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Bromination of 2,1,3-Benzothiadiazole with *N*-Bromosuccinimide

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ABSTRACT

2,1,3-benzothiadiazole is widely used in conducting polymer research. 4,7-Dibromo-2,1,3-benzothiadiazole or 4-bromo-2,1,3-benzothiadiazole can be used for valuable blocks in the main-chain to improve electronic property of resultant polymers. However, the bromination of 2,1,3-benzothiadiazole need Br_2. Br_2 is difficult to handle because high reactivity and toxicity in practical synthesis. We propose simple and convenience method using *N*-bromosuccinimide for bromination of benzothiadiazole.

Keywords: Bromination; benzothiadiazole,

1. Introduction

Bromination of organic compound is important study to carry out various cross-coupling reaction for construction of desired polymer structure. 2,1,3-Benzothiadiazole has been paid attention to prepare donor-acceptor polymer. Pilgram et al. studied on bromination of 2,1,3-benzothiadiazole [1]. They used bromine for the bromination.

However, in previous faithful reports, all bromination method of 2,1,3-benzothiadiazole were carried out using bromine in accordance with first report [2-4]. Bromine need to have careful treatment because of high reactivity. Therefore, we employ *N*-bromosuccinimide (NBS) for the reaction in this study. NBS is a solid form and easy to handle. However, NBS is lower reactivity than that of bromine. 2,1,3-Benzothiadiazole can not be brominated by NBS in mild condition, such as reaction in organic solvent.

We quest improved bromination of 2,1,3-benzothiadiazole with NBS in a certain condition.

2. Experimental

2.1. Bromination of 2,1,3-benzothiadiazole

2,1,3-Benzothiadiazole 1.43 g (10.5 mmol) and 47% hydrobromic acid 12.5 mL were stirred and refluxed at 120 °C. After 1 h, NBS 3.56 g (20.0 mmol) was added slowly. After 3 h, the mixture was visually changed to be colorless. The mixture was quenching by KOH solution and extracted with diethyl ether and dichloromethane. The organic phase was dried with $MgSO_4$, filtered, and evaporated. The pale yellow solid was obtained.

2.2. Instrument

NMR date were measured with a JNM-ECS-400 NMR Spectrometer (JEOL, Japan).

2.3. Materials

NBS was purchased from Wako Chemical (Japan), and used as received. 2,1,3-benzothiadiazole and bromic acid were purchased from Tokyo Chemical (TCI, Japan), and used as received.

3. Result and discussion

3.1. NMR

The crude product was measured with NMR. This data reviels that the ratio of products are to be 2,1,3-benzothiadiazole (1), 4-bromo-2,1,3-benzothiadiazole (2), and 4,7-dibromo-2,1,3-

benzothiadiazole (3). The NMR result are shown in Figure 1. The composition ratio of resultants is evaluated by integration in the NMR. These value are summerized in Table 1. This result indicates that reaction with NBS allows production of 4-bromo-2,1, 3-benzothiadiazole.

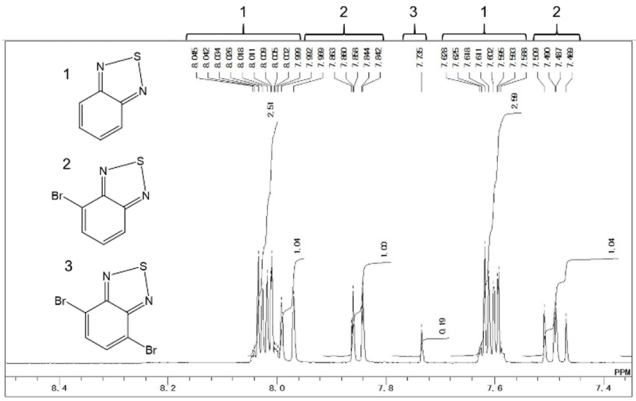

Figure 1. The crude product of 2,1,3-benzothiadiazole bromination with *N*-bromosuccinimide (NBS).

Table 1. Composition ratio of compound evaluates with ^{1}H NMR.

	1	2	3
Integrated value	(2.51+2.59) /4 = 1.28	(1.04+1.00+1.04) /3 = 1.03	0.19/2 = 0.10
ratio	53.1%	42.7%	4.2%

4. Conclusions

A reaction with NBS can brominate 2,1,3-benzothiadiazole with moderate reactive condition.

References

1. Kurt, P., Zupan, M., and Skiles, R., Bromination of 2,1,3-benzothiadiazoles. *J. Heterocyc. Chem.* 7.3, 629-633 (1970).
2. Bertrand, H. C., Clède, S., Guillot, R., Lambert, F., and Policar, C. Luminescence modulations of rhenium tricarbonyl complexes induced by structural variations. *Inorg. Chem.* 53.12, 6204-6223 (2014).
3. Bijleveld, J. C., Shahid, M., Gilot, J., Wienk, M. M., and Janssen, R. A. Copolymers of Cyclopentadithiophene and Electron-Deficient Aromatic Units Designed for Photovoltaic Applications. *Adv. Func. Mater.,* 19.20, 3262-3270 (2009).
4. Chao, D., and Ling, J., Amphiphilic Copolymers of Polyfluorene Methacrylates Exhibiting Tunable Emissions for Ink□Jet Printing. *Macromol. Rap. Commun.* 37.16, 1352-1356 (2016).

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