Synthesis of hydroxy, epoxy, nitrato and methoxy derivatives of tetralins and naphthalenes

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Stereoselective syntheses are described for *cis,trans,cis*-2,3,5-tribromo-1,4-dihydroxytetralin, *trans,trans,cis*-2,3,5-tribromo-1,4-dihydroxytetralin, *trans,trans,trans*-1,4-dihydroxy-2,3-dibromotetralin, *trans,trans,trans*-1-hydroxy-2,3,4-tribromotetralin, *cis,cis,cis*-1,2-epoxy-3,5-dibromo-4-hydroxytetralin, *anti*-1,2:3,4-diepoxytetralin, 1-hydroxy-4-bromonaphthalene, *trans,trans,trans*-1,4-dinitrato-2,3-dibromotetralin, 1-nitrato-2,3,4-tribromotetralin, 2,3-dibromonaphthalene and 1-methoxy-4-nitrato-2,3-dibromonaphthalene. These isomeric arene oxides and disubstituted naphthalenes provide excellent precursors for a number of 1,4- and 2,3-disubstituted naphthalene derivatives that are difficult to prepare using other routes. The structures of the naphthalene and tetralin derivatives were assigned by NMR and other techniques.

Keywords: tetralin and naphthalene derivatives, arene oxides, 1,4-dinitrato-2,3-dibromotetralins, 1,4-dihydroxy-2,3-dibromotetralins

Attention has recently focused on arene oxides and particularly epoxy diols related to arene dioxides as possible ultimate mutagens and/or carcinogens.[1] The same stereochemical situation present in triptolide, an epoxide ring and a hydroxyl group two positions removed on the same face of a six-membered ring, may also be invoked to explain the metabolism induced binding of carcinogenic polycyclic aromatic hydrocarbons to cellular macromolecules.[2] The arene oxide was also isolated firstly from a biological system.[3]

In spite of the many published studies of the biological activity of tetrahydrodiol and tetrahydro epoxides there is still little known about their chemical reactivity and the mechanisms of their reactions. In this work, we describe the first isolation and identification of an arene oxide from pentabromotetralin and many other derivatives of tetralin from tetrabromotetralin. It is also our objective to elaborate the conversions developed and to illustrate the potential utility of isomeric naphthalene oxides for synthesis of polysubstituted naphthalene derivatives that are difficult to synthesise using other routes.

As a consequence of our continuing interest in the photobromination of aryl compounds[4] and in particular the conversion of bromonaphthalenes into methoxy, hydroxy and cyano naphthalene derivatives[5] we have investigated the precursors to arene oxides and other naphthalene and tetralin derivatives.

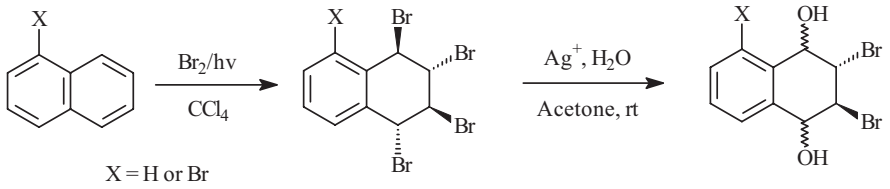
Results and discussion

In our strategy for the synthesis of arene oxides, we sought to utilise a unified approach to single isomers of 1,4-dihydroxynaphthalene derivatives, containing the 2,3,5-tribromo-1,4-dihydroxy and 2,3-dibromo-1,4-dihydroxy-tetrahydronaphthalene moieties. These arise from 1,2,3,4-tetrahydro derivatives, which were previously synthesised by the photobromination of 1-bromonaphthalene and naphthalene, respectively (Scheme 1).[4,6]

The strain energy (SE) of dihydroxytetralins (**1**, **2**, **3** and **4**) indicate that the compound **1** has the most stable structure (3.95 kcal/mol, total strain energy) whereas the compound **4** is of much higher energy as a consequence of the Van der Waals effect among the atoms (*cis*-orientation of C1–OH, C3–Br and C2–Br, C4–OH) which causes a strong steric effect. Strong steric repulsion between hydroxyls and bromine atoms can also be seen nicely in compound **4** by comparison of bond angles between the O1–C1–C2 and C3–C4–O2 with compounds **1**, **2** and **3** in Table 1.

The important feature of the compound **4** is a marked interaction between the hydroxyl group and bromine atoms. The calculated strain energy of 8.00 kcal/mol for compound **4** predicts the existence of this strong interaction. It is, however, not surprising that this isomer was not detected in the reaction products. On the other hand, we were also not able to detect any trace of a mono hydroxyl compound in the reaction mixture after a careful search by NMR spectroscopy.

The correct configuration of pentabromotetralin **5** was previously reported[7] and compound **5** was converted into the 1,4-dihydroxy derivatives **2** and **3**. Conversion of diol **3** into a monoepoxide (**6**) provides verification that **3** incorporates a *trans,trans,cis* orientation of tetralin (Scheme 3). On the basis of the X-ray study of monoepoxide **6**[8] which has an all-*cis* configuration, we assigned the configuration of the dihydroxytetralin derivative (**3**). The *trans*-hydroxyl at the benzylic C-1 position of **3** forming **6** indicated the stereochemistry of the compound **3** (Scheme 3).



X = H 96%

X = Br 56%

Scheme 1

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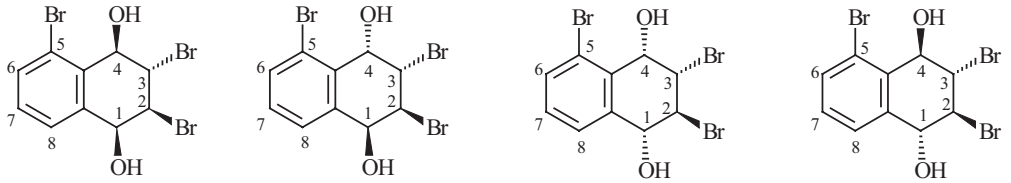
Table 1 Calculations of strain energies (SE, in kcal/mol), bond lengths (C1–C2, C2–C3 and C3–C4, respectively), bond angles (O1(Br)–C1–C2 and C3–C4–(Br)O2, respectively), dihedral angles (H1–C1–C2–H2, H2–C2–C3–H3 and H3–C3–C4–H4, respectively) and coupling constants of 1,2,3,4-tetrahydronaphthalene derivatives by using ChemOffice 6.0 (Chem3D Ultra 6.0, ChemDraw Ultra Version 6.0.1) computer program. All coupling constants (*J*) are given in Hertz (Hz)

Cpds	SE	Bond lengths/Å	Bond angles/°	Dihedral angles/°
1	3.95	1.518, 1.518, 1.520	109.4, 108.4	53.03, 58.65, 79.04
2	5.46	1.520, 1.518, 1.527	109.1, 109.0	54.72, 56.30, 38.70
3	6.70	1.520, 1.516, 1.523	109.1, 107.8	84.33, 58.64, 56.81
4	8.00	1.520, 1.517, 1.520	110.0, 109.3	75.17, 62.11, 75.53
5	20.38	1.520, 1.523, 1.523	111.6, 111.4	78.26, 62.51, 71.26
6	20.77	1.481, 1.521, 1.523	117.3, 108.4	0.77, 10.09, 51.96
8	16.87	1.522, 1.525, 1.522	112.2, 112.3	75.84, 61.87, 76.45
9	3.90	1.520, 1.520, 1.520	110.1, 110.1	75.68, 62.61, 75.76
10	13.52	1.522, 1.522, 1.521	109.5, 112.7	79.87, 61.90, 72.48
11	18.45	1.480, 1.483, 1.480	116.2, 116.3	4.60, 47.79, 4.41
13	9.19	1.522, 1.519, 1.525	109.5, 109.9	70.25, 59.67, 79.91
14	9.32	1.524, 1.521, 1.526	110.4, 109.7	52.78, 57.17, 77.89
17	11.68	1.524, 1.518, 1.528	109.2, 108.9	52.14, 55.24, 46.31



1 **2** **3** **4**

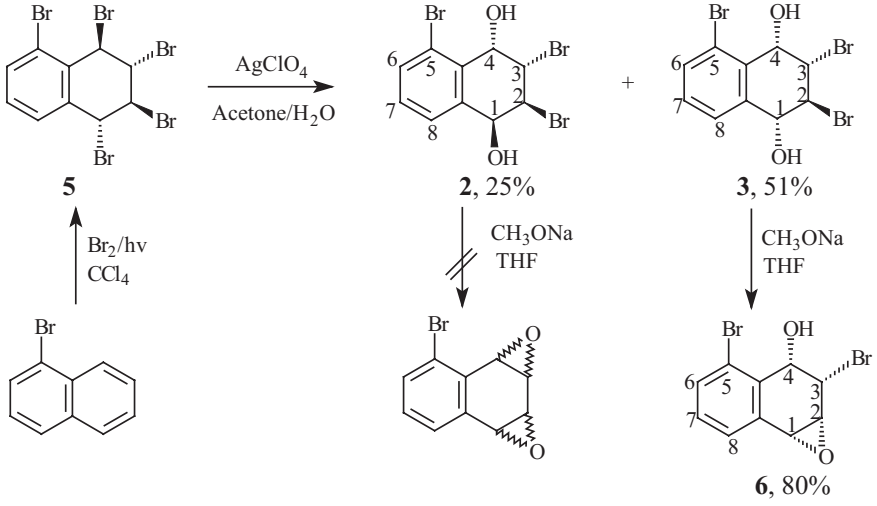
Scheme 2

The ^{1}H NMR spectra of the *trans* diol **2** display *cis* splitting patterns typical of those exhibited by the corresponding dihydroxy derivatives that have *cis* stereochemistry ($J_{2,1}$ = 3.8 Hz). Evidence to support the *cis* relationship between H1 and H2 as well as between H3 and H4 in **2** was obtained by treatment of this diol with sodium methoxide in THF. Compound **2** failed to give any epoxy derivative in contrast to the *cis* diol **3** as shown in Scheme 3. The ^{13}C NMR spectrum of the *trans* diol **2** is also in good agreement with the proposed structure.

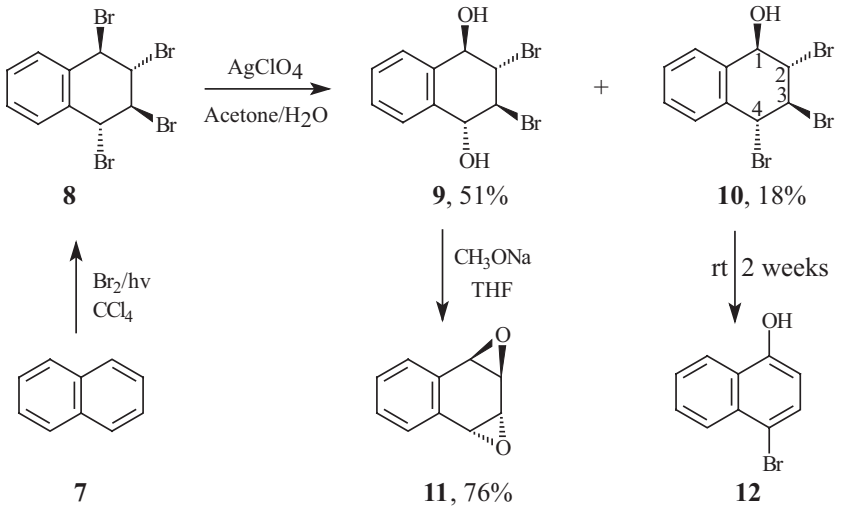
The NMR spectra of the *cis* diol **3** has a *cis* coupling constant ($J_{4,3}$ = 2.6 Hz) for the H3 and H4 protons and a *trans* diaxial coupling constant ($J_{1,2}$ = 8.3 Hz) for the H1 and H2 protons which is in accord with the conformation. Abraham *et al.* [9] have reported complete ^{1}H NMR spectroscopy analysis of all of the possible conduritol derivatives and found similar couplings: *cis* coupling (J = 2.1 Hz, for Conduritol-C[10]) and *trans* coupling (J = 11.0 Hz for Conduritol-F[11]). These comparisons indicate clearly that the isolated asymmetrical dihydroxy **3** has *trans* orientation ($J_{2,3}$ = 12.0 Hz) for H2 and H3.

To our knowledge, **2**, **3** and **6** are novel derivatives of tetralin and these stereoisomers are chemically interesting as precursors for the synthesis of polysubstituted tetralin and naphthalene derivatives which are difficult to access.

Compound **8** was previously synthesised as a sole product by the photobromination of naphthalene (**7**).[6,12] After successful synthesis and isolation of compound **8** using the known procedure[6b] with minor modification, we treated this compound with silver ion in aqueous acetone solution which resulted in the formation of compounds **9** and **10**. Compound **9** has previously been synthesised[13] by treatment of 1,4-naphthaquinone with excess bromine in Et_2O. The newly synthesised all-*trans*-diol dibromide **9** was converted into *anti*-1,2: 3,4-naphthalene dioxide (**11**) and compound **10** into 1-hydroxy-4-bromonaphthalene (**12**) (Scheme 4).



Scheme 3



Scheme 4

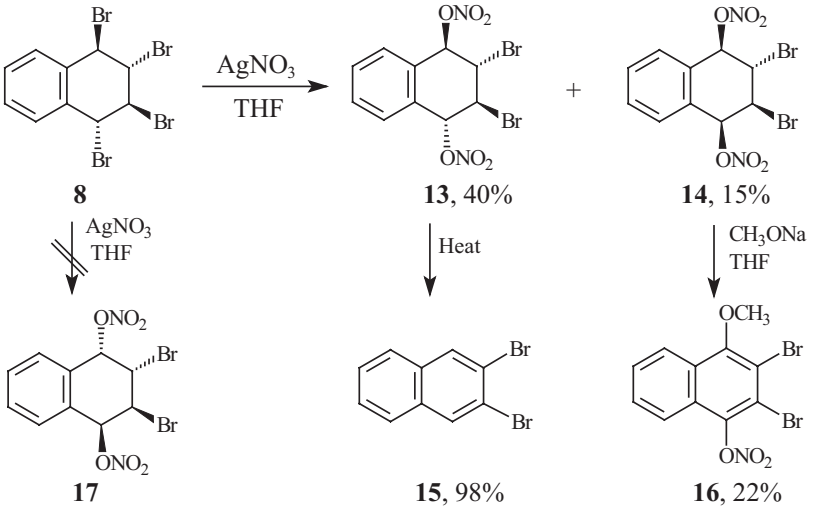
The NMR spectra of tetrabromotetralin **8**, all-*trans* diol **9** and *anti*-naphthalene dioxide **11** exhibit an AA'BB' or AA'XX' splitting pattern which is in full accord with the symmetry of the proposed structures. The five line ^{13}C NMR spectra are also in agreement with the proposed structures. Further evidence to support the *trans*,*trans*,*trans* orientation in **9** was obtained by treatment of this diol with sodium methoxide in THF to give the *anti* dioxide **11**. Evidence for the monohydroxy **10** structure is that it is unstable and readily loses HBr at room temperature to give 4-bromo-1-hydroxynaphthalene **12**.

The presently described synthesis of **11** offers several advantages over previous methods.[14,15] For instance, it begins with a readily available starting material (naphthalene) and is efficient and readily scalable; **8** can be prepared in high yield (95%) which opens up an entry to dihydroxy derivatives (**9** and **10**) and subsequently to the epoxy naphthalenes.

The $J_{2,3}$ coupling constants of 4.1 and 1.5 Hz determined for the compounds **6** and **11**, respectively, which are lower than suggested by the Karplus equation owing to the influence of the electronegative oxygen atoms, are almost identical with those of the corresponding arene dioxides and similar systems.[14] The $J_{2,3}$ coupling constant of 12.0 Hz determined for the compound **3** is higher than suggested by the Karplus equation, but in line with similar systems (Table 1).[6,9]

Compound **8** was converted into *trans*,*trans*,*trans*-1,4-dinitrato-2,3-dibromonaphthalene (**13**) and *trans*,*trans*,*cis*-1,4-dinitrato-2,3-dibromonaphthalene (**14**) by reaction with silver nitrate. The splitting patterns for the methine protons and the five lines, of which three lines belong to the aryl carbons, are fully in agreement with the symmetry of the proposed structure **13**. Unlike the other possible symmetrical structure **17**, it is also apparent from the 1,3-proton splitting pattern ($J_{1,3} = J_{2,4} = 1.8$ Hz) observed in the ^1H NMR spectrum that a *trans* configuration must exist between the protons on C2 and C3; *i.e.* H1 and H3 as well as H2 and H4 bear *cis* stereochemistry (Scheme 6 and Table 1). The ^1H NMR coupling constants ($J_{1,2} = 3.4$ Hz, $J_{3,4} = 3.9$ Hz) obtained for the 1,4-dinitrato-2,3-dibromo compound **14** are consistent with the proposed structure and the literature for compounds of the same stereochemistry.[1d] Furthermore, it is also evident from the ^1H NMR spectra that the structure **14** is the only possible unsymmetrical isomer.

The direct heating of the compound **13** (140°C for 10 min and 220°C for 5 min) resulted in the formation of 2,3-dibromonaphthalene (**15**). 2,3-Dibromonaphthalene is an important intermediate for conversion into further functional groups (*e.g.* 2,3-dimethoxynaphthalene, 2,3-dicyanonaphthalene and 2,3-di(methylthio)naphthalene) and 2,3-naphthalyne is conveniently generated by treating 2,3-dibromonaphthalene



Scheme 5

with phenyllithium.[16] The structural assignment **15** is inferred from NMR coupling constants and chemical shift data which compare favourably with those reported by LeHoullier and co-worker.[16] Compound **14** was treated with sodium methoxide in THF to give an unexpected product, 1-methoxy-4-nitrato-2,3-dibromonaphthalene (**16**) in relatively low yield. The rest of the residue is unseparable polymeric material (Scheme 5). The unexpected aromatised product **16** was confirmed using the NMR spectroscopic data and micro analysis. Zweig and co-workers[17] had established that a characteristic downfield shift from 7.6 to 8.1 is experienced by the aromatic proton in the 8-position *peri* to the 1-methoxy substituent which may be used to differentiate the 1-methoxy substituent from the 4-nitrato substituent.

It is noteworthy that dinitratotetralin (**14**), in contrast to dihydroxytetralin (**9**), undergoes substitution reaction at the C-4 position. This may be attributed to the nitrate as a good leaving group.

The steric interactions of the bromo atoms presumably cause reaction to take place preferentially from the *trans* direction. Therefore, the yield of the product **13** is higher (40%) than the yield of the product **14** (15%).

Conclusions

In this work, we describe the first isolation and identification of diols (**2** and **3**), an arene oxide (**6**), dinitrato (**13** and **14**) and 1-hydroxy-2,3,4-tribromo (**10**) of tetralin derivatives and 4-nitrato-1-methoxy-2,3-dibromonaphthalene (**16**) from the readily available starting materials naphthalene and 1-bromonaphthalene. We also improved the yield of tetrabromonaphthalene (**8**), all-*trans* diol dibromide (**9**) and *trans* dioxide (**11**) by modification of known procedures. The preparation of 2,3-dibromonaphthalene (**15**) provides an excellent example of the potential utility of this compounds as precursors for other 2,3-disubstituted naphthalenes (*i.e.*, 2,3-dimethoxy, 2,3-dicyano, 2,3-di(methylthio), 2,3-diphenoxy-naphthalene derivatives). 4-Bromo-1-hydroxynaphthalene (**12**) was also isolated by the decomposition of compound **10** at room temperature. Compound **12** is useful as a precursor for 1-hydroxy-4-substituted naphthalene derivatives.

Experimental

General

Commercial reagents were purchased from standard chemical suppliers and purified to match the reported physical and spectral data. Classical column chromatography was performed using Merck 60 (70-230 Mesh) silica gel. Thin layer chromatography was carried out on Merck silica gel F_{254} 0.255 mm plates and visualised under UV light. Melting points were determined on a Thomas-Hoover capillary melting point apparatus. IR spectra were recorded on an Jasco FT-IR 430 instrument. NMR spectra were recorded on a Bruker instrument 400 MHz for ^{1}H and 100 MHz for ^{13}C NMR. The elemental analysis carried out with a CHNS-932 (LECO) analyser and mass spectra using a micromass VG Platform-II spectrometer in electron impact (EI) mode.

Trans,trans,trans-1,2,3,4,5-pentabromotetralin (**5**): This isomer was prepared by the procedure which has been recently published[4] except minor modification as follows. The pentabromotetralin (**5**) was prepared by the photobromination of 1-bromonaphthalene using an internal type photochemical reaction apparatus (250 W, projector lamp) in CCl_4 (35 ml) at –50°C (acetone/cardice). After reaction, ^{1}H NMR studies indicated that reaction mixture consisted of two pentabromides and a minor 1,5-dibromonaphthalene. The isomer **5** was separated by recystallisation from methylene chloride-petroleum ether (1:1, 30 ml) in a refrigerator (–5°C) in 12 h to obtain colourless crystals of compound **5** (56%) (m.p. 96°C). Then the rest of the mixture was chromatographed on silica gel and eluted with hexane-benzene (95:5) solvent system to obtain pure isomers as reported in our recent paper.[4]

Cis,trans,cis-2,3,5-tribromo-1,4-dihydroxytetralin (**2**) *and trans, trans,cis-2,3,5-tribromo-1,4-dihydroxytetralin* (**3**): A solution of $AgClO_4$ (1.70 g, 8.20 mmol) in aqueous acetone (7 ml acetone/3 ml H_2O) was added to a stirred solution of pentabromotetralin (**5**) (1.1 g, 2.09 mmol) in acetone (10 ml) over 10 min and protected from the light. The resulting mixture was stirred at room temperature for 2 days. The precipitated AgBr was removed by filtration. To the organic phase was added chloroform (30 ml) and the organic phase was washed with water (2 × 15 ml) and dried over $MgSO_4$. After removal of the solvent, the residue was chromatographed on silica gel (200 g) eluted with ethyl acetate-hexane (10:90) to give stereoisomers **2** and **3**. The first eluted dihydroxy compound **2** was obtained in a yield of 300 mg (25%) and the last eluted dihydoxy compound **3** was obtained in a yield of 600 mg (51%).

CAUTION: Appropriate precautions were taken with solutions and residues which may contain perchlorate to guard against explosion.

2: Colourless solid; m.p. 168–169°C; [Found: C, 30.2; H, 2.05. $C_{10}H_9O_2Br_3$ requires C, 29.96; H, 2.24%]; ν_{max}(KBr) 3866, 3779, 3455, 3050, 1944, 1797, 1500, 1322, 1191, 956, 900, 779, 613, 528, 451; δ_H (400 MHz, $CDCl_3$ and d_6-DMSO) 7.65 (1H, d, J = 7.8 Hz, H8), 7.51 (1H, d, J = 7.8 Hz, H6), 7.21 (1H, t, J = 7.8 Hz, H7), 5.48 (1H, t, $J_{4,OH}$ = 4.5 Hz, H4), 5.15 (1H, dd, $J_{1,2}$ = 3.8 Hz, $J_{1,OH}$ = 5.3 Hz, H1), 4.70 (1H, dd, $J_{2,1}$ = 3.8 Hz, $J_{2,3}$ = 7.1 Hz, H2), 4.25 (1H, dd, $J_{3,2}$ = 7.1 Hz, H3), 4.00 (1H, d, $J_{OH,4}$ = 4.5 Hz, C4–OH), 3.78 (1H, d, $J_{OH,1}$ = 5.3 Hz, C1–OH); δ_C (100 MHz, $CDCl_3$ and d_6-DMSO) 139.40, 132.9, 132.6, 131.3, 124.5, 123.9, 71.0, 60.4, 53.2, 47.7.

3: Colourless solid; m.p. 185–186°C; [Found: C, 30.0; H, 2.1. $C_{10}H_9O_2Br_3$ requires C, 29.96; H, 2.24%]; ν_{max}(KBr) 3889, 3257, 2939, 2879, 1961, 1897, 1710, 1589, 1564, 1452, 1340, 1251, 1228, 1132, 1047, 889, 754, 603; δ_H (400 MHz, $CDCl_3$ and d_6-DMSO) 7.60 (1H, d, J = 7.8 Hz, H8), 7.55 (1H, d, J = 7.8 Hz, H6), 7.23 (1H, t, J = 7.8 Hz, H7), 5.55–5.25 (2H, br, 2 X OH), 5.24 (1H, d, $J_{4,3}$ = 2.6 Hz, H4), 4.90 (1H, d, $J_{1,2}$ = 8.3 Hz, H1), 4.72 (1H, dd, $J_{2,3}$ = 12.0 Hz, $J_{2,1}$ = 8.3 Hz, H2), 4.48 (1H, dd, $J_{3,2}$ = 12.0 Hz, $J_{3,4}$ = 2.6 Hz, H3); δ_C (100 MHz, $CDCl_3$ and d_6-DMSO) 141.2, 135.5, 133.1, 130.9, 128.2, 124.9, 75.7, 71.9, 59.5, 58.9.

Cis,cis,cis-1,2-epoxy-3,5-dibromo-4-hydroxytetralin (**6**): 1,4-Dihydroxy-2,3,5-tribromotetralin (0.529 g, 1.32 mmol) was dissolved in dry THF (10 ml). To the solution was added sodium methoxide (0.157 g, 3 mmol). The reaction mixture was stirred magnetically for 92 h under nitrogen gas atmosphere at 0°C (ice bath). The reaction progress was monitored by TLC. After completion of the reaction, the solvent was removed at reduced pressure and the residue was filtered onto a short silica gel column (10 g) and eluted with ethyl acetate-hexane (1:9) to give the title compound. The compound **6** was recrystallised from chloroform:hexane to give colourless crystals (0.34 g, 80%) (m.p. 135–136°C); [Found: C, 37.6; H, 2.3. $C_{10}H_8O_2Br_2$ requires C, 37.50; H, 2.50%]; ν_{max}(KBr) 3504, 3095, 3020 2995, 1620, 1600, 1490, 1450, 1428, 1400, 1390, 1350, 1100, 900; δ_H (400 MHz, $CDCl_3$) 7.70, (1H, dd, $J_{8,6}$ = 1.0 Hz, $J_{8,7}$ = 8.0 Hz, H8), 7.50 (1H, dd, $J_{6,8}$ = 1.0 Hz, $J_{6,7}$ = 8.0 Hz, H6), 7.25 (1H, t, J = 8.0 Hz, H7), 5.14 (1H, ddd, $J_{4,OH}$ = 12.0 Hz, $J_{4,3}$ = 2.1 Hz, $J_{4,2}$ = 1.8 Hz, H4), 4.43 (1H, d, $J_{1,2}$ = 4.0 Hz, H1), 4.16 (1H, d, $J_{2,1}$ = 4.0 Hz, H2), 4.14 (1H, dd, $J_{3,2}$ = 4.1 Hz, $J_{3,4}$ = 2.1 Hz, H3), 2.90 (1H, d, $J_{OH,4}$ = 12.0 Hz, OH); δ_C (100 MHz, $CDCl_3$) 136.5, 134.7, 133.3, 130.6, 129.9, 126.1, 70.6, 60.5, 57.6, 49.2; *m/z* (CI, NH_3) 338 (100), 320/322 (10), 206 (50), 144 (45%); *m/z* (EI, M^+) 320 (100), 303 (90), 275 (80), 239 (20), 193 (50), 132 (95%).

Trans,trans,trans-1,2,3,4-tetrabromotetralin (**8**): A solution of naphthalene (8.0 g, 62.5 mmol) in CCl_4 (80 ml) in an internal type photochemical reaction apparatus was cooled to 0°C (ice-bath). A device for absorbing the evolved HBr was attached to the side arm. The magnetically stirred solution was irradiated with a sun lamp (150 W projector lamp, cooled by circulating water) and a solution of Br_2 (30 g, 9.61 mmol) in CCl_4 (40 ml) was added dropwise. The reaction mixture was irradiated for 20 min. Reaction progress was monitored by TLC. After completion of the reaction, the solvent and excess bromine were removed. The reaction product was recrystallised from dichloromethane-hexane in a refrigerator. The title compound was obtained as colourless crystals (27 g, 96%); m.p. 104–105°C (decomp) (Lit.[6] 103–105°C). NMR measurements agreed with those reported in the literature.[6]

Trans,trans,trans-2,3-dibromo-1,4-dihydroxytetralin (**9**) *and 2,3, 4-tribromo-1-hydroxytetralin* (**10**): A solution of $AgClO_4$ (2.9 g, 14.1 mmol) in aqueous acetone (7 ml acetone/3 ml H_2O) was added to a stirred solution of tetrabromotetralin (**8**) (3.0 g, 6.7 mmol) in acetone (15 ml) over 15 min and protected from the light. The resulting mixture was stirred at room temperature for a day. The precipitated AgBr was removed by filtration. To the organic phase was added chloroform (50 ml) and the organic phase was

washed with water (2 × 30 ml) and dried over $CaCl_2$. After removal of the solvent, the residue was chromatographed on silica gel (200 g) eluted with ethyl acetate-hexane (1 : 4) to give 2 different isomers. The former eluted isomer (**9**) was obtained (1.1 g, 51%), and then the latter eluted isomer (**10**) was obtained (400 mg, 18%).

9: Colourless solid; m.p. 186–187°C (acetone–hexane) (lit.[13] 185–187°C); R_f = 0.58; ν_{max}(KBr) 3342, 3070, 2971, 2871, 2703, 2487, 1974, 1943, 1845, 1654, 1637, 1581; δ_H (400 MHz, d_6-acetone) 7.57 (2H, A part of AA'BB' system, H5 and H8), 7.34 (2H, B part of AA'BB' system, H6 and H7), 5.30 (1H, br, OH), 5.04 (2H, A part of AA'BB' system, H1 and H4), 4.46 (2H, B part of AA'BB' system, $J_{1,2}$ = 2.3 Hz, $J_{2,3}$ = 5.6 Hz, H2 and H3); δ_C (100 MHz, d_6-acetone) 137.5, 128.8, 127.5, 74.8, 61.9.

10: Colourless solid; m.p. 164–165°C (acetone–hexane); R_f = 0.40; [Found: C, 31.2; H, 2.3, $C_{10}H_9Br_3O$ requires C,31.21; H, 2.36%]; ν_{max}(KBr) 3272, 3025, 2969, 2938, 2913, 2692, 2441, 1508, 1486, 1454, 1346, 1317, 1245, 1089, 1070, 954, 921, 894, 862, 811, 719,694, 590,530; δ_H (400 MHz, d_6-acetone) 7.54 (1H, m, H8), 7.55 (1H, m, H5), 7.30 (2H, m, H6 and H7), 5.60 (1H, d, $J_{4,3}$ = 4.2 Hz, H4), 5.03 (1H, dd, $J_{1,2}$ = 3.4 Hz, H1), 4.91 (1H, dd, $J_{2,1}$ = 3.4 Hz, $J_{2,3}$ = 11.2 Hz, H2), 4.50 (1H, dd, $J_{3,4}$ = 4.2 Hz, $J_{3,2}$ = 11.2 Hz, H3); δ_C (100 MHz, d_6-acetone) 136.4, 132.7, 128.7, 128.5, 127.7, 127.1, 75.1, 55.2, 49.2, 48.1.

Anti-1,2:3,4-naphthalenedioxide (**11**): 1,4-Dihydroxy-2,3-dibromotetralin (0.174 g, 0.54 mmol) was dissolved in dry THF (15 ml). To the solution was added sodium methoxide (0.073 g, 1.3 mmol). The reaction mixture was stirred magnetically for 2 h under nitrogen gas atmosphere at 0°C (ice-bath). The reaction progress was monitored by TLC. After completion of the reaction, the solvent was removed at reduced pressure and the residue was washed with diethylether (2 × 35 ml) and water (2 × 40 ml). The organic phase was dried (Na_2SO_4) and evaporated. The compound **11** was recrystallised from diethyl ether–hexane (1 : 9, 5 ml) to give colourless crystals (0.65 g, 76%), m.p. 102–103°C, (Lit.,[14,15] 99–100°C, from ether–pentane); ν_{max}(KBr) 2998, 2923, 2852, 1725, 1606, 1492, 1475, 1419, 1346, 1299, 1265, 1247, 1214, 1184, 1139, 1120, 1105, 1047, 971; δ_H (400 MHz, $CDCl_3$) 7.37–7.25 (4H, AA'BB', ArH), 3.91 (2H, dd, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 1.5 Hz, H2 and H3), 3.63 (2H, dd, H1 and H4); δ_C (100 MHz, $CDCl_3$) 132.0, 131.9, 129.8, 55.1, 52.3; *m/z* (EI, M^+) 160 (10), 131 (100), 103 (60), 77 (85), 63 (40), 51 (70%).

4-Bromo-1-hydroxynaphthalene (**12**): The compound **10** was decomposed at the room temperature to give 4-bromo-1-naphthol **12** in a good yield The complete conversion was monitored by TLC at room temperature and took place over about two weeks. The compound was recrystallised methylene chloride–hexane (yield: *ca* 90%), m.p. 130–131°C; [Found: C, 53.95; H, 3.1. $C_{10}H_7BrO$ requires C, 53.84; H, 3.16%]; ν_{max}(KBr) 3282, 1593, 1487, 1346, 1259, 1184, 1120, 1070, 1045, 921, 767, 717, 590, 505; δ_H (400 MHz, $CDCl_3$) 8.30 (1H, dd, $J_{5,6}$ = 8.6 Hz, $J_{5,7}$ = 0.6 Hz, H5), 8.10 (1H, d, $J_{8,7}$ = 8.5, Hz, H8), 7.89 (1H, br s, OH), 7.63 (1H, d, $J_{3,2}$ = 8.1 Hz, H3), 7.56 (2H, ddd, $J_{6,5}$ = 8.6 Hz, $J_{6,7}$ = $J_{7,8}$ = 8.5 Hz, H6 and H7), 6.90 (1H, d, $J_{2,3}$ = 8.1 Hz, H2); δ_C (100 MHz, $CDCl_3$) 153.6, 133.0, 130.4, 128.1, 126.8, 126.7, 125.9, 123.2, 111.3, 109.2.

Trans,trans,trans-2,3-dibromo-1,4-dinitratotetralin (**13**) *and cis, trans,trans-2,3-dibromo-1,4-dinitratotetralin* (**14**): Tetrabromotetralin (2.5 g, 558 mmol) was dissolved in THF (30 ml). To the solution silver nitrate (2.1 g, 12.3 mmol) was added. The reaction mixture was stirred magnetically at room temperature and protected from light. The reaction progress was monitored by TLC and completed after 3 days. The mixture was filtered and evaporated (1.35 g). The nitroxytetralin mixture was separated in a silica gel column chromatography (200 g) with hexane–ethyl acetate (90 : 10, 2 L) to give two isomers. The former eluted isomer indicated the compound **13** (0.92 g, 40%). The latter eluted isomer indicated the compound **14** (0.34 g, 15%).

13: Colourless needles; R_f = 0.80; m.p. 106–107°C (chloroform–hexane); [Found: C, 29.2; H, 2.05; N, 6.6. $C_{10}H_8Br_2N_2O_6$ requires C, 29.15; H, 1.96; N, 6.80%]; ν_{max}(KBr) 2969, 1639, 1487, 1349, 1315, 1276, 1184, 1117, 1065, 979, 835, 764, 739, 714, 606; δ_H (400 MHz, $CDCl_3$), 7.45 (2H, m, H5, H8), 7.36, (2H, m, H6, H7), 6.31 (2H, dd, $J_{1,2}$ = 3.3 Hz, $J_{1,3}$ = 1.8 Hz, H1, H4), 7.40 (2H, dd, $J_{2,1}$ = 3.3 Hz, $J_{2,4}$ = 1.8 Hz, H2, H3); δ_C (100 MHz, $CDCl_3$) 131.2, 129.5, 129.3, 81.2, 46.0; *m/z* (EI, M^+) 412 (100), 350 (20), 286 (60), 268 (95), 253 (80%).

14: Colourless needles; R_f = 0.70; m.p. 130–132°C (chloroform–hexane); [Found: C, 29.3; H, 1.85; N, 7.05. $C_{10}H_8Br_2N_2O_6$ requires C, 29.15; H, 1.96; N, 6.80%]; ν_{max}(KBr) 1660, 1497, 1275, 1093, 984, 839, 669, 447; δ_H (400 MHz, $CDCl_3$) 7.50–7.40 (4H, AA'BB' system, ArH), 6.48 (1H, d, $J_{1,2}$ = 3.4 Hz, H1), 6.36 (1H, d, $J_{4,3}$ = 3.9 Hz, H4), 4.84 (1H, dd, $J_{3,4}$ = 3.9 Hz, $J_{3,2}$ = 7.3 Hz, H3), 4.78 (1H, dd, $J_{2,1}$ = 3.4 Hz, $J_{2,3}$ = 7.3 Hz, H2); δ_C (100 MHz, $CDCl_3$) 131.2, 131.1, 130.1, 130.1, 128.7, 128.4, 81.7, 77.9, 47.4, 47.3; m/z (412 (M^+) 412 (100), 350 (20), 286 (60), 270 (20), 253 (95%).

2,3-Dibromonaphthalene (**15**): The compound **13** (576 mg, 2.0 mmol) in an open glass-tube was heated in an oil bath to 140°C for 10 min and to 220°C for 5 min. The dark-coloured material was filtered through a short silica gel column (20 g) with hexane. After evaporation of the solvent, the ^1H NMR analysis indicated that the dinitroxy derivative had been converted completely into 2,3-dibromonaphthalene (392 mg, 98%); m.p. 138–140°C (Lit.[16] 139–140°C); ν_{max}(KBr) 2923, 1648, 1581, 1558, 1536, 1494, 1425, 1342, 1305, 1274, 1195, 1132, 958, 946, 887, 858, 754, 680, 590; δ_H (400 MHz, $CDCl_3$) 8.06 (2H, s, H1, H4), 7.65 (2H, A part of AA'BB' system, H5 and H8), 7.41 (2H, B part of AA'BB' system, H6 and H7); δ_C (100 MHz, $CDCl_3$) 133.5, 132.6, 127.6, 127.3, 122.4.

2,3-Dibromo-4-nitrato-1-methoxynaphthalene (**16**): Dinitratotetralin **14** (2.50 g, 6.07 mmol) was dissolved in THF (15 ml). To the solution, sodium methoxide (0.98 g, 18.2 mmol) was added and the mixture was stirred magnetically at room temperature. The reaction was monitored by TLC and completed after 6 h. The residue was washed with water (2 × 30 ml) and dichloromethane (2 × 25 ml). The organic phase was separated, dried ($CaCl_2$) and evaporated. The crude product was chromatographed on a silica gel column (135 g silica gel) (hexane–ethyl acetate, 9 : 1, 1.5 L) to give the title compound **16** (0.5 g, 22%); m.p.: 154–155°C (hexane–chloroform); R_f = 0.41 (hexane–ethyl acetate, 9 : 1); [Found: C, 35.0; H, 1.7; N, 3.55. $C_{11}H_7Br_2NO_4$ requires C, 35.05; H, 1.87; N, 3.72%]; ν_{max}(KBr) 1631, 1450, 1363, 1274, 1230, 1062, 1027, 964, 846, 825, 771, 721, 551; δ_H (400 MHz, $CDCl_3$) 8.11 (1H, dd, $J_{8,7}$ = 6.8 Hz, $J_{8,6}$ = 2.1 Hz, H8), 8.04 (1H, d, $J_{5,6}$ = 6.6 Hz, H5), 7.70 (2H, ddd, $J_{6,7}$ = $J_{7,6}$ = 7.1 Hz, $J_{7,5}$ = 2.2 Hz, $J_{6,8}$ = 2.1 Hz, H6 and H7), 4.29 (3H, s, OMe); δ_C (100 MHz, $CDCl_3$) 179.6, 179.0, 159.4, 134.7, 134.3, 131.3, 131.3, 127.6, 127.3, 122.6, 62.3.

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