Pergamon

Tetrahedron 58 (2002) 5603–5609

TETRAHEDRON

Selective bromination of 1-bromonaphthalene: efficient synthesis of bromonaphthalene derivatives

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Received 19 February 2002; revised 9 May 2002; accepted 30 May 2002

Abstract—Selective and specific preparation methods are described for 1,4-dibromonaphthalene, 1,5-dibromonaphthalene and 1,3,5-tribromonaphthalene. The reaction of 1-bromonaphthalene and naphthalene with stoichometric quantities of bromine by using a minimum amount of solvent (methylene chloride) at −30 and −50°C smoothly affords 1,4-dibromonaphthalene in 90% yield. Photobromination of 1-bromonaphthalene in CCl_4 at −30°C gives 1,2,3,4,5-pentabromo-1,2,3,4-tetrahydronaphthalenes, whereas 1,5-dibromonaphthalene is obtained at reflux (77°C) in 80% yield under the same conditions. Dehydrobromination of the pentabromide by *t*-BuOK affords 1,3,5-tribromonaphthalene as a sole product (91%). 1,5-Dibromo- and 1,3,5-tribromonaphthalenes were efficiently converted to the corresponding methoxy naphthalene derivatives.

1. Introduction

An ideal chemical process from a clean technology viewpoint would involve a stoichiometric reaction between substrate and reagent, proceed at ambient temperature and pressure, require no solvent, produce by-products that easily separate and give high yields of a single isomer. Unfortunately, it is rarely possible to achieve such a process. A particular problem arises in the case of electrophilic aromatic substitution reactions, which frequently require large quantities of Lewis acid 'catalysts' that are destroyed during work-up, need elevated temperatures, cause corrosion problems, and produce mixtures of *ortho* and *para* isomers as well as polysubstitution products. Such reactions are becoming an embarrassment to the industry and commercially viable alternatives are urgently required.[1] Thus, specific and selective bromination is important both in intermediate and product synthesis. The control of the reactivity, selectivity and yield and the use of sufficiently mild industrial conditions are all factors that must be taken into account.

Bromonaphthalenes have become increasingly important as a triplet excitation acceptor with useful phosphorescent properties.[2] They are also useful as a precursor for other substituted naphthalene derivatives such as phenols,[3] amines,[4] ethers[5] and organometallics.[6] However, in spite of the potential importance of them, existing methods for their preparation are not very practical. In consequence, only a very limited range of commercial di- and trisubstituted naphthalenes are available, and these are generally very expensive. Therefore, we have sought a better synthesis of di- and tribromonaphthalenes.

Bromination of aromatic compounds with elemental bromine is well-known. Aromatic bromination generally requires a catalyst and often gives mixtures of products. Monohalogenation of benzenoid aromatics generally does not need any catalyst unlike benzene although, further halogenation generally needs a catalyst. Therefore, the synthesis of bromosubstituted naphthalenes is restricted by the starting naphthalene because reactivity towards bromine is reduced after some steps. Most of the halonaphthalene derivatives have been synthesised from substituted naphthalene derivatives (amino, nitro, sulfo, trimethylsilyl, etc.).[7]

We wish to report a new, simple, quick and general procedure for the preparation of bromonaphthalenes (e.g. 1,4-dibromonaphthalene (1,4-DBN, **3**), 1,5-dibromonaphthalene (1,5-DBN, **4**) and 1,3,5-tribromonaphthalene (1,3,5-TBN, **5**). We have also clarified conditions for the nuclear bromination of 1-bromonaphthalene (1-BN, **2**).

2. Results and discussions

We studied bromination of 1-bromonaphthalene (**2**) under different reaction conditions by changing reaction period, amount and type of solvents and density of light (Table 1). First, 1-BN was treated with bromine at −15°C in the dark by keeping a molar ratio 1:100 of 1-BN **2** to solvent (CH_2Cl_2) (entry 1). Electrophilic bromination was quite slow and complete in 9 days. After completion of bromination (>95% conversion), 1,4-DBN **3** and 1,5-DBN **4** were

Keywords: photobromination; bromonaphthalenes; methoxynaphthalenes.

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0040–4020/02/$ - see front matter
PII: S0040-4020(02)00549-5

Table 1. Bromination of 1-Bromonaphthalene

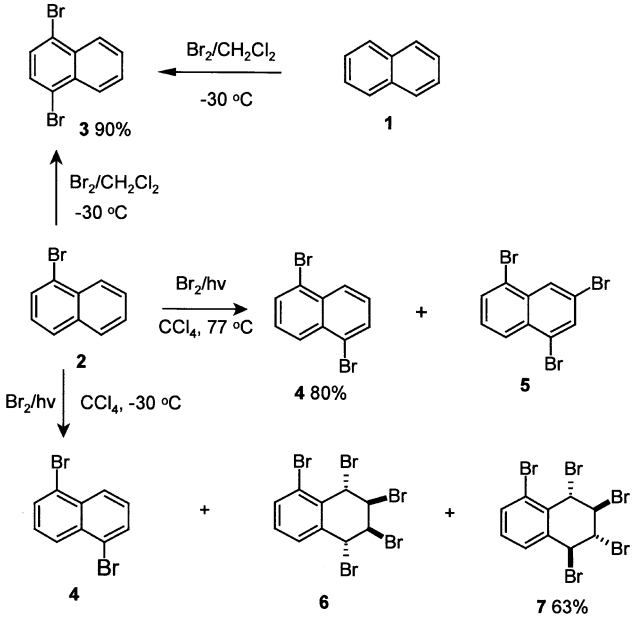
Entry	Reagent	Substrate/solvent	Reaction time	Temperature	Ratio of the products (%)[a]			
					3	**4**	**5**	**6** and **7**
1	Br_2 (1.1 equiv.)	1-BN/CH_2Cl_2: 1/100	9 days	−15°C in dark	90	10	–	–
2	Br_2 (1.1 equiv.)	1-BN/CH_2Cl_2: 1/15	30 h	−15°C in dark	90	10	–	–
3	Br_2 (1.1 equiv.)	1-BN/CH_2Cl_2: 1/15	2 days	−30°C or −50°C in dark	98	2	–	–
4	Br_2 (1.1 equiv.)	1-BN/$CHCl_3$: 1/15	2 days	−15°C in dark	88	12	–	–
5	Br_2 (2.5 equiv.)	1-BN/CCl_4	45 min	−30°C	–	10	–	90 (14/76)
6	Br_2 (2.5 equiv.)	1-BN/CCl_4	75 min	0°C	–	30	–	70 (18/52)
7	Br_2 (2.5 equiv.)	1-BN/CCl_4	2 h	30°C	–	69	–	31
8	Br_2 (1.5 equiv.)	1-BN/CCl_4	2.5 h	77°C	–	92	8	–

[a] Ratio of the products was established by ^{1}H NMR spectroscopy. The conversions of all reactions was >95%.

formed in a ratio of 90:10 as assigned by ^{1}H NMR spectroscopy. In order to accelerate the reaction we decided to carry out the bromination under more concentrated conditions (entry 2). A 1:15 molar ratio of substrate (1-BN)-solvent (CH_2Cl_2) (seven times more concentrated) was used and the reaction was complete in a shorter time (30 h) to give almost the same product ratio.

On the other hand, the low temperature bromination (−30 and −50°C, entry 3) of 1-BN under the same conditions is an effective and convenient preparation method for 1,4-DBN, because it reduced the formation of 1,5-DBN (product ratio: 98:2 for 1,4-DBN and 1,5-DBN, respectively) and 1,4-DBN was easily isolated in a high yield (90%). When using $CHCl_3$ as a solvent, we obtained the same results except relatively longer reaction period in comparison with entry 2 (entry 4). However, surprisingly, no reaction was observed in CCl_4.

The procedure described in entry 3 was repeated for naphthalene by using 1 equiv. of bromine. The reaction gave 1-bromonaphthalene and 1,4-DBN (ca. 95:5, assigned by ^{1}H NMR spectroscopy). Reaction of naphthalene with 2 equiv. of bromine gave the same results as in entry 3.

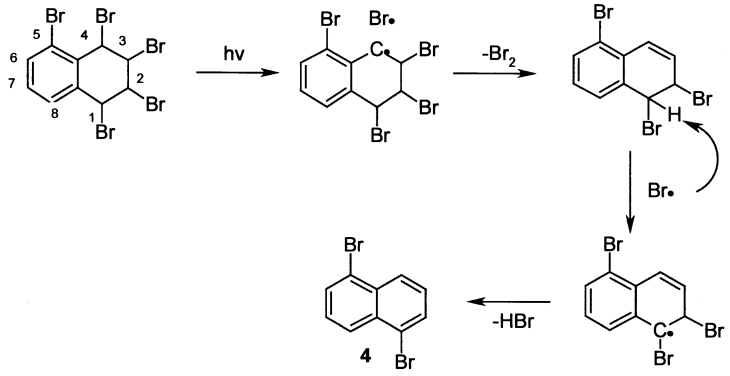


Scheme 1.

Dibromination of naphthalene with molecular bromine is unsatisfactory, but Yanovskaya[8] reported the quantitative preparation of 1,4-DBN by the reaction of naphthalene with dioxane dibromide, in a 1:2 molar ratio, at 40°C. However, Bayer et al.[9] subsequently showed that this method of preparation is neither quantitative nor specific for 1,4-dibromonaphthalene, and 1,5-dibromonaphthalene and 2-bromonaphthalene were also 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.[10] Recently we described[11] more convenient synthetic methodology for 1,4-DBN based on photobromination of tetralin and subsequent double HBr elimination of the formed product, i.e. 1,1,4,4,-tetrabromotetralin. However, the present method seems to be more convenient in view of no special reaction procedure and device and usage of minimum solvent.

The fact that electrophilic bromination was suppressed in an apolar solvent (CCl_4) turned our attention to bromination using radicals. Therefore, we studied photochemical bromination of 1-BN in an apolar solvent (CCl_4). 1-BN was subjected to bromination in an immersion-well photochemical apparatus with internal projector lamp (250 W). The photobromination resulted in the formation of addition (pentabromides **6** and **7**) and addition–elimination products (**4** and **5**). Interestingly, product ratio dramatically changed depending on reaction temperature. While the ratio of pentabromides **6** and **7** was 31:69 at 30°C (entry 7), it was 70:30 at 0°C (entry 6). Photobromination at lower temperature (−30°C, entry 5) is an efficient method for obtaining the normal addition product, i.e. pentabromides **6** and **7** (product ratio is 10, 14 and 76% for 1,5-DBN, pentabromide **6** and pentabromide **7**). The mainly formed pentabromide **7** was isolated in 56% yield after crystallization of the crude mixture. After chromatography on silica gel and recrystallization, 1,5-DBN, pentabromide **7** and **6** were isolated in 8, 7 (total 63% yield of **7**) and 10% yields, respectively.

Four aliphatic and three aromatic signals in the ^{1}H NMR spectra are in agreement with 1,2,3,4,5-pentabromo-1,2,3,4-tetrahydronaphthalenes **6** and **7**. The observation of 10 lines in the ^{13}C NMR spectra of the pentabromides **6** and **7** is also in accord with the proposed structures. However, it is not possible to establish stereochemistry of the stereoisomeric compounds **6** and **7** on the basis of the spectral data because thereotically nine different pentabromides could be formed.



Scheme 2.

Therefore, the structural assignments of stereoisomers **6** and **7** were established by X-ray crystallographic analysis. The X-ray analysis clearly indicates **6** has *trans*,*cis*,*trans*-whereas **7** has *trans*,*trans*,*trans* configuration.[13]

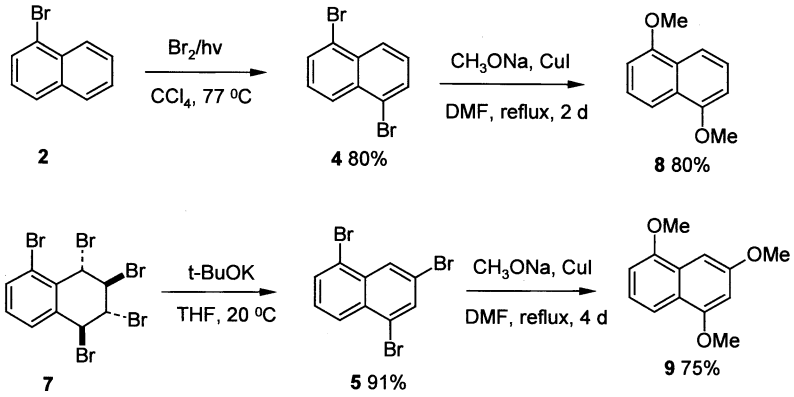
Exhaustive photobromination of 1-BN in refluxing CCl_4 in an internal type irradiation produces a high yield synthesis of 1,5-DBN **4**. The reaction mixture yielded 1,5-DBN **4** and 1,3,5-tribromonaphthalene (1,3,5-TBN, **5**) in a ratio of 92:8 (entry 8). Fractional crystallization gave pure 1,5-DBN **4** in 80% yield (Scheme 1).

1,5-DBN **4** may be formed either by direct electrophilic substitution of 1-BN **2** or by elimination of HBr and Br_2 from the addition products **6** and **7**. In order to test the second possibility, the pentabromides were heated at reflux in CCl_4 in the dark for 7 days. However we did not observe any dehydrobromination and debromination. However, externally visible light irradiation of pentabromides **6** or **7** in CCl_4 resulted in formation of 1,5-DBN **4**. A plausable mechanism for the formation of 1,5-DBN **4** is rationalized below. We assume that initially a benzylic radical forms at C_1 position where the bromide at C_8 facilitates its leaving due to steric effects of the bromide at C_1. Then Br_2 leaves to form a double bond. The visible light initiates formation of molecular bromine which appears with bromine colour. The formed bromine abstracts a hydrogen atom from the C_5 position to form HBr. The radical species are finally aromatized by elimination of bromine radical (Scheme 2).

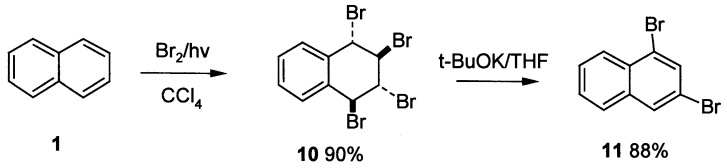
Pentabromides **6** and **7** have the requisite skeletal arrangement and functionality to permit the easy introduction of two double bonds to form naphthalene derivatives. Therefore, we subjected the pentabromide **7** to a dehydrobromination with 2 moles of potassium *tert*-butoxide and isolated 1,3,5-tribromonaphthalene (**5**) as a sole product in a high yield (91%) (Scheme 3). However dehydrobromination of pentabromide **6** under the same conditions resulted in the formation of several di- and tribromonaphthalene derivatives (possible four bromonaphthalene isomers) which we were unable to isolate and identify.

Dehydrobromination of the pentabromides **6** and **7** can lead to six tribromonaphthalene and four dibromnapthalene isomers. The dehydrohalogenation of **7** gave selectively only one product while other isomer (**7**) lead to product multiplicity. We observed the same behaviour for the dehydrobromination of *trans*,*trans*,*trans*-1,2,3,4-tetrabromo-1,2,3,4-tetrahydronaphthalene (**10**), in which 1,3-dibromonaphthalene (**11**) was obtained as a sole product (Scheme 4).[14] We assume that the same configuration of both compounds (**7** and **11**) of bromine atoms may be responsible for the same selectivity.

The ^1H NMR spectrum of compound **5** consists of five characteristic signals which indicate that two of them with singlet are consistent with the position of Br_1 and Br_3. The fact that the resonance of H_4 (8.42, s) and H_8 (8.55, d) shift downfield indicates the position of Br_1 and Br_5 resulting from a Van der Waals interaction between Br_1 and H_8 (or



Scheme 3.



Scheme 4.

Br_5 and H_4). On the other hand, 1,3,5-tribromonaphthalene (**5**) exhibits a similar signal system with that of 1,3-dibromonaphthalene (**11**)[14] due to the same positions of Br_1 and Br_3.

1,5-Dibromonaphthalene is an important intermediate for conversion to further functional groups. For instance, conjugated polymers incorporating naphthalene units through the 1,5-positions have shown potential as electroluminescence materials.[15] Although a few routes[16] were introduced for preparation of 1,5-DBN, they have no preparative importance. It was reported that 1,5-dibromonaphthalene (**4**) was obtained by removing the amino group of 1,5-amino derivatives of naphthalene.[17] Our method has several advantages. It begins with a readily available starting material, it is efficient, and readily applicable to large-scale preparation which opens up an entry to 1,5-disubstituted naphthalene derivatives. Moreover, the solvent and excess bromine are recyclable in this procedure. Finally, pentabromides **6** and **7** and bromonaphthalenes **3**–**5** are starting points for the polyfunctionalization of naphthalenes, due to their ready conversion to other derivatives.

Having obtained 1,5-DBN and 1,3,5-TBN in a high yield, we wished to demonstrate its value as a precursor of other useful compounds. Copper-assisted nucleophilic substitutions of 1,5-DBN and 1,3,5-TBN by methoxide ion easily and efficiently converted into their methoxy derivatives **8** and **9** as a sole products (Scheme 3).

The structure of bromonaphthalenes **4** and **5** rests on ^1H and ^{13}C NMR spectral data of **8** and **9**. The existence of three methoxy groups are in accord with structure **9**. Resonances of H_8 and H_6 are doublets at 6.66 and 7.56 (J=8 Hz), respectively. H_7 appears as a triplet at 7.05 (J=8 Hz). H_2 and H_4 exhibit only *meta* coupling (J_m=2 Hz, δ: 6.35 and 6.96 for H_2 and H_4, respectively) due to the bromine atom attached to C_3. The 13 lines, of which three lines belong to the methoxy groups, are fully in agreement with trimethoxide **9**.

Methoxynaphthalenes have great synthetic importance in several ways, i.e. for 1,5-dimethoxynaphthalene; in the synthesis of other substituted naphthalene derivatives,[18] electron donors,[19] the ring-enlargement with halocarbenes to benzotropone derivatives[20] and natural products.[21] They are usually prepared from hardly accesible 1,5-dihydroxynaphthalene. Therefore, our method appears to be more convenient and practical.

3. Conclusions

Mayo et al proposed that there are at least three primary reactions of bromine with naphthalene, at least two mechanisms of substitution and two mechanisms of addition.[12] We assume that earlier workers did not properly consider and overlooked the influence of the solvent polarity, reaction period and quantity of solvent upon the reaction route. This work revealed that selectivity and reactivity can be controlled and changed by the temperature, amount and type of solvent, reaction time and type of irradiation (i.e. internally or externally).

In summary, the regiospecific ring bromination of 1-bromonaphthalene was efficiently achieved. Efficient and novel syntheses are described for 1,4-DBN **3**, 1,5-DBN **4**, 1,3,5-TBN **5** and pentabromide **7**. We assume that other aromatic benzenoid hydrocarbons can selectively and efficiently be converted to their bromoderivatives under mild conditions without using any catalyst. We are currently extending this methodology to biphenylene, antracene, phenantrene, brominated naphthalenes and quinolines.

4. Experimental

4.1. General

Commercial reagents were purchased from standard Chemical Suppliers and purified to match the reported physical and spectral data. Melting points were determined on a Thomos–Hoover capillary melting points apparatus. Solvents were concentrated at reduced pressure. NMR spectra were recorded on spectrometers operating at 200 and 400 MHz for ^1H and 50 or 100 MHz for ^{13}C NMR. Chemical shifts are given in ppm (δ scale), coupling constants (J) and in Hz. The bromination reaction was conducted in an efficient fume cupboard. 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.

4.2. General procedure for photobromination

All photobrominations were carried out in a borosilicate glass cylindrical vessel with two necks, attached with a dimrot cooler and dropping funnel, in which a tube was immersed (immersion-well type reactor). For irradiation, this tube contained a 150 or 250 W projector lamp, surrounded by a glass tube, cooled by water circulation. The device for absorbing the evolved hydrogen bromide was attached to the side arm.

4.3. Polar brominations of 1-bromonaphthalene

4.3.1. Entry 1. The solution of 1-Bromonaphthalene (**2**) (2.07 g, 10 mmol) in CH_2Cl_2 (35 mL) was cooled to 0°C (ice bath). The device for absorbing the evolved hydrogen

bromide was attached to the reaction flask. The drying tube which was attached to the reaction apparatus was filled with KOH (outside) to absorb releasing HBr and $CaCl_2$ (inside). To the solution which is protected from light was added dropwise Br_2 (1.76 g, 11 mmol) in CH_2Cl_2 (30 mL) over 20 min. HBr was evacuated during the reaction. The reaction content was allowed to stand at −15°C in the freezer. Reaction progress was checked by ^1H NMR and TLC. The bromination was complete in 9 days. The solvent was evaporated and the residue was filtered and purified in short Al_2O_3 column (10 g). ^1H NMR spectroscopy indicated that crude material consisted of 1,4-DBN and 1,5-DBN in a ratio of 90:10, respectively. After careful crystallization of the residue from CH_2Cl_2 (15 mL)/petroleum ether (light, 60 mL) by standing in the freezer (−15°C) during 3–4 days 1,4-DBN 2.57 g (80%) was collected in a pure colourless needles, mp 80–82°C (lit.[4] 83–83.5°C), (Found: C, 42.12; H, 2.18. $C_{10}H_6Br_2$ requires C, 42.00; H, 2.11%); δ_H (250 MHz, $CDCl_3$) 8.80–8.20 (4H, AA′BB′ system, ArH), 8.20 (2H, s, ArH); δ_C (50 MHz, $CDCl_3$) 134.88, 132.06, 130.16, 129.76, 124.84.

4.3.2. Entry 2. To the solution of 1-BN (2.07 g, 10 mmol) in CH_2Cl_2 (7 mL) was added dropwise bromine (1.76 g, 11 mmol) in CH_2Cl_2 (3 mL). The molar ratio of 1-BN/CH_2Cl_2 was taken as 1:15. Further reaction details are identical to the above procedure. The bromination was complete in 24 h to give the same product ratio and isolated amount of 1,4-DBN described in entry 1.

4.3.3. Entry 3. The solution of 1-BN (2.07 g, 10 mmol) in CH_2Cl_2 (7 mL) was cooled to −30°C. To the solution was added initially cooled (−30°C) Br_2 (1.1 equiv., 1.76 g, 11 mmol) in CH_2Cl_2 (3 mL). The ratio of 1-BN–CH_2Cl_2 was 1:15. The reaction mixture was allowed to stand in a freezer at −30°C for 2 days in the dark. It was seen that some of the product recrystallized. After removal of the solvent at reduced pressure, analysis by ^1H NMR spectroscopy indicated that the 1-BN converted to 1,4-DBN completely and formed 1,4-DBN and 1,5-DBN in a ratio 98:2, respectively. Reaction material was dissolved in CH_2Cl_2 (15 mL) and diluted with petroleum ether (60 mL, light 40–60°C) (CH_2Cl_2−PE; 1:4) and allowed to stand in the freezer (−15°C). Fractional crystallization in a few days gave pure 1,4-DBN in a yield of 90% (2.57 g).

The reaction was repeated at −50°C to give the same result except almost all the product crystallized during the reaction.

4.3.4. Entry 4. 1-BN (2.07 g, 10 mmol) was dissolved in $CHCl_3$ (7 mL) in a reaction flask and cooled to 0°C. To the solution was added bromine (1.1 equiv. mol, 1.76 g, 11 mmol) in $CHCl_3$ (3 mL) the reaction mixture was left in the freezer (−15°C). The bromination was complete in 2 days. The solvent was evaporated and the residue was filtered through Al_2O_3 (10 g). Analysis of the residue (2.57 g) by ^1H NMR spectroscopy showed complete conversion and formation of 1,4-DBN and 1,5-DBN in a ratio of 88:12, respectively.

The bromination was repeated by using CCl_4 as a solvent under the reaction conditions described above. However no conversion was observed.

4.4. Photobrominations of 1-bromonaphthalene

4.4.1. Entry 5. 1-BN (2.07 g, 10 mmol) was dissolved in CCl_4 (35 mL) in a photochemical apparatus (60 mL) and the solution cooled to −30°C. A solution of Br_2 (4.0 g, 25 mmol) in CCl_4 (15 mL) was added dropwise over 15 min to the magnetically stirred solution which was irradiated with a sun lamp (250 W projector lamp). After the reaction mixture was irradiated for 45 min, the solvent and excess bromine were removed in vacuo (below 5°C). ^1H NMR analysis of the residue indicated formation of pentabromide **6**, pentabromide **7** and 1,5-DBN **4** in a ratio of 14:76:10. Recrystallization from CH_2Cl_2–hexane (1:1, 30 mL) by allowing the mixture to stand overnight in the fridge afforded 2.1 g pentabromide **7** as colourless crystals, mp 96°C. The recrystallization procedure was repeated for the mother liquor diluted with hexane (10 mL) at frezeer (−15°C). Totally 3.0 g, (56%) of pentabromide **7** was collected. After removing the solvent, crude mixture (3.25 g) was chromatographed on silica gel (250 g), eluted with benzene–hexane (5:95) to give 1,5-DBN (229 mg, 8%), pentabromide **7** (384 mg, 7%; total yield: 3.384 g, 63%), a mixture of pentabromides **6** and **7** (1.98 g) and pure pentabromide **6** (527 mg, 10%) which was crystallized from CH_2Cl_2–hexane (1:1, 30 mL) as a colourless solid, mp 128°C.

Pentabromide ***6***. Colourless solid; (Found: C, 75.72; H, 22.78. $C_{10}H_7Br_5$ requires C, 75.86; H, 22.81%); ν_{max} (KBr) 3052, 3042, 2954, 2951, 1560, 1452, 1113, 896, 806, 768, 726; δ_H (200 MHz, $CDCl_3$) 7.86 (1H, d, J=8.3 Hz, C-8), 7.65 (1H, d, J=8.3 Hz, C-6), 7.33 (1H, t, J=8.3 Hz, C-7), 5.98 (1H, d br, J=2.5 Hz), 5.82 (1H, d, J=8.3 Hz), 5.33 (1H, t, J=2.5 Hz), 4.8 (1H, dt, J=8.3, 2.5 Hz); δ_C (50 MHz, $CDCl_3$) 137.34, 135.21, 134.51, 132.93, 132.07, 126.34, 57.07, 53.37, 52.93, 47.94.

Pentabromide ***7***. Colourless solid; (Found: C, 75.60; H, 22.72. $C_{10}H_7Br_5$ requires C, 75.86; H, 22.81%); ν_{max} (KBr) 3040, 2954, 2949, 1562, 1450, 1113, 896, 816, 768, 720; δ_H (200 MHz, $CDCl_3$) 7.68 (1H, d, J=7.9 Hz, C-8), 7.58 (1H, d, J=7.9 Hz, C-6), 7.26 (1H, t, J=7.9 Hz, C-7), 5.75 (1H, d, J=3.2 Hz), 5.59 (1H, d, J=9.3 Hz), 5.37 (1H, dd, J=9.3, 3.2 Hz), 4.9 (1H, t, J=3.2 Hz); δ_C (50 MHz, $CDCl_3$) 138.29, 135.87, 133.81, 133.37, 133.23, 127.59, 57.83, 55.03, 54.55, 51.50.

4.4.2. Entry 6. Magnetically stirred solution of 1-BN (1.04 g, 5 mmol) in CCl_4 (25 mL) cooled to 0°C in the photochemical apparatus (45 mL). A solution of Br_2 (2.0 g, 12.5 mmol) in CCl_4 (10 mL) was added dropwise within 15 min. The reaction mixture was internally irradiated with 150 W projector lamp for ca. 70 min. The reaction progress was monitored by ^1H NMR. After the reaction the excess bromine and solvent were completely evaporated by vacuo. The residue was dissolved in $CHCl_3$ and filtered through a short Al_2O_3 (10.0 g) column using hexane. ^1H NMR analysis of the reaction mixture (2.0 g) revealed products **5**–**7** in a ratio 30:18:52, respectively.

4.4.3. Entry 7. 1-BN (2.07 g, 10 mmol) was dissolved in CCl_4 (40 mL) in photochemical apparatus (60 mL). To the magnetically stirred solution was added bromine (3.98 g, 25 mmol) in CCl_4 (10 mL) within 30 min at 30°C while irradiating by projector lamp (250 W). The reaction progress was monitored by ^1H NMR. After the completion of reaction (total 2 h) and the removing the solvent, the ^1H NMR analysis indicated formation of 1,5-DBN and the pentabromide **7** in a ratio of 69:31, respectively.

4.4.4. Entry 8. To the magnetically stirred solution of 1-BN (1.33 g, 7.5 mmol) in CCl_4 (25 mL) in a photochemical apparatus (45 cm^3) at 0°C (ice bath) was added bromine (1.8 g, 11.25 mmol) in CCl_4 (15 mL) within 1 h while irradiating by a projector lamp (250 W). The reaction progress was monitored by ^1H NMR. Reaction mixture was totally irradiated for 2.5 h. After removing the solvent and excess bromine, the residue was filtered on a short Al_2O_3 column (10 g) eluted with hexane. The ^1H NMR analysis of the residue indicated the formation of 1,5-DBN and 1,3,5-TBN in a ratio of 92:8. Repeated crystallization of the reaction mixture from CH_2Cl_2–petroleum ether (1:2, 100 mL) in the freezer at (−15°C) in 3 days gave 1,5-DBN (1.47 g, 80%) in a pure form, (pale yellow crystals, mp 129–130°C (lit.[22] 131°C); ν_{max} (KBr) 3060, 1795, 1488, 1322, 1189, 900, 701; δ_H (250 MHz, $CDCl_3$) 8.24 (2H, d, J=8.0 Hz, ArH), 7.84 (2H, d, Hz, ArH), 7.46 (2H, t, J=8.0 ArH); δ_C (50 MHz, $CDCl_3$) 135.07, 132.89, 129.39, 129.31, 125.02.

4.5. Bromination of naphthalene

Naphthalene was treated with one and two equiv. of bromine in CH_2Cl_2 at −30°C in a separate reaction flask. Substrate–solvent molar ratio was taken in a ratio of 1:15. Reaction of naphthalene with one equiv. bromine was completed in 2 days to give 1-BN and 1,4-DBN **3** in ratio of 90:5, respectively, besides unreacted naphthalene 5% (conversion 95%), as assigned ^1H NMR spectroscopy. The reaction of naphthalene with 2 equiv. of bromine was complete in 3 days. After removing the solvent, precipitated residue was recrystallized from CH_2Cl_2–petroleum ether. 1,4-Dibromonaphthalene (**3**) was obtained in a yield of 90%. Reaction conditions and crystallization procedure were the same as described in entry 3.

4.6. Heating pentabromides 6 and 7

A solution of a mixture of pentabromides **6** and **7** (120 mg, 0.225 mol) in CCl_4 (7 mL) in a sealed glass-tube was heated at 70°C for 7 days in the dark. ^1H NMR analysis of the reaction mixture indicated that pentabromides **6** and **7** remained without change.

4.7. Irradiation of pentabromides 6 and 7

A mixture of pentabromide **6** and **7** (527 mg, 1 mmol) was dissolved in CCl_4 (30 mL) in a 50 mL of reaction flask. To a magnetically stirred solution at reflux temperature of CCl_4 was irradiated externally with projector lamp (250 W) for 2 h. The reaction progress was monitored by TLC or ^1H NMR. Evolving hydrogen bromide was observed and bromine appeared during reaction. After completion of the conversion, the solvent was removed by vacuo. The precipitate was filtered by a short silica gel (5 g) column by eluting petroleum ether. ^1H NMR analysis of the crude material indicated existence of 1,5-DBN **4** and 1,3,5-TBN **5** in a ratio of 89:11, respectively.

4.7.1. Preparation of 1,3,5-tribromonaphthalene (5). Pentabromide **7** (4.0 g, 7.6 mmol) in dry THF (25 mL) was treated with potassium *tert*-butoxide (4.154 g, 18.4 mmol, 2.5 equiv.) in dry THF (25 mL). The mixture was stirred at room temperature overnight. After worked up (3×50 mL ether), dried and evaporated, the residue was filtered by using a short silica gel (10 g) column eluting with light petroleum ether. 1,3,5-Tribromonaphthalene (5) was obtained and the product was recrystallized from chloroform–light petroleum in a yield of 91% (2.56 g) as a colourless solid, mp 107–108°C; (Found: C, 32.72; H, 1.18. $C_{10}H_5Br_3$ requires C, 32.91; H, 1.35%); ν_{max} (KBr) 3073, 1606, 1479, 1353, 1189, 1079, 877, 819; δ_H (400 MHz, $CDCl_3$) 8.42 (1H, s, H_4), 8.19 (1H, d, J=8.0 Hz, H_8), 7.95 (1H, s, J=1.6 Hz, H_2), 7.85 (1H, d, J=8.0 Hz, H_6), 7.43 (1H, t, J=8.0 Hz, H_7); δ_C (100 MHz, $CDCl_3$) 134.06, 134.02, 132.26, 132.14, 129.99, 128.15, 127.73, 124.14, 122.20; m/z (CI, NH_3) 367 (95 MH^+), 286 (100), 236 (15), 206 (25), 69 (15%).

Same dehydrobromination procedure was repeated for pentabromide **6**. A product mixture was obtained, which unable to isolate and to identify.

4.7.2. Preparation of 1,5-dimethoxynaphthalene (8). Freshly cut sodium (4.84 g, 210.4 mmol) was added under nitrogen gas to dry methanol (30 mL). When dissolution was complete, the warm solution was diluted with dry dimethylformamide (DMF, 60 mL) followed by the addition of vacuum-dried cuprous iodide (960 mg, 5.0 mmol). After dissolution, 1,5-DBN **4** (2.32 g, 8.32 mmol) in dry DMF (30 mL) was added. The reaction mixture was stirred magnetically for 2 days under a nitrogen gas atmosphere at reflux (ca. 90°C). After cooling to room temperature, H_2O (100 mL) and diethyl ether (100 mL) were added to the reaction mixture. The organic layer was separated, washed with H_2O (3×35 mL), and dried over $CaCl_2$. The solvent was removed and the product was passed through a short column packed with silica gel (15 g) with eluting petroleum ether. Recrystallization from a mixture of CH_2Cl_2 and petroleum ether (bp 40–50°C) in the refrigerator (5°C) yielded 1,5-dimethoxynaphthalene (**8**) (1.8 g, 80%) as colourless needles, mp 180–181°C (lit.[23] 182–184°C); (Found: C, 76.67; H, 6.60. $C_{12}H_{12}O_2$ requires C, 76.57; H, 6.43%); δ_H (200 MHz, $CDCl_3$) 4.01 (6H, s, OCH_3), 6.86 (2H, d, J=8.0 Hz, C-2,6), 7.40 (2H, t, J=8.0 Hz, C-3,7), 7.86 (2H, d, J=8.0 Hz, C-4,8); δ_C (100 MHz, $CDCl_3$) 57.54, 106.57, 116.22, 127.15, 128.65, 157.27; m/z (CI, NH_3) 189 (100 MH^+), 173 (50), 145 (10), 115 (75), 102 (25%).

4.7.3. Preparation of 1,3,5-trimethoxynaphthalene (9). Freshly cut sodium (0.74 g, 32 mmol) was added to dry methanol (30 mL) under nitrogen gas. After complete dissolution, dry dimethylformamide (DMF, 30 mL) was added, followed by vacuum dried cuprous iodide (0.52 g, 2.7 mmol) and 1,3,5-TBN **5** (1.0 g, 2.7 mmol) in dry DMF

(50 mL). The reaction mixture was magnetically stirred under a nitrogen-gas atmosphere at reflux (ca. 90°C) for 4 days. The reaction progress was monitored by TLC. After cooling to room temperature, to the reaction mixture was added H_2O (60 mL) and diethyl ether (120 mL). The organic layer was washed with H_2O (3×50 mL), and dried over $MgSO_4$. The solvent was removed and the crude product was passed through short silica gel column. Recrystallization of the sample from CH_2Cl_2–petroleum ether (bp 40–50°C) (1:1, 10 mL) in the freezer yielded 1,3,5-TMN **9** (450 mg, 75%) as colourless needles; mp 89–90°C; (Found: C, 71.60; H, 6.70. $C_{13}H_{14}O_3$ requires C, 71.54; H, 6.47%); ν_{max} (KBr) 3060, 2938, 2830, 1594, 1403, 1267, 1155, 1024, 865; δ_H (400 MHz, $CDCl_3$) 3.75 (3H, s, OCH_3), 3.78 (3H, s, OCH_3), 3.81 (3H, s, OCH_3), 6.35 (1H, d, J=2.0 Hz), 6.66 (1H, d, J=8.0 Hz), 6.96 (1H, d, J=2.0 Hz), 7.05 (1H, t, J=8.0 Hz), 7.56 (1H, d, J=8.0 Hz); δ_C (100 MHz, $CDCl_3$) 56.12, 56.25, 56.32, 93.38, 99.16, 106.38, 115.46, 123.87, 126.33, 128.19, 155.80, 157.93, 159.36.

Acknowledgements

The authors are indebted to Gaziosmanpasa University, Department of Chemistry and the University Research Foundation (Grant Nr: 98/31) for financial support.

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