Chinese Chemical Letters 25 (2014) 435–437

Contents lists available at ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet

Original article

Bromodimethylsulfonium bromide: A brominating reagent for the conversion of anthracene into 9,10-dibromoanthracene

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ARTICLE INFO

Article history:
Received 29 July 2013
Received in revised form 28 October 2013
Accepted 5 November 2013
Available online 8 December 2013

Keywords:
Bromodimethylsulfonium bromide
Brominating reagent
9,10-Dibromoanthracene

ABSTRACT

Bromodimethylsulfonium bromide (BDMS) was used as an efficient brominating reagent for the synthesis of 9,10-dibromoanthracene in dichloromethane. The desired products were obtained in excellent yields.

1. Introduction

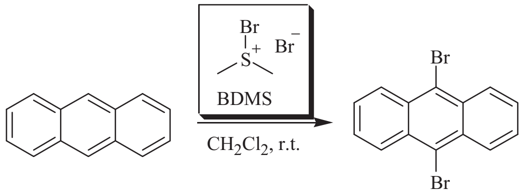
Anthracenes have been extensively investigated in many fields, *e.g.*, material chemistry [1–4], thermochromic or photochromic fields [5], and organic light-emitting devices [6–12]. Furthermore, anthracene derivatives have been used in optical, electronic, and magnetic switches when combined with polymers, films, and crystals [13,14]. In biological systems, anthracene scaffolds are also employed for probing DNA cleavage [15]. 9,10-Dibromoanthracene has been used as an important component in fluorescent and light-emitting polymers [16]. Traditional methods for the preparation of 9,10-dibromoanthracene involve the bromination of aromatic hydrocarbons of anthracene *via* the electrophilic substitution of Br_2 [17]. Recently, several improved methods have been reported for constructing 9,10-dibromoanthracene in the presence of $ZnBr_2/NaBiO_3$ [18], DBU/Br_2/HBr [19], or Br_2/AcOH [20]. However, molecular bromine has several limitations including its volatile, irritating and corrosive nature that makes it a less than preferable reagent.

Bromodimethylsulfonium bromide (BDMS) can be considered a convenient storage of molecular bromine, which exhibits both the properties of a brominating reagent as well as an effective catalyst [21]. It is easier to handle compared to the hazardous molecular bromine. In addition, BDMS exhibits efficient catalytic properties, which might be due to its ability to generate *in situ* dry HBr in the reaction medium, and acts as an efficient pre-catalyst for various acid-catalyzed organic transformations. In continuation of our recent work on the development of useful new synthetic methodologies using bromodimethylsulfonium bromide (BDMS) [22], we have observed that the treatment of anthracene with bromodimethylsulfonium bromide at room temperature in dichloromethane afforded the corresponding 9,10-dibromoanthracene (Scheme 1).

2. Experimental

2.1. Synthesis of 9,10-dibromoanthracene

General procedure for the synthesis of 9,10-dibromoanthracene: A mixture of anthracene (10.0 mmol) and BDMS (24.0 mmol) in CH_2Cl_2 (10.0 mL) was stirred for appropriate amount of time at room temperature [CAUTION!! The reaction produces HBr and a gas trap (bubbler containing 1 mol/L NaOH solution) should be used, preferably in a fumehood]. When the reaction completed as indicated by TLC analysis, the reaction product was collected by



Scheme 1. Synthesis of 9,10-dibromoanthracene.

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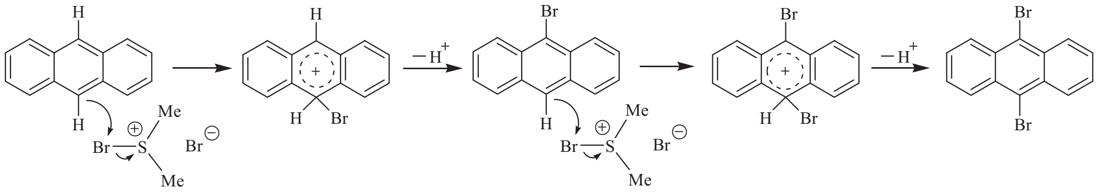
http://dx.doi.org/10.1016/j.cclet.2013.12.009



Scheme 2. Plausible mechanism for formation of 9,10-dibromoanthracene in the presence of BDMS.

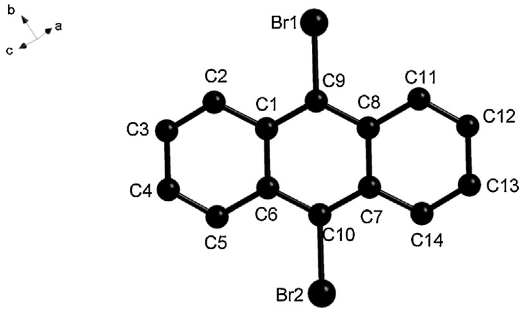


Fig. 1. The molecular structure of 9,10-dibromoanthracene.

Table 1
Optimization of the reaction condition for the synthesis of 9,10-dibromoanthracene.

Entry	Solvent	Catalyst loading	Time (h)	Yield (%)[a]
1	DMSO	200 mol%	12	12
2	CH_3CN	200 mol%	2	40
3	THF	200 mol%	3	56
4	1,4-Dioxane	200 mol%	2.5	30
5	Ethyl acetate	200 mol%	5	70
6	CH_2Cl_2	200 mol%	0.5	85
7	CH_2Cl_2	240 mol%	0.5	96

[a] Isolated yield.

filtration. The yellow solid was dried *in vacuo* for 2 h to give the compound. Mp: 222–224 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (4H), 7.66 (4H).

2.2. Cystallographic studies

X-ray single-crystal diffraction data for 9,10-dibromoanthracene were collected on an APEX II CCD at 173(2) K with a graphite-monochromated Mo Kα radiation (k = 0.71073 Å). The structure was solved by the direct methods and refined by full-matrix leastsquares fitting on F2 by SHELXTL-97. The molecular structure of 9,10-dibromoanthracene is shown in Fig. 1.

3. Results and discussion

Initially, we investigated the reaction of anthracene and bromodimethylsulfonium bromide in DMSO as a solvent. Unfortunately, the reaction did not proceed as planned. However, we were delighted to find that the reaction proceeded well when DMSO was replaced with carbon tetrachloride. In the screening of different solvents to identify the most suitable solvent for this transformation, DCM was found to be superior to other solvents such as acetonitrile, THF, 1,4-dioxane, and ethyl acetate in terms of both reaction times and yields obtained (Table 1, entries 1–5).

This reaction was found to complete within 30 min and was amenable to be carried out on a multi-gram scale. For example, no loss of yield was observed when the experiment was conducted on a 10 g (96%) or on a 100 g (96%) scale. In all cases, the 9,10-dibromoanthracene formed was found to be of good quality and purity (mp 222–224 °C, Lit. 226 °C [19,20]). Subsequently, we applied this unpurified 9,10-dibromoanthracene in lithiation chemistry with no problems. Also, a plausible mechanism for the formation of 9,10-dibromoanthracene is shown in Scheme 2.

In the current studies, synthesis of 9,10-dibromoanthracene requires heating with bromine in carbon tetrachloride giving the desired compound in 83–88% yield [23], while Graebe and Liebermann reported a preparation using carbon disulphide as the reaction solvent [24]. Perhaps the most reliable and commonly used approach for the preparation of 9,10-dibromoanthracene involves the reaction of anthracene with bromine in dry dioxane, giving 9,10-dibromoanthracene in 99% yield [25]. However, in each of these cases there are problems associated with the use of toxic molecular bromine.

4. Conclusion

In summary, we have developed an improved synthesis of 9,10-dibromoanthracene that uses mild conditions and inexpensive, nonvolatile BDMS as a brominating reagent.

Acknowledgments

This work was supported financially by the Natural Science Foundation of Tianjin (Nos. 12JCZDJC34300, 11JCYBJC03600), Young Scientist Fund (No. 21001080).

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