Synthesis of hexabromo, hydroxy, epoxy, methoxy and nitroxy derivatives of tetralins and naphthalenes

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Stereoselective synthesises are described for naphthalene and tetralin derivatives. Hexabromo **2** and **3**, monomethoxy **7**, dimethoxy **6**, dihydroxy **4** and dinitroxy **10** derivatives of tetralin have been obtained. Base-promoted elimination reactions of **6** and **4** provided monomethoxy **8** and **9** and diepoxy **5** naphthalenes respectively. The structures of these products were determined by ^{1}H and ^{13}C NMR spectra, mass spectra and micro analysis.

Keywords: tetralin and naphthalene derivatives/arene oxide

Naphthalenes play an important role as structural units or key intermediates in naturally occurring alkaloids and have attracted the interest of synthetic and natural product chemists for their biological activity.[1]

Bromonaphthalenes have become increasingly important as triplet excitation acceptors with useful phosphorescent properties.[2] They are also useful precursors for other substituted naphthalene derivatives such as phenols,[3] amines,[4] ethers[5] and organometallics.[6]

Epoxides are essential intermediates and building blocks in organic synthesis. Many methods have been developed for the direct epoxidation of double bonds, mainly using peracids, hydrogen peroxide, and dialkyldioxiranes. Many epoxidations have been described[7] but none involve hexabromonaphthalene. We now report for the first time epoxidation of the compound.

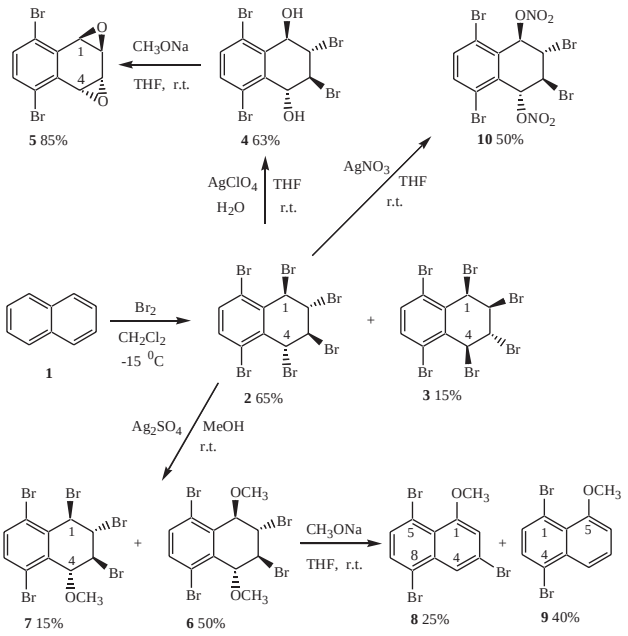
Since the initial demonstration that an arene oxide is a key intermediate in the metabolism of naphthalene by mammals,[8] substantial interest has developed in the chemistry, biochemistry, and pharmacology of arene oxides.[9] Subsequent reports have implicated arene oxides in the metabolism of several other polycyclic aromatic hydrocarbons. Arene oxides are capable of transforming cells in culture and are potent frame shift mutagens in bacterial test systems.[10] In addition, substantial evidence has accumulated which implicates metabolically formed arene oxides as the causative agents which account for the toxicity of several aromatic hydrocarbons.[10]

In this work we describe the isolation and identification of dibromoepoxide and synthetically important derivatives of tetralin and napthalene from hexabromotetralin by silver mediated reactions. It is our objective to elaborate the conversions developed and to illustrate the potential utility of the hexabromide isomer **2** for the synthesis of hexasubstituted tetralin derivatives that are otherwise difficult to access.

Results and discussion

First, we synthesised the starting compound **2** by bromination of naphthalene. A 1:15 molar ratio of substrate (naphthalene)–solvent (CH_2Cl_2) was used to give the hexabromides **2** and **3** in a yield of 65 and 15% respectively (Scheme 1). These compounds **2** and **3** were isolated by fractional crystallisation and column chromatography. Their structures were elucidated based on spectroscopic analysis and by comparison with the same compounds reported by Balci and coworkers.[11]

Due to the weakness of the carbon–bromine bond and the reactivity of the benzylic positions, we wished to investigate the substitution of benzylic bromides with hydroxy, nitroxy and methoxyl groups and we also intended to use base-mediated elimination of the obtained compounds to yield corresponding synthetically valuable products.



Scheme 1

Hydroxy derivatives of naphthalenes have importance not only for natural products[12] but also for their pharmacological properties[13] and they are useful precursors of other naphthalene derivatives as well. Treatment of hexabromide **2** with silver ion in aqueous THF solution formed diol **4** (Scheme 1) which was isolated by column chromatography and purified by crystallisation. ^{1}H and ^{13}C NMR spectroscopic studies of **4** indicate its high symmetry. For the symmetrical diol, two possible structures can be considered which are *trans,trans,trans*- **4** and the *cis,trans,cis*-configuration. To form the epoxide, bromine and hydroxyl have to be *trans* to one another. Therefore the epoxide **5** obtained from **4** indicated that **4** has the *trans,trans,trans*-configuration. The ^{1}H NMR spectrum of this compound shows two sets of signals. The aromatic protons appear as a singlet and the aliphatic protons give rise to an AA'BB' system and the signal belongs to the O–H groups which resonate at 5.02 as a broad singlet. The five lines in the ^{13}C NMR spectra are also in agreement with the proposed structure.

Treating diol **4** with sodium methoxide under nitrogen afforded the *anti*-diepoxy derivative **5** in high yield (85%). Because of the *trans* alignment of the hydroxyls and bromines and the *trans* alignment of the two hydroxyls in compound **4**, *anti*-diepoxide **5** formed (Scheme 1). The ^{1}H NMR spectrum of *anti*-diepoxide **5** exhibits an AA'BB' splitting pattern of the aliphatic protons. 1,4-H's appear at lower magnetic field than the 2,3-H's. This has to do with the electronegativity of the sp^2 carbon atom as compared with the sp^3 carbon atom and the

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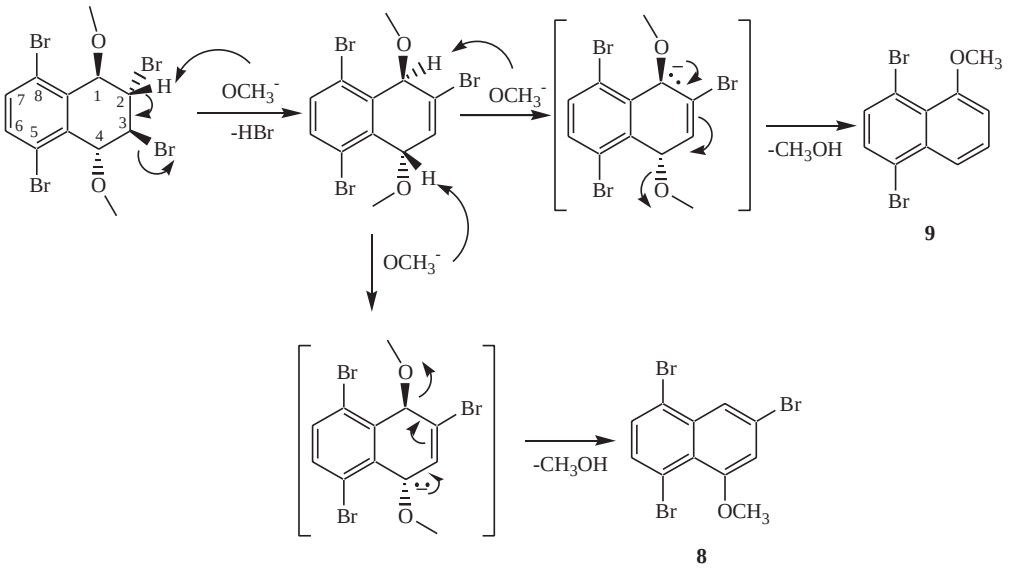

Scheme 2

ring current effect of the neighbouring benzene ring which is stronger for protons 1,4-H than for protons 2,3-H. Therefore, 1,4-H's resonate 0.14 ppm more down field than 2,3-H's. The five lines in the ^{13}C NMR spectrum also accord with the proposed structure of the *anti*-diepoxide **5**.

Methoxynaphthalenes have great synthetic importance for natural products,[14] for electron donors,[15] the ring-enlargement with halocarbenes to benzotropone derivatives,[16] and precursors for other substituted naphthalene derivatives such as naphthoquinones.[17]

Treatment of hexabromide **2** with Ag_2SO_4 in dried MeOH at room temperature under a nitrogen atmosphere afforded the corresponding dimethyl ether compound **6** with monomethyl ether compound **7** in 50% and 15% yield, respectively (Scheme 1). The ^1H NMR spectrum of **6** confirms the proposed structure. Aromatic protons appear as a singlet, aliphatic protons give rise to an AA'BB' system and methoxyl protons were observed as a singlet. Six line ^{13}C NMR spectra are also in agreement with the proposed structures. It is also obvious that due to the configuration retention of bromines bounded to C2- and C3-atoms there are two possible symmetrical isomeric structures, *trans,trans,trans* **6** and *cis,trans,cis.* Reaction proceeds by an S_N1 mechanism and due to the bulky bromines, the methoxyl groups attack *trans* to form the corresponding product **6**. ^1H and ^{13}C NMR studies indicate that the other compound obtained as a side product has only one methoxyl group whose position was determined by comparison with the coupling constant of **6** (for **6** J_{34} = 2.4 Hz; for **7** J_{34} = 2.7Hz).

Base-induced elimination of dimethyl ether **6** formed 1-methoxy-3,5,8-tribromide **8** and 1-methoxy-5,8-dibromide **9** (Scheme 1) which were easily separated by column chromatography. Since the bromine and methylether are bulky groups and repel each other, it is noteworthy that MeOH elimination occurred as well as HBr elimination (Scheme 2). The ^1H-NMR spectrum of **8** consists of three characteristic signals. H2 and H4 with a doublet (J_{24} = 1.8 Hz, *meta* coupling) consistent with the position of Br bound to C3. Moreover, the hydrogen corresponding to a doublet at 7.02 could be located at C2, which appears shielded due to the electron releasing effects of the OMe group at the *ortho* position. Signals of H4 were observed downfield (8.05, d) due to the van der Waals interaction of (C_8–Br)–H4 and (C_3–Br)–H4. In the ^{13}C NMR spectrum, the observation of 10 aromatic resonances (six quaternary and four methine carbons) and one sp^3 carbon (methoxyl group) is fully in agreement with the structure 1-methoxyl-3,5,8-tribromide **8.**

The ^1H NMR spectrum of the other product **9** has three neighbouring aromatic protons which show the typical AMX-spin system with two *3J* coupling constants (*ortho-coupling*) and one *4J* coupling constant (*meta-coupling*). H7 appears at 7.50 as a triplet due to the electron-releasing effects of the OMe group at the *ortho* position, H6 appears shielded at 6.97 (J_{67} = 7.7 Hz, J_{68} = 0.85 Hz). Methoxyl protons appeared at 3.96 as a singlet. In the ^{13}C NMR spectrum, the presence of 10 aromatic resonances (from five quaternary and five methine carbons) and one sp^3 carbon resonance (methoxyl group) accord with the proposed structure **9.**

Compound **2** was converted into the 1,4-dinitroxy **10** by the reaction with silver nitrate (Scheme 1). 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. Micro analysis and the mass spectrum also confirm the proposed structure.

Experimental

General remarks: Commercial reagents were purchased from standard chemical suppliers and purified to match the reported physical and spectroscopic data. Solutions were concentrated at reduced pressure. Column chromatography was performed on Fluka silica gel 60 (0.04–0.063 mm) and on Merck aluminium oxide 90 active neutral (0.063–0.200 mm). Thin layer chromatography (TLC) 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. NMR spectra were recorded on a Bruker DPX-400 instrument, 400 MHz for ^1H and 100 MHz for ^{13}C NMR. All chemical shifts (δ) are deduced from $CDCl_3$ or CD_3COCD_3 solvent signals, δ in ppm. *J* is in Hz. The following abbreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet; brs, broad singlet; dd, doublet of doublets. Elemental analysis was carried out with a CHNS-932 (LECO) analyser and mass spectra using a micromass VG Platform-II spectrometer in electron impact (EI) and chemical ionisation (CI) modes. Chem Draw Ultra 6.0 program was used for drawing molecules.

*Bromination of naphthalene***:** Bromine (18.7 g, 6.0 ml, 117 mmol) in CH_2Cl_2 (8 ml) was added dropwise over 10 min to a solution of naphthalene **1** (3.0 g, 23.4 mmol) in CH_2Cl_2 (15 ml) at 0 °C.

CAUTION: Due to the carcinogenity and toxicity of bromides and the HBr which is produced from the reaction, all bromination reactions should be performed in an efficient fume hood and chemicals handled with appropriate precautions! The HBr outlet from the reaction vessel should be connected to a HBr gas trap (bubbler containing 1.0 M NaOH solution.

The reaction mixture was left in the freezer (–15 °C) for 7 days. After completion of the reaction, unreacted bromine and solvent were removed at reduced pressure at 20 °C. The crude product was fractionally crystallised from THF/hexane to give the hexabromide **2** (7.0 g). This was separated by filtration and the residue was recrystallised from THF-hexane to give the asymmetric product **3** (1.0 g). The remainder was subjected to silica gel (190 g) column chromatography. Eluting with hexane gave **2** (2.2 g) and **3** (1.1 g) in the total yield of 65% and 15% respectively.

(1R, 2S*, 3S*, 4R*, 5, 8)-hexabromo-1, 2, 3, 4-tetrahydronaphthalene* (**2**): Yield: 9.2 g (65%); colourless needle crystals from THF/hexane; m.p. 129–130 °C (lit. m.p.125–128 °C[11] from THF/methylene chloride). R_f = 0.80 (hexane/EtOAc: 9/1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.51 (s, 2H, ArH), 6.01 (A part of AA'BB' system, 2H, H1, H4), 5.40 (B part of AA'BB' system, 2H, H2, H3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 137.3, 137.1, 127.1, 56.4, 52.5. $C_{10}H_6Br_6$ (605.58): calcd. C 19.83, H 1.00; found C 19.81. H 1.02

(1R,2R*, 3R*, 4S*, 5, 8)-hexabromo-1, 2, 3, 4-tetrahydronaphthalene* (**3**): Yield: 2.1 g (15%); colourless crystals from THF/ether; m.p. 168–170 °C (decomp.) (lit. m.p.165–172 °C[11], decomp., methylene chloride/hexane); R_f = 0.63 (hexane/EtOAc: 9/1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.42–7.37 (m, 2H, H6, H7), 5.73 (d, J_{43} = 4.2 Hz, 1H, H4), 5.54 (d, J_{12} = 2.9 Hz, 1H, H1), 5.14 (dd, J_{23} = 11.3 Hz, J_{21}= 2.9 Hz, 1H, H2), 4.17 (dd, J_{34} = 4.2 Hz, J_{32} = 11.3 Hz, 1H, H3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 138.5, 137.3, 136.7, 136.2, 126.5, 124.1, 58.7, 55.7, 54.1, 52.8. $C_{10}H_6Br_6$ (605.58): calcd. C 19.83, H 1.00; found C 19.80. H 1.03

Treatment of hexabromide **2** *with Ag_2SO_4, synthesising methoxy derivatives*: To a solution of hexabromide **2** (2.21 g, 3.65 mmol) in dry methanol (40 ml) was added Ag_2SO_4 (2.39 g, 7.66 mmol) under a nitrogen atmosphere. The resulting reaction mixture was stirred magnetically at room temperature for 3 days. Reaction progress was monitored by TLC for consumption of the starting material. The residual solid was removed by filtration. After removal of the solvent the crude product was submitted to column chromatography (silica gel, 100 g). Elution with hexane– EtOAc (9/1, 2.0 l) gave two products.

(1R, 4R*)-dimethoxy-(2S*, 3S*, 5, 8)-tetrabromo-1, 2, 3, 4-tetrahydronaphthalene* (**6**): Yield: 0.85 g (46%); Colourless needles; m.p. 138–139 °C (from dichloromethane-hexane); R_f = 0.64 (hexane/EtOAc :9/1). IR : ν (KBr) = 2927, 1741, 1458, 1436, 1357, 1338, 1255, 1186, 1135, 1076, 1024, 952, 937. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.37 (s, 2H, H6, H7), 4.92 (A part of AA'BB' system, 2H, H1, H4), 4.90 (B part of AA'BB' system, 2H, H2, H3), 3.78 (s, 6H, OMe). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 54.7 (OMe), 64.2 (C2, C3), 81.2 (C1, C4), 124.7 (C5, C8), 135.0 (C7, C6), 137.7 (C9, C10). $C_{12}H_{12}Br_4O_2$ (507.84): calcd. C 28.38, H 2.38; found C 28.30, H 2.32.

(1R, 2S*, 3S*)-5, 8-pentabromo-(4R*)-methoxy-1, 2, 3, 4-tetrahydronaphthalene* (**7**): Yield: 0.30 g (15%); yellow solid; m.p. 176–177 °C (from dichloromethane-hexane); R_f = 0.025 (hexane/EtOAc :9/1). IR: ν (KBr) = 3444, 3068, 2985, 2917, 2819, 1732, 1570, 1435, 1385, 1352, 1334, 1280, 1224, 1196, 1169, 1126, 1080, 1016, 998, 960, 918, 904, 811, 771, 746, 671, 655, 630, 532, 501, 418. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.48 (s, 2H, H6, H7), 5.34 (brs, 1H, H1), 5.08 (dd, J_{43} = 2.7 Hz, J_{42} = 1.3 Hz, 1H, H4), 4.96 (dd, J_{21} = 1.3 Hz, J_{23} = 1.4 Hz, 1H, H2), 4.87 (dd, J_{34} = 2.7 Hz, J_{32} = 1.4 Hz, 1H, H3), 3.56 (s, 3H, OMe). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 135.6, 135.4, 135.4, 133.4, 127.0, 126.2, 80.7, 72.6, 58.2, 45.1, 43.0. $C_{11}H_9Br_5O$ (556.71): calcd. C 23.73, H 1.63; found C 23.70, H 1.61.

Hydrolysis of hexabromide **(2)** *with $AgClO_4$*: To a stirred solution of hexabromide **2** (3.0 g, 4.95 mmol) in THF (40 ml) was added a solution of $AgClO_4 \times H_2O$ (2.45 g, 10.9 mmol) in aqueous THF (7 ml THF/3 ml H_2O). The resulting mixture was stirred at room temperature for 2 days and protected from the light. The precipitated AgBr was removed by filtration and then the solution was dried over calcium chloride. After removal of the solvent, the residue was purified by silica gel column chromatography (100 g). Eluted with hexane/ethyl acetate (4:1) afforded the title compound **4**.

(2S, 3S*, 5, 8)-tetrabromo-1, 2, 3, 4-tetrahydronaphthalene-(1R*, 4R*)-diol* (4): Yield: 1.5 g, (63%); yellow prism crystals; m.p. 188–189 °C (from acetone–hexane); R_f = 0.44 (hexane/EtOAc: 4/1). IR: ν (KBr) = 3839, 3546, 3419, 3000, 2935, 1432, 1390, 1236, 1220, 1191, 1170, 1128, 1041, 1018, 997, 896, 821, 779, 748, 671, 636, 524. ^{1}H-NMR (CD_3COCD_3, 400 MHz): δ = 7.61 (s, 2H, H6, H7), 5.43 (A part of AA'BB' system 2H, H1, H4), 5.05 (B part of AA'BB' system, 2H, H2, H3), 5.02 (brs, 2OH). ^{13}C NMR (CD_3COCD_3, 100 MHz): δ = 136.6 (C9, C10), 135.5 (C6, C7), 126.2 (C5, C8), 72.8 (C1, C4), 49.4 (C2, C3). MS (CI): *m/z* = 481 (5), 480 (8), 479 (6) [M$^+$], 419 (9), 418 (5), 381 (5), 338 (15), 321 (30), 320 (53), 319 (30), 303 (33), 302 (66), 301 (32), 287 (28), 286 (58), 285 (30), 240 (38), 222 (82), 160 (92), 144 (100), 132 (40), 115 (56), 86 (30), 72 (25). $C_{10}H_8Br_4O_2$ (479.79): calcd. C 25.03, H 1.68; found C 25.05, H 1.66.

Anti-1, 2:3, 4-dioxide-5, 8-dibromo-1, 2, 3, 4-tetrahydronaphthalene (**5**): To a solution of diol **4 (**0.42 g, 0.87 mmol) in freshly distilled THF (10 ml) was added a solution of sodium methoxide (0.11 g, 2.17 mmol) in THF (10 ml). The mixture was stirred at ambient temperature under nitrogen for 6 h. Reaction progress was monitored by TLC for consumption of the starting material. Diethyl ether (30 ml) and H_2O (25 ml) were added to the reaction mixture and the resulting precipitate was removed by filtration. The organic layer was separated, washed with H_2O (3 × 25 ml), dried over $CaCl_2$, and concentrated at reduced pressure. The crude product was chromatographed using an aluminium oxide (20 g) column, eluted with hexane to give the desired product which was recrystallised from chloroform-hexane yielded colourless needles (0.24 g, 85%); m.p. 206–207 °C (chloroform/hexane); R_f = 0.79 (hexane/EtOAc : 4/1). IR: ν (KBr) = 3066, 3002, 1470, 1415, 1340, 1253, 1197, 1182, 1164, 1120, 1105, 979, 931, 871. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.45 (s, 2H, H6, H7), 4.16 (A part of AA'BB' system, J_{12} = 3.56 Hz, J_{13} = 1.44 Hz, 2H, H1, H4), 4.02 (B part of AA'BB' system, J_{23} = 1.42 Hz, 2H, H2, H3). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 51.6 (C2, C3), 55.0 (C1, C4), 126.5 (C5, C8), 133.5 (C9, C10), 135.1 (C6, C7). MS (EI): *m/z* = 320 (7), 318 (15), 316 (7) [M$^+$], 291 (15), 289 (35), 287 (15), 262 (10), 260 (10), 209/211 (35), 182/184 (35), 102 (75), 74 (100). $C_{10}H_6Br_2O_2$ (317.96): calcd. C 37.77, H 1.90; found C 37.75, H 1.92.

Elimination of dimethoxide (6):To a solution of dimethylether **6** (0.55 g, 1.1 mmol) in freshly distilled THF (10 ml) was added a solution of sodium methoxide (0.13 g, 2.3 mmol) in dried THF (10 ml). The mixture was stirred at ambient temperature for 5 h. Reaction progress was monitored by TLC for consumption of the starting material. Diethyl ether (25 ml) and H_2O (25 ml) were added to the reaction mixture and the resulting precipitate was removed by filtration. The organic layer was separated, washed with H_2O (3 × 20 ml) and dried over $CaCl_2$. The filtrate was concentrated *in vacuo* to give two products separated by column chromatography using SiO_2 (50 g) eluted with hexane (2.0 l).

3, 5, 8-Tribromo-1-methoxynaphthalene (**8**): Yield: 0.11 g (25%); pale yellow solid; m.p. 122–123 °C (from chloroform/hexane); R_f = 0.53 (hexane). IR: ν (KBr) = 3002, 1597, 1573, 1554, 1489, 1460, 1442, 1423, 1383, 1350, 1290, 1255, 1195, 1178, 1126, 1088, 993, 906, 837, 822, 808, 765, 665, 580, 534. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.05 (d, J_{42} = 1.8 Hz, 1H, H4), 7.58 (d, J_{67} = 8.1 Hz, 1H, H6), 7.53 (d, J_{76}= 8.1 Hz, 1H, H7), 7.02 (d, J_{24} = 1.8 Hz, 1H, H2), 3.95 (3H, s, OMe). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 56.3 (OCH_3), 111.8 (C2), 117.1 (C8), 121.6 (C5), 122.6 (C3), 123.2 (C4), 123.9 (C9), 131.9 (C6), 133.5 (C7), 135.9 (C10), 156.9 (C1). $C_{11}H_7Br_3O$ (394.88): calcd. C 33.46, H 1.79; found C 33.48, H 1.77.

1, 4-Dibromo-5-methoxynaphthalene (**9**): Yield: 0.137 g (40%); green solid; m.p. 54–55 °C (chloroform/hexane); R_f = 0.34 (hexane). IR: ν (KBr) = 3000, 2932, 2909, 2829, 1855, 1732, 1608, 1576, 1560, 1491, 1458, 1431, 1396, 1354, 1296,1265, 1203, 1178, 1113, 1074, 997, 897. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.90 (dd, J_{87} = 8.6 Hz, J_{86} = 0.85 Hz, 1H, H8), 7.59 (d, J_{23} = 8.1 Hz, 1H, H2), 7.53 (d, 1H, H3), 7.50 (t, 1H, H7), 6.97 (d, J_{67} = 7.7 Hz, 1H, H6), 3.96 (s, 3H, OMe). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 56.2 (OMe), 108.3 (C6), 116.8 (C1), 121.0 (C8), 122.9 (C4), 125.2 (C9), 128.3 (C7), 130.9 (C2), 133.2 (C3), 135.2 (C10), 156.3 (C5). $C_{11}H_8Br_2O$ (315.99): calcd. C 41.81, H 2.55; found C 41.78, H 2.57.

(2S, 3S*)-5, 8-tetrabromo-(1R*, 4R*)-dinitroxy-1, 2, 3, 4-tetrahydronaphthalene* (**10**): To a solution of hexabromide **2** (3.0 g, 4.95 mmol) in dried THF (40 ml) was added $AgNO_3$ (1.85 g, 10.9 mmol). The reaction mixture was stirred magnetically at room temperature and protected from the light. The reaction progress was monitored by TLC and completed after 3 days. The mixture was filtered and evaporated. The residue was allowed to crystallise from dichloromethane and hexane mixtures in refrigerator. Dinitroxy **10** (0.7 g) was obtained and the residue recovered from the mother liguor (1.5 g) was purified by silica gel (150 g) column chromatography, eluting with hexane/EtOAc (9:1) to give the dinitroxy **10** (0.71 g, 1.41 g, 50%) as a yellow crystals; m.p. 214–215 °C (dichloromethane/hexane); R_f = 0.56 (hexane/EtOAc: 8/1).

IR: ν (KBr) = 3905, 3839, 3735, 3482, 3274, 3081, 2971, 2900, 2688, 2642, 2593, 2539, 2345, 1924, 1868, 1791, 1735, 1654, 1569, 1484, 1440, 1384, 1319, 1272, 1197, 1174, 1135, 1025, 958, 941. ^{1}H NMR ($CDCl_3$, 400 MHz): δ =7.70 (s, 2H, H6, H7), 6.56 (A part of AA'BB' system, 2H, H1, H4), 5.02 (B part of AA'BB' system, 2H, H2, H3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 40.0 (C2, C3), 79.1 (C1, C4), 127.1 (C5, C8), 129.5 (C9, C10), 137.0 (C6, C7). MS (EI): *m/z* = 572 (2), 570 (4), 568 (2) [M^+], 383, 381 (15), 318 (22), 289, 291 (40), 209, 211 (20), 193, 195 (25), 113 (45), 74 (100). $C_{10}H_6Br_4N_2O_6$ (569.78): calcd. C 21.08, H 1.06, N 4.92; found C 21.05, H 1.08, N 4.87.

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