

Silica-Supported Quinolinium Tribromide: a Recoverable Solid Brominating Reagent for Regioselective Monobromination of Aromatic Amines

Zheng Li,* Xiunan Sun, Lue Wang, Yanbo Li and Yuanhong Ma

Gansu Key Laboratory of Polymer Materials, College of Chemistry and Chemical Engineering,
Northwest Normal University, Lanzhou, Gansu, 730070 P. R. China

Sintetizamos tribrometo de quinolina suportado em sílica, que mostrou ser um reagente de bromação eficiente, estável e reutilizável para a monobromação regioselectiva de aminas aromáticas. Esse processo tem a vantagem de apresentar alto rendimento sob condições moderadas e usando procedimentos experimentais simples.

Silica-supported quinolinium tribromide was synthesized and found to be an efficient, stable, and recoverable solid brominating reagent for the regioselective monobromination of aromatic amines. This protocol has advantages of high yield, mild condition and simple work-up procedure.

Keywords: bromination, aromatic amine, silica-supported quinolinium tribromide

Introduction

Bromination of aromatic substrates has received significant interest in recent years due to the increasing commercial importance of bromo-organics in the synthesis of a large number of natural products as well as in the manufacture of pharmaceuticals, agrochemicals and other specialty chemicals. Bromo-organics are key intermediates in the preparation of organometallic reagents and play vital roles in transition metal coupling reactions.¹ Bromo-organics can also be used as potent antitumor, antibacterial, antifungal, antineoplastic, antiviral and antioxidising agents.² The conventional bromination of aromatic substrates typically uses liquid bromine as brominating reagent under harsh reaction conditions.³ However, liquid bromine is a corrosive reagent and can be difficult to manipulate on small scale, thus special care is required for its storage and transportation. Recently, a variety of new methods for the bromination of aromatic compounds have been reported in the literature ranging from NBS,⁴ KBr/mineral acid,⁵ [bmim]Br₃,⁶ NaBr/NaClO₂,⁷ KBr/PhCH₂Ph₃PHSO₅,⁸ KBr/H₂O₂,⁹ *N*-methylpyrrolidin-2-one hydrotribromide/H₂O₂,¹⁰ RBr/NaH,¹¹ hexamethylenetetramine-Br₂,¹² *N,N,N',N'*-tetrabromobenzene-1,3-disulfonylamide or poly(*N*-bromobenzene-1,3-disulfonylamide),¹³ 1,2-dipyridiniumditribromide-ethane,¹⁴ ethylenebis(*N*-

methylimidazolium) ditribromide,¹⁵ 1-butyl-3-methylpyridinium tribromide,¹⁶ *tert*-butylhydroperoxide/HBr,¹⁷ LiBr/(NH₄)₂Ce(NO₃)₆,¹⁸ KBr/NaBO₃·4H₂O,¹⁹ 2-methyl-4-poly(styrylmethyl)thiazolium hydrotribromide,²⁰ LiBr/(diacetoxyiodo)benzene,²¹ alkalimetal bromide/NaIO₄,²² bromodimethylsulfonium bromide,²³ HBr/H₂O₂,²⁴ 1,8-diazabicyclo[5.4.0]undec-7-ene hydrobromide perbromide,²⁵ metal bromides/sodium bismuthate,²⁶ *N*-octyl quinolinium tribromide²⁷ and pyridinium hydrobromide perbromide.²⁸ However, some methods still suffer from drawbacks of difficult handling, low selectivity, low yield and corrosion.

Very recently, silica-supported reagents and catalysts,²⁹ especially the silica-supported brominating reagent,³⁰ were investigated, which had the advantages of high efficiency, high activity and easy handling.

In continuation of our study on the chemical transformation using silica-supported reagent, in this paper, we report a new bromination method which uses silica-supported quinolinium tribromide (SQTB) instead of liquid bromine as an alternative electrophilic bromine source to deliver a stoichiometric amount of bromine to aromatic amines and regioselectively synthesize monobromination products under mild condition.

Experimental

IR spectra were recorded using KBr pellets on a Digilab FTS 3000 FTIR spectrophotometer and

*e-mail: lizheng@nwnu.edu.cn

^1H NMR spectra on a Mercury-400BB instrument using CDCl_3 or $\text{DMSO}-d_6$ as solvents and Me_4Si as internal standard. Melting points were observed in an electrothermal melting point apparatus. Gas chromatography was determined on Shimadzu GC 2010. The course of reaction and purity of products were checked by TLC.

Preparation of silica chloride

Silica chloride was prepared according to modified literature method.³¹ Silica gel (80-200 mesh) was washed with 1 mol L^{-1} HCl, followed by deionized water, 30% H_2O_2 and then again deionized water. After being washed, the silica was dried overnight at 100°C in vacuum to give preconditioned silica gel. To preconditioned silica gel (10 g), in a round bottomed flask equipped with a condenser and a drying tube, thionyl chloride (40 mL) was added and the reaction mixture was refluxed for 48 h. The unreacted thionyl chloride was distilled off and the resulting grayish white powder was dried at 100°C in vacuum and stored in a tightly capped bottle. This silica chloride can be used for months without losing its activity.

Preparation of silica-supported quinoline

Silica-supported quinoline was prepared according to modified literature method.³¹ Silica chloride (5 g) was added to the solution of 8-hydroxyquinoline (7.3 g, 50 mmol) and triethylamine (5.1 g, 50 mmol) in 20 mL of acetonitrile, and the slurry was refluxed for 24 h. Then, the mixture was filtered and the solid was washed with dichloromethane ($3 \times 20 \text{ mL}$) and deionized water ($3 \times 50 \text{ mL}$), and then dried at 100°C in vacuum to give the product. The silica supporting capacity for quinoline is *ca.* 1.2 mmol g^{-1} , which was estimated by carbon elemental analysis.

Preparation of silica-supported quinolinium tribromide

To the silica-supported quinoline (5 g, 6 mmol based on the supported quinoline), hydrobromic acid (48 wt.% in water, 6.7 g, 40 mmol) was added. The mixture was stirred vigorously at room temperature for 12 h. Then sodium bromate (0.75 g, 5 mmol) was added, and the resulting mixture was refluxed for 48 h. Then, the mixture was filtered, the solid was washed with deionized water ($3 \times 50 \text{ mL}$) and dried at 100°C in vacuum to give the product. The silica supporting capacity for quinolinium tribromide is *ca.* 1.2 mmol g^{-1} , which was estimated by

carbon elemental analysis. IR $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr): 3429, 2926, 1631, 1454, 1361, 1104, 976, 805.

General procedure for the monobromination of aromatic amines using silica-supported quinolinium tribromide

To an aromatic amine (1 mmol) in 20 mL of acetonitrile, silica-supported quinolinium tribromide (1 g, 1.2 mmol based on the supported quinolinium tribromide) was added. The mixture was stirred at room temperature or at reflux for appropriate time indicated in Table 2 until the reaction was completed as monitored by TLC. The resulting mixture was filtered to recover the spent silica-supported quinolinium tribromide, which was washed by CH_2Cl_2 ($3 \times 10 \text{ mL}$) and regenerated by further reaction with hydrobromic acid and sodium bromate. The filtrate was evaporated off the solvent under reduced pressure and extracted with ether ($4 \times 10 \text{ mL}$). The ether solution was washed with deionized water ($4 \times 10 \text{ mL}$), dried by magnesium sulfate and then evaporated off ether to give the crude product, which was recrystallized from ethanol to give the pure product. The analytical data for representative compounds are shown below.

2-Bromo-4-methoxybenzenamine (entry 9)

^1H NMR (CDCl_3 , 400 MHz) δ 3.73 (s, 3H, CH_3), 4.20 (br s, 2H, NH_2), 6.25-6.70 (m, 3H, Ar-H). IR $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr): 3392, 3299, 1594, 1478.

4-Bromo-*N,N*-dimethylbenzenamine (entry 10)

^1H NMR (CDCl_3 , 400 MHz) δ 2.91 (s, 6H, CH_3), 6.55 (d, J 8.8 Hz, 2H, Ar-H), 7.27 (d, J 8.8 Hz, 2H, Ar-H). IR $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr): 3094, 15892, 1502, 1358, 1225.

N-(4-bromophenyl)-benzamide (entry 14)

^1H NMR (CDCl_3 , 400 MHz) δ 7.47-7.57 (m, 7H, Ar-H), 7.80 (br s, 1H, NH), 7.85-7.87 (m, 2H, Ar-H). IR $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr): 3331, 1645, 1518.

2-Amino-6-bromobenzothiazole (entry 16)

^1H NMR ($\text{DMSO}-d_6$, 400 MHz) δ 7.22 (d, J 9.2 Hz, 1H, Ar-H), 7.31 (d, J 9.2 Hz, 1H, Ar-H), 7.63 (s, 2H, NH_2), 7.78 (s, 1H, Ar-H). IR $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr): 3457, 3089, 1634, 1534, 1447, 1306, 1107.

3-Bromo-9-ethyl-carbazole (entry 19)

^1H NMR (CDCl_3 , 400 MHz): δ 1.40-1.44 (t, 3H, J 7.2 Hz, CH_3), 4.32-4.35 (q, 2H, J 7.2 Hz, CH_2), 7.24-7.53 (m, 5H, Ar-H), 8.03-8.05 (m, 1H, Ar-H), 8.20 (s, 1H, Ar-H). IR $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr): 2968, 1626, 1466, 1447, 1225.

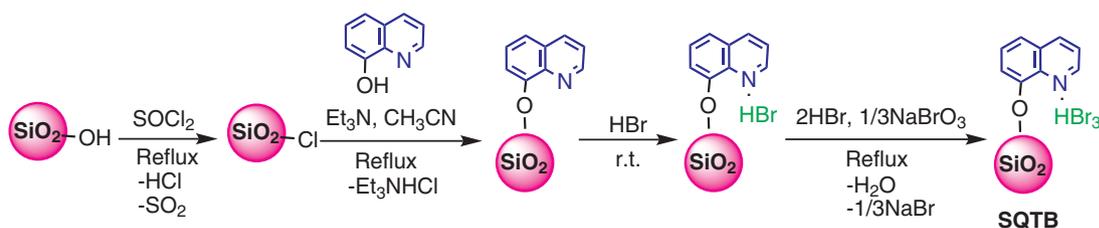
Results and Discussion

Preparation of silica-supported quinolinium tribromide (SQTB)

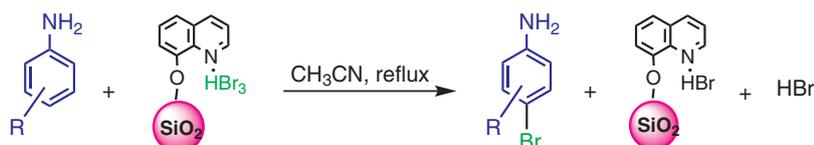
Silica-supported quinolinium tribromide was synthesized by the reflux of preconditioned silica gel in thionyl chloride first to give silica chloride, then silica chloride was further reacted with 8-hydroxyquinoline in acetonitrile under refluxing condition to yield silica-supported quinoline. Silica-supported quinoline was further treated with hydrobromic acid at room temperature to form silica-supported quinolinium bromide, which was then refluxed with the mixture of hydrobromic acid and sodium bromate to afford silica-supported quinolinium tribromide (SQTB) in high yield (Scheme 1). It is noteworthy to mention that the silica supporting capacity for quinolinium tribromide is affected by solvents. The CH_2Cl_2 , CHCl_3 , CCl_4 , THF and CH_3CN were tested for the supporting reaction. It was found that the reaction in acetonitrile gave the best result (Table 1). SQTB is a stable solid and has no offensive odor of typical bromine.

Table 1. The effect of solvents on the silica supporting capacity for quinolinium tribromide

Entry	Solvent	Silica supporting capacity for quinolinium tribromide (mmol g ⁻¹)
1	CH_2Cl_2	0
2	CHCl_3	0.1
3	CCl_4	0.1
4	THF	0.4
5	CH_3CN	1.2



Scheme 1.



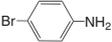
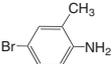
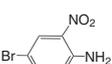
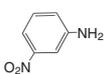
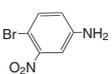
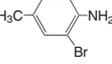
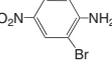
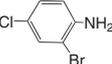
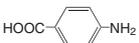
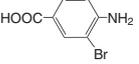
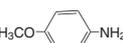
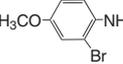
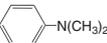
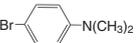
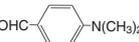
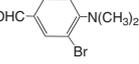
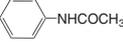
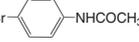
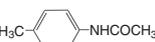
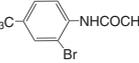
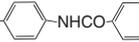
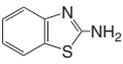
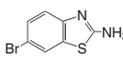
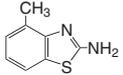
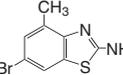
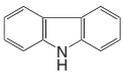
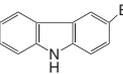
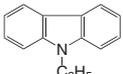
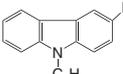
Scheme 2.

Monobromination of aromatic amines using silica-supported quinolinium tribromide (SQTB)

In order to explore the application of SQTB as a brominating reagent, aniline was selected as a model substrate. It was found that aniline reacted with SQTB in acetonitrile efficiently at reflux condition leading to regioselective monobromination, preferentially in the *para* position due to stereoelectronic effects (Table 2, entry 1), producing *p*-bromoaniline in high yield (Scheme 2). Moreover, due to use of the reagent in a stoichiometric amount, no polybromination occurred with SQTB. Although the unsupported quinolinium tribromide³² reported in the literature could also be an oxidizing agent for amines, no oxidizing products were observed for SQTB under the studied conditions. It is important to mention that the solvents play an important role in the bromination reaction by SQTB. The reaction hardly proceeded in CH_2Cl_2 , $\text{C}_2\text{H}_5\text{OH}$, DMF, 1,4-dioxane, DMSO and CS_2 . However, the reaction in CH_3CN afforded product in high selectivity, nearly complete conversion. Therefore, CH_3CN was selected as the reaction solvent. Furthermore, the spent SQTB could be easily recovered from the reaction system only by filtration, and then could be easily regenerated by further reaction with hydrobromic acid and sodium bromate. The bromination ability of the reagent was renewed. For example, the recycled SQTB, that was used under the conditions of Table 2 for the bromination of aniline, afforded in the second, third and fourth runs 90, 89 and 87% of *p*-bromoaniline, respectively.

In similar fashion, the reactions of a variety of aromatic amines with SQTB were investigated. It was found that the reactions are general and applicable to several substituted anilines containing different groups, such as methyl, methoxy, chloro, nitro and carboxyl

Table 2. Monobromination of aromatic amines with silica-supported quinolinium tribromide (SQTB)^a

Entry	Aromatic amine	Reaction condition	Product	mp (lit.) (°C)	Yield ^b (%)
1		2 h 80°C		66-68 (63-64) ⁶	90
2		2 h 80°C		57-58 (55-57) ⁶	92
3		5 h 80°C		105-106 (109-112) ¹²	95
4		5 h 80°C		132-133 (131) ³³	93
5		2 h 80°C		Oil (Oil) ⁶	92
6		5 h 80°C		100-101 (100-102) ¹²	94
7		3 h 80°C		61-62 (64-66) ⁸	89
8		7 h 80°C		201-202 (214) ³⁴	88
9		2 h 80°C		Oil (Oil) ³⁵	92
10		2 h 80°C		50 (50-52) ⁶	96
11		8 h 80°C		Oil (Oil) ¹²	92
12		12 h 80°C		166-168 (167-168) ⁸	90
13		12 h 80°C		114 (117) ³⁶	91
14		10 h 80°C		195-197 (203) ³⁷	89
15		2 h 80°C		107-109 (102-103) ⁶	94
16		6 h r.t.		201-203 (209-210) ³⁸	90
17		6 h r.t.		205-206 (212) ³⁹	92
18		5 h r.t.		193-195 (189-191) ⁴⁰	94
19		5 h r.t.		79-80 (81-82) ⁴¹	87

^a All products were identified by GC, ¹H NMR, IR and comparison with authentic samples; ^b Yields refer to the isolated products.

groups. If the substituents are electron-rich groups, the reaction time is shorter than the electron-withdrawing groups (Table 2, entries 2-9). When the *para* position of the substituted anilines is occupied, the reactions lead to selective monobromination in the *ortho* position (Table 2, entries 5-9).

In order to explore the generality of the method developed for the monobromination of activated aromatic substrates, experiments for reactions of secondary or tertiary anilines or amides with SQTB were also conducted. They were also effective and gave the corresponding monobromination products in excellent yield (Table 2, entries 10-14). Furthermore, in a similar fashion, the reactions of 1-aminonaphthalene, 2-aminobenzothiazole, 2-amino-4-methyl-benzothiazole, carbazole and 9-ethylcarbazole with SQTB were also attempted. Corresponding monobromination products were also obtained in high yield (Table 2, entries 15-19).

In comparison with other brominating reagents according to Eissen's method,⁴² SQTB used in this protocol has similar property to sol-gel entrapped pyridinium hydrobromide perbromide reported by Levin,³⁰ both of which could be easily recovered from the reaction systems, regenerated by further reactions with hydrobromic acid/sodium bromate or bromine, and reused many runs without obvious loss of activities. Employing SQTB as a transport medium for bromine could reduce the hazardous potential of using molecular bromine.⁴³ The cost and environmental impact of SQTB could be minimized by its recyclability. However, producing by-product (sodium chloride) in the preparation of SQTB and using volatile solvent (acetonitrile) in the brominating reactions are still the insufficiency of this protocol.

In conclusion, the silica-supported quinolinium tribromide was found to be an efficient, regioselective, stable and recoverable solid brominating reagent for the monobromination of aromatic amines including primary, secondary and tertiary amines, as well as amides and heterocycles. The ease of work up, high yield and high selectivity are the features of this reagent.

Acknowledgments

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