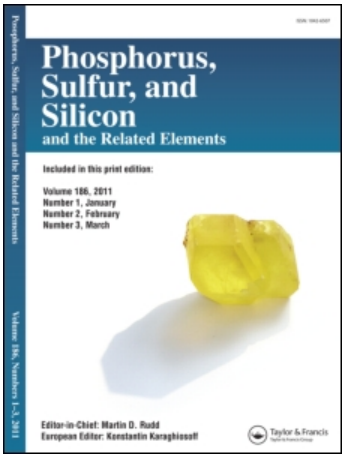

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Microwave-Assisted Solvent-Free Synthesis of Quinolines Using *N*-Bromosulfonamides

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MICROWAVE-ASSISTED SOLVENT-FREE SYNTHESIS OF QUINOLINES USING *N*-BROMOSULFONAMIDES

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Quinolines were readily prepared under new convenient conditions using poly(N,N′-dibromo-N,N′-dimethylenebenzene-1,3-disulfonamide) (PBBS) or N,N,N′,N′-tetra bromo benzene-1,3-disulfonamide (TBBDA) as efficient reagents from 2-aminobenzophenones and ketones or phenylacetylene under microwave/solvent-free conditions in good to excellent yields.

Keywords Acetylacetone; 2-aminobenzophenone; PBBS; quinolines; TBBDA

INTRODUCTION

High-throughput screening has created a critical demand to develop practical routes for rapid chemical synthesis of natural product-like molecules. To secure such practice, the discovery and invention of new synthetic methods for accessing some natural product entities in more efficient ways has been a fertile area of organic synthesis.[1–8] The quinoline nucleus is a backbone of many natural products and pharmacologically significant compounds displaying a broad range of biological activity.[9,10] They are found to possess a wide spectrum of biological activities and are used as antimalarial, antibacterial, antiasthmatic, antihypertensive, and tyrosine kinase inhibiting agents.[11–13]

In addition to the medicinal importance, polyquinolines derived from quinolines are found to undergo hierarchical self-assembly into a variety of nano- and mesostructures with enhanced electronic and photonic functions.[14–17] Consequently, various methods such as Skraup, Doebner–von Miller, Friedlander, and Combes methods have been developed for the preparation of quinoline derivatives.[18–25] In recent years, iodine[26]; Lewis acids such as $AuCl_3$,[27] $Bi(OTf)_3$,[28] and $Ag_3PW_{12}O_{40}$[29]; a combination of acidic catalysts and microwave irradiation[30,31]; ionic liquids[32]; chlorotrimethylsilane[33]; dodecylphosphonic acid[34]; and 1-methylimidazolium trifluoroacetate[35] have also been utilized to be effective for this synthesis. However, many of these procedures also suffer from harsh reaction conditions,

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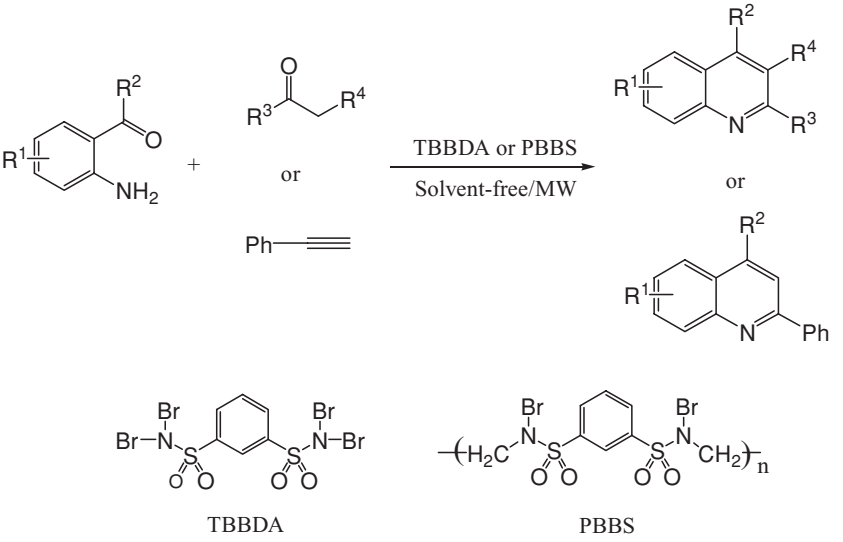
long reaction times, low yields, difficult workup, and the use of stoichiometric and/or relatively expensive reagents.

RESULTS AND DISCUSSION

In continuation of our studies towards the development of new environmentally friendly synthesis of quinolines through *N*-halo reagents, we now report *N,N,N′,N′*-tetra bromobenzene-1,3-disulfonamide (TBBDA) and poly(*N,N′*-dibromo-*N,N′*-dimethylene benzene-1,3-disulfonamide) (PBBS)[36–40] as efficient reagents for the preparation of quinolines from 2-aminobenzophenones and different ketones or phenylacetylene under microwave/solvent-free conditions (Scheme 1).

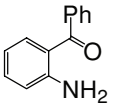
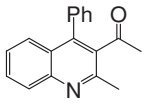
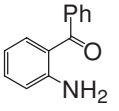
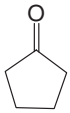
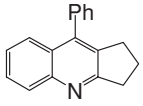
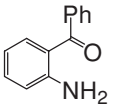
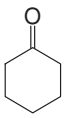
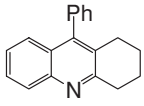
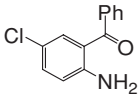
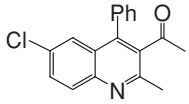
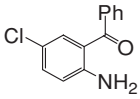
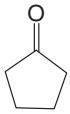
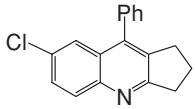
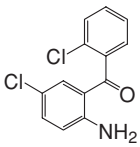
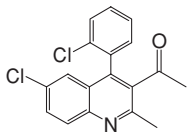
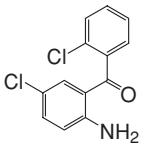
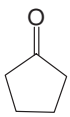
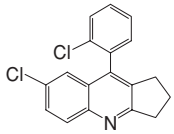
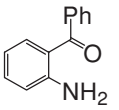
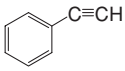
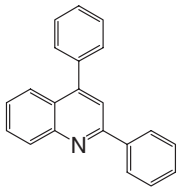
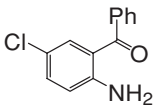
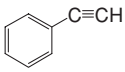
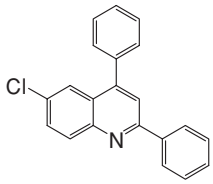


Scheme 1

Quinoline derivatives were prepared from different 2-aminobenzophenones and various α-methylene carbonylic compounds or phenylacetylene. Several 2-aminobenzo phenones were converted to quinolines using TBBDA or PBBS with good to high yields without byproducts. The results are presented in Table I. For chemoselectivity, a reaction was inserted between 2-aminobenzophenone and either ethylacetoacetate and methylacetoactate, but no obvious product was obtained.

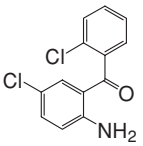
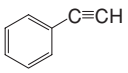
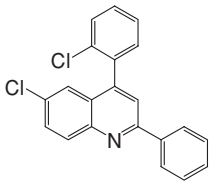
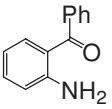
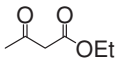
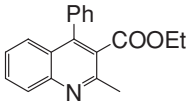
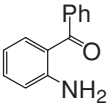
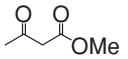
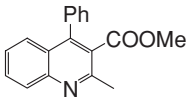
For the optimization of reaction conditions, 2-amino-5-chlorobenzophenone and acetylacetone were selected as model substrates because the other substances have almost the same characteristics. It was found that, in the absence of solvent, the reaction is completed in the presence of 0.45 mmol of TBBDA and irradiation by microwave for 9 min. The product was obtained in 94% yield (Table I, entry 4). To demonstrate the generality of the method, we next extended the scope of this reaction to other model compounds, the results of which are summarized in Table I. As is obvious from Table I, this method is equally effective for both cyclic and acyclic ketones.

Table I Synthesis of various quinolines by TBBDA and PBBS under microwave/solvent-free conditions

Entry	2-Aminoaryl ketone	Ketone or Acetylene	Product	TBBDA Time[min]	TBBDA Yield[a] (%)	PBBS Time[min]	PBS Yield[a] (%)	Ref.
1				5	97	9	93	34
2				6	95	8.5	90	34
3				8	94	10	91	34
4				9	94	13	88	34
5				9	93	16	87	34
6				15	88	20	83	29
7				17	86	20	80	29
8				11	91	13	86	31
9				16	90	19	87	31

(Continued on next page)

Table I Synthesis of various quinolines by TBBDA and PBBS under microwave/solvent-free conditions *(Continued)*

Entry	2-Aminoaryl ketone	Ketone or Acetylene	Product	TBBDA Time[min]	TBBDA Yield[a] (%)	PBBS Time[min]	PBBS Yield[a] (%)	Ref.
10				20	90	24	85	31
11				12	—[b]	12	—[b]	—[b]
12				10	—[b]	15	—[b]	–[b]

[a]Products were characterized by their physical properties, comparison with authentic samples, and by spectroscopic methods.

[b]No reaction.

Also, this reaction is very clean and free from side reactions, such as self-condensation of ketones, which are normally observed under basic conditions.

As shown in Table I, this method is effective for phenylacetylene. 2-Aminoaryl ketones such as 2-aminobenzophenone, 2-amino-5-chlorobenzophenone, and 2-amino-2′,5-dichlorobenzophenone reacted smoothly with phenylacetylene to produce a range of quinoline derivatives in good to excellent yields.

Since TBBDA and PBBS contain halogen atoms, which are attached to nitrogen atoms, it is very possible that they release X^+ in situ, which in turn can act as a catalyst in the reaction medium.[36–40] Therefore, the mechanism shown in Scheme 2 can be suggested for the reaction of phenyl acetylene with 2-amino acetophenone derivatives.[31]

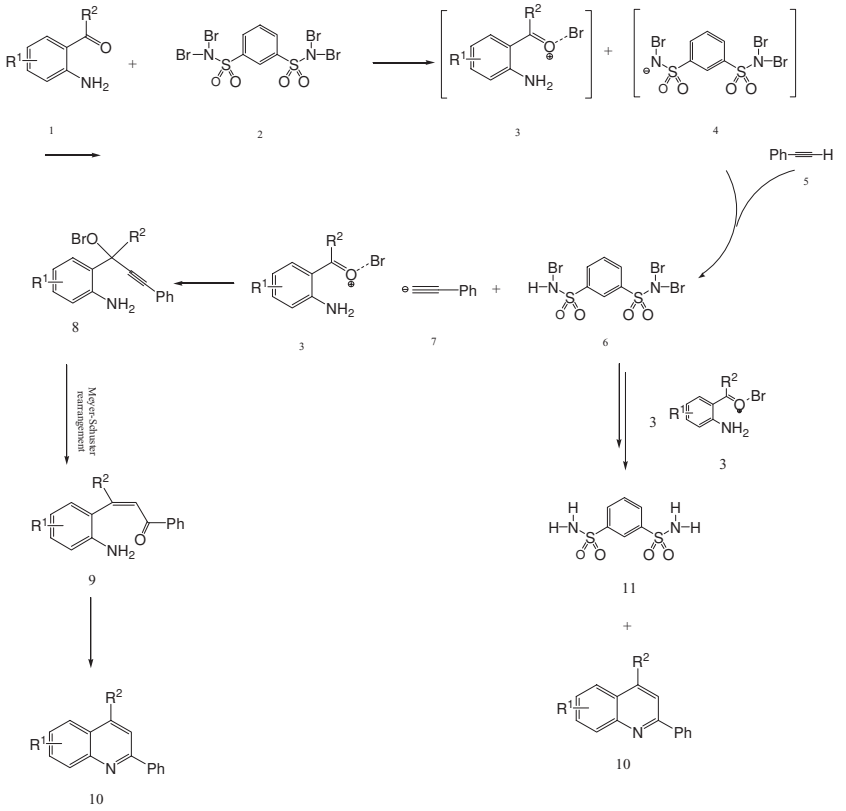
CONCLUSIONS

In conclusion, we now report TBBDA and PBBS as efficient reagents for the preparation of quinolines from *o*-aminoarylketones and different ketones or phenylacetylene under solvent-free/microwave irradiation conditions. This method not only provides an excellent complement to quinoline synthesis, but also avoids the use of hazardous and environmentally unfriendly acids or bases.

TBBDA and PBBS are inexpensive and nonhazardous reagents. They work under heterogeneous conditions, and can conveniently be handled and removed from the reaction mixture by simple filtration.

EXPERIMENTAL

2-Amino-5-chlorobenzophenone (0.23 g, 1 mmol), acetophenone (0.6 g, 5 mmol) or phenylacetylene (0.82 g, 8 mmol), and *N,N,N′,N′*-tetrabromobenzene-1,3-disulfonamide



Scheme 2

(0.25 g, 0.45 mmol) or PBBS (0.25 g, 0.60 mmol) were mixed together and irradiated under microwave conditions at a power output of 900 W (LG Co. microwave, 230v ~50 Hz, RF output 900 W). After completion of the reaction [Table I, monitored by TLC (5:1, n-hexane:acetone)], CH_2Cl_2 (10 mL) was added, and the sulfonamide was removed by filtration. Evaporation of the solvent under reduced pressure followed by purification using preparative thin layer chromatography afforded the pure product.

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