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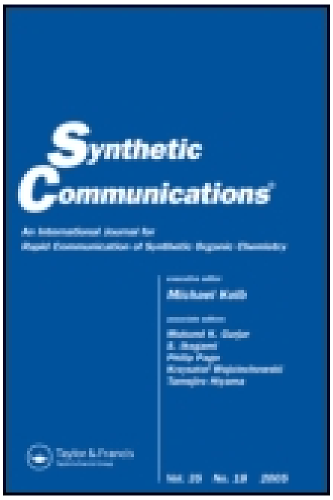

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AN IMPROVED PROCEDURE FOR THE PREPARATION OF 9,10-DIBROMOANTHRACENE

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AN IMPROVED PROCEDURE FOR THE PREPARATION OF 9,10-DIBROMOANTHRACENE

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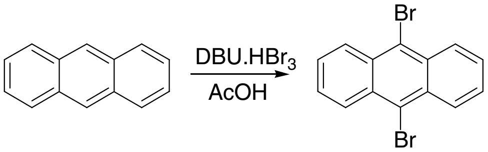
ABSTRACT

An improved procedure is described for the dibromination of anthracene, affording 9,10-dibromoanthracene with yields >95%.

9,10-Dibromoanthracene has been used extensively as a component in fluorescent and light-emitting polymers.[1] In the course of some studies directed towards the synthesis of 9,10-disubstituted anthracene derivatives we required significant quantities of 9,10-dibromoanthracene as our key starting material and opted to prepare this compound ourselves by adopting a recent procedure reported by Muathen (Scheme 1).[2]



Scheme 1.

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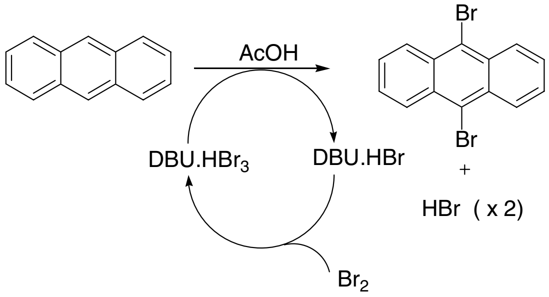
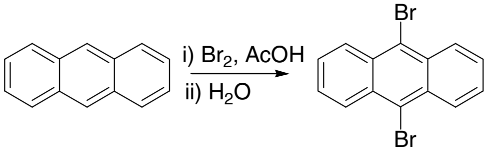
This involved the bromination of anthracene by heating at reflux in acetic acid with DBU.HBr$_3$, which in turn had to be prepared from the reaction of DBU and bromine in the presence of HBr in acetic acid. Although this reaction proceeded well in our hands (91% yield unpurified), it required an additional step to prepare DBU.HBr$_3$. It occurred to us that it may be possible to use a catalytic quantity of DBU, since the reagent DBU.HBr$_3$ should be easily generated *in situ* and then subsequently regenerated once electrophilic aromatic substitution had taken place (Scheme 2).



Scheme 2.

However, in the control reaction whereby bromine was added to a heated solution of anthracene in acetic acid, bromination proceeded efficiently giving the desired product in 97% yield. This meant that direct bromination of the anthracene was occurring and it was subsequently demonstrated that addition of bromine in acetic acid dropwise to a stirred suspension of anthracene in acetic acid at room temperature gave the desired product in 95% yield after workup (Scheme 3).



Scheme 3.

The reaction was found to be complete within 30 minutes 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 1 g (94%) or on a 10 g (94%) scale. In all cases, the 9,10-dibromoanthracene formed was found to be of good quality and purity (mpt. 220–222°C, Lit.[2] 226°C).

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No attempt was made to purify the material and we have subsequently used this unpurified product in lithiation chemistry with no resulting problems.

Aside from those reactions that necessitate the synthesis of exotic brominating agents, other methods exist in the literature for the direct bromination of anthracene. The current *Organic Syntheses* preparation of 9,10-dibromoanthracene requires heating with bromine in carbon tetrachloride giving the desired compound in 83–88% yield,[3] while Graebe and Liebermann reported a preparation using carbon disulphide as the reaction solvent.[4] Perhaps the most efficient existing synthetic route to 9,10-dibromoanthracene involves the reaction with bromine in dry dioxane, giving 9,10-dibromoanthracene in 99% yield.[5] However, in each of these cases there are problems associated with the toxicity, expense and inflammable nature of the solvents used.

In summary we have developed an improved synthesis of 9,10-dibromoanthracene that uses mild conditions and inexpensive, non-toxic acetic acid as solvent.

General Procedure for the Preparation of 9,10-Dibromoanthracene

Bromine (17.9 g, 5.8 mL, 0.112 mol) in acetic acid (50 mL) was added dropwise over a period of 5 minutes to a vigorously stirred* suspension of anthracene (10.0 g, 0.056 mol) in acetic acid (300 mL) at room temperature [**CARE!!** The reaction evolves HBr and is best connected to a HBr gas trap (bubbler containing 1 M NaOH solution) preferably in a fumehood]. The reaction was left to stir for 30 minutes during which a canary yellow precipitate formed. Water (300 mL) was added,** the suspension left to stir for 10 minutes, then filtered and washed with a little water. The yellow solid was dried *in vacuo* for 24 hours to give the title compound (17.70 g, 94%); mpt 220–222°C (lit.[2] 226°C); δ_H (200 MHz; CDCl$_3$; Me$_4$Si) 8.57 (4H, AA′XX′ system, ArCH$_{1,4,5,8}$), 7.62 (4H, AA′XX′ system, ArCH$_{2,3,6,7}$); m/z (EI) 333.8992 (M$^+$ C$_{14}$H$_8$Br$_2$ requires 333.8993), 255 (6%), 174 (16), 168 (11), 149 (5).

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*When conducting experiments on a larger scale, overhead stirring is necessary to ensure efficient mixing.

**Addition of water was necessary to achieve complete precipitation of the product. The optimal volume added was found to be approximately the same as the acetic acid used.

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