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RESEARCH ARTICLE

Selective and efficient oxidation of sulfides and thiols with a 1,1,3,3-tetramethylguanidine/Br_2 complex

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The 1,1,3,3-tetramethylguanidine/Br_2 complex has been found to be an efficient reagent for the selective oxidation of aliphatic and aromatic sulfides to the corresponding sulfoxides and the oxidative coupling of thiols to disulfides. 1,1,3,3-Tetramethylguanidine can be recovered at the completion of the reaction and reused.

Keywords: 1,1,3,3-Tetramethylguanidine/Br_2 complex; Oxidation; Sulfide; Thiol

1. Introduction

Selective oxidations of sulfides to sulfoxides and thiols to disulfides are of interest from both biological [1–5] and synthetic chemistry points of view [6–10]. Although a large number of oxidizing agents can effect the conversion of sulfides to sulfoxides and the oxidative coupling of thiols to disulfides [11], the susceptibility of sulfoxides and disulfides to further oxidation narrows the choice of reagents for these processes. Therefore, the discovery of new oxidants for the selective transformation of sulfides to sulfoxides and thiols to disulfides is of importance in synthetic organic chemistry.

The use of molecular bromine for the oxidation of sulfides and thiols is restricted because the formation of HBr (as a reduction product) can affect the selectivity of the reaction. Under acidic conditions the main product becomes contaminated by the formation of side products such as sulfonic acids, sulfinic acids and bromo substituted sulfides and sulfoxides [12]. Therefore, if bromine is to be used as an oxidant, it is necessary that these problems be circumvented by carrying out the reactions under conditions where HBr is not released as a free acid.

Recently, we have described the use of the hexamethylenetetramine/Br_2 complex as a bromine-based oxidant for the selective oxidation of organic compounds [13–15]. In those reactions hexamethylenetetramine acts as an HBr acceptor. We now wish to report on the use of the 1,1,3,3-tetramethylguanidine/Br_2 (TMGB) complex as another safe, recoverable and

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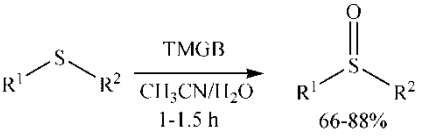
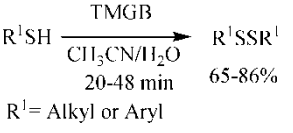
efficient reagent for the oxidation of sulfides and thiols, as summarized in Scheme 1. The amine part of this complex acts as an HBr acceptor, preventing the solution from becoming acidic. The formation of 1,1,3,3-tetramethylguanidinium hydrobromide as the reaction proceeds seems to accelerate the rate of oxidation, possibly by increasing the ionic strength of the solution. After the reaction is complete, 1,1,3,3-tetramethylguanidinium is easily recovered.





SCHEME 1

2. Results and discussion

The 1,1,3,3-tetramethylguanidine/Br_2 complex is readily prepared by the dropwise addition of a hexane solution of bromine to a hexane solution of 1,1,3,3-tetramethylguanidine at room temperature. The amount of activated Br_2 in this reagent, as determined by thiosulfate titration, was found to be approximately 35% of the total amount of bromine present; i.e., the oxidation of one mole of sulfide requires about three moles of TMGB.

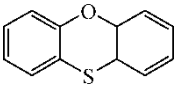
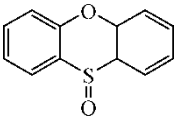
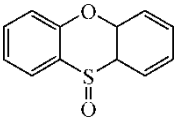
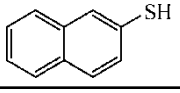
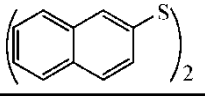
As indicated in table 1, various alkyl and aryl sulfides and thiols are converted into the corresponding sulfoxides and disulfides in good yields when the reactions are carried out in

Table 1. Oxidation of sulfides and thiols with the 1,1,3,3-tetramethylguanidine/Br_2 complex.

					M.p. or B.p.(°C)	
Entry	Reductant	Product	Time (h)	% Yield	Found	Reported [ref.]
1	$(CH_3)_2S$	$(CH_3)_2SO$	1.10 (h)	79	187–189	189–191 [21]
2	$(CH_3CH_2)_2S$	$(CH_3CH_2)_2SO$	1.10 (h)	81	101–104	103–106 [21]
3	$(CH_3(CH_2)_2)_2S$	$(CH_3(CH_2)_2)_2SO$	1.20 (h)	76	22–24	24.5–25.5 [22]
4	$(CH_3(CH_2)_3)_2S$	$(CH_3(CH_2)_3)_2SO$	1.10 (h)	78	28–32	29–31.6 [22]
5			1.30 (h)	84	232–235	235–237 [22]
6	$PhSCH_3$	$PhSOCH_3$	1.20 (h)	66	31–33	33–34 [23]
7	p-$BrC_6H_4SCH_3$	p-$BrC_6H_4SOCH_3$	1.20 (h)	83	74–77	74–76 [23]
8	p-$O_2NC_6H_4S\ CH_3$	p-$O_2NC_6H_4SO\ CH_3$	1.20 (h)	79	145–147	140–142 [23]
9	$PhSCH_2CH_3$	$PhSOCH_2CH_3$	1.40 (h)	88	144–146	146 [23]
10	$PhCH_2SCH_2Ph$	$PhCH_2SOCH_2Ph$	1.50 (h)	81	133–135	133–135 [23]
11	$PhCH_2SPh$	$PhCH_2SOPh$	1.10 (h)	78	120–121	123–124 [23]
12	PhSPh	PhSOPh	1.00 (h)	87	71–75	70.5 [24]

(*continued*)

Table 1. Continued.

Entry	Reductant	Product	Time (h)	% Yield	M.p. or B.p.(°C) Found	Reported [ref.]
13			1.10 (h)	82	151–153	153–155 [25]
14	$PhCH_2SOPh$	No reaction	24 (h)			
15		No reaction	24 (h)			
16	$CH_3(CH_2)_4SH$	$(CH_3(CH_2)_4S)_2$	0.33 (h)	71	127–130	128–130 [26]
17	$CH_3(CH_2)_7SH$	$(CH_3(CH_2)_7S)_2$	0.5 (h)	76	71–75	74–75 [23]
18	$C_6H_{11}SH$	$(C_6H_{11}S)_2$	0.66 (h)	65	122–127	125–130 [24]
19	$PhCH_2SH$	$(PhCH_2S)_2$	0.33 (h)	68	68–71	69–72 [24]
20	PhSH	$(PhS)_2$	0.5 (h)	72	59–61	61–62 [24]
21	p-$CH_3C_6H_4SH$	(p-$CH_3C_6H_4S)_2$	0.58 (h)	71	43–44	45–46 [26]
22	o-ClC_6H_4SH	(o-$ClC_6H_4S)_2$	0.3 (h)	86	85–87	87–88 [27]
23			0.42 (h)	83	138–139	139 [28]

aqueous acetonitrile at room temperature for 2 hours or less. This is a highly useful reaction for the preparation of sulfoxides, which are important intermediates in the synthesis of many organic compounds [16]. As indicated by the data in table 1 (entries **14** and **15**), sulfoxides are resistant to further oxidation to sulfones under these conditions.

3. Conclusion

A new bromine-based oxidant for the selectively oxidation of sulfides and thiols to their corresponding sulfoxides and disulfides has been discovered. The reaction proceeds without any over-oxidation to sulfones or sulfonic acids. This reagent, which it can be recycled and handled much more easily than liquid bromine, is a convenient alternative to other *N*-haloamines [17–20]. Our investigations toward specificity of these kind of reactions and their extension to the oxidation of other organic compounds are in progress.

4. Experimental

4.1 *General*

Melting points were measured using an Electrothermal 9100 apparatus and are uncorrected; IR spectra were recorded using a Shimadzu IR-470 spectrometer; and, ^{1}H NMR spectra were recorded in $CDCl_3$ using a Bruker DRX-300 Avance spectrometer at 300.13 MHz. All products, known compounds, were characterized by IR and ^{1}H NMR spectral data and the observation that their melting points are consistent with literature values.

4.2 *Preparation of 1,1,3,3-tetramethylguanidine/Br_2*

A solution of Br_2 (0.480 g, 3 mmol) in hexane (2 ml) was added dropwise to a magnetically stirred solution of 1,1,3,3-tetramethylguanidine (0.345 g, 3 mmol) in hexane (15 ml). The solution was then stirred at room temperature for 30 min. A yellow oil which formed was separated and washed twice with hexane (2 × 10 ml). The product (0.795 g, 96%) was used without further purification for the oxidation of sulfides and thiols.

4.3 *Oxidation of sulfides*

In a typical reaction, methyl phenyl sulfide (0.124 g, 1 mmol) was added to the mixture of 1,1,3,3-tetramethylguanidine/Br_2 (0.790 g, 2.9 mmol) in aqueous acetonitrile (CH_3CN/H_2O; 3:1 V/V, 20 ml). The mixture was stirred at room temperature for 80 min, while the progress of the reaction was followed by TLC. Upon completion, the reaction mixture was treated with saturated aqueous sodium thiosulfate (5 ml) to reduce any residual oxidant. The product was extracted into CH_2Cl_2 (2 × 10 ml) and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave a product (0.123 g, 88%) of sufficient purity for most purposes; mp 31–33°C (ref. [23]: 33–34°C). IR (KBr) (ν_{max}, cm^{-1}) 3070, 3000, 2920, 1450, 1406, 1093, 1050. ^1H NMR [300 MHz, $CDCl_3$] δ 2.70 (s, 3H, CH_3), 7.35–7.71 (m, 5 arom. H) ppm.

4.4 *Oxidation of thiols*

In a typical procedure *p*-methyl thiophenol (0.124 g, 1 mmol) was added to a mixture of 1,1,3,3-tetramethylguanidine/Br_2 (0.790 g, 2.9 mmol) in aqueous acetonitrile (CH_3CN/H_2O; 3:1 V/V, 20 ml). The mixture was stirred at room temperature for 35 min, while the progress of the reaction was followed by TLC. Upon completion, the reaction mixture was treated with saturated aqueous sodium thiosulfate (5 mL) to reduce any residual oxidant. The product was extracted into CH_2Cl_2 (2 × 10 ml) and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave a product (0.087 g, 71%) of sufficient purity for most purposes; mp 43–44°C (ref. [26]: 45–46°C). IR (KBr) (ν_{max}, cm^{-1}) 3029, 2912, 1488, 1396. ^1H NMR [300 MHz, $CDCl_3$] δ 2.35 (s, 6H, $2CH_3$), 7.13 (d, $J = 8.1$ Hz, 4 arom. H), 7.41 (d, $J = 8.2$ Hz, 4 arom. H) ppm.

4.5 *Recovery of 1,1,3,3-tetramethylguanidine*

The aqueous layer obtained from the above reaction mixtures was treated with saturated aqueous sodium thiosulfate (5 mL) to reduce excess oxidant. Then, saturated sodium carbonate (5 mL) was added to neutralized the HBr and the liberated 1,1,3,3-tetramethylguanidine was extracted into CH_2Cl_2 (2 × 10 ml). This solution was dried over anhydrous magnesium sulfate and the solvent evaporated under vacuum to give 1,1,3,3-tetramethylguanidine (0.217 g, 63%).

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