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RESEARCH ARTICLE

Alternative pathway to brominate 2,1,3-benzothiadiazole: Preparation of 4,7-dibromobenzo[*c*]-1,2,5-thiadiazole via N-bromosuccinimide

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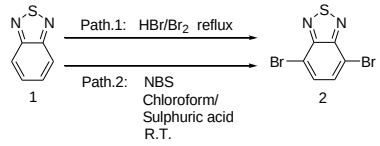
Graphical abstract



Abstract

This present work reports an alternative pathway to brominate the 2,1,3-benzothiadiazole (BT). The conventional method to brominate a phenyl/benzene ring is to use the bromine solution (Br_2) together with hydrobromic acid (HBr). This is because the phenyl/benzene rings exhibit high stability due to the delocalized π-conjugation, which the substitution of bromines into the rings can only be done through a strong bromination source, e.g. the Br_2/HBr. Besides that, there is another bromine source, known as N-bromosuccinimide (NBS), which is normally used for bromination of thiophene rings but not the phenyl/benzene ring. The bromination ability of NBS is relatively mild than the Br_2/HBr. Herein, this research shows that bromination of benzene/phenyl ring through NBS is possible under a drastic condition that involved the usage of 96% concentrated sulphuric acid and chloroform at room temperature. This alternative pathway can be used when there is limit access to the Br_2 and bromination through NBS is relatively less dangerous than the Br_2/HBr.

Keywords: Bromination, 2,1,3-benzothiadiazole, N-bromosuccinimide, HBr/Br_2

INTRODUCTION

The bromination of 2,1,3-benzothiadiazole (BT) was first introduced by Pilgram and co-workers in 1970. It was found that bromine successively substituted into the BT at 4th and 7th positions. This pioneer work was done by dropwise addition of bromine solution into a solution mixture that contains BT in 47% HBr at 126-130ºC. With the aid of gas-liquid chromatography, Pilgram group found that 4-bromo-BT was formed in the first half period of reaction, after which 4,7-dibromo-BT began to form (Pilgram *et al.*, 1970). Nowadays, this method still remains as the most common method for researchers to brominate the BT unit (Blouin *et al.*, 2008; Helgesen *et al.*, 2009; Westrup *et al.*, 2016).

The electrophilic aromatic bromination is commonly done by Br_2/HBr system, which is the most commonly used bromine source by researchers (Beaupré & Leclerc, 2013; Blouin *et al.*, 2008; Bundgaard & Krebs, 2007; Kutkan *et al.*, 2016). However, there are several intrinsic drawbacks for this system. First, the use of halogens under harsh reaction conditions are considered as toxic, corrosive, and hazardous approach for bromination (Li *et al.*, 2016; Mendoza *et al.*, 2016). Next, the formation of equimolar HBr as the by-product result in the dissipation of the half amount of bromine atom from Br_2 (Li *et al.*, 2016).

The development of mild and effective reagents and reaction conditions are highly welcomed in organic synthesis as they are less polluting, inexpensive, and easy to obtain, and more environmental friendly. Recently, scientists have modified and discovered other alternative bromine source to replace the Br_2/HBr system. For example, bromination can be done by using N-bromosuccinimide (NBS) (Bose & Mal, 2014; Wang *et al.*, 2012; Yadav *et al.*, 2004), organic ammonium tribromides, such as tetrabutyl ammonium tribromide (Chaudhuri *et al.*, 1998), alkylammonium bromide(Mendoza *et al.*, 2016), Br_2/HNO_3(Andrievsky *et al.*, 2014), and etcetera. Moreover, some "green" bromination methods also been introduced, such as the photocatalytic bromination which involved the usage of microporous organic polymers (MOPs)(Li *et al.*, 2016) and the oxidative halogenation using catalysts with oxygen or H_2O_2 (Podgoršek *et al.*, 2009; Yonehara *et al.*, 2011). Besides that, some researchers applied different metal-based catalysts in bromination, such as copper (France *et al.*, 2005; Hao & Liu, 2015; Xu *et al.*, 2017; Yang *et al.*, 2009), iron(Wang *et al.*, 2014), vanadium(Podgoršek *et al.*, 2009), gold (Mo *et al.*, 2010), indium (Moriya *et al.*, 2012), and etcetera. However, some of the catalysts are difficult to obtain, highly toxic, and expensive.

Generally, NBS is used as the bromine source for the 5-membered-ring compounds such as thiophene (Choi *et al.*, 2015; Helgesen *et al.*, 2009; Zhang, 2004; Zhou *et al.*, 2015). Strong acidic condition is essential to generate the elemental bromonium ion (Br^+) from the NBS. This is because adequate amount of hydrogen ions (H+) is needed to protonated the NBS in order to release the high electrophilic Br^+. The mechanism scheme is clearly shown in the following **Figure 1** (Eguchi *et al.*, 1994).

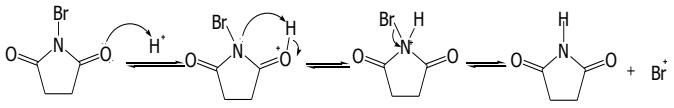


Fig. 1 Protonation of NBS and generation of Br^+ (Eguchi *et al.*, 1994).

There are several papers reported in 19th century about the bromination of benzene/phenyl rings using NBS(Duan *et al.*, 1999; Eguchi *et al.*, 1994; Lambert *et al.*, 1965). In 2005, Brown and co-workers (2005) have successfully brominated an aromatic compound, isoquinoline by using NBS in concentrated sulphuric acid, H_2SO_4. According to this report, 5-bromoisoquinoline was synthesized through dropwise addition of the isoquinoline into concentrated sulphuric acid under nitrogen condition. No reflux was involved and the highest temperature throughout the entire experiment did not exceed 30°C. Moreover, dry ice-acetone bath was applied during addition of NBS to the reaction mixture (Brown & Gouliaev, 2005).

In 2009, there was a research paper reported the usage of NBS to brominate 4-(5-octylthiophene-2-yl)benzo[c][1,2,5]thiadiazole in DMF/chloroform solvent. However, this reaction was done at 60°C for 2 days. The reaction is time consuming and the solvent DMF used is classified as highly harmful solvent (Sonar *et al.*, 2009). Hence, some modification is done in this research to replace the harmful DMF and shorten the reaction time.

EXPERIMENTAL

Materials

The 2,1,3-benzothiadiazole, N-bromosuccinimide, toluene, chloroform, hexane, sulphuric acid were purchased from Sigma-Aldrich while the hydrobromic acid, HBr and bromine water, Br_2 were purchased from R&M chemicals. Sodium thiosulphate, sodium carbonate, sodium hydrocide, sodium chloride were purchased from QRëC™.

Synthesis Procedures

The schematic diagram shown in Figure 3 summarized the two different pathway to brominate the BT **(1)**.

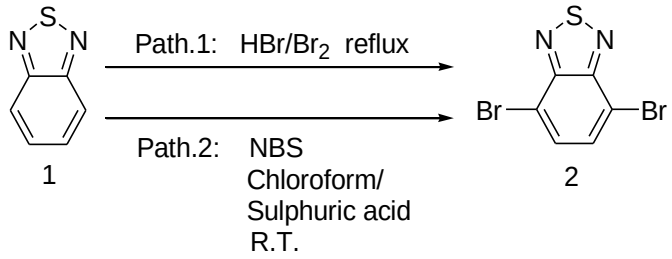


Fig. 3 Schematic diagram for bromination of **(1)** via two different pathways.

Pathway 1: The conventional method

Synthesis of 4,7- dibromobenzo[*c*][1,2,5]thiadiazole **(2)** was obtained from a modified procedure by Pilgram et al., 1970 (Pilgram *et al.*, 1970).

A mixture of 2,1,3- benzothiadiazole, BT (20.00 g, 147 mmol) and hydrobromic acid HBr (48 %, 60 ml) was heated under N_2 to 100 °C with stirring before Br_2 (22.60 ml, 440 mmol) was added dropwise over a period of one hour. When product started precipitating, further amount of HBr (40 ml) was added to facilitate stirring and allowed the mixture to stir under reflux for further 2 hours. The hot reaction mixture was filtered and the precipitate was washed with distilled water for several times. Then the filtrate was cooled to precipitate further product, filtered and the solid was washed with water. The filtrate was poured onto a solution of sodium thiosulphate $Na_2S_2O_3$ (10 % w/w) to destroy the remaining bromine. The obtained orange solid product was recrystallised from ethanol and then recrystallised from a mixture of chloroform/hexane (2:1) to obtain 4,7- dibromo- 2,1,3-benzothiadiazole (2) as pale yellow solid (needle- like micro-crystals). Yield: 39.5 g (γ=91 %)

Pathway 2: The alternative method

2,1,3-benzothiadiazole, BT **(1)** (5.00 g, 36.72 mmol, 1.00 equiv.) was added into a 250ml, 3-necked, round bottom flask with a 1-cm Teflon-coated magnetic stir-bar and connected to a nitrogen inlet. After that, 100 mL of 96% concentrated sulphuric acid were added, followed by 100 mL of chloroform. The solution mixture was stirred for 20 minutes at room temperature in order to uniformly dissolve the solid-formed BT.

Next, N-bromosuccinimide, NBS (14.38 g, 80.78 mmol, 2.20 equiv. of **1**) was added into the stirring solution mixture in several small portions, the next portion was only added after the previous portion had completely dissolved. The oxygen was removed by vacuum pump for a few minutes, before the nitrogen gas was inputted through a surgical needle which traversed crossed a rubber stopper from a nitrogen-filled balloon. The set-up for this bromination was shown in **Figure 2**.

Fig. 2 Set-up for the bromination.

After that, the reaction mixture was stirred at room temperature for 18 hours. After 18 hours, 20 g of Na_2CO_3 was added into the reaction mixture in many small portions, the subsequence portion was only added after the carbon dioxide formed by the former portion had completely evolved from the solution mixture. (*Be careful about the formation of massive carbon dioxide gas.) After that, the resulting solution was transferred to a 500 mL Erlenmeyer flask which placed in ice-bath. 300 mL of ice-cold distilled water was dropwisely added into the cold solution mixture while stirred with a glass rod. (*Addition of huge amount of distilled water in one input will result in the sudden increased in temperature and produced massive gas).

The resulting white suspension was transferred to a 1 L separating funnel, and extracted with three 200 mL portions of toluene. Another 200 mL of toluene was added into the Erlenmeyer flask to wash out the remaining white precipitate. After that, everything was transferred to the 500 mL separating funnel, and washed with another three 150 mL distilled water. The collected organic layers were combined and transferred to another 1 L separating funnel, the layer was washed with three 150 mL of 1 M sodium hydroxide, NaOH solution and three 100 mL of distilled water. The washed organic layer was transferred to a beaker, stirred and dried over 4 g of sodium carbonate, Na_2SO_4 for 15 minutes. The resulting mixture was filtered and the remaining toluene solvent was removed by rotatory evaporator. The white cotton-liked solid was obtained and recrystallized from chloroform: hexane (2:1) solution. The resulting off-white crystallize solid, the compound **(2)** (10.29 g, 95.3%) was tested for its melting point and purity. Finally, it was characterized by FTIR, ^{1}H-NMR, and ^{13}C-NMR.

RESULTS AND DISCUSSION

First of all, the reaction mechanism for the bromination of **(iii)** was illustrated in Figure 4. The **(2)** was obtained through a series of electrophilic aromatic substitution of bromonium ions, Br^+. The Br^+ cations were selectively substituted at the 4th- and 7th- positions of **(1)** due to the activating feature of the imine groups present in the compound.

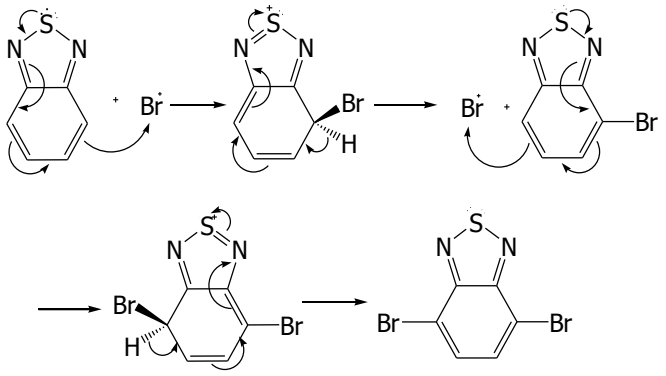


Fig. 4 The reaction mechanism for bromination of **(1)**.

Although the appearance of product **(2)** synthesized via the alternative method (Pathway 2) is slightly different from the product obtained through conventional method (Pathway 1), both products were analyzed and characterized by FTIR, ^{1}H-NMR and ^{13}C-NMR. The result obtained was compared and explained in this section.

Melting Point (MP)
Pathway 1: 186-191ºC
Pathway 2: 184-186 ºC
The MP range of (2) from pathway 2 is slightly lower than pathway 1 but both shared the same MP at 186ºC.

Fourier Transform Infrared (FTIR)
Pathway 1 (cm^{-1}): 3078, 3033, 1661, 1595, 1498, 1475, 1375, 1309, 1272, 1183, 1121, 1080, 1019, 934, 873, 842, 824, 793, 743, 730, 705, 686, 656, 632, 615, 585
Pathway 2 (cm^{-1}): 3078, 3048, 1652, 1587, 1498, 1476, 1374, 1309, 1273, 1183, 1141, 1079, 1018, 935, 873, 842, 824, 796, 743, 705, 617, 609, 585

The FTIR bands obtained from both products were almost similar to each other. The bands higher than 3000 cm^{-1} belong to the sp^2 hybridized C-H stretching vibration while the bands located in the range of 1600-1400 cm^{-1} represented the aromatic C=C stretching vibration. Band located approx. 1650 cm^{-1} indicates the present of C=N group. Bands presented in the range of 1342-1266 cm^{-1} and 1250-1020 cm^{-1} denoted the present of C-N stretching, while 1080-1000 cm^{-1} indicated the present of bromo-substituted aromatic rings. Finally, bands present in the range of 690-515 cm^{-1} represent the present of C-Br stretching. The comparison FTIR spectra of **(1)** and **(2)** were shown in Figure 5.

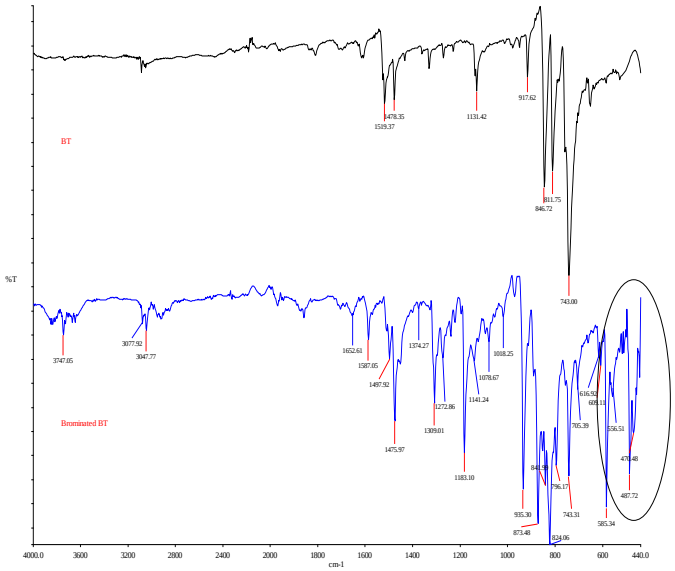


Fig. 5 The FTIR spectra of precursor **(1)** (black) and product **(2)** (blue) obtained from the alternative pathway (Pathway 2).

Nuclear Magnetic Resournace (NMR)
Pathway 1:
^{1}H-NMR (500MHz, $CDCl_3$, ppm) δ 7.74 (s, 2H)
^{13}C-NMR (500MHz, $CDCl_3$, ppm) δ 153.1, 132.4, 114.0

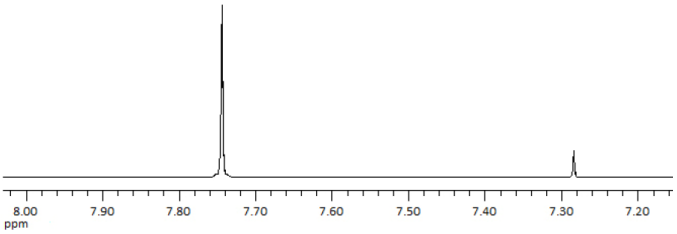


Fig. 6 The ^{1}H-NMR of the brominated product **(2)** synthesized from pathway 1.

Pathway 2:
^{1}H-NMR (500MHz, $CDCl_3$, ppm) δ 7.73 (s, 2H)
^{13}C-NMR (500MHz, $CDCl_3$, ppm) δ 153.0, 132.4, 113.9

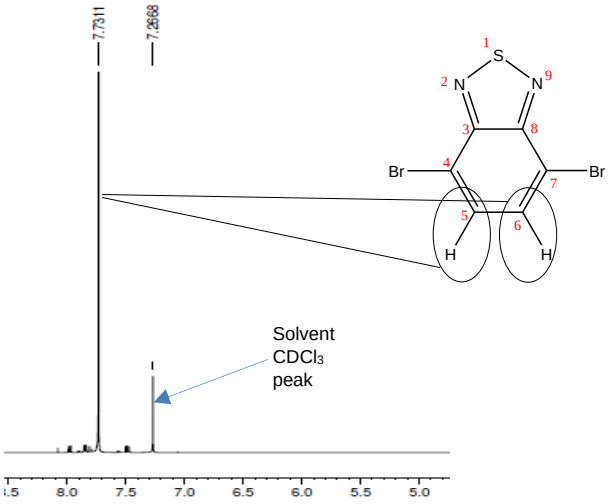


Fig. 7 The ^{1}H-NMR of the brominated product **(2)** synthesized from pathway 2.

The ^{1}H-NMR spectra of (2) obtained from two different pathways as shown in Figure 6 and Figure 7 exhibit similar peaks. Both ^{1}H-NMR spectra displayed a singlet peak at around 7.74 ppm, which corresponds to the two protons located at 5th and 6th positions on the product (2). The peak at 7.27 ppm is the $CDCl_3$ solvent peak. This indicates that the product (2) obtained from the proposed alternative pathway is identical to the brominated product obtain from previously reported method. Hence, pathway 2 is applicable for the bromination of BT **(1)**. NBS is an alternative bromine source for BT bromination.

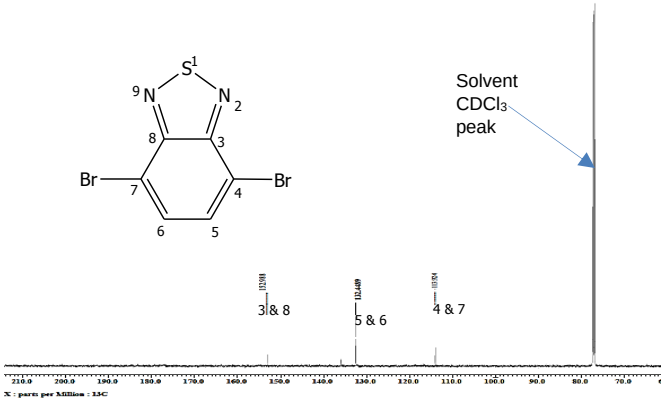


Fig. 8 The ^{13}C-NMR spectrum of brominated product **(2)** synthesized from pathway 2.

Based on the ^{13}C-NMR spectrum shown in Figure 8, the chemical structure of the product (2) obtained through the alternative pathway was further confirmed. The three peaks located at 153.0 ppm, 132.4 ppm, and 113.9 ppm represented the carbon at 3rd- & 8th- positions, 5th- & 6th- positions, and 4th- & 7th- positions of the (7), respectively. The peak presents around 70-80 ppm belongs to the $CDCl_3$ solvent residue signal.

CONCLUSION

2,1,3-Benzothiadiazole is able to brominate at its 4th and 7th position by using NBS in chloroform/96%concentrated sulphuric acid at room temperature under nitrogen conditions instead of applying the conventional method that used Br_2/HBr system.

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