LETTER

NJC
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Tetra-*n*-alkylammonium bromates—new and efficient reagents for deoximation

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Received (in Toulouse, France) 18th June 2004, Accepted 14th September 2004
First published as an Advance Article on the web 15th November 2004

Tetra-*n*-alkylammonium bromates were prepared from the corresponding bromides for the first time and were used for deoximation of oximes to the corresponding carbonyl compounds.

Quaternary ammonium salts are versatile phase-transfer catalysts and some of them have been used to assist oxidation of a variety of organic compounds using inexpensive primary oxidants such as O^2,[1] NaOCl,[2] H_2O_2,[3] $KMnO_4$[4] and others.[5,6] Research efforts are now directed towards modifying the usual quaternary ammonium salts and using them as reagents rather than as catalysts. In our search for low-cost, selective yet efficient and easy-to-handle oxidizing agents, we observed that the tetra-*n*-alkylammonium bromides can be converted to the corresponding bromates by the simple procedure of passing chlorine gas through an alkaline solution of the bromide. Using this simple procedure two such bromates, namely tetra-*n*-propylammonium bromate and tetra-*n*-butylammonium bromate, were prepared. These bromates are low-melting solids with excellent storage stability and responded to all analytical test for bromates.[7] These bromates were found to be soluble both in water and in organic solvents. Bromates are seldom used as oxidants in organic synthesis, primarily because of their insolubility in organic solvents. The favourable solubility characteristics of these tetra-*n*-alkylammonium bromates not only offered the opportunity for their use as primary oxidants for organic substrates but also made product recovery easy. As a first application of these versatile oxidizing agents, we used these reagents for the oxidative deoximation of several oximes to the parent carbonyl compounds.

Oximes are crystalline compounds and are used for the isolation, purification and characterisation of the parent carbonyl compounds.[8,9] Besides protecting a carbonyl group,[10] oximation gives the product oxime, which can be used as intermediates for the preparation of nitriles,[11] of amides *via* the Beckmann rearrangement or to activate the carbonyl group.[12] Considering that oximes can be prepared from non-carbonyl precursors and from compounds having active methylene groups by reported methods,[13,14] deoximation becomes a very important procedure not only for the regeneration of the parent carbonyl but also for conversion of compounds of the type Z–CH_2–Z′ to Z–CO–Z′ where Z and Z are electron-withdrawing groups, thus leading to new methods for the preparation of carbonyl compounds from hydrocarbon sites.

The classical acid-catalysed hydrolysis of oximes as a method of deoximation proved to be unsatisfactory, especially when acid-sensitive functional groups are present in the molecule.[15] Some methods have been reported for the oxidative deoximation and notable among them are the use of 2,6DCPCC,[16] TMSCl,[17] 3-carboxypyridine chlorochromate,[18] dimethyloxirane,[19] Mn(*O*-Ac)$_2$[20] and *t*-butylhydroperoxide.[21] Despite the great improvements reported, these methods suffer from the disadvantages of using harsh reaction conditions, costly reagents and elaborate recovery procedures. Herein, we wish to report that tetra-*n*-alkylammonium and tetra-*n*-butylammonium bromates, prepared for the first time, act as a new class of cost-effective reagents for oxidative deoximation (Scheme 1, Table 1).

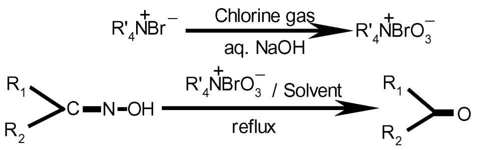
It is noteworthy that, unlike other methods of deoximation, the major drawbacks of overoxidation of aldehydes to carboxylic acid and the formation of by-products resulting from oxidation of the solvent were not observed. Camphor oxime could be converted to camphor, α,β-unsaturated oximes were deoximated without oxidation of the double bond. Furthermore, acid- and base-sensitive groups remained unaffected and finally the solvent toluene was not oxidized. The water solubility of the unreacted reagent and by-products made product recovery easy. In conclusion, bromates, which are not used extensively in the oxidation of organic substrates primarily due to their insolubility in organic solvents, can be used for this purpose when present as a counterion in quaternary ammonium salts.

Experimental

All reagents and solvents were purified by methods reported in the literature.[7] The quaternary ammonium bromides were procured from E. Merck, Inc. Melting points were recorded in an apparatus from Scientific Devices, India, type MP-D, in open capillaries and ^{1}H NMR spectra were recorded in an EM 360, 60 MHz spectrometer. C,H,N analysis of the bromates were obtained from the facility available at RRL, Jorhat.

Conversion of the tetra-*n*-alkylammonium bromide to bromate

The bromide (0.01 mol; 3.14 or 3.70 g for the propyl or butyl, respectively) was dissolved in 50 ml of 5% aqueous NaOH and chlorine gas was passed through the solution till a yellow (orange for the butyl case) oil separated, which solidified on standing. The yellow (orange) solid was filtered and dried. On neutralising the filtrate with dilute HCl, a second crop of the yellow (orange) bromate was obtained.



Scheme 1 Deoximation of oximes with tetra-*n*-alkylammonium bromate.

DOI: 10.1039/b409319d

Table 1 Deoximation of various oximes to the carbonyl compounds

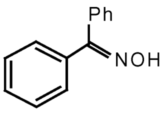
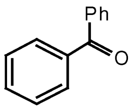
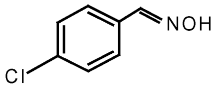
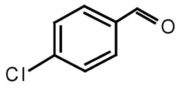
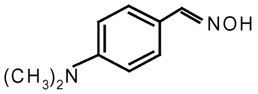
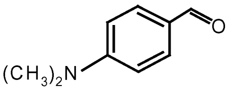
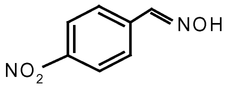
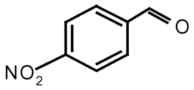
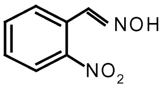
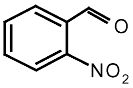
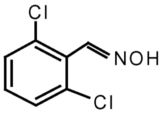
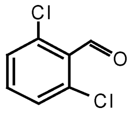
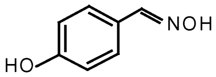
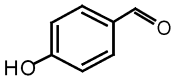
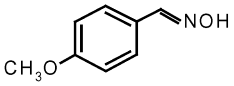
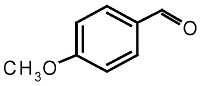
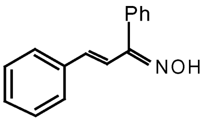
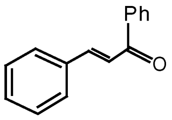
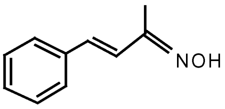
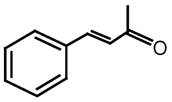
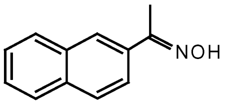
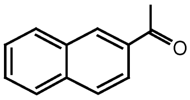
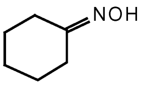
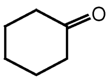
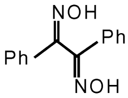
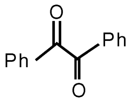
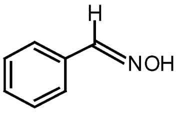
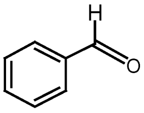
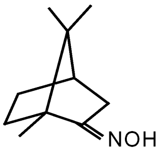
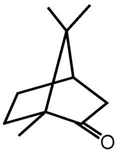
			Reflux time[a]/h		% Yield[a]		M.p. or b.p.[b]/°C	
Entry	Substrate	Product	I	II	I	II	Obs.	Lit.[6]
1			3	3	85	82	48	48
2			2.5	3	89	85	46	47
3			2.5	3	79	82	72	73
4			2.5	3	84	80	108	106
5			1.5	2	92	78	46	44
6			2.5	2.5	78	76	74	71
7			2.5	3	92	81	116	117
8			1.5	2	78	74	249[c]	247[c]
9			2.5	2.5	92	90	56	58
10			2.5	1.5	80	76	42	42
11			1.5	1.5	86	81	52	53
12			2.5	2	76	80	158[c]	156[c]

Table 1 (*continued*)

Entry	Substrate	Product	Reflux time[a]/h		% Yield[a]		M.p. or b.p.[b]/°C	
			I	II	I	II	Obs.	Lit.[6]
13			1	1.5	89	87	97	95
14			1.5	2	88	83	180[c]	179[c]
15			1.5	2	71	78	179	179

[a] I denotes tetra-*n*-propylammonium bromate and II is with tetra-*n*-butylammonium bromate. [b] Products identified by their m.p./b.p., ^{1}H NMR and IR. [c] Boiling point.

Tetra-*n*-propylammonium bromate. M.p. 114–116 °C; ^{1}H NMR ($CDCl_3$): δ 1.2 (m, 12 H), 2.3 (m, 8 H), 4.5 (m, 8 H); anal. found C, 46.4%; H, 8.92%; N, 4.18%; calcd C, 45.86%; H, 8.98%; N, 4.46%.

Tetra-*n*-butylammonium bromate. M.p. 61–62 °C; ^{1}H NMR ($CDCl_3$): δ 1.3 (m, 12 H), 2.3 (m, 8 H), 3.6 (m, 8 H), 4. 8 (m, 8 H); anal. found: C, 50.8%; H, 9.92%; N, 3.93%; calcd C, 51.88%; H, 9.79%; N, 3.78%.

Oxidative deoximation of oximes with tetra-*n*-alkylammonium bromates

In a representative procedure, 0.001 mol of the oxime and 0.001 mol of the tetra-*n*-alkylammonium bromate were dissolved in 15 ml of toluene and refluxed (Table 1). The progress of the reaction was monitored by TLC in prepared silica gel plates using authentic samples of the starting and target compounds as references. A mixture of ethyl acetate–hexane (1 : 9) was used as the eluent. After completion of the reaction, the solvent was removed under reduced pressure and the solid obtained was dissolved in minimum volume of ethanol and poured into ice cold water. The product was washed several times with water. In the cases that liquid carbonyl compounds were the end product, they were separated from the solvent and by-products by fractional distillation under reduced pressure. The products were identified by determining their m.p., b.p., ^{1}H NMR and IR spectra and comparing them with those obtained from authentic samples.

Acknowledgements

The authors are grateful to UGC, New Delhi for financial assistance.

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