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Poly(*N*-bromo-*N*-ethylbenzene-1,3-disulfonamide) and *N,N,N′,N′*-tetrabromobenzene-1,3-disulfonamide as efficient reagents for synthesis of quinolines

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ABSTRACT

Poly(*N*-bromo-*N*-ethylbenzene-1,3-disulfonamide) [PBBS] and *N,N,N′,N′*-tetrabromobenzene-1,3-disulfonamide [TBBDA] were used as efficient reagents for the synthesis of quinolines in excellent yields from 2-aminoaryl ketones and carbonyl compounds under aqueous and solvent-free conditions.

1. Introduction

Quinolines are an important group of heterocyclic compounds. Several derivatives have been found to possess useful biological activities such as antimalarial, antibacterial, anti-asthmatic, antihypertensive, and anti-inflammatory.[1] In addition, quinolines are valuable synthons for the preparation of nano-and meso structures with enhanced electronic and photonic functions.[2] As a result of their importance as substructures in a broad range of natural and designed products, significant effort continues to be directed toward the development of new quinoline-based structures and new methods for their construction.[3] Thus, the synthesis of quinolines is an important and useful task in organic chemistry. The Friedländer annulation is a straightforward method for the synthesis of these compounds[4] which involves a condensation followed by a cyclodehydration between 2-aminoarylketones and α-methylene ketones, and is catalyzed by both acids and bases. In recent years, iodine,[5] Lewis acids[6] such as $ZnCl_2$, $SnCl_2$, $Bi(OTf)_3$, $Ag_3P-W_{12}O_{40}$, $AuCl_3$, and $CeCl_3{\cdot}7H_2O$, a combination of acidic catalysts and microwave irradiation,[7] ionic liquids,[8] chlorotrimethylsilane,[9] dodecylphosphonic acid,[10] and 1-methylimidazolium trifluoroacetate,[11] have been utilized for this synthesis. However, many of these procedures suffer from harsh reaction conditions, long reaction times, low yields, difficulties in work-up, and the use of stoichiometric and/or relatively expensive reagents.

In continuation of our interest in the application of*N,N,N′,N′*-tetrabromobenzene-1,3-disulfonamide [TBBDA] and poly(*N*-bromo-*N*-ethylbenzene-1,3-disulfonamide) [PBBS],[12] in organic synthesis,[12–16] we report here a convenient method for the preparation of quinolines from 2-aminoarylketones and various ketones in the presence of TBBDA and PBBS under (i) aqueous and (ii) solvent-free conditions (Scheme 1). Among the solvents (EtOH, H_2O, CH_3CN, and toluene) screened, H_2O proved to be the best (Table 1). Under solvent-free conditions, most of the reactions proceeded to afford the corresponding product in less time, however, the yield was slightly lower.

Substituted quinolines were prepared from appropriate 2-aminoarylketones and various α-methylene carbonyl compounds. 2-Aminobenzophenones were converted to quinolines using TBBDA or PBBS in good to high yields without any by-product formation. The results are presented in Table 2.

N,N,N′,N′-Tetrabromobenzene-1,3-disulfonamide [TBBDA] and poly(*N*-bromo-*N*-ethylbenzene-1,3-disulfonamide) [PBBS] are inexpensive and non-hazardous reagents. They react under heterogeneous conditions, are conveniently handled, and can be removed from the reaction mixture by simple filtration.

In conclusion, we have described an efficient method for the synthesis of quinolines via Friedländer annulation utilizing TBBDA and PBBS. This method provides an excellent complement to quinoline synthesis and also avoids the use of hazardous acids or bases.

2. Experimental

2.1. General procedure for quinoline synthesis using TBBDA and PBBS in the presence of H_2O

2-Aminoarylketone (0.5 mmol), carbonyl compound (0.5 mmol), and H_2O (5 mL) were placed in a 25 mL round-bottomed flask.

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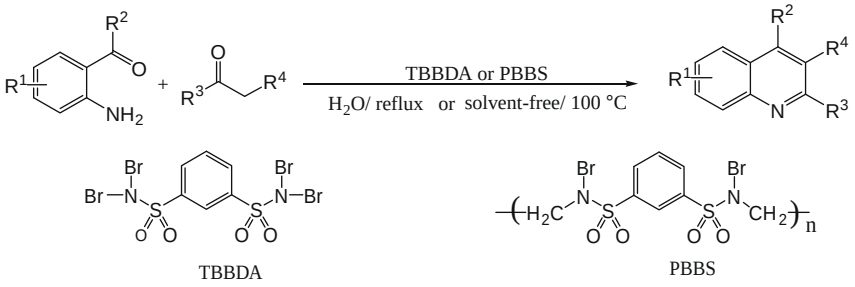


Scheme 1.

Table 1
Reaction times and yields of 1-(2-methyl-4-phenylquinoline-3-yl)ethanone using TBBDA in various solvents

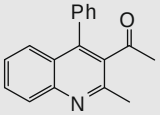
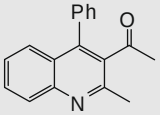
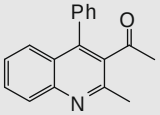
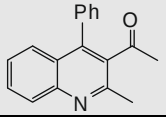
Entry	Product	Solvent	Time (h)	Yield (%)
1		Toluene	10	66
2		CH_3CN	10	74
3		EtOH	6	92
4		H_2O	4	94

Table 2
Synthesis of various quinolines using TBBDA and PBBS in H_2O and under solvent-free conditions

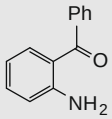
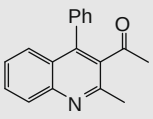
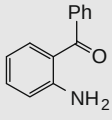
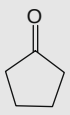
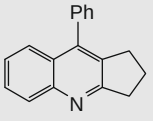
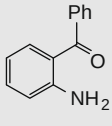
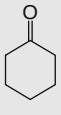
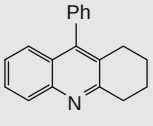
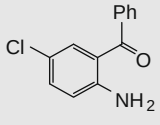
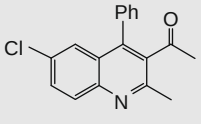
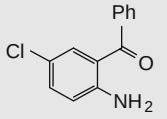
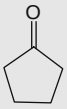
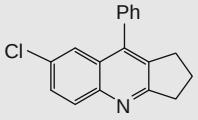
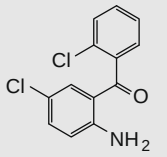
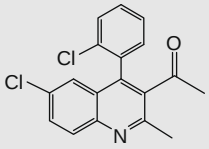
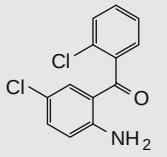
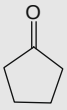
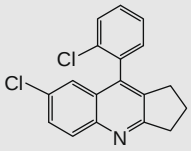
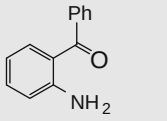
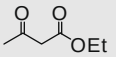
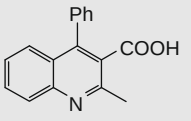
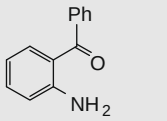
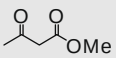
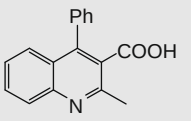
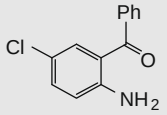
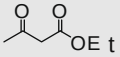
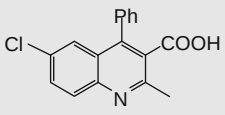
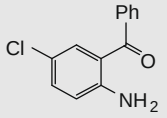
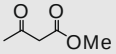
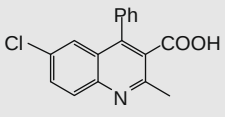
Entry	2-Aminoaryl ketone	Ketone	Product	TBBDA(H_2O)		PBBS(H_2O)		TBBDA (solvent-free)		PBBS (solvent-free)		Ref.
				Time (h)	Yield[a] (%)	Time(h)	Yield[a] (%)	Time (h)	Yield[a] (%)	Time (h)	Yield[a] (%)	
1				4	94	6	91	2.5	90	4	84	10
2				4.5	94	7	87	3.5	90	5	86	10
3				6	86	8.5	80	4	82	6.5	84	10
4				5	94	7	90	3	92	4.5	83	10

Table 2 (*continued*)

Entry	2-Aminoaryl ketone	Ketone	Product	TBBDA(H_2O)		PBBS(H_2O)		TBBDA (solvent-free)		PBBS (solvent-free)		Ref.
				Time (h)	Yield[a] (%)	Time(h)	Yield[a] (%)	Time (h)	Yield[a] (%)	Time (h)	Yield[a] (%)	
5				4	95	6.5	92	2.5	91	4	83	10
6				7.5	87	10	81	5	83	7	80	6e
7				8	84	10.5	80	6	82	8.5	81	6e
8				6	91	9	85	–		–		
9				6.5	92	8.5	87	–		–		
10				7	92	9.5	85	–		–		
11				7	94	9	87	–		–		

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

TBBDA (0.25 g, 0.45 mmol) or PBBS (0.25 g) was added to the solution with stirring. The reaction was heated at reflux and after completion [Table 2, monitored by TLC (5:1, *n*-hexane/acetone)], the flask was cooled to room temperature, and the precipitated sulfonamide was removed by filtration. Dichloromethane (10 mL) was added and the organic layer was separated and dried (Na_2SO_4). Evaporation of the solvent under reduced pressure followed by purification by preparative thin layer chromatography afforded the pure quinoline.

2.2. General procedure for quinoline synthesis using TBBDA and PBBS under solvent-free conditions

A mixture of the 2-aminoarylketone (0.5 mmol), carbonyl compound (0.5 mmol), and TBBDA (0.25 g, 0.45 mmol) or PBBS (0.25 g) was placed in a test-tube at 100 °C and stirred. After completion of the reaction [Table 2, monitored by TLC (5:1, *n*-hexane/acetone)], CH_2Cl_2 (10 mL) was added, and the precipitated sulfonamide was removed by filtration. Evaporation of the solvent under reduced pressure followed by purification by preparative thin layer chromatography afforded the pure quinoline.

$C_{17}H_{13}O_2N$ (entries 8 and 9): mp 215–218 °C; IR (KBr): ν 3350–2700 (COOH), 1706 (CO), 1654 (C=N) cm^{-1}; ^1H NMR [$CDCl_3$, FT-90 MHz]: δ 12.63 (s, 1H, COOH), 7.50–7.00 (m, 9H, aromatic), 2.28 (s, 3H, CH_3); ^{13}C NMR [$CDCl_3$, FT-90 MHz]: δ 31.80, 116.67, 120.04, 123.07, 127.10, 128.69, 129.16, 131.54, 132.40, 134.47, 138.42, 149.46, 152.20, 201.84; MS (*m*/*z*) 262 (M^+). Anal. Calcd for $C_{17}H_{13}O_2N$: C, 77.56; H, 4.94; N, 5.32%. Found: C, 77.77; H, 4.89; N, 5.12.

$C_{17}H_{12}O_2NCl$ (entries 10 and 11): mp 269–272 °C; IR (KBr): ν 3400–2700 (COOH), 1716 (CO), 1649 (C=N) cm^{-1}; ^1H NMR [$CDCl_3$, FT-90 MHz]: δ 12.90 (s, 1H, COOH), 7.46–7.24 (m, 8H, aromatic), 2.24 (s, 3H, CH_3); ^{13}C NMR [$CDCl_3$, FT-90 MHz]: δ 31.60, 118.16, 121.01, 126.60, 126.80, 128.90, 131.78, 133.81, 135.20, 136.83, 144.70, 146.40, 147.90, 200.20; MS (*m*/*z*) 297 (M^+). Anal. Calcd for $C_{17}H_{12}O_2NCl$: C, 68.57; H, 4.03; N, 4.70%. Found: C, 68.14; H, 4.21; N, 5.02.

Acknowledgment

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