Bromination of Naphthalene. Preparation of 1,3-Dibromonaphthalene†

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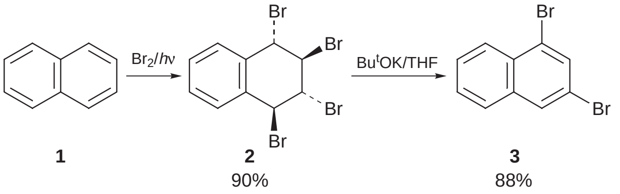
Photobromination of naphthalene with molecular bromine gives only one stereoisomer α,2β,3α,4β-tetrabromo-1,2,3,4-tetrahydronaphthalene (yield 90%); dehydrobromination of which results in the formation of 1,3-dibromonaphthalene in 88% yield.

Dibromonaphthalenes are important key intermediates in the industrial and laboratory preparation for hydroxy, amine, ether, nitrile, alkyl, organic acid and organometallic derivatives of naphthalenes. Bromonaphthalenes have become increasingly important as triplet excitation acceptors with useful phosphorescence properties.[1] Haloderivatives of naphthalene have attracted much attention in view of medicinal interest.[2] Despite their synthetic importance, the preparation of dibromo substituted naphthalene derivatives are very limited in the literature. For this reason interest in our laboratory has been focused on the bromination reaction of naphthalene and synthesis of dibromosubstituted naphthalene derivatives.[3]

Some attempts have previously been made to brominate of naphthalene and Orndorff and Moyer[4] prepared a crystalline naphthalene tetrabromide in 3% yield while another study increased the yield to 30%.[5] Mayo and Hardy[6] investigated the bromination of naphthalene in several solvents to distinguish between addition and substitution reactions in terms of polar and free radical mechanisms. We now describe an efficient bromination of naphthalene and a new and quick method for the synthesis for 1,3-dibromonaphthalene.

An excess of bromine was added to a solution of naphthalene in CCl_4 while irradiating using an internal type irradiation (150 W projector lamp) photochemical reaction apparatus below 10°C (Scheme 1). After removing the solvent, the reaction mixture was directly subjected to crystallization from dichloromethane–hexane. We isolated tetrabromide **2** in pure form in a high yield *ca.* 90%.



Scheme 1

Proton and carbon NMR studies of the tetrabromide **2** indicated the formation of a highly symmetrical compound. Aliphatic and aromatic protons show two AA′BB′ systems in the ^{1}H NMR spectrum of compound **2**. The ^{13}C NMR resonances of the CHBr carbons, olefinic CH carbons and quaternary carbons are at the expected shifts. The tetrabromide was assigned by X-ray analysis to be α,2β,3α,4β-tetrabromo-1,2,3,4-tetrahydronaphthalene.[7]

Mayo and Hardy[6] proposed that there are at least three primary reactions of bromine with naphthalene, at least two mechanisms of substitution and at least two mechanisms of addition. In earlier studies, in photobromination of naphthalene using a sun lamp 1-bromonaphthalene was observed as a polar addition product as well as tetrabromide as a radical addition product. However, the reactions were performed under external light irradiation which requires longer reaction time during which the polar addition product, *i.e.* 1-bromonaphthalene, and some observation of configuration isomerization among tetrabromostereoisomers was observed. Also the reaction conditions can led to formation of the secondary products. We realized that using internal type irradiation provides a very high density of light which leads to very effective addition a shorter time. Therefore, we assume that the reaction completely place takes by a radical mechanism in internal type photobromination. High bromine concentration is also important for rapid addition and to obtain only one stereoisomer (tetrabromide **2**) instead of a stereoisomeric mixture. We achieved the best yield of tetrabromide **2** using a molar ratio of 1:4:15 naphthalene, bromine and solvent, respectively.

After successful synthesis of the desired tetrabromide, the double dehydrobromination of **2** achieved efficiently using potassium *tert*-butoxide. With 2 mol potassium *tert*-butoxide we isolated 1,3-dibromonaphthalene **3** as the sole product in a yield of 88% (Scheme 1). Structural assignment of **3** was achieved by means of proton and carbon NMR which indicated its unsymmetrical structure.

Dehydrobromination of the tetrabromide can lead to three dibromonaphthalene isomers: 1,4-, 2,3- and 1,3-dibromonaphthalenes, of which the only 1,3-dibromo structure is unsymmetrical. The NMR spectra are thus consistent with the 1,3-dibromo compound. The fact that the resonance of H^8 (δ 8.18) shifts downfield indicates the position of Br^1, the downfield shift resulting from a van der Waals interaction between Br^1 and H^8. In addition, two resonance signals with small a constant coupling ($J_{23} = 1.9$ Hz, *meta* coupling) are consistent with the 1.3-bromo structure. Four singlets and six doublets in the ^{13}C NMR spectrum in the olefinic region are also in agreement with the proposed unsymmetrical structure.

It was reported that 1,3-dibromonaphthalene was obtained by removing of the amino group by diazotization from 1-amino-2,4-bromonaphthalene,[8] as well as some modifications of this method.[9]

The presently described synthesis of **3** offers several advantages over previous methods. For instance, it begins with a readily available starting material and is efficient and readily applicable to large-scale preparation which opens up an entry to 1,3-disubstituted naphthalene derivatives. After reaction, the solvent and excess bromine are recyclable in this procedure. Finally, tetrabromide **2** and dibromide **3** are starting points for the polyfunctionalization of naphthalene, due to their ready conversion to other derivatives.

Experimental

Commercial reagents were purchased from standard chemical suppliers and purified to match the reported physical and spectral data.

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Melting points were determined on a Thomas–Hoover capillary melting points apparatus. Solvents were concentrated at reduced pressure. NMR spectra were recorded on a Varian-Gemini 2000 spectrometer at 200 MHz for ^{1}H and 50 MHz for ^{13}C NMR. Irradiations were carried out in an immersion-well reactor with an internal light source by using a 24 V and 150 W projector lamp. The bromination reaction was conducted in an efficient fume cupboard.

Bromination of Naphthalene.—As the result of several experiments, we recommend the following procedure for the bromination of naphthalene. A solution of naphthalene (1.92 g, 15 mmol) in CCl_4 (30 cm^3) in an internal type photochemical reaction apparatus (cylindrical immersion-well reactor, 50 cm^3) was cooled to 0 °C (ice bath). The device for absorbing the evolved hydrogen bromide 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 (9.6 g, 60 mmol, 4 equiv.) on CCl_4 (14 cm^3) was added dropwise during 1 h. The reaction mixture was irradiated for 1.5 h. Reaction progress was monitored by ^{1}H NMR spectroscopy and TLC. It was seen that most of reaction product **2** precipitated during the reaction. After completion of the addition, the solvent and excess bromine were removed *in vacuo* (below 15 °C). The precipitated reaction product was recrystallised from CH_2Cl_2–hexane in a refrigerator. 1,2,3,4-tetrabromo-1,2,3,4-tetrahydronaphthalene **2** was obtained in a yield of 90% (6.04 g): mp 104–105 °C (decomp); δ_H($CDCl_3$) 7.61–7.43 (AA′BB′, 4H, aryl H), 5.71 (A part of AA′XX′ system, 2 H, CHBr), 5.00 (X part of AA′XX′ system); δ_C($CDCl_3$) 133.38, 130.59, 130.17, 54.54, 50.71 (Found: C, 27.22; H, 1.73, $C_{10}H_8Br_4$ requires C, 26.82; H, 1.8%).

Preparation of 1,3-*Dibromonaphthalene* **3**.—Tetrabromide **3** (5.0 g, 11.17 mmol) in dry THF (50 ml) was treated with potassium *tert*-butoxide (3.19 g, 28 mmol) in dry THF (30 ml). The mixture was stirred at room temperature overnight. After working up (3 × 100 ml ether), drying and removing of the solvent, the residue was filtered by using a short silica gel (10 g) column eluting with light petroleum (bp = 40–60 °C). 1,3-Dibromonaphthalene was obtained in crystalline form (chloroform–light petroleum) in a yield of 88% (2.81 g): mp 63–64 °C (lit.,[9] 64 °C from EtOH). δ_H ($CDCl_3$) 8.18 (d, $J_{78} = 7.4$ Hz, 1H, H^7), 7.97 (m, 1H, H^4), 7.88 (d, $J_{24} = 1.9$ Hz, 1H, H^2), 7.73 (dd, $J_{56} = 6.8$, $J_{57} = 2$ Hz. 1H, H^5), 7.64–7.50 (m, 2H, H^6, H^7); δ_C ($CDCl_3$) 137.13 (s). 134.50 (d), 132.63 (s), 131.89 (d), 129.73 (d), 129.63 (d), 129.44 (d), 129.21 (d), 125.51 (s), 120.89 (s) (Found, C, 42.38; H, 2.17. $C_{10}H_6Br_2$ requires C, 42.00; H, 2.11%).

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