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# A Concise Synthesis of the 2,3-Dimethylene-1,4-methano-1,2,3,4-tetrahydronaphthalene and its Reaction with Singlet Oxygen

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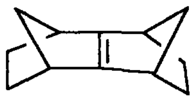
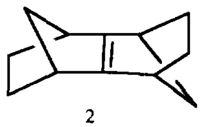
**Abstract:** Palladium-catalyzed carbomethoxylation of benzonorbornadiene (7) yielded dimethyl-1,4-methano-1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylate (9) which was transformed in three steps into 2,3-dimethylene-1,4-methano-1,2,3,4-tetrahydronaphthalene (4) in a high yield. Reaction of **4** with singlet oxygen resulted in the formation of epoxy-endoperoxide (12). X- ray crystallographic analysis demonstrated that epoxide ring is exo as methylene bridge. For the first time, the epoxy-endoperoxide formation from the "one pot" reaction of a diene with singlet oxygen was observed. The epoxy-endoperoxide formation mechanism was discussed. CoTPP (Cobalt(II)tetraphenylporphyrin) catalyzed rearrangement of epoxy-endoperoxide gave hydroxy-aldehyde (13) which was oxidized into dialdehyde (14).

Pyramidalized alkenes are molecules containing carbon-carbon double bonds in which one or both of the $sp^2$ carbon atoms do not lie in the same plane as the attached atoms. The study of *syn-* and-*anti* -sesquinorbornanes(1,2) and 10-oxabenzo-syn-sesquinorbornene (3 )has revealed a combination of some expected steric effects of the bridges with newly discovered stereoelectronic properties of the π system[1,2]. Much of the literature on the pyramidalization of alkenes through1988 is covered in the review by Borden[3].



1



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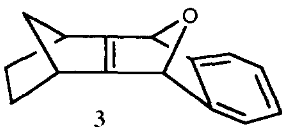
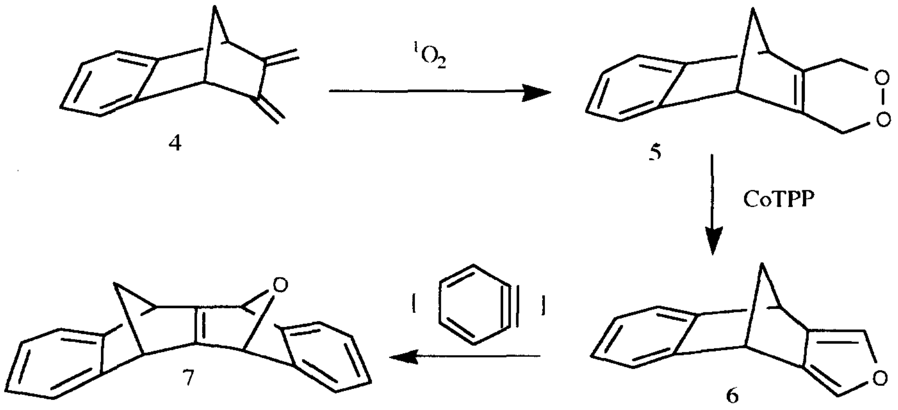


3

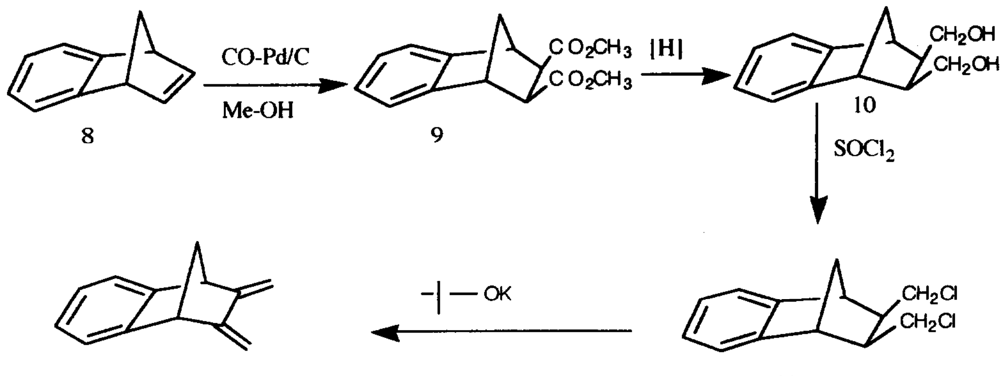
We were interested in the synthesis of **7** in order to study the pyramidalization in the C-C double bond. We prepared some furan derivatives by the Co(II)tetraphenylporphyrin(CoTPP) catalyzed rearrangement of endoperoxides obtained by the reaction of exocyclic dienes witn singlet oxygen[4].Following the same methodology we wanted to synthesize compound **6** whose treatment with benzyne would lead to product **7** (scheme: 1).



Scheme: 1

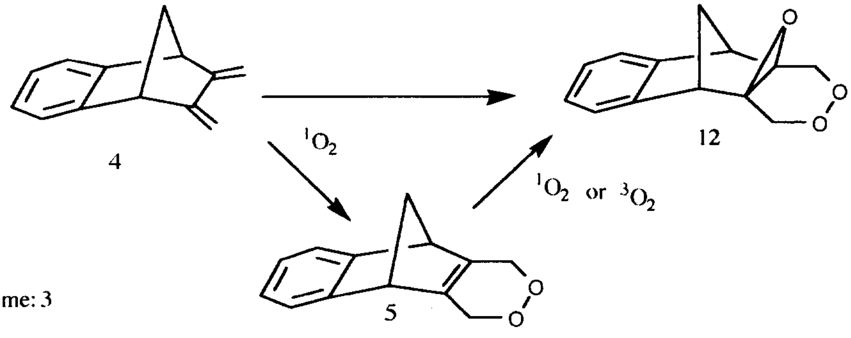
Previously, compound **4** was obtained in seven steps.First, the known *endo-cis* adduct[5] of indene and maleic anhydride was prepared. Then, the *endo-cis* adduct was hydrolyzed and esterified (diazomethane) to the *cis* -dimethyl ester before izomerization to *trans* -ester and it was subjected to general reduction-tosylation-elimination procedures[6] to obtain diene **4**. Indene and maleic anhydride are cheap but the yield of adduct is low and the yield tends to get lower in the stages of hydrolysis, esterification and ester izomerization ; it is especially low in the stage of izomerization because of the polymerization taking place. When the *cis*- bis(hydroxymethyl) derivatives obtained from *cis*- ester, was subjected to p-toluenesulfonation it gave tetrahydrofuran derivatives competitively with the p-di-tosylation product[6]. We now report the synthesis of diene **4** in four steps starting from the benzonorbornadiene in good yield (scheme: 2).

Stille et al[7]. have reported the reaction of cyclic and acyclic olefins with carbon monoxide in methanol to form 1,2- and 1,3-diester in the presence of catalytic amount of $PdCl_2$ and stoichiometric amounts of $CuCl_2$. Vogel et al[8]. found that $PdCl_2$ can be replaced by 10 %Pd/C . Under the usual conditions (3-4 atm.CO, 0,02 mol-equiv. 10%Pd/C, 4 mol- equiv. $CuCl_2$, abs. MeOH, 20-25°, 24h ) the benzonorbornadiene(8), which was synthesized according to Friedman's[9] procedure, was bis-carbomethoxylated and esterified to the dimethyl 1,4-methano-1,2,3,4-tetrahydronaphthalene-*exo*- *cis* -2,3-dicarboxylate (9) in a 57 % yield. The structure of **9** was deduced from its melting point, $^1H$- and $^{13}C$-NMR spectra and by comparing these with the *endo* -di-ester which is known in the literature[5]. After purification by crystallization,**9** was reduced to the *cis*- diol(10) with $LiAlH_4$/ THF in a 75 % yield. Reaction of **10** with $SOCl_2$/ pyridine yielded *exo-cis* dichloride(11) in a 75 % yield, which eliminated two equivalents of HCl in excess t-BuOK/ THF, yielding the exocyclic diene **4** in a 80 % yield. Ester izomerization could be avoided if the reduction and reaction with $SOCl_2$/ pyridine were carried out under strict control of concentration and temperature (see experimental part) .



Scheme: 2

Singlet oxygen undergoes 1,4-cycloaddition to conjugated dienes to give cyclic peroxides and is added to mono olefins to form 1,2-dioxetans and hydroperoxides[10]. When **4** was submitted to photooxygenation at room temperature in carbon tetrachloride solution containing tetraphenylporphyrin (TPP) as sensitizer after 24 hours the $^1H$- NMR spectrum indicated the complete consumption of the starting material. The reaction mixture was chromatographed on silica gel column with ether/petroleum ether (1/1) as eluent. Examination of the fractions revealed that the only product was **12** (40 % yield ), the material balance consisting of polymer. Careful re-examination of crude reaction mixture confirmed that the chromatographic product was also that formed from the photooxygenation(scheme:3). Photooxygenation of **4** in chloroform and methylene chloride using TPP gave the same product(12).



Scheme: 3

The structure of **1 2** was established on the basis of its $^1H$-and $^{13}C$-NMR spectrum.The $^1H$- and $^{13}C$-NMR spectral data of compound was completely in agreement with the structure. There were two AB and one AA'BB'systems, one of AB system belonging to the methylenic bridge protons. It was located between $\partial = 2.21\text{-}1.78$ ppm ( $J_{AB} = 9.2$ Hz ). This AB system was further split by the bridgehead protons to triplets ($J_{12} = 1.56$ Hz ).The other AB system belongs to the methylenic protons in the peroxide ring was located between ∂ = 4.46-4.10 ppm ($J_{AB}$ = 13 Hz). Bridgehead protons resonated as a br singlet at 3.47 ppm. Aromatic protons gave rise to as a AA′BB′ system between ∂ = 7.29-7.08 ppm as expected. Mass spectral analysis (70 eV) showed a molecular ion of *m/e* 216. X-ray crystallographic analysis demonstrated that the epoxide ring is *exo* as methylene bridge. The asymmetric unit contains an unusual number(3) of independent molecules, which have slightly different stereochemistry (Fig. 1). Thus, we observed for the first time epoxy-endoperoxide formation from the "one-pot " reaction of a diene with singlet oxygen .

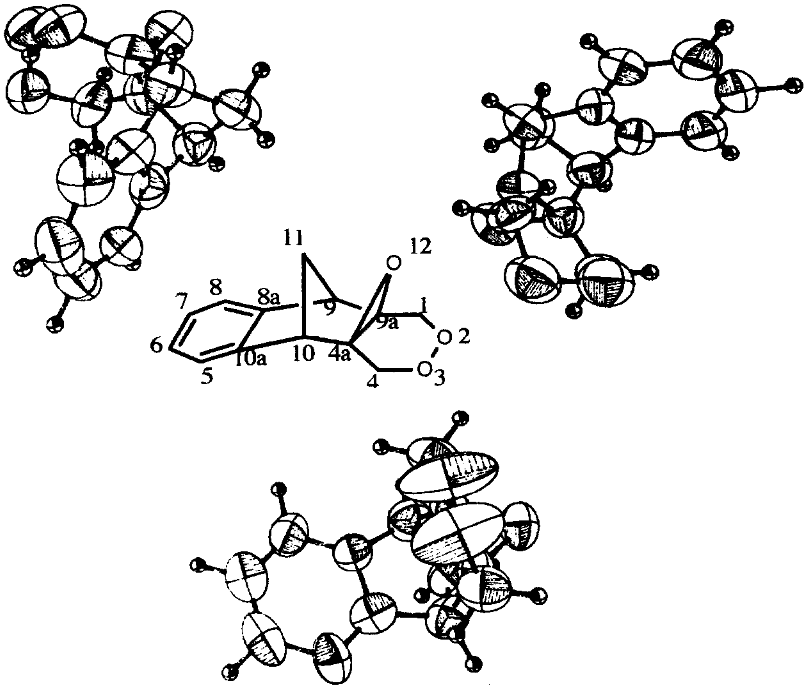
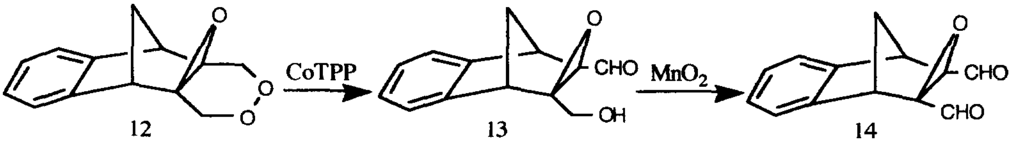


Figure 1. X-ray crystal Structure of 12

To explain how product **1 2** derived from **5** with singlet or triplet oxygen , the reaction was stopped after 2 hours and reaction mixture was chromatographed under the same conditions. However, it was observed that the same product (12) had formed. If the rate determining step were the formation of **1 2** from **5**, then endoperoxide (5) would be obtained and its reaction would be studied with singlet and triplet oxygen . This was the expected situation because Vogel has shown that when diene units are fused onto rigid and structurally similar norbornyl frameworks significant reactivity differences are observed. More specifically, in the 2,3-dimethylenenorbornane introduction of a double bond between C(5) and C(6), due to the hyperconjugative interaction of the endocyclic double bond with the diene, alters the energies and/or the shape of diene frontier orbitals and the Diels- Alder reactivity is appreciable affected[11]. Compound **4** has also an endocyclic double bond which is a π bond of benzene ring. It has been suggested that singlet oxygen undergoes electrophilic addition to the double bond to give a fugitive perepoxide which subsequently captures a allylic hydrogen thereby forming the hydroperoxide[12]. When allylic hydrogen atoms are unavaliable the perepoxide rearranges to a dioxetan[13]. The latter sequence has been offered to explain the formation of epoxide from the reaction of adamantylideneadamantane with singlet oxygen in the presence of pinacolone as a potential oxygen trapping agent. Steric effects in the adamantane skeleton were thought to prevent the rearrangement and therefore the perepoxide reacted with pinacolone in Baeyer- Villiger fashion to give the epoxide and t-butyl acetate[14]. Jefford has carried out the reaction of singlet oxygen with norbornene[15] and 2- phenylnorbornene[16] in a variety of solvents including pinacolone, and obtained norbornene-epoxide and 2-phenylnorbornene-epoxide respectively, but no t-butyl acetate could be detected.It has been reported that either the perepoxide is not formed or, if it is, then pinacolone is not sufficiently electrophilic to produce a Baeyer-Villiger type intermediate. This is contrary to the earlier report. In carrying out the tests for singlet oxygen as authentic oxidation species, Jefford has showed that 2-phenylnorbornene undergoes auto-oxidation[16] and gives 2-phenylnorbornene-epoxide. As a result, the formation of **12** can be explained by the formation of peroxide **5** which can originate from [4+2]-cycloaddition of singlet oxygen to **4**, followed by epoxidation of the double bond with singlet or triplet oxygen. It is difficult to account for the formation of the epoxide. Similar results have been observed in the reaction of 2,3-dimethylene-1,4-epoxy-1,2,3,4-tetrahydronahthalene with singlet oxygen[17].Further experiments in this area are in progress.



Scheme: 4

Cobalt(II) tetraphenylporphyrin catalyzes the rearrangement of unsaturated bicyclic endoperoxides to bisepoxides[18], and of monocyclic endoperoxides to furans[4,19]. The application of this reaction to epoxy-endoperoxide(12) resulted in the formation of expected hydroxy-aldehyde(13), (in nearly quantitative yield),which was oxidized into dialdehyde(14) in a 20 % yield with $MnO_2$ in benzene(scheme:4). Both of these compounds were characterized by means of spectral data. A probable mechanism for the rearrangement of **12** to **13** involves catalytic cleavage of the peroxide bond, presumably by electron transfer, followed by a hydrogen shift and loss of CoTPP. Because CoTPP had caused no reaction on the epoxide ring its configuration must remain unchanged. These reactions may be interesting in view of the products formed because they are benzonorbornadiene-epoxides bearing aldehyde, alcohol(13) and dialdehyde(14) functional groups on the epoxide ring.

## Experimental Section

**General**: Solvents were concentrated at reduced pressure and melting points were uncorrected. Infrared spectra were obtained from films on NaCl plates for liquids or from solution in 0.1 mm cells or KBr pellets for solids on a Perkin-Elmer 337 infrared recording spectrophotometer. The $^1$H-NMR and $^{13}$C-NMR spectra were recorded by Varian EM-200 NMR spectrometer and were reported $\partial$ units with $(CH_3)_4Si$ as internal standard. Mass spectrum was recorded at the University of East Anglia. X-ray data were collected by standard techniques. All column chromatography was performed on silica gel (60 mesh ), while TLC was carried out on 0.2 mm silica gel 60 $F_{254}$ plates.

### *Dimethyl-1,4-methano-1,2,3,4-tetrahydronaphthalene-exo-cis-2,3-dicarboxylate(9)*

Benzonorbornadiene[9] (15 g ,0.105 mol ), 54 g (0.4 mol ) $CuCl_2$ , 10 % Pd/C (0.75 g ,0.7 mmol ) , 10.6 g (0.1 mol ) trimethylorthoformate and 250 ml anh. methanol were placed in a 1 l.autoclave. After careful degassing , the mixture was pressurized with CO (5 atm ) and stirred for 24 h. at RT. CO pressure was maintained at 4-5 atm. After removal of the solvent by evaporation, 250 ml water and 250 ml $CHCl_3$ were added. The solid was filtered off. The organic layer was washed with sat. aq. $NaHCO_3$ solution ( 3 x 100 ml ). Water layer was washed with (2 x 100 ml ) $CHCl_3$ and organic layers were combined and dried over $MgSO_4$. After removal of solvent the yellowish residue was recrystallized from ethylacetate. Yield 16g (57 % ) white crystals,mp 107-108 $^0$C ( literature[5] value 110$^0$C ). IR. (KBr ): 3010, 2980, 1740, 1420, 1340, 1200, 1050 cm$^{-1}$.$^1$H-NMR (200 MHz- $CDCl_3$ ) $\partial$ 7.1 - 7.3 (AA´BB´- system , aromatic, 4H ), 3.7 (s, ester-methyl, 6H ), 3.6 ( s, bridgehead, 2H ), 2.75 (s, methyne, 2H ), 1.8 - 2.5 (AB- system, bridge, 2H ) ppm.

### *exo-cis-2,3-Bis(hydroxymethyl)-1,4-methano-1,2,3,4-tetrahydronaphthalene (10)*

To a vigorously stirred suspension of $LiAlH_4$ 0.8 g ( 21 mmol ) in 60 ml anh. THF maintained at 0 $^0$C a suspension of **9** (4 g, 15 mmol ) in 30 ml THF was added portionwise (0.5-1h ). The mixture was allowed to reach RT. and stirred at RT under a nitrogen atmosphere. After 6 h. water was added dropwise and mixture heated under reflux for one minute and filtered through 20 g. silica gel. The solid (silica gel and aluminum salts ) was extracted with $CHCl_3$. The filtrates were combined and dried over $MgSO_4$. After filtration the solvent was evaporated and 2.4 g diol **(10)** was obtained as a white powder in a 75 % yield. Pure enough for the next step, mp 168-169$^0$C ( $CHCl_3$ ). $^1$H-NMR (200 MHz-$CDCl_3$ )$\partial$ 7.2 - 7.0 (AA´BB´- system, aromatic, 4H ) , 3.95 - 3.85 (AB- system, methylene, 4H ), 3.65 (s, bridgehead, 2H ), 3.05 (br s, methyn, 2H ), 1.8 - 1.6 ( AB- system, bridge, 2H ) ppm. Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.89. Found: C, 76.21; H, 7.95.

### *exo-cis-2,3-Bis(chloromethyl)-1,4-methano-1,2,3,4-tetrahydronaphthalene (11)*

To a stirred mixture of anh. pyridine (1.6 g, 20 mmol ) and $SOCl_2$ (9 g, 75 mmol ), 2 g (9.8 mmol ) of **10** was added portionwise, without cooling. More $SOCl_2$ (15 g, 125 mmol ) was added and the mixture was heated to 60-70 $^0$C for 2 h. After cooling to RT the mixture was added to 100 ml $CH_2Cl_2$. The excess of $SOCl_2$ was destroyed slowly by dropwise addition of water (20 ml ) under external cooling and reflux. The organic layer was washed with water (3 x 50 ml ) and dried (MgSO4). After evaporation of solvent 1.6 g (75 % yield ) of **11** was obtained as a yellowish-white powder, pure enough for the next step, mp 86 - 87$^0$C ($CH_2Cl_2$- p.ether ). IR. (KBr ): 2930, 2835, 1455, 1290, 1075, 1010 cm$^{-1}$. $^1$H-NMR (200 MHz- $CDCl_3$ ) $\partial$ 7.26 - 7.1 (AA´BB´- system, aromatic, 4H ), 3.9 - 3.45 (AB - system , methylenic, 4H ), 3.45 (br s, bridgehead, 2H ), 2.16 - 2.09 (m, methyne, 2H ), 1.88 - 1.74 (AB- system, bridge, 2H ) ppm. $^{13}$C-NMR (200MHz-$CDCl_3$ ) $\partial$ 147.97, 126.66, 121.47, 48.35, 47.30, 45.67, 43.61 ppm. Anal. Cald for $C_{13}H_{14}Cl_2$: C, 64.74; H, 5.85. Found: C, 64.80; H, 5.97

### *2,3-Dimethylene-1,4-methano-1,2,3,4-tetrahydronaphthalene (4).*

Solid t-BuOK (4 g, 36 mmol ) was added to a stirred solution of **11** (1.7 g, 7 mmol ) in 20 ml anh. THF cooled to 0 $^{o}$C The mixture was stirred at RT for 12 h. The end of elimination was checked by TLC. Water (15 ml ) was added portionwise until complete dissolution of KCl. The brownish mixture was extracted with petroleum ether (3 x 25 ml ). The organic extract were combined and washed with water (3 x 25 ml ). After drying ($MgSO_4$) the solution was evaporated to dryness. 0.95 g (80 % yield ) of **4** was obtained. Courless needles, mp 83 - 84$^{o}$C ( lit$^{6a}$. 83$^{o}$C )

### *1,2,3,4,4a,9,9a,10-Oktahydro-9,10-exo-methano-4a,9a-exo-epoxy-2,3-dioxaantracene(12 )*

To a stirred solution of **4** ( 0.8 g, 4.8 mmol ) in 30 ml carbon tetrachloride was added 5 mg of TPP(tetraphenylporphyrin). The resulting mixture was irradiated with a projection lamp (150 watt ) while oxygen is being passed through solution and the mixture was stirred for 24 hours at room temperature. Solvent was removed by evaporation. The formed precipitate (consisting of **12** and polymer) was submitted to silica gel column chromatography (80 g ) eluting with ether/petroleum ether (1/1).From fractions 7 to 12 we isolated 450 mg epoxy-endoperoxide in a 45 % yield. Yellowish crystals from $CH_2Cl_2$/petroleum ether , m p 120 $^{o}$C IR. (KBr ): 2910, 1455, 1420, 1260, 965, 880,770 $cm^{-1}$; $^{1}$H-NMR (200MHz- $CDCl_3$ ) ∂ 7.29 - 7.08 (AA'BB'- system, aromatic, 4H ), 4.46 - 4.10 (AB- system, methylenic, 4H ), 3.47 (s, bridgehead,2H ), 2.21- 1.78 ( AB- system, bridge, 2H ) ppm ; $^{13}$C-NMR (200 MHz-$CDCl_3$ ) ∂ 147.89, 126.90, 123.66, 70.16, 63.08, 46.71, 43.27 ppm. MS (70 eV ), m/e (relative intensity ) 216 (11.56 ), 198 (17.80 ), 186 (9.69 ), 170 (15.81 ), 157 (17.19 ), 141 (61.19 ),129 (96.66 ), 116 (base ), 102 (6.07 ), 91 (8.04 ), 77 (11.09 ), 63 (11.90 ), 51 (5.16 ), 39 (7.07 ). Anal. Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59. Found: C, 71.89 ; H, 5.60.

### *1,2,3,4-Tetrahydro-2-formyl-3-hydroxymethyl-1,4-exo-methano-2,3-exo-epoxynaphthalene(13)*

A solution of **12** (0.3 g, 1.4 mmol ) in 50 ml. of methylene chloride was cooled to 0 $^{o}$C. While cooling and stirring, a solution of CoTPP (15 mg ) in 5 ml of $CH_2Cl_2$ was added within 10 min. The reaction mixture was stirred at room temperature for 30 min. and was filtered through a short silica gel column (20 g ) eluting with methylene chloride/petroleum ether (80/20 ). Removal of the solvents gave 285 mg of hydroxy-aldehyde (95 % yield). IR .($CHCl_3$ ): 3600, 2960, 2250, 1710, 1380, 1035, 900 $cm^{-1}$; $^{1}$H-NMR (200 MHz- $CDCl_3$ ) ∂ 9.44 (s, aldehyde,1H ) , 7.45 - 7.06 (m, aromatic,4H ), 4.00 - 3.76 (AB- system, methylenic,2H ), 3.68 (s, bridgehead, 1H ) , 3.46 (s, bridgehead, 1H ), 2.17 - 1.65 (AB- system,bridge, 2H ), 2.02 (br s,alcohol, 1H ) ppm; $^{13}$C-NMR (200 MHz-$CDCl_3$) ∂ 196.62, 148.06, 147.68, 126.92, 126.60, 124.86, 123.36, 78.76, 73.87, 58.46, 47.23, 45.63, 42.30 ppm. Anal. Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59. Found; C, 71.97; H, 5.69

### *1,2,3,4-Tetrahydro-1,4-exo-methano-2,3-exo-epoxy-2,3-diformylnaphthalene(14)*

Freshly prepared active $MnO_2$ (2.5 g, 29 mmol) was added to a solution of **13** (240 mg, 1.1 mmol) in 10 ml benzene within 10 min. The reaction mixture was refluxed for 5 hours and then filtered. The precipitate was extracted with methylene chloride. The combined organic layers were evaporated. The residue was separated through a short silica gel column (20 g ) eluting with methylene chloride/petroleum ether (65/35).Concentration of solvents gave **14** (48 mg, 20 % yield ). IR ($CHCl_3$ ) : 2900, 2240, 1715, 1460, 1380, 1060, 900 $cm^{-1}$; $^{1}$H-NMR (200 MHz- $CDCl_3$) ∂ 9.45 (s, aldehyde, 2H ); 7.50-7.05 ( AA'BB'- system, aromatic, 4H ), 3.82 (s, bridgehead 2H ), 2.12-1.72 (AB- system, bridge,2H ) ppm; $^{13}$C-NMR (200MHz-$CDCl_3$ ) ∂ 193.50, 146.65, 127.01, 124.80, 77.35, 45.50, 41.47 ppm. Anal. Cacd for $C_{13}H_{10}O_3$ : C, 72.89; H, 4.70. Found: C, 72.43; H, 4.76.

Table 1. Fractional atomic coordinates and equivalent thermal parameters
Ueq is the mean of the principal axes of the thermal ellipsoid

| | x | y | z | Ueq(Å$^2$) |
|---|---|---|---|---|
| Molecule (a) | | | | |
| C1 | 0.1033(8) | 0.1192(7) | 0.9327(5) | 0.1013(44) |
| O2 | 0.2031(6) | 0.0678(4) | 0.9307(4) | 0.1120(29) |
| O3 | 0.2048(6) | 0.0366(4) | 0.8496(4) | 0.1074(27) |
| C4 | 0.2444(8) | 0.1064(6) | 0.8052(6) | 0.0966(39) |
| C4a | 0.1800(7) | 0.1871(6) | 0.8118(6) | 0.0840(34) |
| C5 | 0.0014(9) | 0.1177(6) | 0.6471(5) | 0.0910(36) |
| C6 | -0.0940(11) | 0.0683(6) | 0.6410(7) | 0.1055(44) |
| C7 | -0.1641(9) | 0.0741(7) | 0.6998(9) | 0.1147(49) |
| C8 | -0.1401(8) | 0.1256(8) | 0.7689(7) | 0.1046(43) |
| C8a | -0.0468(8) | 0.1737(6) | 0.7732(5) | 0.0817(34) |
| C9 | 0.0053(7) | 0.2377(6) | 0.8364(5) | 0.0922(35) |
| C9a | 0.1072(7) | 0.1930(6) | 0.8740(5) | 0.0816(34) |
| C10 | 0.1192(7) | 0.2337(6) | 0.7361(5) | 0.0844(34) |
| C10a | 0.0237(7) | 0.1731(5) | 0.7120(5) | 0.0847(34) |
| C11 | 0.0573(7) | 0.3043(6) | 0.7776(5) | 0.0955(39) |
| O12 | 0.2110(5) | 0.2393(4) | 0.8805(4) | 0.1024(27) |
| Molecule (b) | | | | |
| C1' | -0.1602(8) | 0.4367(6) | 0.1290(5) | 0.1001(40) |
| O2' | -0.1543(8) | 0.4244(9) | 0.2109(6) | 0.1938(58) |
| O3' | -0.0778(9) | 0.4311(10) | 0.2608(5) | 0.2060(64) |
| C4' | 0.0295(9) | 0.4179(6) | 0.2525(5) | 0.0942(38) |
| C4a' | 0.0479(7) | 0.4198(5) | 0.1630(5) | 0.0788(33) |
| C5' | 0.0860(8) | 0.1959(6) | 0.1612(5) | 0.0877(37) |
| C6' | 0.0106(10) | 0.1308(7) | 0.1420(7) | 0.1026(45) |
| C7' | -0.0798(9) | 0.1395(6) | 0.0844(7) | 0.1001(45) |
| C8' | -0.0995(7) | 0.2200(6) | 0.0438(6) | 0.0880(36) |
| C8a' | -0.0244(7) | 0.2837(6) | 0.0618(5) | 0.0866(39) |
| C9' | -0.0215(7) | 0.3773(6) | 0.0321(4) | 0.0826(35) |
| C9a' | -0.0457(7) | 0.4310(5) | 0.1043(5) | 0.0741(32) |
| C10' | 0.1272(7) | 0.3595(6) | 0.1259(5) | 0.0933(37) |
| C10a' | 0.0654(7) | 0.2748(5) | 0.1213(4) | 0.0750(29) |
| C11' | 0.1048(8) | 0.3883(5) | 0.0341(5) | 0.0837(36) |
| O12' | 0.0270(5) | 0.5022(4) | 0.1243(3) | 0.0950(25) |
| Molecule (c) | | | | |
| C1'' | 0.0873(7) | 0.6004(5) | 0.5478(4) | 0.0921(32) |
| O2'' | 0.0400(5) | 0.6031(4) | 0.4649(4) | 0.1175(26) |
| O3'' | 0.0543(5) | 0.6918(4) | 0.4338(3) | 0.1130(29) |
| C4'' | 0.1661(6) | 0.6981(5) | 0.4160(4) | 0.0853(27) |
| C4a'' | 0.2452(6) | 0.6765(5) | 0.4866(4) | 0.0800(31) |
| C5'' | 0.2544(6) | 0.8838(5) | 0.5610(4) | 0.0905(31) |
| C6'' | 0.1949(7) | 0.9252(5) | 0.6180(5) | 0.0894(31) |
| C7'' | 0.1578(6) | 0.8795(5) | 0.6811(5) | 0.0863(27) |
| C8'' | 0.1774(6) | 0.7912(5) | 0.6909(5) | 0.0908(34) |
| C8a'' | 0.2353(6) | 0.7519(4) | 0.6351(4) | 0.0816(27) |
| C9'' | 0.2753(6) | 0.6605(5) | 0.6293(4) | 0.0862(30) |
| C9a'' | 0.2052(7) | 0.6260(5) | 0.5532(4) | 0.0855(29) |
| C10'' | 0.3349(6) | 0.7349(5) | 0.5250(4) | 0.0880(31) |
| C10a'' | 0.2716(6) | 0.7971(5) | 0.5724(4) | 0.0778(28) |
| C11'' | 0.3857(6) | 0.6765(6) | 0.5960(5) | 0.0981(32) |
| O12'' | 0.2669(5) | 0.5843(3) | 0.4951(3) | 0.1054(21) |

Table 2. Bond lengths (Å), bond angles (o) and selected torsion angles (o) with e.s.d.'s in parantheses.

Molecule (a)

| | | | |
|---|---|---|---|
| O12 - C4a | 1.420 (11) | C10a- C5 | 1.385 (12) |
| O12 - C9a | 1.456 (11) | C10a- C8a | 1.412 (13) |
| O2 - O3 | 1.440 ( 9) | C10a- C10 | 1.521 (12) |
| O2 - C1 | 1.465 (13) | C9a - C9 | 1.501 (12) |
| O3 - C4 | 1.431 (12) | C9a - C1 | 1.514 (13) |
| C11 - C9 | 1.610 (13) | C9 - C8a | 1.534 (12) |
| C11 - C10 | 1.545 (13) | C8 - C8a | 1.362 (14) |
| C4a - C9a | 1.448 (13) | C8 - C7 | 1.407 (18) |
| C4a - C10 | 1.568 (12) | C5 - C6 | 1.394 (16) |
| C4a - C4 | 1.496 (13) | C6 - C7 | 1.380 (19) |

| | | | |
|---|---|---|---|
| C9a -O12 -C4a | 60.5 (6) | C1 -C9a -C4a | 118.9 (8) |
| C1 -O2 -O3 | 108.0 (6) | C1 -C9a -C9 | 122.3 (8) |
| C4 -O3 -O2 | 105.8 (6) | C8a -C9 -C9a | 104.1 (7) |
| C10 -C11 -C9 | 93.6 (7) | C11 -C9 -C9a | 100.7 (7) |
| C10 -C4a -C9a | 105.8 (7) | C11 -C9 -C8a | 99.4 (7) |
| C4 -C4a -O12 | 116.6 (7) | C9a -C1 -O2 | 108.1 (8) |
| C4 -C4a -C9a | 118.7 (8) | C7 -C8 -C8a | 116.7 (1.0) |
| C4 -C4a -C10 | 122.4 (8) | C9 -C8a -C10a | 105.1 (8) |
| C10 -C4a -O12 | 116.1 (7) | C8 -C8a -C10a | 122.7 (9) |
| C9a -C4a -O12 | 61.0 (6) | C8 -C8a -C9 | 132.3 (9) |
| C10 -C10a-C8a | 108.8 (7) | C10a-C10 -C4a | 101.7 (7) |
| C5 -C10a-C8a | 119.1 (8) | C11 -C10 -C10a | 99.1 (7) |
| C5 -C10a-C10 | 131.9 (9) | C11 -C10 -C4a | 100.5 (7) |
| C9 -C9a -O12 | 118.5 (7) | C4a -C4 -O3 | 112.8 (8) |
| C9 -C9a -C4a | 106.4 (7) | C6 -C5 -C10a | 119.2 (9) |
| C4a -C9a -O12 | 58.5 (5) | C7 -C6 -C5 | 119.8 (1.0) |
| C1 -C9a -O12 | 115.0 (7) | C6 -C7 -C8 | 122.2 (1.0) |

| | | | |
|---|---|---|---|
| C4a -C4 -O3 -O2 | -53.8(9) | C8 -C8a -C10a-C10 | 180.0(9) |
| C9a -C1 -O2 -O3 | -60.0(9) | C10 -C4a -C9a -C1 | 145.3(8) |
| C9 -C9a -C4a-C4 | -140.0(8) | C5 -C10a-C8a -C9 | 177.0(8) |
| C1 -O2 -O3 -C4 | 80.3(8) | | |

Molecule (b)

| | | | |
|---|---|---|---|
| O12'- C9a' | 1.446 (10) | C9a'- C9' | 1.534 (13) |
| O12'- C4a' | 1.437 (10) | C8a'- C9' | 1.519 (12) |
| O2' - O3' | 1.182 (13) | C8a'- C8' | 1.405 (12) |
| O2' - C1' | 1.353 (16) | C10'- C11' | 1.553 (13) |
| O3' - C4' | 1.372 (13) | C10'- C4a' | 1.524 (11) |
| C10a'- C8a' | 1.401 (11) | C11'- C9' | 1.587 (12) |
| C10a'- C10' | 1.541 (13) | C5' - C6' | 1.433 (13) |
| C10a'- C5' | 1.362 (13) | C4a'- C4' | 1.511 (13) |
| C9a'- C1' | 1.535 (12) | C8' - C7' | 1.385 (14) |
| C9a'- C4a' | 1.428 (11) | C6' - C7' | 1.385 (15) |

| | | | |
|---|---|---|---|
| C9a'-O12'-C4a' | 59.4 (5) | C11'-C9'-C9a' | 102.0 (6) |
| C4'-O3'-O2' | 127.9 (1.0) | C9'-C11'-C10' | 92.7 (6) |
| C1'-O2'-O3' | 129.2 (1.0) | C4a'-C4'-O3' | 110.6 (7) |
| C9'-C8a'-C10a' | 106.0 (7) | C4a'-C9a'-O12' | 60.6 (5) |
| C8'-C8a'-C10a' | 122.5 (8) | C9'-C9a'-O12' | 115.8 (7) |
| C8'-C8a'-C9' | 131.3 (8) | C9'-C9a'-C4a' | 105.0 (7) |
| C10'-C10a'-C8a' | 107.1 (7) | C1'-C9a'-O12' | 117.5 (7) |
| C5'-C10a'-C8a' | 120.3 (8) | C1'-C9a'-C4a' | 121.2 (7) |
| C5'-C10a'-C10' | 132.5 (7) | C1'-C9a'-C9' | 121.3 (7) |
| C10'-C4a'-O12' | 116.9 (7) | C4a'-C10'-C10a' | 102.5 (7) |
| C9a'-C4a'-O12' | 60.0 (5) | C11'-C10'-C10a' | 99.8 (6) |
| C9a'-C4a'-C10' | 107.1 (7) | C11'-C10'-C4a' | 99.7 (7) |
| C4'-C4a'-O12' | 114.3 (7) | C6'-C5'-C10a' | 117.0 (8) |
| C4'-C4a'-C10' | 123.6 (7) | C6'-C7'-C8' | 119.3 (9) |
| C4'-C4a'-C9a' | 118.0 (8) | C9a'-C1'-O2' | 108.7 (8) |
| C9a'-C9'-C8a' | 104.7 (6) | C7'-C6'-C5' | 123.1 (9) |
| C11'-C9'-C8a' | 99.2 (7) | C7'-C8'-C8a' | 117.6 (8) |

| | | | |
|---|---|---|---|
| C4a'-C4'-O3'-O2' | 18.0(1.8) | C10'-C4a'-C9a'-C1' | 142.2(8) |
| C9'-C9a'-C4a'-C4' | -145.2(8) | C5'-C10a'-C8a'-C9' | 179.8(8) |
| C8'-C8a'-C10a'-C10' | -177.9(8) | C1'-O2'-O3'-C4' | -29.9(2.2) |
| C9a'-C1'-O2'-O3' | 19.7(1.7) | | |

Molecule (c)

| | | | |
|---|---|---|---|
| O3''-O2'' | 1.494 (9) | C10a''-C10'' | 1.520 (11) |
| O3''-C4'' | 1.439 (10) | C8a''-C9'' | 1.513 (10) |
| O12''-C4a'' | 1.466 (9) | C8a''-C8'' | 1.378 (11) |
| O12''-C9a'' | 1.451 (10) | C9''-C9a'' | 1.544 (10) |
| O2''-C1'' | 1.435 (8) | C9''-C11'' | 1.541 (11) |
| C4a''-C4'' | 1.473 (9) | C5''-C6'' | 1.419 (11) |
| C4a''-C9a'' | 1.491 (11) | C9a''-C1'' | 1.491 (12) |
| C4a''-C10'' | 1.511 (10) | C10''-C11'' | 1.563 (11) |
| C10a''-C8a'' | 1.376 (10) | C6''-C7'' | 1.390 (11) |
| C10a''-C5'' | 1.377 (11) | C7''-C8'' | 1.403 (11) |

| | | | |
|---|---|---|---|
| C4''-O3''-O2'' | 106.7 (5) | C8''-C7''-C6'' | 121.6 (7) |
| C9a''-O12''-C4a'' | 61.5 (5) | C9a''-C1''-O2'' | 109.2 (6) |
| C10''-C4a''-C9a'' | 106.8 (6) | C10''-C11''-C9'' | 94.5 (5) |
| C10''-C4a''-O12'' | 115.8 (6) | C6''-C5''-C10a'' | 115.9 (7) |
| C9a''-C4a''-O12'' | 58.8 (5) | C4a''-C9a''-O12'' | 59.8 (5) |
| C9a''-C9''-C8a'' | 103.1 (6) | C8''-C8a''-C10a'' | 121.6 (7) |
| C7''-C6''-C5'' | 120.8 (7) | C8''-C8a''-C9'' | 131.1 (7) |
| C4a''-C4''-O7 | 111.8 (6) | C9''-C8a''-C10a'' | 107.3 (6) |
| C10a''-C10''-C4a'' | 102.4 (6) | C5''-C10a''-C8a'' | 123.2 (7) |
| C11''-C10''-C4a'' | 100.1 (6) | C5''-C10a''-C10'' | 129.4 (7) |
| C11''-C10''-C10a'' | 99.2 (6) | C10''-C10a''-C8a'' | 107.3 (6) |
| C11''-C9''-C8a'' | 100.1 (6) | C4''-C4a''-O12'' | 113.3 (6) |
| C11''-C9''-C9a'' | 100.8 (6) | C4''-C4a''-C9a'' | 118.2 (6) |
| C1''-C9a''-O12'' | 114.6 (6) | C4''-C4a''-C10'' | 125.4 (7) |
| C1''-C9a''-C4a'' | 119.8 (6) | C1''-O2''-O3'' | 108.2 (5) |
| C1''-C9a''-C9'' | 125.8 (7) | C9''-C9a''-O12'' | 114.9 (7) |
| C7''-C8''-C8a'' | 116.8 (7) | C9''-C9a''-C4a'' | 103.2 (6) |

| | | | |
|---|---|---|---|
| C4a''-C4''-O3''-O2'' | -55.5(7) | C9a''-C1''-O2''-O3'' | -57.6(7) |
| C9''-C9a''-C4a''-C4'' | -147.0(7) | C10''-C4a''-C9a''-C1'' | 146.8(7) |
| C4''-O3''-O2''-C1'' | 78.9(7) | C8''-C8a''-C10a''-C10'' | 178.1(7) |
| C5''-C10a''-C8a''-C9'' | -177.0(7) | | |

Table 3. Experimental data and structure refinement parameters.

### Crystal data

$C_{13}H_{12}O_3$
Mr=216.238
Monoclinic
$P\ 1\ 2_1/a\ 1$
a=12.248(3) Å
b=15.587(2) Å
c=16.666(2) Å
B =96.75(2)°
V =3159.64(96) $Å^3$
Z=12

Mo Kα radiation
λ=0.70930 Å
Cell parameters from 25 reflections
θ=6-9°
μ=0.09 $mm^{-1}$
T=293 K
Rod-shaped
0.12 X 0.15 X 0.40 mm
Yellow
Dx=1.364

### Data collection

Enraf-Nonius CAD-4 diffractometer
w/2θ scans
Absorption correction:
none
6421 measured reflections
4929 independent reflections
2137 observed reflections
$[F \geq 3\sigma(F)]$

θmax=48°
h= -11 --> 11
k= 0 --> 16
l= 0 --> 18
3 standard reflections
frequency:180 min
intensity variation 1%
Rint = 0.0428

### Refinement

Refinement on F
Final R=0.055
wR=0.050
1088 reflections
433 parameters
S not calculated
Weighting scheme:
w = 1 / ( σ **2 (F) + .01 F*F )
H atoms positions not refined

$(\Delta/\sigma)_{max}$= 0.385
$\rho_{max}$= +0.22 e $Å^{-3}$
$\rho_{min}$= -0.09 e $Å^{-3}$
Atomic scattering factors from
international Tables for X-ray
Crystallography (1974, Vol. IV)
Extinction correction:
none

H atoms were geometrically positioned 1.08 Å from the corresponding atoms. Non-H atoms were refined using the blocked full-matrix method. Initially a unit weighting scheme was used, but in the final stages of the refinement the weights were assigned using the method described in SHELX76 (Sheldrick,1976) package.[20]

The programs used were SHELX76 (Sheldrick,1976),[20] SHELXS86 (Sheldrick, 1990)[21] and ORTEP (Johnson,1976).[22]

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