BROMINATION OF TETRALIN. SHORT AND EFFICIENT SYNTHESIS OF 1,4-DIBROMONAPHTHALENE

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Received October 21, 1999
Accepted September 14, 2000

High-temperature bromination of tetralin (1,2,3,4-tetrahydronaphthalene) with bromine resulted in benzylic bromination to give 1,4-dibromo-1,2,3,4-tetrahydronaphthalene (**4**) as a major product and several secondary products. Photolytic bromination of tetralin and subsequent double dehydrobromination of 1,1,4,4-tetrabromo-1,2,3,4-tetrahydronaphthalene (**10**) gave 1,4-dibromonaphthalene (**11**) as the sole product in a high yield. 1,4-Dibromonaphthalene is efficiently converted to the corresponding methoxy (**12** and **13**) and cyano (**14** and **15**) derivatives of naphthalene.

Key words: Bromine; Photobromination; Bromination; Halogenation; Naphthalenes; Tetralin; Aromatic nucleophilic substitution.

1,4-Dibromonaphthalene (1,4-DBN) has become increasingly important as a triplet excitation acceptor with useful phosphorescent properties[1]. It is also useful as a precursor for other 1,4-disubstituted naphthalene derivatives such as phenols[2], amines[3], aryl ethers[4], alkyl ethers[5] and organometallics[6]. However, in spite of the potential importance of 1,4-DBN, existing methods for its preparation are not very practical. In consequence, only a very limited range of commercial 1,4-disubstituted naphthalenes is available, and they are generally very expensive. Therefore, we have sought a better synthesis of 1,4-DBN.

Dibromination of naphthalene with molecular bromine is unsatisfactory, but Yanovskaya[7] reported the quantitative preparation of 1,4-DBN by the reaction of naphthalene with dioxane dibromide, in a 1 : 2 mole ratio, at 40 °C. However, Bayer *et al.*[8] subsequently showed that this method

of preparation is neither quantitative nor specific for 1,4-dibromonaphthalene, 1,5-dibromonaphthalene and 2-bromonaphthalene also being formed. Bromination of naphthalene with alumina-supported copper (II) bromide appeared to be more promising, but the 1,4-DBN could not easily be separated from the by-products[9].

High temperature bromination conditions may increase the reactivity to encourage production of geminal dibromides at benzylic positions. In connection with our interest in high temperature bromination reactions of unsaturated systems[10] we would like to extend the work to hydroaromatic hydrocarbons. Although benzylic bromination of alkylbenzenes is well known, it usually requires irradiation with UV light in the presence of a free radical catalyst and often gives mixtures of products. It appeared likely, however, that tetralin could be cleanly converted to 1,1,4,4-tetrabromo-1,2,3,4-tetrahydronaphthalene without the complication of overbromination. The tetrabromide should then be capable of undergoing HBr elimination to give 1,4-DBN. We therefore studied this reaction and we now report a superior synthesis of 1,4-DBN by this approach. We have also clarified some other features of the reaction and we have demonstrated the synthetic utility of 1,4-DBN by using it as a precursor for a number of other compounds.

EXPERIMENTAL

Commercial reagents were purchased from standard chemical suppliers and purified to match the reported physical and spectral data. Melting points were determined on a Thomas–Hoover capillary melting points apparatus. The NMR spectra were recorded on spectrometers operating at either 200 or 400 MHz for ^{1}H and 50 or 100 MHz for ^{13}C NMR. Chemical shifts are given in ppm (δ-scale), coupling constants (*J*) in Hz. All column chromatography was performed on silica (60–230 mesh, Merck). TLC was carried out on Merck 0.2 mm silica gel 60 F_{254} analytical alumina plates. All bromination reactions were conducted in an efficient fume cupboard.

Thermal Bromination of Tetralin

To a solution of tetralin (**1**; 1.00 g, 7.5 mmol) in CCl_4 (25 ml) was added a solution of bromine (2.40 g, 30.3 mmol) in CCl_4 (15 ml) and the mixture was heated under reflux (77 °C) for about 10 min. When the colour of the bromine had disappeared, the reaction was stopped and the solvent was removed *in vacuo*. The residue was allowed to crystallise from petroleum ether (30 ml) in a refrigerator. *1,4-Dibromo-1,2,3,4-tetrahydronaphthalene* (**4**; 1.36 g, 63%) was isolated, m.p. 87–89 °C (ref.[11] 89–93 °C). The dibromide slowly decomposed with the evolution of hydrogen bromide on standing at room temperature. This process was slowed by storage in a refrigerator.

The residue recovered from the mother liquor was subjected to silica gel (90 g) column chromatography, eluting with hexane. *1-Bromonaphthalene* (**2**; 156 mg, 10%), *naphthalene* (**3**;

135 mg, 14%), and *1,2,4-tribromo-1,2,3,4-tetrahydronaphthalene* (**6**; 140 mg, 5%) were eluted successively. Recrystallisation of **6** from hexane gave needle-like colourless crystals, m.p. 59–60 °C. ^{1}H NMR ($CDCl_3$): 2.85 (dtd, *J*(3a,3b) = 14.5, *J*(3b,2) = *J*(3b,4) = 6.2, *J*(3b,1) = 1.4, 1 H, H3b); 3.30 (ddd, *J*(3a,3b) = 14.5, *J*(3a,4) = 9.6, *J*(3a,2) = 2.8, 1 H, H3a); 4.82 (m, 1 H, H2); 5.55 (dd, *J*(3b,1) = 1.4, *J*(1,2) = 2.9, 1 H, H1); 5.63 (dd, *J*(4,3a) = 9.6, *J*(4,3b) = 6.2, 1 H, H4); 7.26–7.66 (m, 4 H, aryl). ^{13}C NMR ($CDCl_3$): 40.2 (t), 47.2 (d), 52.1 (d), 52.8 (d), 130.9 (d), 131.5 (d), 132.9 (d), 133.1 (d), 135.2 (s), 136.6 (s). For $C_{10}H_9Br_3$ (369) calculated: 32.56% C, 2.46% H; found: 31.97% C, 2.68% H.

Then, elution of the column with chloroform gave *2-bromo-1,2,3,4-tetrahydronaphthalen-1-ol* (**5**; 140 mg, 8%), colourless crystals, m.p. 111–112 °C (chloroform) (ref.[12] 110 °C). ^{1}H NMR ($CDCl_3$): 2.28 and 2.51 (AB, *J*(3a,3b) = 13.7, 2 H, H3a and H3b); 2.60 (s, OH); 3.00 (m, 2 H, H4a and H4b); 4.35 (ddd, *J*(2,3a) = 3.3, *J*(2,3b) = 9.5, *J*(1,2) = 7.0, 1 H, H2); 4.91 (d, *J*(1,2) = 7.0, 1 H, H1); 7.60, 7.35 and 7.14 (m's, 4 H, aryl). ^{13}C NMR ($CDCl_3$): 28.4 (t), 30.0 (t), 56.5 (d), 74.4 (d), 127.0 (d), 128.3 (d), 128.5 (d), 128.8 (d), 135.2 (s), 135.7 (s). For $C_{10}H_{11}BrO$ (227) calculated: 52.89% C, 4.88% H; found: 52.67% C, 4.81% H. 1,4-Dibromo-1,2,3,4-tetrahydronaphthalene has been prepared previously by the reaction of 1,2,3,4-tetrahydronaphthalene with *N*-bromosuccinimide, as reported by Djerassi[11], but the exact stereochemistry of the product (*cis* or *trans*) has not been determined[13]. On the other hand, Blount[14] reported formation of 1,2-dibromo-1,2,3,4-tetrahydronaphthalene in about 30% yield on bromination of 1,2,3,4-tetrahydronaphthalene with bromine without solvent at 95 °C. The difference presumably arises as a result of enhanced elimination of HBr from 1-bromo-1,2,3,4-tetrahydronaphthalene in Blount's hotter and more concentrated conditions, followed by addition of bromine to the 1,2-dihydronaphthalene thus formed.

Bromination of 1,2-Dihydronaphthalene

A solution of 1,2-dihydronaphthalene (**8**; 130 mg, 1.00 mmol) in $CHCl_3$ (3 ml) was treated with bromine (176 mg, 1.1 mmol). After removal of the solvent *in vacuo*, recrystallisation of the residue from CH_2Cl_2–petroleum ether afforded *trans-1,2-dibromo-1,2,3,4-tetrahydronaphthalene* (**9**; 261 mg, 95%), m.p. 66 °C (ref.[15] 70 °C). ^{1}H NMR ($CDCl_3$): 7.13–7.36 (m, 4 H, aryl H's); 5.68 (t, 1 H, *J*(1,2) = *J*(1,3) = 1.5); 4.94–4.98 (m, 1 H); 3.20–3.30 (m, 1 H); 2.75–3.01 (m, 2 H); 2.14–2.29 (m, 1 H). ^{13}C NMR ($CDCl_3$): 136.5 (s), 134.9 (s), 133.3 (d), 131.2 (d), 130.9 (d), 128.7 (d), 79.7 (d), 79.1 (d), 78.4 (d), 53.6 (d), 27.2 (t), 26.5 (t).

Photobromination of 1,2-Dibromo-1,2,3,4-tetrahydronaphthalene

To a solution of 1,2-dibromo-1,2,3,4-tetrahydronaphthalene (**9**; 145 mg, 0.50 mmol) in $CDCl_3$ (0.5 ml) in an NMR tube bromine (0.88 g, 0.55 mmol) was added. The mixture was irradiated by a projector lamp (150 W) for 15 min. HBr gas was rigorously evacuated during the reaction. The residue obtained after removal of the solvent was recrystallised from CH_2Cl_2–petroleum ether to give *1,2,4-tribromo-1,2,3,4-tetrahydronaphthalene* (**6**; 156 mg, 85%).

Hydrolysis of 1,2-Dibromotetralin (**9**)

A solution of 1,2-dibromo-1,2,3,4-tetrahydronaphthalene (**9**; 145 mg, 0.50 mmol) in $CHCl_3$ (20 ml) was mixed with silica gel 60 (20 g) and H_2O (0.5 ml). The resulting mixture was stirred for 2 days. The solution was filtered and the solvent was removed *in vacuo*. The resi-

due was crystallised from $CHCl_3$ to give *trans-2-bromo-1,2,3,4-tetrahydronaphthalen-1-ol* (**5**) (91 mg, 80%).

Bromination of Naphthalene (**3**)

To a refluxing solution of naphthalene (**3**; 6.4 g, 50 mmol) in tetrachloromethane (60 ml) in a reaction flask a solution of bromine (17.57 g, 110 mmol) in CCl_4 (30 ml) was dropped over 1 h. The reaction mixture was stirred for another 1 h at the reflux temperature of CCl_4 (77 °C), then cooled to room temperature, and the solvent was removed *in vacuo*. On distillation of the reaction mixture *in vacuo*, *1-bromonaphthalene* (**2**) was collected at 130 °C/10 mm Hg to provide pure material in a yield of 90% (9.31 g).

Photobromination of 1,2,3,4-Tetrahydronaphthalene (**1**)

A solution of tetralin (3.96 g, 30 mmol) in CCl_4 (75 ml) in an internal type photochemical reaction apparatus (immersion-well reactor, 100 ml) was cooled to 0 °C with an ice bath. A device for absorbing the hydrogen bromide evolved was attached to a side arm. The content was irradiated by a projector lamp (150 W, cooled by running water) and stirred magnetically while a solution of Br_2 (21.6 g, 135 mmol) in CCl_4 (20 ml) was added during 0.5 h. The reaction mixture was irradiated for 1.5 h in total. HBr was rigorously removed during the reaction. The reaction progress was monitored by ^{1}H NMR spectroscopy or TLC. After removal of the solvent, the residue was crystallised from CCl_4 at 0 °C, and was identified as *1,1,4,4-tetrabromo-1,2,3,4-tetrahydronaphthalene* (**10**; 12.36 g, 92%), white crystalline material, m.p. 63 °C (decomp.) from CCl_4. ^{1}H NMR ($CDCl_3$): 7.90 (2 H, H5, H8); 7.37 (2 H, H6, H7); 3.23 (s, 4 H, aliphatic). ^{13}C NMR ($CDCl_3$): 139.2 (s), 132.8 (d), 132.3 (d), 62.8 (d), 49.5 (t). For $C_{10}H_8Br_4$ (448) calculated: 26.82% C, 1.95% H; found: 26.03% C, 2.10% H. The tetrabromide **10** slowly decomposed with evolution of hydrogen bromide to give 1,4-dibromonaphthalene on standing at room temperature or at 0 °C.

1,4-Dibromonaphthalene

To a stirred solution of 1,1,4,4-tetrabromo-1,2,3,4-tetrahydronaphthalene (**10**; 11.2 g, 25 mmol) in dry, freshly distilled THF (110 ml) a solution of potassium *tert*-butoxide (6.16 g, 55 mmol) in dry, freshly distilled THF (60 ml) was added over 20 min. The resulting reaction mixture was stirred magnetically at room temperature overnight. The mixture was diluted with water (100 ml) and the solution was extracted into ether (300 ml), then the extract was washed with water and dried with $MgSO_4$. After removal of the solvent, the residue was filtered through a short silica gel column (30 g) (hexane) and recrystallised from hexane to give clear yellow crystals of 1,4-dibromonaphthalene (**11**; 6.79 g, 95%), m.p. 80 °C (ref.[3] 83–83.5 °C). ^{1}H NMR ($CDCl_3$): 7.62 (s, 2 H); 8.23–7.62 (AA′BB′, 4 H). ^{13}C NMR ($CDCl_3$): 123.1 (s), 128.3 (d), 128.7 (d), 130.6 (d), 133.4 (s). For $C_{10}H_6Br_2$ (286) calculated: 42.00% C, 2.11% H; found: 42.84% C, 2.50%H.

1-Bromo-4-methoxynaphthalene (**12**)

Freshly cut sodium (460 mg, 20 mmol) was added under nitrogen gas to dry methanol (30 ml). When dissolution was complete, the warm solution was diluted with dry dimethylformamide (DMF) (30 ml) followed by the addition of vacuum-dried cuprous iodide (475 mg,

2.5 mmol). After dissolution, 1,4-DBN (**11**; 1.43 g, 5.0 mmol) in dry DMF (50 ml) was added. The reaction mixture was stirred magnetically under a nitrogen atmosphere at reflux (*ca* 90 °C). Reaction progress was monitored by TLC and starting material was consumed within 12 h. After cooling to room temperature, H_2O (50 ml) and diethyl ether (100 ml) were added to the reaction mixture. The organic layer was separated, washed with H_2O (3 × 50 ml), and dried over $MgSO_4$ for 1 h. The solvent was removed and the crude product was purified by chromatography (SiO_2, petroleum ether). 1-Methoxy-4-bromonaphthalene (**12**; 1.16 g, 80%) was obtained as a light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): 4.00 (s, 3 H, OCH_3); 6.68 (d, AB, 1 H, H2); 7.65 (d, *J*(2,3) = 8, 1 H, H3); 7.48–7.64 (m, 2 H, H6, H7); 8.15–8.30 (m, 2 H, H5, H8). ^{13}C NMR ($CDCl_3$): 57.6, 98.2, 105.0, 106.3, 123.8, 124.4, 127.0, 128.0, 129.6, 131.3, 157.2. This compound has been prepared previously by several routes, such as methylation of the corresponding naphthol[16] or bromination of 1-methoxynaphthalene[17].

1,4-Dimethoxynaphthalene (**13**)

Freshly cut sodium (690 mg, 30 mmol) was added under nitrogen gas to dry methanol (30 ml). When dissolution was complete, the warm solution was diluted with dry dimethylformamide (DMF) (30 ml) followed by the addition of vacuum-dried cuprous iodide (950 mg, 5 mmol). After dissolution, 1,4-DBN (**11**; 1.43 g, 5 mmol) in dry DMF (50 ml) was added. The reaction mixture was stirred magneticaly under a nitrogen gas atmosphere at reflux (*ca* 90 °C) for 36 h. Reaction progress was monitored by TLC and starting material was consumed within 12 h to form mainly 1-methoxy-4-bromonaphthalene (**12**) as assigned by TLC. Formation of 1,4-dimethoxynaphthalene (**13**) was completed in 36 h. After cooling to room temperature, H_2O (50 ml) and diethyl ether (100 ml) were added to the reaction mixture. The organic layer was separated, washed with H_2O (3 × 50 ml), and dried over $MgSO_4$ for 1 h. The solvent was removed and the crude product was passed through a short column packed with Al_2O_3 (10 g). Recrystallisation from a mixture of CH_2Cl_2 and petroleum ether (b.p. 40–50 °C) in the refrigerator yielded 1,4-dimethoxynaphthalene (**13**; 752 mg, 80%) as colourless needles, m.p. 76–77 °C (ref.[18] 86–87.5 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): 3.94 (s, 3 H); 6.68 (s, 2 H, H2, H3); 7.47–7.51 (AA′BB′, 2 H, H6, H7); 8.18–8.22 (AA′BB′, 2 H, H5, H8). ^{13}C NMR ($CDCl_3$): 57.5, 106.6, 116.2, 127.1, 128.6, 157.3.

1-Bromo-4-cyano-naphthalene (**14**)

1,4-DBN (**11**; 1.43 g, 5 mmol) dissolved in freshly distilled DMF (40 ml) was mixed with dry CuCN (0.805 g, 9 mmol). The reaction mixture was stirred magnetically at the reflux temperature of the solvent under an N_2 atmosphere for 12 h. Reaction progress was monitored by TLC for consumption of the starting material. After the reaction mixture had cooled to room temperature, benzene (40 ml) and water (40 ml) were added. The muddy mixture was separated by suction filtration. The mud was extracted with ether (4 × 30 ml) and the ether layers were subjected to suction filtration each time. The aqueous phase was extracted with benzene (40 ml) and the combined organic layers were washed with 10% aqueous $FeCl_3$ (100 ml) and 10% aqueous NaOH, respectively. The organic phase was dried over Na_2SO_4. After removal of the solvent, the residue was chromatographed on a SiO_2 column eluted with petroleum ether. The material was recrystallised from dichloromethane–light petroleum ether (1 : 1, 15 ml) in a refrigerator to yield pure compound (810 mg, 70%), m.p. 103–104 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.74 (d, *J*(3,2) = 8, 1 H, H3); 7.71–7.78 (m, 2 H, H6, H7); 7.84

(d, *J*(2,3) = 8, 1 H, H2); 8.23–8.26 (m, 1 H, H5 or H8); 8.31–8.35 (m, 1 H, H5 or H8). ^{13}C NMR ($CDCl_3$): 111.0, 117.1, 126.0, 128.4, 128.5, 130.0, 130.2, 130.5, 133.1, 134.0, 134.1.

1,4-Dicyanonaphthalene (**15**)

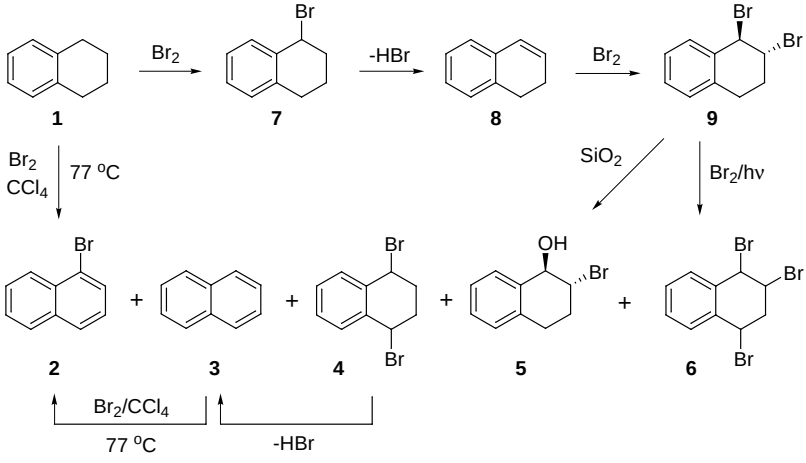
1,4-DBN (**11**; 1.80 g, 6.2 mmol) dissolved in freshly distilled DMF (30 ml) was mixed with dry CuCN (1.68 g, 15 mmol). The reaction mixture was stirred magnetically at the reflux temperature of the solvent under an N_2 atmosphere for 20 h. Reaction progress was monitored by TLC for completion of formation of the dicyanonaphthalene. The reaction mixture was cooled to room temperature, and into it were poured benzene (40 ml) and water (40 ml). A muddy mixture was formed and the muddy part was separated by suction filtration. The muddy part was extracted with ether (4 × 40 ml) and the ether layers were separated from the muddy part by suction filtration each time. The aqueous phase was extracted with benzene (30 ml) and the combined organic layers were washed with 10% aqueous $FeCl_3$ (100 ml) and 10% aqueous NaOH, respectively. The organic phase was dried over Na_2SO_4. After removal of the solvent, the crude product was chromatographed using a SiO_2 column eluted with petroleum ether. The material obtained was recrystallised from dichloromethane–light petroleum ether (1 : 1, 15 ml) in a refrigerator to yield pure compound **15** (890 mg, 80%), m.p. 205–206 °C (ref.[19] 208 °C). ^{1}H NMR ($CDCl_3$): 3.94 (s, 3 H); 6.68 (s, 2 H, H2, H3); 7.47–7.651 (AA′BB′, 2 H, H6, H7); 8.18–8.22 (AA′BB′, 2 H, H5, H8). ^{13}C NMR ($CDCl_3$): 116.2, 117.1, 126.4, 131.4, 132.4, 133.0.

RESULTS AND DISCUSSION

In an initial experiment, 1,2,3,4-tetrahydronaphthalene (**1**) was subjected to bromination by 4 equivalents of bromine in refluxing carbon tetrachloride for 10 min, by which time the bromine colour had disappeared. The resulting crude product was crystallised from petroleum ether, which provided the dibromo compound **4** as the major product (63%). The rest of the mixture was submitted to silica gel column chromatography. After careful repeated chromatography, followed by fractional crystallisation, four additional products were isolated and characterised as **2**, **3**, **5**, and **6** (Scheme 1).

In order to characterise these products properly, and also to provide information about the way how they were formed, several additional experiments were conducted. Naphthalene (**3**) and 1-bromonaphthalene (**2**) were characterised by comparison with authentic materials. It appeared likely that **3** was formed by elimination of HBr from dibromo product **4**, and indeed compound **4** eliminated hydrogen bromide spontaneously to form naphthalene both in its solid state and in solution. Therefore, we concluded that naphthalene could be formed by double HBr elimination from **4** during the reaction and during column chromatography. Compound **2** could possibly have been formed by direct bromination of **3** during the reaction or by double elimination of HBr from compound **5**. In order to

check whether **2** could be produced by direct bromination of naphthalene forming from **4** in the conditions occuring during the reaction, a solution of one mole equivalent of bromine in CCl_4 was dropped to a refluxing solution of naphthalene in CCl_4. The reaction product was distilled *in vacuo* to obtain pure **2** in a yield of *ca* 90%, thereby demonstrating the possibility that it could have been formed in this way.



SCHEME 1

The elemental analysis of compound **6** was in reasonable agreement with the proposed tribromide structure (Scheme 1). H2 shows a multiplet comprising the couplings with H1, H3a, and H3b. In signal group at 5.63 ppm (dd, H4) the low coupling (6.2 Hz) appears between H4 and H3b, while large coupling (9.6 Hz) H4 and H3a. The methylene protons at C3 appear as an AB system. The A part, which is the signal group of H3a, is split into doublets of doublets of doublets. The geminal coupling, J(3a,3b), is *ca* 14.5 Hz. The second doublet splitting originates from coupling to H4 (J(3a,4) = 9.6) and the third doublet (J(2,3a) = 2.8) originates from coupling to H2. The B part of the AB spin system in split into doublets of triplets of doublets. The triplet splitting (J = 6.2) is due to nearly equal values of the dihedral angles between H3b and H2/H4. One of the doublet splitting is due to the geminal coupling (J(3a,3b)) and the second doublet splitting (J(1,3b) = 1.4) originates from the H1. The fact that such long-range coupling exists between H1 (δ 5.55) and H3b is due to a *W* arrangement as confirmed double resonance experiments. The chemical shifts of the ^{13}C NMR resonances of compound **6** were also consistent with the expected chemical shifts. Therefore, the structure of **6** was confirmed as that shown in Scheme 1.

The elemental analysis of **5** was consistent with its being a bromo alcohol[20]. IR analysis confirmed that a hydroxy group was present and the melting point was the same as that reported previously for 2-bromo-1,2,3,4-tetrahydronaphthalen-1-ol[12]. Therefore, it seemed that this product had been formed by partial hydrolysis of 1,2-dibromo-1,2,3,4-tetrahydronaphthalene (**9**). Benzylic bromides can be hydrolysed easily during column chromatography to the corresponding bromo alcohols[21], and the retention of stereochemistry probably results from intermediate bromonium ion formation.

The ^{1}H NMR spectrum[12] of bromo alcohol **5** showed three multiplets at δ 7.60, 7.35 and 7.14 due to aromatic protons. The H1 and H2 resonances occurred as an AB system. The H1 resonance was a doublet at δ 4.91 (J(1,2) = 7.0). Irradiation of the signal at δ 3.00, which was assigned to the two protons on C4 as a multiplet, showed that the signal groups at δ 2.28 and 2.51 belong to protons on C3, which appear as an AB system (J(3a,3b) = 13.7). When the H1 signals were irradiated, the doublet of doublets of doublets of H2 (δ 4.35) changed to a doublet of doublets (J(2,3a) = 3.3, J(2,3b) = 9.5). Finally, the hydroxy group resonates at δ 2.60. The *trans*-configuration of the hydroxy group and the bromo substituent in the bromo alcohol was assigned by X-ray crystallographic analysis (Fig. 1).

The molecular structure with atom-numbering scheme for compound **5** is shown in Fig. 1. The crystallographic data and the bond lengths and angles

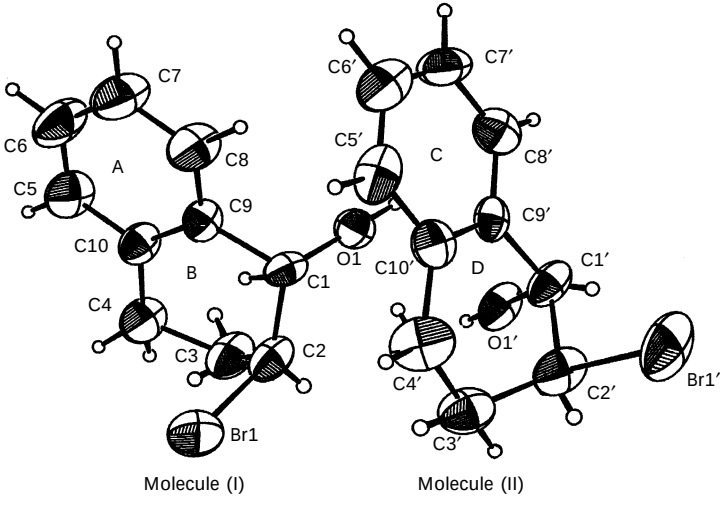


FIG. 1

Crystal structure of compound **5** with atom-numbering scheme. The thermal ellipsoids are drawn at the 50% probability level

are given in Tables I and II. The asymmetric unit contains two molecules. The intermolecular close contact between the oxygen atoms [O1···O1′ is 2.724(8) Å] of molecules (I) and (II) causes a hydrogen bond. In molecule (II), the O1′–C1′ [1.33(1) Å] and C2′–Br1′ [1.893(9) Å] bond lengths are shorter than in molecule (I) but the C2′–C3′ bond length [1.68(1) Å] is abnormally longer. The C9′–C1′–O1′ [104.3(7)°], C2′–C1′–O1′ [100.2(7) °], and Br1′–C2′–C1′ [99.1(6)°] bond angles are smaller while the Br1′–C2′–C3′ bond angle [115.5(6)°] is larger than the corresponding ones [1.53(1), 2.05(1), 1.38(1) Å and 112.1(7), 112.8(7), 114.1(6), 105.6(7)°, respectively] in molecule (I). The C (C5′,C6′,C7′,C8′,C9′,C10′) and A (C5,C6,C7,C8,C9,C10) rings are planar while D (C1′,C2′,C3′,C4′,C9′,C10′) and B (C1,C2,C3,C4,C9,C10) rings are non-planar with maximum deviations of C2′ [0.266(9) Å] and C2 [0.318(10) Å] from the best least-squares planes. Some of the dihedral angles between the best least-squares planes of the molecules (I) and (II) are A/C = 78.0(3), B/C = 79.8(3), A/D = 73.9(3), and B/D = 75.7(3)°. The C–Br bond lengths and C–C–Br bond angles in the non-planar rings and also the bond lengths and angles in the planar rings are generally in good agreement with the corresponding ones[22].

It appeared likely that compounds **5** and **6** may have arised from further reactions of 1,2-dibromo-1,2,3,4-tetrahydronaphthalene (**9**), itself formed from 1,2-dihydronaphthalene (**8**) following dehydrobromination of 1-bromo-1,2,3,4-tetrahydronaphthalene (**7**). In order to test this possibility, 1,2-dihydronaphthalene (**8**) was reacted with molecular bromine in CH_2Cl_2 to provide *trans*-1,2-dibromo-1,2,3,4-tetrahydronaphthalene[24] (**9**) in nearly quantitative yield. Photobromination of **8** with a projector lamp afforded the 1,2,4-tribromo compound **6**, while hydrolysis of **9** over silica gave the bromo alcohol **5**, demonstrating that this route is indeed a possible one for production of these compounds. The understanding gained from this analysis of the reaction products of the short-time bromination of tetralin in refluxing tetrachloromethane enabled us to design better experiments to provide tetrabromotetralin.

Simple use of extra bromine and prolonged duration of reaction at the reflux temperature of CCl_4 did indeed produce tetrabromotetralin (**10**), but along with a large amount of polymeric material. In order to minimise the *in situ* loss of HBr, which was probably responsible for initiating the production of the polymeric by-product, we carried out the reaction under photolytic conditions at low temperature. To a solution of tetralin in CCl_4 *ca* 4.5 mole equivalents of bromine were added while the solution was irradiated internally with a 150 W projector lamp at 0 °C. The process resulted in the substitution of all four benzylic hydrogen atoms with bromine atoms

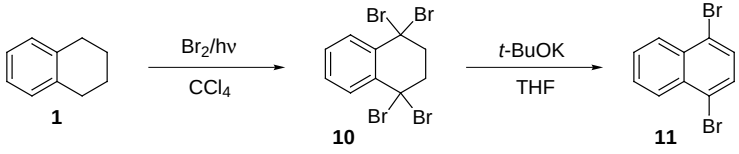
TABLE I
Crystallographic and experimental data[23] of bromo alcohol **5**

Empirical formula	$C_{10}H_{11}BrO$
Formula weight	227.11
Crystal colour	colourless
Crystal dimensions, mm	0.20 × 0.15 × 0.10
Crystal system	monoclinic
Lattice parameters:	
a, Å	10.690(1)
b, Å	8.939(1)
c, Å	19.704(2)
β, °	95.73(1)
V, Å^3	1 873.45(33)
Space group	$P2_1/n$
Z	8
D_x, g ml^{-1}	1.61
μ(MoK), mm^{-1}	4.29
Temperature, K	293
F(000)	912
λ(MoKα), Å	0.71073
Residuals *R*; R_w	0.063; 0.072
No. of reflections used	2 760
No. of parameters	217
Goodness of fit	0.98
Minimum residual density, e Å^{-3}	–0.63
Maximum residual density, e Å^{-3}	0.57
Treatment of hydrogen atoms	Geometric calculation
Refinement	Full-matrix least-squares (MolEN)
Measurement	Enraf–Nonius CAD-4 diffractometer
Program system	CAD-4 Express Software
Structure determination	Mo1EN

TABLE II
Bond distances (in Å) and angles (in °) for bromo alcohol **5**

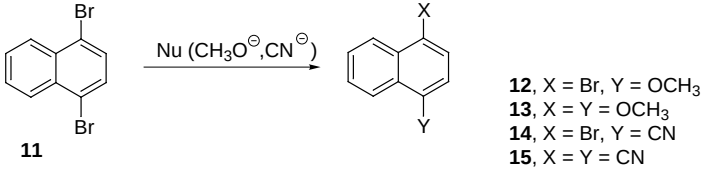
Atoms	Bond distances	Atoms	Bond distances
Br1′–C2′	1.893(9)	C6′–C7′	1.43(2)
Br1–C2	2.05(1)	C7′–C8′	1.38(1)
O1′–C1′	1.33(1)	C9–C10	1.35(1)
O1–C1	1.53(1)	C9–C1	1.53(1)
C10′–C9′	1.42(1)	C9–C8	1.34(1)
C10′–C4′	1.55(1)	C10–C4	1.49(1)
C10′–C5′	1.41(1)	C10–C5	1.41(1)
C9′–C1′	1.53(1)	C4–C3	1.57(1)
C9′–C8′	1.46(1)	C3–C2	1.38(1)
C1′–C2′	1.52(1)	C2–C1	1.57(1)
C2′–C3′	1.68(1)	C8–C7	1.41(1)
C3′–C4′	1.47(1)	C7–C6	1.33(2)
C5′–C6′	1.41(1)	C6–C5	1.33(1)
Atoms	**Angles**	**Atoms**	**Angles**
C9′–C10′–C4′	125.9(8)	C10–C9–C1	124.1(8)
C9′–C10′–C5′	117.8(8)	C10–C9–C8	117.1(9)
C4′–C10′–C5′	116.3(8)	C1–C9–C8	118.7(8)
C10′–C9′–C1′	122.0(8)	C9–C10–C4	120.3(8)
C10′–C9′–C8′	122.9(8)	C9–C10–C5	119.6(8)
C1′–C9′–C8′	115.1(8)	C4–C10–C5	120.0(8)
O1′–C1′–C9′	104.3(7)	C10–C4–C3	111.7(8)
O1′–C1′–C2′	100.2(7)	C4–C3–C2	114.2(9)
C9′–C1′–C2′	111.9(7)	Br1–C2–C3	105.6(7)
Br1′–C2′–C1′	99.1(6)	Br1–C2–C1	114.1(6)
Br1′–C2′–C3′	115.5(6)	C3–C2–C1	109.0(8)
C1′–C2′–C3′	116.1(7)	O1–C1–C9	112.1(7)
C2′–C3′–C4′	112.7(8)	O1–C1–C2	112.8(7)
C10′–C4′–C3′	113.4(8)	C9–C1–C2	110.3(7)
C10′–C5′–C6′	119.1(9)	C9–C8–C7	122.5(9)
C5′–C6′–C7′	122.9(9)	C8–C7–C6	120(1)
C6′–C7′–C8′	119.6(9)	C7–C6–C5	119(1)
C9′–C8′–C7′	117.6(9)	C10–C5–C6	122.2(9)

to give 1,1,4,4-tetrabromo-1,2,3,4-tetrahydronaphthalene (**10**) in high yield (92%). The structure of **10** was established unambiguously by its ^{1}H NMR spectrum. The four aliphatic protons resonated as a singlet at δ 3.2. The aromatic protons showed an AA′BB′ pattern at δ 7.57 and 8.22. An efficient double dehydrobromination of **10** was achieved by using 2 mole equivalents of potassium *tert*-butoxide, giving 1,4-dibromonaphthalene (**11**), isolated in a yield of 95% (Scheme 2). The ^{1}H and ^{13}C NMR spectra showed the expected symmetry in the molecule.



SCHEME 2

Having obtained 1,4-dibromonaphthalene (1,4-DBN; **11**) in high yield by a very convenient procedure, we wished to demonstrate its value as a precursor of other useful compounds[25]. Copper-assisted nucleophilic substitutions by methoxide and cyanide ions easily and efficiently converted 1,4-DBN (**11**) into its methoxy (**12** and **13**) and cyanide (**14** and **15**) derivatives as sole products (Scheme 3).



SCHEME 3

The structure of naphthalene rests on ^{1}H and ^{13}C NMR spectral data of **13** and **15** in which AA′BB′ system of the aromatic protons and the singlets for the H2 and H3 protons confirming the symmetrical structures are observed. In NMR spectra of bromocyanide **12** and methoxybromide **14**, H2 and H3 protons showed an AB pattern at δ 7.74, 7.84 and δ 6.68, 7.65 with J(2,3) = 8.0, respectively.

Selectively transformation of 1,4-DBN (**11**) into methoxybromide **12** and bromocyanide **14** opened up synthesis of various cyanide and methoxy derivatives of naphthalene due to bromo substituent. Methoxynaphthalenes have great synthetic importance in several points, *i.e.*, for 1,4-dimethoxynaphthalene; in synthesis of other substituted naphthalene derivatives[26]

and natural products[27], as sensitiser[28] and electron donors[29] and in the ring-enlargement[30] with halocarbenes to benzotropone derivatives. They are usually prepared from hardly accessible 1,4-dihydroxynaphthalene and, therefore, our method appear to be more convenient and practical.

In conclusion, exhaustive benzylic photobromination of tetralin, followed by elimination of HBr under basic conditions, allows the high yield synthesis of 1,4-dibromonaphthalene. This method of synthesis has several advantages over existing methods. It begins with a readily available starting material, it is efficient, and it is applicable to large-scale work. The product is a useful precursor of other 1,4-disubstituted naphthalenes.

The authors are indebted to the University Research Fund of the Department of Chemistry, Gaziosmanpasa University (grant No. 1994/2) and The Scientific and Technical Research Council of Turkey (TUBITAK; grant No. TBAG-1322) for financial support. O. Ç. also thanks the British Council in Turkey for supporting co-operation with the University of Wales Swansea.

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