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The Reactions of 3, 7-Dinitrodibenzobromolium Salt with Some Amines

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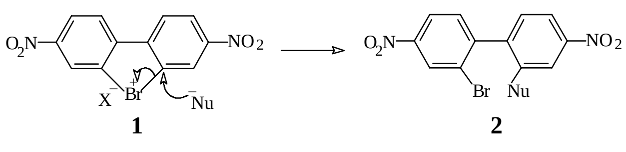
Abstract: The reactions of 3,7-dinitrodibenzobromolium salt with some amines were studied. A reaction mechanism based on the structure of the major product **6** and the minor product **7** was proposed. The reaction was considered to proceed *via* a substituted benzyene intermediate.

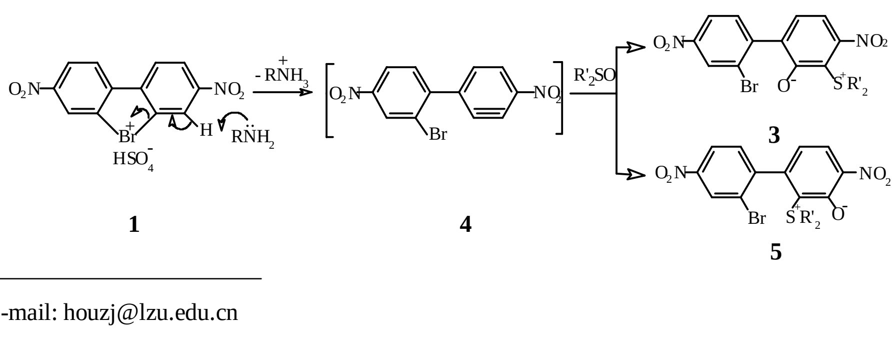
Keywords: 3, 7-Dinitrodibenzobromolium salt, amine, benzyene, reaction mechanism.

We have reported the reaction of 3, 7-dinitrodibenzobromolium salt with various nucleophiles and the formation of the major product **2** was explained to be *via* the nucleophilic attack of the carbon next to the bromide followed by the leaving of the Br^+ group (**Scheme 1**)[1,2]. Later, it was found out that the major product of the reaction between **1** and some sulfoxides in the presence of equal molar of basic nucleophile was 2-sulfoniophenolate **3**. Therefore, a mechanism of the formation of **3** was proposed to be through substituted benzyene **4** as an intermediate (**Scheme 2**)[3]. Since compound **5** which is the regio isomer of **3** was not isolated, we could not confirm the above mechanism.

Scheme 1



Scheme 2



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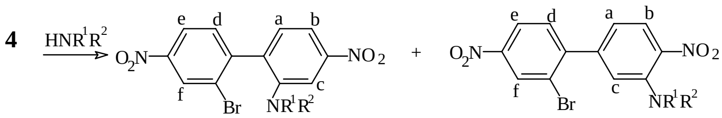
In order to get enough proof for this mechanism, the following reactions were designed and performed. The reason, compound **1** did not give the intermediate **4**, is that the excess amount of the amine was reacted with the intermediate **4** to give the regio isomers **6** and **7** (**Scheme 3**).

The reactions of **1** with a series of primary and secondary amines were studied. We found that for each reaction, **6** was the major product, **7** was a minor product. The Rf value of both compounds was very close. The spectrum data showed that compound **7** was the regio isomer of compound **6**. The yields of the products were listed in **Table 1**. Since the differences of the chemical shifts of the aromatic protons of **6** and **7** were obvious, the structures can be easily deduced by simple analysis of the aromatic substitution effect and the relating coupling constants. The electron-withdrawn effect of the nitro group gave rise to the difference of the yield between **6** and **7**[4]. Obviously, these results strongly supported the mechanism that the reaction was proceeded through the intermidiate **4**.

Scheme 3



6 **7**

Table 1 The yields of **6** and **7**

Amine	Major product (yield*%)	Minor product (yield* %)
n-BuNH$_2$	**6a** (41)	**7a** (19)
c-HexNH$_2$	**6b** (50)	**7b** (13)
Piperidine	**6c** (43)	**7c** (14)
PhNH$_2$	**6d** (54)	**7d** (26)
BnNH$_2$	**6e** (40)	**7e** (15)

*Isolated yield

Experimental

IR were recorded using Nicolet 170-SX spectrometer. ^{1}H NMR spectra were recorded on an Avance DRX 200 instrument ($CDCl_3$ was used as the solvent with TMS as an internal chemical shift reference). MS measurements were performed on HP 5890 spectrometer. Melting points were determined on Kofler hot-stage apparatus. The thermometer was uncorrected. Compound **1** was prepared according to ref. 5.

General procedure

A mixture of compound **1** (0.5 mmol), amine (10 mmol) was stirred at r.t. for 6 h. The reaction mixture was poured into cold water (30 mL), filtered and washed with water to give a brown filter cake. The filtrate was extracted with ethyl acetate (5 mL×3). The filter cake was dissolved in the organic layer of the extraction and filtered. The filtrate was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel chromatography with petroleum/ethyl acetate (5/1) as an elute to give **6** and **7** (yields of **6** and **7** were listed in **Table 1**), respectively. **6a**: orange crystals, mp 106-107°C. ^{1}H NMR: 0.93 (t, 3H, J = 7.2 Hz, CH_3), 1.20 - 1.70 (m, 4H, $CH_3C\mathbf{H}_2C\mathbf{H}_2$–), 3.19 (t, 2H, J = 7.2 Hz, $NHC\mathbf{H}_2$–), 7.12 (d, 1H, J_{ab} = 8.3 Hz, H_a), 7.51 (d, 1H, J_{de} = 8.4 Hz, H_d), 7.58 (d, 1H, J_{bc} = 2.0 Hz, H_c), 7.63 (dd, 1H, J_{ab} = 8.3 Hz, J_{bc} = 2.0 Hz, H_b), 8.31 (dd, 1H, J_{de} = 8.4 Hz, J_{ef} = 2.2 Hz, H_e), 8.62 (d, 1H, J_{ef}=2.2 Hz, H_f). MS (*m/z*): 395, 393 (M^+, 32, 33), 352, 350 ($[M-C_3H_7]^+$, 61, 65), 271 ($[M-Br-C_3H_7]^+$, (70), 270 (100). **6b**: orange crystals, mp 150-151°C. ^{1}H NMR: 1.06-2.18 (m, 10H, $-(CH_2)_5-$), 3.28 - 3.60 (m, 2H, N**H**C**H**), 7.08 (d, 1H, J_{ab} = 8.4 Hz, H_a), 7.51 (d, 1H, J_{de} = 8.4 Hz, H_d), 7,56 (d, 1H, J_{bc} = 2.0 Hz, H_c), 7.59 (dd, 1H, J_{ab} = 8.4 Hz, J_{bc} = 2.0 Hz, H_d), 8.31 (dd, 1H, J_{de} = 8.4 Hz, J_{ef} = 2.4 Hz, H_e), 8.60 (d, 1H, J_{ef} = 2.4 Hz, H_f). MS (*m/z*): 421,419 (M^+, 53,53), 378, 376 ($[M-C_3H_7]^+$, 96, 100). The melting point of **6c** was consistent to that reported in the literature[1]. **6d**: orange crystals, mp 120-122°C. ^{1}H NMR: 5.31 (1H, brs, N**H**), 7.10 (d, 1H, J_{ab} = 8.4 Hz, H_a), 7.14 - 7.39 (m, 5H, Ph**H**), 7.57 (d, 1H, J_{de} = 8.4 Hz, H_d), 7.78 (dd, 1H, J_{ab} = 8.4 Hz, J_{bc} = 2.2 Hz, H_b), 8.07 (d, 1H, J_{bc} = 2.2 Hz, H_c), 8.31 (dd, 1H, J_{de} = 8.4 Hz, J_{ef} = 2.2 Hz, H_e), 8.61 (d, 1H, J_{ef} = 2.2 Hz, H_f). MS (*m/z*): 415, 413 (M^+, 20, 22), 334 ($[M-Br]^+$ 25), 288 ($[M-Br-NO_2]^+$, 29), 241 (55), 149 (52), 44 (100). ν_{max}: 3348 (NH), 1618, 1573,1492 (Ar), 1523,1344 (NO_2). **6e**: orange crystals, mp 154-155°C. ^{1}H NMR: 4.40 (s, 2H, $PhC\mathbf{H}_2$), 7.13 (d, 1H, J_{ab} = 8.2 Hz, H_a), 7.31(brs, 5H, Ph**H**), 7.51 (d, 1H, J_{de} = 8.5 Hz, H_d), 7.56(d, 1H, J_{bc} = 2.0 Hz, H_c), 7.65 (dd, 1H, J_{ab} = 8.2 Hz, J_{bc} = 2.0 Hz, H_b), 8.30 (dd, 1H, J_{de} = 8.5 Hz, J_{ef} = 2.1 Hz, H_e), 8.60 (d, 1H, J_{ef} = 2.1 Hz, H_f). MS (*m/z*): 429, 427 (M^+, 11, 12), 91 (100). **7a**: orange crystals, mp 111-112°C. ^{1}H NMR: 1.00 (t, 3H, J = 7.0 Hz, CH_3), 1.10-1.90 (m, 4H, $CH_3C\mathbf{H}_2C\mathbf{H}_2$–), 3.08 - 3.46 (m, 2H, $C\mathbf{H}_2NH$–), 6.58 (dd, 1H, J_{ab} = 8.4 Hz, J_{ac} = 2.2 Hz, H_a), 6.80(d, 1H, J_{ac} = 2.2 Hz, H_c), 7.50(d, 1H, J_{de} = 8.4 Hz, H_d), 8.21(dd, 1H, J_{de} = 8.4 Hz, J_{ef} = 2.2 Hz, H_e), 8.23 (d, 1H, J_{ab} = 8.4 Hz, H_b), 8.53 (d, 1H, J_{ef} = 2.2 Hz, H_f). MS (*m/z*): 395,393 (M^+, 17, 17), 352, 350 ($[M-CH_3CH_2CH_2]^+$, 100, 100). **7b**: orange crystals, mp 174-175°C. $^!$H NMR: 0.7-2.3 (m, 10H, $-(CH_2)_5-$), 3.35 - 3.75 (m, 1H, C**H**NH-), 6.95 (d, 1H, J_{ac} = 2.2 Hz, H_c), 7.51 (d, 1H, J_{de} = 8.4 Hz, H_d), 8.22 (dd, 1H, J_{de} = 8.4 Hz, J_{ef} = 2.2 Hz, H_e), 8.24 (d, 1H, J_{ab} = 8.4 Hz, H_b), 8.55 (d, 1H, J_{ef} = 2.2 d, Hz, H_f). MS (*m/z*): 421, 419 (M^+, 15, 15), 378, 376 (51, 50), 55 (100). **7c**: orange crystals, mp 127-128°C. ^{1}H NMR: 1.68 (brs, 6H, $-CH_2-(C\mathbf{H}_2)_3-CH_2-$), 3.10 (m, 4H, $-C\mathbf{H}_2-N-C\mathbf{H}_2-$), 6.95 (dd, 1H, J_{ab} = 8.6 Hz, J_{ac} = 2.0 Hz, H_a), 7.10 (d, 1H, J_{ac} = 2.0 Hz, H_c), 7.49 (d, 1H, J_{de} = 8.4 Hz,H_d), 7.80 (d, 1H, J_{ab} = 8.6 Hz, H_b), 8.22 (dd, 1H, J_{de} = 8.4 Hz, J_{ef} = 2.2 Hz, H_e), 8.55 (d, 1H, J_{ef} = 2,2 Hz,H_f). MS (*m/z*): 407, 405 (M^+, 5, 5), 390, 388 (100, 99), 360, 358 (21, 19). **7d**: orange crystals, mp 162-164°C. ^{1}H NMR: 6.77 (dd, 1H, J_{ab} = 8.8 Hz, J_{ac} = 1.8 Hz, H_a), 7.19 (d, 1H, J_{ac} = 1.8 Hz, H_c), 7.25 - 7.50 (m, 6H, H_d, Ph**H**), 8.19 (dd, 1H, J_{de} = 8.4 Hz, J_{ef} = 2.2 Hz, H_e), 8.31 (d, 1H, J_{ab} = 8.8 Hz, H_b), 8.52 (d, 1H, J_{ef} = 2.2 Hz, H_f), 9.59(brs, 1H, NH). MS (*m/z*): 415,413 (M^+, 90, 95), 241 (100), 121 (53). **7e**: orange crystals, mp 158-160 °C. ^{1}H NMR: 4.58 (d, 2H, J = 5.6 Hz, $PhCH_2$), 6.68 (dd, 1H, J_{ab} = 8.8 Hz, J_{bc} = 1.8 Hz, H_a), 6.82 (d, 1H, J_{ac} = 1.8 Hz, H_c), 7.36 (brs, 5H, $C_6\mathbf{H}_5$, H_d), 7.38 (d, 1H, J_{de} = 8.4 Hz， H_d)， 8.19 (dd, 1H, J_{de} = 8.4 Hz, J_{ef} = 2.2 Hz, H_e), 8.29 (d, 1H, J_{ab} = 8.8 Hz, H_b), 8.51(d, 1H, J_{ef} = 2.2 Hz, H_f). MS (*m/z*): 429, 427 (M^+, 18, 20), 411 (19), 409 (18), 381 (19), 379 (17), 284 (14), 105 (75), 91 ($PhCH_2^+$, 100).

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