Short communication

An Efficient Microwave-Induced Solvent-Free Organic Bromination Using Tetrabutylammonium Tribromide

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Abstract

Microwave-induced solvent-free brominations of organic substrates have been carried out with tetrabutylammonioum tribromide, $(C_4H_9)_4N^+(Br_3^-)$. Reactions are facile, affording products in high yields within very short reaction times.

Keywords: Microwave (MW); bromination; tetrabutylammonium tribromide (TBATB); environmentally benign reaction

1. Introduction

In recent times, due to growing environmental awareness[1–3] microwave-induced chemical synthesis has become a useful alternative to conventional synthetic procedures.[4–7] In this context a few reports are also available on microwave-induced organic brominations with reagents such as bromine and NBS.[8–11] However, these days, organic bromination reactions are often carried out using organicammonium tribromides (OATBs).[12–16] Among the different OATBs developed so far, tetrabutylammonium tribromide (TBATB), $(C_4H_9)_4N^+(Br_3^-)$, is the most versatile reagent.[17–29] TBATB is regarded as a 'greener' substitute of bromine because it is stable, crystalline, easy to handle and has worked well as a brominating agent, allowing bromination of a wide array of organic substrates.[30] In an effort to further explore the scope of TBATB as brominating reagent, we recently performed some reactions under microwave conditions using a few test substrates. Encouraged by the initial results,[31] a detailed study has now been done and reported in this communication.

2. Experimental

The reagent, tetrabutylammonium tribromide (TBATB), $(C_4H_9)_4N^+(Br_3^-)$, used for these bromination reactions was synthesized following one of our already reported preparation procedures.[23]

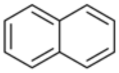
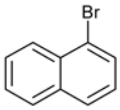
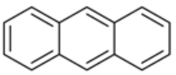
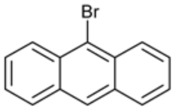
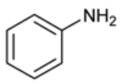
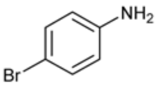
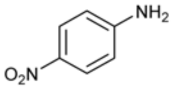
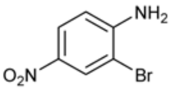
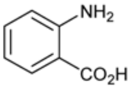
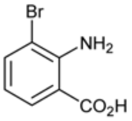
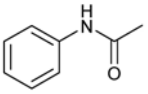
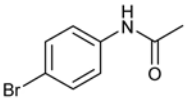
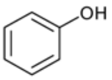
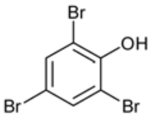
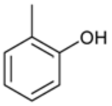
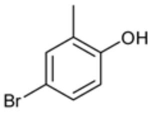
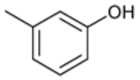
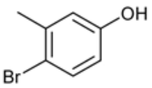
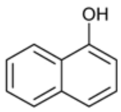
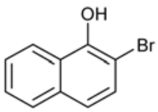
2. 1. General Procedure for Bromination Reactions Under Microwave Conditions

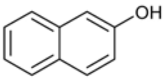
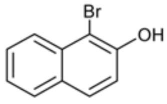
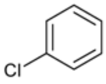
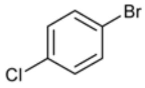
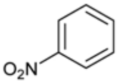
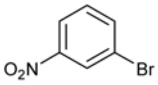
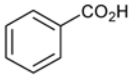
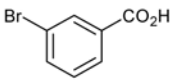
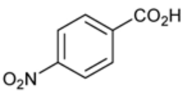
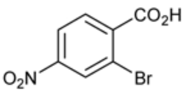
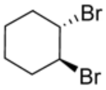
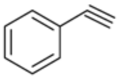
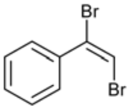
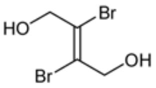
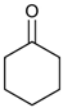
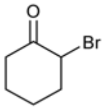
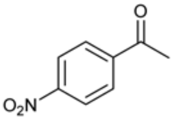
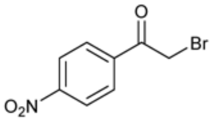
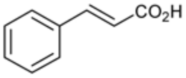
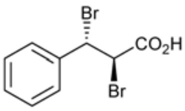
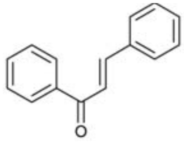
The reactions were carried out in a monomode reactor (Synthewave 402® Prolabo). In a typical reaction, 1 mmol of organic substrate was mixed thoroughly with 1 mmol of TBATB, with light grinding in order to ensure complete homogeneity. The mixture was then inserted into the microwave chamber and the reaction was carried out maintaining the power at 40% and reaction temperature at 90 °C. The progress of the reaction was monitored by TLC using ethylacetate-hexane solvent system (volume ratio varied for different substrates). Once the reaction was completed, the reaction mixture was diluted with ethyl acetate (30 mL) and filtered through a short column of silica gel in order to remove the spent reagent. The crude product thus obtained was subjected to column chromatography over a pad of silica gel using ethyl acetate-hexane solvent system as eluent. The products were identified by comparison of their melting points, IR absorption and NMR spectra with the authentic samples.[32]

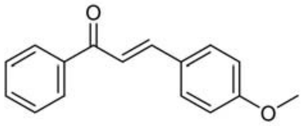
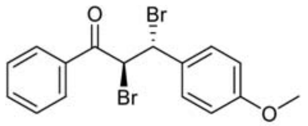
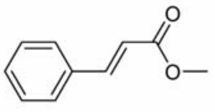
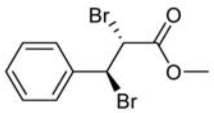
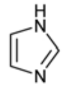
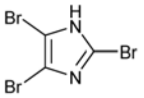
3. Results and Discussion

In order to study the versatility of TBATB as brominating agent under microwave conditions, representative examples of different types of organic substrates were taken (see Table 1). It was observed that bromination reactions under microwave conditions were very facile and the products were obtained in moderate to high yields. Similar experiments performed after homogenization of the reaction mixtures by grinding, followed by conventional heating at 90 °C showed no reaction within the same reaction time as needed for microwave conditions.

Table 1: Microwave accelerated bromination of organic substrates using TBATB under neat reaction conditions.[a]

Entry	Substrate	Product	Time (s)	Yield[b] (%)
1			120	62
2			93	92
3			50	83
4			70	85
5			50	55
6			93	85
7			96	76
8			336	60
9			265	72
10			93	70

Entry	Substrate	Product	Time (s)	Yield[b] (%)
11			153	81
12			60	55
13			76	45
14			196	40
15			110	35
16			60	95
17			180	90
18			120	65
19			60	70
20			213	56
21			60	70
22			83	87

Entry	Substrate	Product	Time (s)	Yield^b (%)
23			90	68
24			160	62
25			105	72

^{a}Reaction conditions: microwave power, 40%; temperature, 90 °C; solvent-free conditions. ^{b}Isolated yields.

As we can see from Table 1, when reactions were carried out on unsubstituted aromatic compounds like naphthalene and anthracene (entries 1 and 2), only monobrominated products were obtained. With aromatic amino compounds such as aniline, 4-nitroaniline, 2-aminobenzoic acid and acetanilide (entries 3 to 6), regioselectivity was maintained and monobrominated products were formed in moderate to high yields. Microwave bromination reactions were also performed on phenol and some of its derivatives (entries 7 to 11). In case of cresols, only monobromo products were obtained regioselectively, which is probably because of the higher *o,p*-directing power of the OH substituent. However, it has been reported earlier that mixtures of products are obtained when liquid bromine is used as reagent.[12] Fused ring phenolic compounds (α- and β-naphthols, entries 10 and 11) afforded the expected bromo-products in high yields. Bromination was also possible on deactivated benzene systems such as chloro and nitrobenzene (entries 12 and 13). Moderate yields of products were also obtained with benzoic acid (entry 14) and 4-nitrobenzoic acid (entry 15). For multiple bonded systems (entries 16–18) the corresponding *trans*-products were obtained in high yields. α-Bromination of ketones was possible by this method as indicated by reactions of cyclohexanone and 4-nitroacetophenone (entries 19 and 20), and α,β-unsaturated systems of different types (entries 21–24) gave the corresponding dibromo products in good yields. Finally, bromination of heterocyclic compounds, such as imidzole, is also possible (entry 25).

4. Conclusions

Microwave-induced brominations with TBATB were successfully carried out on different types of organic substrates under solvent-free conditions. This method could be useful alternative to the existing methods of bromination, because the reactions are facile, with extremely short reaction times and simple purification process, and products are obtained in moderate to high yields.

5. Acknowledgements

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6. References

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Povzetek

Izvedli smo z mikrovalovi iducirane reakcije bromiranja organskih spojin s tetrabutilamonijevim tribromidom, $(C_4H_9)_4N^+(Br_3^-)$, brez uporabe topila. Reakcije so hitre in produkti nastanejo v zelo kratkih reakcijskih časih z visokimi izkoristki.