetramethylanthraquinone* **23b**

KBH_4 (100 mg; 1 equiv) was added to a suspension of **23b** (550 mg) in CH_3OH (170 mL) and the mixture was stirred for 1.5 h. After treatment with H_2O/HCl and extraction with CH_2Cl_2, usual work-up afforded a first crop of crystals of **22b**, approximately 275 mg after washings with a mixture of cyclohexane/ethyl acetate (70:30).

Purification of the residue from the mother liquors by TLC on silica gel gave an additional 130 mg of **22b**. (Total yield: 405 mg, 80%).

• *10-Hydroxy-1,2,3,4-tetramethyl-9-anthrone,* **22b**

Colorless crystals; mp 183–184 °C benzene).

IR (Nujol) 3 410 (OH) and 1 630 cm^{-1} (CO).

^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.30 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 2.43 (d, 1H, J = 5 Hz, OH), 2.55 (s, 3H, CH_3), 2.58 (s, 3H, CH_3), 5.87 (d, 1H, J = 5 Hz, H-10), 7.41–7.46 (m, 1H, H-7), 7.55–7.64 (m, 2H, H-5,6), 7.99 (d, 1H, J = 5 Hz, H-8).

^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 16.1 (CH_3), 16.8 (CH_3), 17.7 (CH_3), 18.2 (CH_3), 65.6 (C-10), 126.9–132.7 (4 ArCH), 129.2–141.5 (8 ArC), 188.4 (C-9, CO).

EIMS (70 eV, m/z, rel intensity): 266 (M^+, 36), 251 (100).

HRMS: calc for $C_{18}H_{18}O_2$ 266.1307, found 266.1305.

Anal calc for $C_{18}H_{18}O_2$: C, 81.17: H, 6.81. Found: C, 81.17: H, 6.82.

Identification of 1,2,3,4-tetramethyl-9,10-dihydroanthracene-9,10-diol, **21b**

Attribution of structure **21b** to the compound which was separated last, and in minute amount, after epoxidation of **18b** by dimethyldioxirane, is based upon its identification with one of the quinols resulting from the reduction by KBH_4 of 1,2,3,4-tetramethylanthraquinone **23b**.

Although this reduction has been previously reported as giving a single quinol which was considered to be the *trans* isomer [2], high resolution ^{1}H NMR detects a second compound in the raw product of the reaction, which is most probably the *cis* stereoisomer of the first. In fact, one observes a double spectrum, composed of two series of closely-placed signals, separated from each other by about 0.04 ppm, which are consistent with the same planar structure. The spectrum of the new compound arising from **18b** is unique and corresponds exactly to one series of signals: the slightly more blended ones. The spectrum of the insoluble compound which remains after several washings of the raw reduction mixture of **23b** with boiling benzene is also unique and corresponds exactly to the other series of signals. Moreover, by chromatographic assays on small SiO_2 plates (eluent: cyclohexane/AcOEt) the compound coming from **18b** can be identified with the minor stereoisomer (the less eluted one) formed in the reduction of **23b**.

It is known that hydride reduction of anthraquinones with *peri*-substituents gives predominantly the *trans*-quinol [14a,b], especially in the case of 1,4-dimethylanthraquinone [15]. It is therefore probable that the main reduction product of **23b** is also the *trans* stereoisomer and that the product coming from **18b** is the *cis*-quinol **21b**.

The spectral data of the reduction products of **23b** were as follows:

Major stereoisomer (quinol considered to be *trans*, mp 214–215 °C).

IR (KBr): 3 309, 3 270 cm^{-1} (shoulder) (OH).

^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.65 (d, 2H, J = 8.6 Hz, OH), 2.32 (s, 6H, CH_3), 2.54 (s, 6H, CH_3), 5.94 (d, 2H, J = 8.6 Hz, H-9,10), 7.43–7.46 and 7.69–7.72 (m, 4H, AA′BB′, H-5 to 8).

^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 16.77 (CH_3), 16.93 (CH_3), 65.90 (C-9,10), 128.61, 128.89 (ArCH-5 to 8), 131.90, 133.66, 136.33, 136.50 (ArC).

Minor stereoisomer (quinol considered to be *cis*, **21b**, mp 191–192 °C).

IR (KBr): 3 303 cm^{-1} (large) (OH).

^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.28 (s, 6H, CH_3), 2.49 (s, 6H, CH_3), 3.09 (d, 2H, J = 6 Hz, OH), 5.89 (d, 2H, J = 6 Hz, H-9,10), 7.34–7.37 and 7.49–7.53 (m, 4H, AA′BB′, H-5 to 8).

^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 15.41 (CH_3), 16.87 (CH_3), 68.46 (C-9,10), 128.47, 128.56 (ArCH-5 to 8), 132.40, 134.94, 135.63, 140.06 (ArC).

• *Acid-catalyzed rearrangement of* anti-*diepoxide* **19d**

anti-Diepoxide **19d** (50 mg) was added to a solution of *p*-toluenesulfonic acid (70 mg, 3 equiv) in THF (10 mL) and the mixture was stirred for 1 h at room temperature. After concentration, separation of the residue by TLC on silica gel (eluent: CH_2Cl_2) afforded 30 mg (60%) of **20d** as crystals which were fairly insoluble in common solvents.

The same rearrangement was observed when **19d** was treated with an acetonitrile solution (1 M) of $LiBF_4$ (6 equiv). Under stirring, **20d** slowly precipitated out from the solution.

• *1-Acetyl-1,2-dimethyl-3-methylidene-4,9-diphenyl-2,3-dihydro-1*H*-benzo[f]inden-2-ol,* **20d**

Colorless crystals, mp 265–267 °C.

IR ($CHCl_3$): 3 440 (OH) and 1 690 cm^{-1} (CO).

^{1}H NMR (300 Mz, DMSO-d_6) δ: 0.76 (s, 3H, CH_3-1), 1.17 (s, 3H, CH_3-2), 1.91 (s, 3H, CH_3-CO), 4.32 (s, 1H, CH_2), 5.10 (s, 1H, CH_2), 5.57 (s, 1H, OH-2), 6.92 (m, 1H) and 7.28–7.66 (m, 13H).

Attributions of signals were based upon positive NOE: from 0.76 (CH_3-1) to 1.17 (CH_3-2), from 1.17 (CH_3-2) to 0.76 (CH_3-1) and 5.57 (OH-2), from 5.10 (H-CH_2) to 4.32 (H-CH_2) and 5.57 (OH-2), and the absence of NOE from 1.91 (CH_3-CO).

Moreover a *cis* relationship between the two methyl groups at positions 1 and 2 could be deduced.

^{13}C NMR (75.5 Mz, DMSO-d_6) δ: 17.0 (CH_3), 27.5 (CH_3), 27.9 (CH_3), 64.8 (C-1), 83.8 (C-2), 108.6 (CH_2), 125.7-130.9 (ArCH), 132.1–154.8 (ArC and C-3), 206.8 (C, CO).

EIMS (70 eV, m/z, rel intensity): 418 (M^+, 7), 375 (100).

HRMS: calc for $C_{30}H_{26}O_2$ 418.1933, found 418.1932.

Note: Although only harmless by-products are believed to be produced using dimethyldioxirane [17], one has to remember that potential hazards always exist when mixing

acetone with peroxidizing agents. Care should therefore be taken with these reagents, in particular when scaling up epoxidation procedures.

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