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Rearrangement of unsaturated cyclic peroxides obtained by photooxygenation of 2,3-dimethylene-7-oxabenzonorbornene and 2,3-dimethylene-1,4-etheno-1,2,3,4-tetrahydronaphthalene

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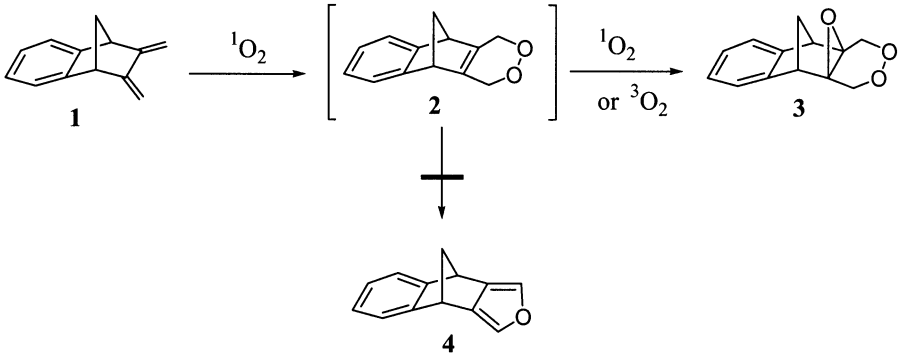
Abstract—Cobalt(II) tetraphenylporphyrin (CoTPP)-catalyzed rearrangement of peroxide **11** obtained by the photooxygenation of **5** gave a mixture of epoxides **15** (or **16**) and **17**. However, CoTPP-catalyzed rearrangement of peroxide **20** arising by photooxygenation of 2,3-dimethylene-1,4-etheno-1,2,3,4-tetrahydronaphthalane **6** gave 1,4-etheno-1,2,3,4-tetrahydronaphtho[*b*]-furan **21**. The different behaviour of these endoperoxides **11** and **20** is discussed in terms of ring strain and the degree of the pyramidalization of the C=C bond.

1. Introduction

Unsaturated bicyclic endoperoxides are readily available by cycloaddition of singlet oxygen to conjugated dienes.[1] The peroxides can be converted both thermally and photochemically to a variety of oxygenated compounds including bis-epoxides.[2] Cobalt(II) tetraphenylporphyrin (CoTPP) catalyzes the rearrangement of unsaturated bicyclic endoperoxides to bis-epoxides.[3] O'Shea and Foote reported that CoTPP-catalyzed rearrangement of monocyclic endoperoxides gives furans in quantitative yield.[4] Recently, we used CoTPP to catalyze the rearrangement of endoperoxides arising by photooxygenation of exocyclic dienes and obtained 3,4-disubstituted furans.[5] Following the same methodology, we wanted to synthesize 3,4-fused furan **4** via 2,3-dimethylene-1,4-methano-1,2,3,4-tetrahydronaphthalene (**1**). However, reaction of **1** with singlet oxygen resulted in the formation of epoxy-endoperoxide (**3**). The expected precursor, endoperoxide **2**, for furan formation, could not be isolated (Scheme 1).[6]

In the previous report,[6] we discussed the epoxy-endoperoxide formation mechanism. To the best of our knowledge, the 'one pot' formation of an epoxy-endoperoxide during photooxygenation of a diene has been observed for the first time. We thought that the methano bridge in diene **1** might be effective in the epoxide formation in some way. To obtain more insight into this problem, we decided to study the photooxygenation reaction of dienes **5** and **6**, where the methylene bridge in **1** is replaced by an



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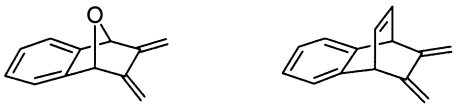
oxygen atom and ethylene group, respectively. Photooxygenation of **5** might reveal the effect of bridge atom to epoxy-endoperoxide formation. On the other hand, diene **6** should provide information as to how the strain of the system can determine the fate of the photooxygenation reaction.



5 **6**

2. Results and discussion

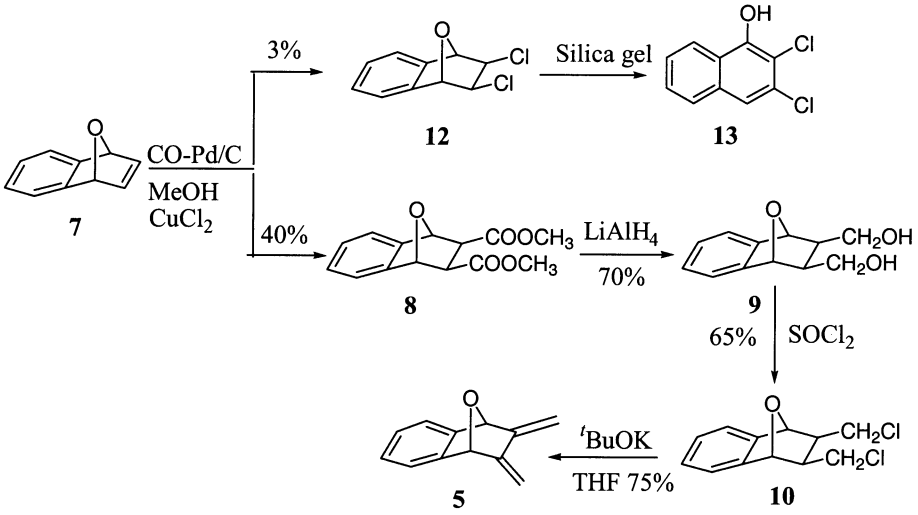
The synthesis of the exocyclic diene **5** is reported in the literature. Luo and Hart[7] synthesized **5** by trapping of isobenzofuran with *cis*-1,4-dichloro-2-butene followed by dehydrohalogenation of the formed adduct. Isobenzofuran was generated in situ by the thermolysis of the adduct formed by the cycloaddition of 7-oxabenzonorbornene to tetraphenylcyclopentadienone. Because of the high cost of the starting materials and low yields, we decided to develop a new synthesis for the title compound **5**, starting from 7-oxabenzonorbornene.

James and Stille[8] have reported that the reaction of cyclic and acyclic olefins with carbon monoxide in the presence of catalytic amount of $PdCl_2$ and stoichiometric amount of $CuCl_2$ in alcohols affords predominantly diesters. Vogel et al.[9] found that $PdCl_2$ can be replaced by 10% Pd/C. We applied these procedures and developed a concise synthesis of the diene **5** in high yield (Scheme 2). In our synthesis, the first step was the carbomethoxylation of 7-oxabenzonorbornene (**7**).

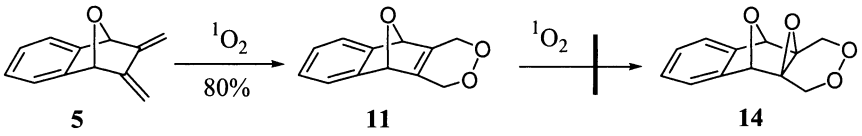
7-Oxabenzonorbornene (**7**) was synthesized according to the procedure of Ziegler.[10] Then, under the usual conditions (3–4 atm CO, 0.02 mol equiv. $CuCl_2$, abs. MeOH, 20–25°C, 48 h) the 7-oxabenzonorbornene was carbomethoxylated and *exo-cis*-2,3-dicarboxylate (**8**) was obtained in 40% yield (Scheme 2). The carbomethoxylation of strained double bond is always accompanied by side reactions.[8] A small quantity (3%) of *exo*,*exo*-dichloro compound **12** was also obtained from this reaction. The mechanism of formation of **12** was not clarified. Dichloro compound **12** rearranged to the naphthalene derivative **13** during column chromatography on silica gel. We assume, that silica gel catalyzes the opening of the oxygen bridge to form a benzylic cation, which can be stabilized by elimination of α-hydrogen atom adjacent to carbocation. Aromatization results in the formation of **13**. Physical and spectroscopic data of **13** were completely in agreement with those reported in the literature.[11]

The structure of the carbomethoxylation product **8** has been elucidated on the basis of ^1H and ^{13}C NMR data and further chemical transformations. Especially, a seven-line ^{13}C NMR spectrum clearly indicated the symmetrical structure and the *syn* addition of the ester groups. The *exo*,*exo* stereochemical assignment for the ester groups was supported by the absence of a measurable coupling between bridgehead protons and the protons adjacent to ester groups. In the next step, **8** was reduced to the *exo*,*exo* diol (**9**) with $LiAlH_4$/THF in 70% yield. Reaction of **9** with $SOCl_2$/pyridine yielded *exo*,*exo* dichloride[7] **10** in 65% yield. The established *exo*,*exo* configuration[7] of this dichloride **10** confirmed the *exo*,*exo* configuration of the starting compound, diester **8**. Base supported elimination of HCl from **10** furnished the exocyclic diene **5** in 75% yield.

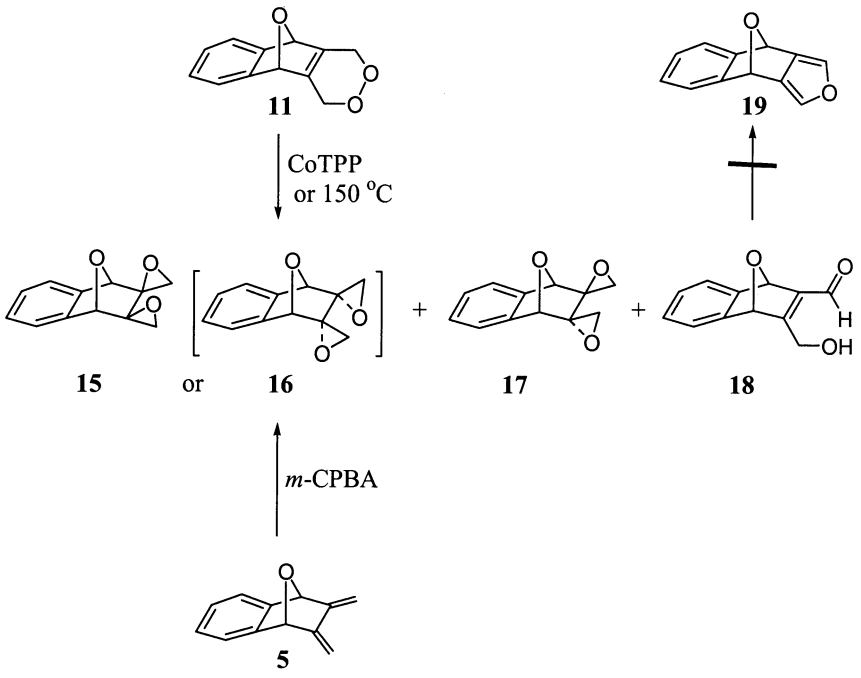
The photooxygenation of diene **5,** in the presence of tetraphenylporphyrin (TPP) as a sensitizer, in carbon



Scheme 2.



Scheme 3.



Scheme 4.

tetrachloride at room temperature gave the endoperoxide **11** in 80% yield contrary to the photooxygenation of the diene **1** (Scheme 3). Careful examination of the crude product by NMR spectroscopy did not reveal the formation of any trace of the further oxidation product epoxy-endoperoxide **14**.

The structure of **11** was established on the basis of its ^{1}H and ^{13}C NMR spectra. Endoperoxide **11** exhibits an AA′BB′-system (δ 6.9–7.2) arising from the aromatic protons and an AB system (δ 4.36–4.96 ppm) for the diastereotopic methylenic protons. The bridgehead protons appear as a singlet at δ 5.6 in accordance with the proposed structure. The ^{13}C NMR spectrum consisting of 6 signals is also in agreement with the structure.

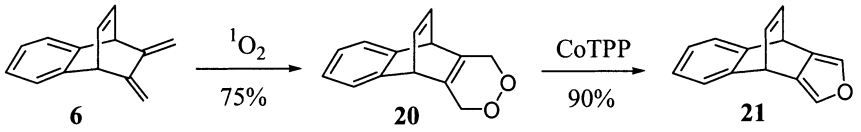
As discussed before, CoTPP catalyzes the rearrangement of monocyclic endoperoxides to furans. In the light of this reaction we treated a solution of **11** in $CDCl_3$ with CoTPP (5–10 mol%) in an NMR tube (Scheme 4) and monitored the reaction with ^{1}H NMR. Unfortunately, we observed the formation of a symmetrical bis-epoxide **15** (or **16**) as the major product (75% yield) (Scheme 4). An asymmetric bis-epoxide **17** and hydroxy-aldehyde **18** were formed as the side products. On standing at room temperature, the aldehyde peak disappeared forming unidentified products. Attempted purification of the aldehyde **18** failed due to its instability on silica.

Similar results have been observed in the rearrangement reactions of peroxides arising from the photooxygenation of 2,3-dimethylene-7-oxanorbornane[12] and 8,9-dimethylene-4-phenyl-2,4,6-triazatricyclo[5.2.1.0^{2,6}]decane-3,5-dione.[13]

The major product, symmetrical bis-epoxide **15** (or **16**), has been characterized properly by ^{1}H and ^{13}C NMR. However, the exact configurational assignment to this bis-epoxide (*exo*,*exo* or *endo*,*endo*) could not be made. Bis-epoxide **15** (or **16**) underwent ring opening reactions upon column chromatography. An independent synthesis of this bis-epoxide was undertaken.

Thermolysis of endoperoxides arising by the photooxygenation of exocyclic dienes is known.[2,14] The endoperoxide **11** was then subjected to thermolysis. For this purpose, the endoperoxide was dissolved in $CDCl_3$ and pyrolyzed at 150°C in a sealed tube. The analysis of the reaction mixture by ^{1}H NMR indicated the formation of a similar bis-epoxide mixture **15** (or **16**) and **17**, which was isolated from the CoTPP reaction (Scheme 4). The same epoxide mixture was also obtained by direct oxidation of exocyclic diene **5** with *m*-chloroperbenzoic acid (Scheme 4).

Our next target was to perform the photooxygenation reaction of exocyclic diene **6** and subject it to CoTPP-catalyzed rearrangement. Diene **6** was synthesized according to the procedure of Butler and Snow.[15] The photooxygenation of **6** in carbon tetrachloride at room temperature was accomplished with TPP as sensitizer. The ^{1}H NMR spectrum of the crude material showed that the endoperoxide **20** was formed



Scheme 5.

as the sole product. Peroxide **20** was purified and isolated by silica gel column chromatography in 50% yield (Scheme 5).

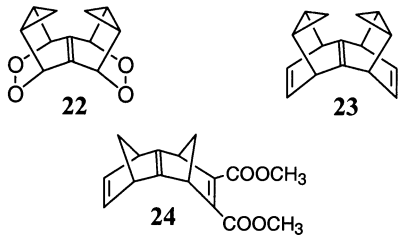
The structure of **20** was established on the basis of the spectral data. The methylene protons gave rise to an AB system between δ 4.70 and 4.85. The singlet at δ 4.70 was assigned to bridgehead protons, and the singlet at δ 6.90 to the olefinic protons. The aromatic protons gave rise to an AA′BB′-system between δ 6.90 and 7.20.

CoTPP-catalyzed rearrangement of **20** resulted in the formation of the expected furan **21** in 90% yield (Scheme 5). Once again, spectral data confirmed the structure of the rearranged product. Aromatic (4H), olefinic (2H) and furan (2H) protons give rise to a multiplet between δ 6.80 and 7.40. Bridgehead protons (2H) resonated at δ 5.0 as broad singlet. Seven peaks in the ^{13}C NMR spectrum, six of them in the sp^2 region support the proposed structure.

3. Conclusion

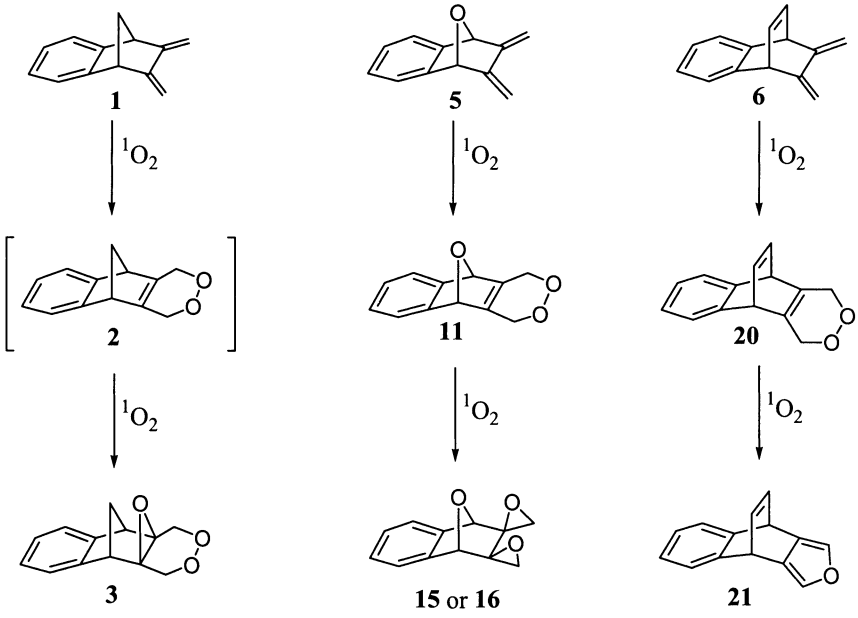
The results show that the reaction of three different exocyclic dienes **1**, **5**, and **6** with singlet oxygen afford the bicyclic endoperoxides **3**, **11**, **20**. Endoperoxides **11** and **20** have been isolated and characterized. However, the endoperoxide **2** could not be isolated. It reacts immediately with oxygen to form exclusively the epoxide **3** (Scheme 6).

It is well known that the reactivity of the double bond in norbornene is characterized by a pronounced preference for *exo* attack. It has been rationalized in terms of geometry of the double bond, which is not completely planar but bent in the *endo* direction. Ermer et al. have shown by neutron diffraction measurements on a norbornene derivative, that the out-of-plane bending (pyramidalization) are 7.3 and 7.5°.[16] In connection with our work on the pyramidalized double bonds, we have recently demonstrated that the central double bond in **22** is more pyramidalized than the central double bond in **23**.[17] This outcome has been explained by the hyperconjugation between the central π-bond and four adjacent C–O bonds, which weaken the central double bond and causes the central C=C bond to lengthen. The weaker double bond is more susceptible to bending.



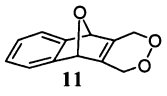
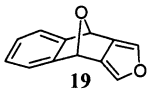
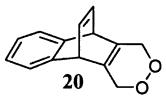
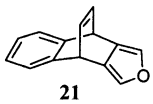
In the case of **2**, we assume that this double bond is also bent due to the annealation of the peroxide linkage and the reactivity of the double bond is increased. The increased reactivity is already reflected by the spontaneous formation of the epoxide **3**. Paquette and Carr[18] have reported that the central double bond in **24** reacts exothermically in air to give the corresponding *exo* epoxide. We can now raise the question of why the endoperoxide **11** does not undergo epoxidation. We assume that the double bond in this system is also quite pyramidalized. We believe that the electrostatic repulsion between the nonbonding electrons of the oxygen-bridge and the nonbonding electrons of incoming molecular oxygen prevents the approach of singlet or triplet oxygen to form the epoxide ring. To find a satisfactory answer to this problem, some calculations, especially transition state energies, have to be carried out.

The second problem was why the endoperoxide **20** forms the corresponding furan **21** while endoperoxide **11** does not. It is clear that the annelation of a furan ring will increase the existing strain in the parent endoperoxides further.



Scheme 6.

Table 1. Strain energies of the compounds **11**, **19**, **20**, and **21** in kcal mol^{-1}

Compounds	 **11**	 **19**	 **20**	 **21**
Total strain energies	34.835	53.346	23.668	35.240

For this purpose we have undertaken MM+ force field calculations for compounds **11**, **19**, **20** and **21**. Optimized geometry and energies[19] for all compounds were calculated by using HyperChem 5.01 for Windows. It can be seen that the total strain energy in **11** increases by about 18.5 kcal mol^{-1} by forming the furan **19**, whereas this increase of strain energy in the case of **20** is about 11.5 kcal mol^{-1} (Table 1) by the annealation of furan ring. We assume that the difference of 7.0 kcal mol^{-1} is responsible for the non-cyclization of **18**.

4. Experimental

Melting points are uncorrected. Solutions were evaporated under reduced pressure with a rotary evaporator, and the residue was chromatographed on silica gel (70–230 Mesh, FLUKA) and neutral alumina. TLC was done on 0.2 mm silica gel 60F_{254} plates. The ^{1}H and ^{13}C NMR spectra were recorded on 200 (50) Varian and 400 (100 MHz) Bruker spectrometers and are recorded in δ units with $SiMe_4$ as internal standard. Infrared spectra were obtained from KBr pellets or from solutions in 0.1 mm cells on Perkin–Elmer 337 Infrared recording spectrophotometer.

4.1. General procedure: A—photooxygenation

A solution of the diene containing TPP as a sensitizer ($3–5\times10^{-4}$ m) in a pyrex tube with a water cooling jacket was irradiated with a projector lamp (150 W). Oxygen was continuously bubbled through the solution during photolysis.

4.2. General procedure: B—Co(II)-catalyzed rearrangement

A solution of peroxide in methylene chloride was cooled to 0°C. While cooling and stirring, a solution of CoTPP, (5–10 mol%) in methylene chloride (5 mL) was added over 10–15 min. Then, the reaction mixture was stirred at rt until TLC showed complete consumption of starting material.

4.2.1. Carbomethoxylation of 7-oxabenzonorbornene: dimethyl *exo*,*exo*-1,4-epoxy-1,2,3,4-tetrahydronaphthalenedicarboxylate (8) and 2,3-bis(chloro)-1,4-epoxy-1,2,3,4-tetrahydronaphthalene (12). 7-Oxabenzonorbornene[10] **7** (22.25 g, 0.155 mol), 83 g (0.61 mol) $CuCl_2$, 10% Pd/C (1.12 g, 1.105 mmol) 16.46 g (0.155 mol) trimethylorthoformate and 1 L anh. methanol were placed in a 3 L autoclave. After careful degassing, the mixture was pressurized with CO (3.5–4 atm) and stirred for 48 h at rt. CO pressure was maintained at 3.5 atm. After removal of the solvent by evaporation, 200 mL water and 500 mL $CHCl_3$ were added. The solid was filtered off. The organic layer was washed with sat. aq. $NaHCO_3$ solution (2×200 mL). The aqueous layer was washed with (2×150 mL) $CHCl_3$ and the organic layers were combined and dried over $MgSO_4$. After removal of solvent, the residue was purified on a silica gel (100 g) column eluted with chloroform/hexane (2/3) to give 16.36 g (0.062 mol, 40%) of *exo*,*exo*-diester **8** as white crystals, mp 150–151°C; [Found: C, 64.23; H, 5.31. $C_{14}H_{14}O_5$ requires C, 64.12; H, 5.38%]; ν_{max} (KBr) 3030, 2960, 1740, 1450, 1350, 1200, 1030 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 6.9–7.1 (AA′BB′-system, aromatic, 4H), 5.4 (s, bridgehead, 2H), 3.5 (s, OCH_3, 6H), 2.7 (s, CH, 2H); δ_C (100 MHz, $CDCl_3$) 171.40, 145.09, 127.68, 119.71, 81.45, 52.40, 49.88; *m*/*z* 262 (3, M^+), 231 (85), 199 (20), 143 (27), 119 (100), 89 (95), 59 (80).

4.2.2. Data for 12. White crystals (1 g, 3%), mp 140–141°C; [Found: C, 55.64; H, 3.68. $C_{10}H_8Cl_2O$ requires C, 55.84; H, 3.75%]; ν_{max} (KBr) 3200, 3100, 3000, 1750, 1500, 1000 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.14–7.28 (AA′BB′-system, aromatic, 4H), 5.3 (s, bridgehead, 2H), 4.1 (s, CH, 2H); δ_C (100 MHz, $CDCl_3$) δ 142.74, 128.41, 120.56, 87.13, 60.52. *m*/*z* 179/181 (48, M^+-HCl), 143 (20), 131 (30), 118 (100), 89 (51).

4.2.3. Data for 13. White crystals, mp 111–112°C[11]; ν_{max} (KBr) 3361, 3080, 1727, 1600, 1550, 1500, 1480, 1450, 1500 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 8.15 (br, d, J=7.1 Hz, aromatic, 1H), 8.05 (br, d, J=7.7 Hz, aromatic, 1H), 7.55–7.47 (m, aromatic, 2H), 7.41 (s, aromatic, 1H), 5,9 (s, OH); δ_C (100 MHz, $CDCl_3$) 146.50, 130.50, 127.71, 126.87, 125,47, 125.17, 124.61, 123.67, 122.73, 122.70.

4.2.4. *exo*,*exo*-2,3-Bis(hydroxymethyl)-1,4-epoxy-1,2,3,4-tetrahydronaphthalene (9). To a vigorously stirred suspension of $LiAlH_4$ (116 mg, 15 mmol) in 25 mL anh. THF maintained at 0°C, a suspension of **8** (410 mg, 10.80 mmol) in 15 mL THF was added portion-wise over 0.5 h. The mixture was allowed to reach rt, and stirred under a nitrogen atmosphere. After 16 h water was added dropwise and the mixture heated under reflux for one minute, then filtered through silica gel (10 g). The solid (silica gel and aluminum salts) was extracted with $CHCl_3$. The organic extracts were combined and dried over $MgSO_4$. After filtration the solvent was evaporated. Recrystallization of the residue from CH_2Cl_2 gave **9** (225 mg, 70%) as a white powder, mp 156–157°C; [Found: C, 70.04; H, 6.72. $C_{12}H_{14}O_3$ requires C, 69.88; H, 6.84%]; ν_{max} (KBr) 3300, 2950, 2400, 1460, 1330, 1200, 1100, 1030 cm^{-1}; δ_H (400 MHz, CD_3OD) 7.0–7.25 (AA′BB′-system, aromatic, 4H), 5.1 (s, bridgehead, 2H), 4.8 (br, s, hydroxyl, 2H), 3.68 (dd, A-part of AB-system, J=10.5, 5.6 Hz) methylenic, 2H), 3.51 (dd, B-part of AB-sytem, J=10.5, 7.3 Hz,

methylenic, 2H), 1.8–1,9 (m, CH, 2H), δ_C (100 MHz, CD_3OD) 146.84, 127.76, 119.91, 82.89, 61.84, 46.67.

4.2.5. *exo*,*exo*-2,3-Bis(chloromethyl)-1,4-epoxy-1,2,3,4-tetrahydronaphthalene (10). To a stirred mixture of anh. pyridine (0.6 g, 7.6 mmol) and $SOCl_2$ (0.8 g, 6.7 mmol), **9** (0.6 g, 2.90 mmol) was added portion-wise without cooling. More $SOCl_2$ (1.6 g, 13.4 mmol) was added and the mixture was heated to 60–70°C for 2 h. After cooling to rt the mixture was added to 60 mL CH_2Cl_2. The excess $SOCl_2$ was destroyed slowly by dropwise addition of water (10 mL) while cooling. The organic layer was washed with water (3×50 mL) and dried over $MgSO_4$. After evaporation of solvent, **10** was obtained as an yellowish powder (0.311 g, 44%), pure enough for the next step, mp 146–147°C (lit.[7] 147–149°C); ν_{max} (KBr) 3000, 2950, 2370, 1460, 1300, 1200, 1000. δ_H (400 MHz, $CDCl_3$) 7.08–7.21 (AA′BB′-system, aromatic, 4H), 5.25 (s, bridgehead, 2H), 3.71 (dd, A-part of AB-system, J=10.6, 4.9 Hz, methylenic, 2H), 3.48 (m, B-part of AB-system, methylenic, 2H), 2.13–2,20 (m, CH, 2H); δ_C (100 MHz, $CDCl_3$) 144.94, 127.49, 119.60, 82.81, 47.75, 43.9. *m/z* 241/243/245 (M^+), 209/207 (50), 171 (15), 153 (20), 128 (41), 118 (100), 89 (61%).

4.2.6. 2,3-Dimethylene-1,4-epoxy-1,2,3,4-tetrahydronaphthalene (5). Solid ^{t}BuOK (1.8 g, 16 mmol) was added to a stirred solution of **10** (0.6 g, 2.46 mmol) in 20 mL anh. THF cooled to 0°C. The mixture was stirred at rt for 12 h. Water (15 mL) was added portion-wise until the complete dissolution of KCl. The brownish mixture was extracted with hexane (3×25 mL). The organic extract was combined and washed with water (3×25 mL). After drying ($MgSO_4$) the solution was evaporated to dryness and 315 mg (75%) **5** obtained. Colorless needles, mp 73–74°C (Lit.[7] 73–74°C); ν_{max} (KBr) 3000, 1500, 1400, 1250 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.05–7.21 (AA′BB′-system, aromatic, 4H), 5.43 (s, bridgehead, 2H), 5.2 (s, olefinic, 2H), 5.08 (s, olefinic, 2H); δ_C (100 MHz, $CDCl_3$) 144.93, 144,77, 127.54, 119.96, 103.31, 83.97.

4.2.7. 1,2,3,4,4a,9,9a,10-Octahydro-9,10-epoxy-2,3-dioxaanthracene (11). A solution of diene **5** (300 mg, 1.48 mmol) and TPP (50 mg) in CCl_4 (50 mL) was photooxidised using the general procedure A given in Section 4.1 for 12 h. After removal of the solvent, the residue was passed through a short silica gel column (20 g) eluting with methylene chloride. Then, endoperoxide **11** was crystallized from methylene chloride/ether (3:1) to give (267 mg, 75%) as white crystals, mp 191.5°C; [Found: C, 71.09; H, 5.07. $C_{12}H_{10}O_3$ requires C, 71.28; H, 4.98%]; ν_{max} (KBr) 2900, 1750, 1200, 1000, 750 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 6.93–7.20 (AA′BB′-system, aromatic, 4H), 5.6 (s, bridgehead, 2H), 4.96 (d, A-part of AB-system, J=14.9 Hz, methylenic, 2H), 4.38 (d, B-part of AB-system, J=14.9 Hz, methylenic, 2H); δ_C (100 MHz, $CDCl_3$) 148.46, 147.30, 125.95, 120.33, 82.88, 70.31; *m/z* 202 (2, M^+), 173 (16), 160 (22), 144 (18), 132 (25), 131 (40), 115 (100), 89 (68%).

4.2.8. 2-*exo*,3-*exo*(or 2-*endo*),3-*endo*-Bis(epoxymethano)-1,4-epoxy-1,2,3,4-tetrahydro-naphthalene (15 or 16). To a solution of **11** (50 mg, 0.247 mmol) in methylene chloride (20 mL) a solution of CoTPP (10 mg) in methylene chloride (5 mL) was added and stirred at 0°C for 1 h. Solvent was evaporated, and the residue was chomatographed on neutral alumina (50 g) eluting with methylene chloride to afford **15** (or **16**) as a white solid (37,5 mg, 75%); mp 137–138°C; [Found: C, 71.22; H, 4.96. $C_{12}H_{10}O_3$ requires C, 71.28; H, 4.98%]; ν_{max} (KBr) 2900, 1700, 1600, 1500, 1250 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.19–7.3 (AA′BB′-system, 4H), 5.00 (s, bridgehead, 2H), 2.82 (d, A-part of AB-system, J=4.0 Hz, epoxide, 2H), 2.54 (d, B-part of AB-system, J=4.0 Hz, epoxide, 2H); δ_C (100 MHz, $CDCl_3$) 143.10, 128.57, 121.10, 84.04, 63.42, 47.66; *m/z* 201 (5, M^+-H), 173 (17), 160 (20), 157 (27), 132 (30), 131 (58), 118 (75), 115 (100), 89 (83).

4.3. Thermolysis of endoperoxide (11)

A solution of the endoperoxide **11** (20 mg, 0.098 mmol) in deuterochloroform (0.7 mL) was placed into a NMR tube. The tube was sealed under vacuum and heated 150°C. The reaction was monitored by ^{1}H NMR and was complete after 2 h. Then the reaction mixture was cooled to room temperature, and the solvent was evaporated. ^{1}H NMR data of the reaction mixture was compared to spectral data obtained from the CoTPP-catalyzed rearrangement reaction. It was shown that the products of two reactions were same.

4.4. Epoxidation of diene (5)

To a magnetically stirred solution of **5** (100 mg, 0.59 mmol) in $CHCl_3$ (25 mL) was added *m*-chloroperbenzoic acid (202 mg, 1.17 mmol) at rt during 5 min. After stirring for 1 h, the solvent was evaporated. The ^{1}H NMR analysis of the crude mixture indicated that the same products **14** (or **15**), **16** were formed as in the CoTPP-catalyzed reaction.

4.4.1. 1,2,3,4,9,10-Hexahydro-9,10-etheno-2,3-dioxaanthracene (20). To a stirred solution of **6** (0.75 g, 4.17 mmol) in CCl_4 (20 mL) TPP (10 mg) was added. The mixture was photooxidised until all the diene was completely consumed (5 h). The solvent was evaporated, and the residue was chromatographed on silica gel eluting with $CHCl_3$/hexane (1/1) to afford **20** as white solid (0.44 g, %75), mp 100–101°C. [Found: C, 79.09; H, 7.65. $C_{14}H_{122}O_2$ requires C, 79.22; H, 5.70%]; ν_{max} (KBr) 3030, 2980, 1450, 1200, 950 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.11 (AA′-part of AA′BB′-system, aromatic, 2H), 6.90 (m, BB′-part of AA′BB′-system and AA′ part of AA′XX′-system, aromatic and olefinic, 4H) 4.70 (m, XX′-part of AA′XX′-system and methylenic, 4H); δ_C (100 MHz, $CDCl_3$) 148.09, 141.1, 140.5, 124.5, 123.08, 72.13, 49.6; *m/z* 211 (30, M^+−H), 181 (25), 153 (100), 128 (50), 82 (45%).

4.4.2. 1,4-Etheno-1,2,3,4-tetrahydronaphtho[*b*]furan (21). A solution of **20** (46 mg, 0.23 mmol) in 0.7 mL $CDCl_3$ was placed into a NMR tube. The tube was sealed under vacum and cooled at 0°C. The reaction was monitored by ^{1}H NMR and was complete after 0.5 h. Evaporation of the solvent gave **21**. It was stable in solution for a week at room temperature. ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.8–7.4 (m, aromatic 4H, olefinic, 2H and furan ring, 2H), 5 ppm (br s, bridgehead 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 147.19, 140.11, 134.23, 132.12, 126.15, 124.16, 42.10.

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