J. Chem. Research (S), 1998, 100–101†

Oxidation of Benzylic and Secondary Alcohols to Carbonyl Compounds by $NaBrO_3$–NH_4Cl Reagent in Aqueous Acetonitrile†

Ahmad Shaabani* and Majid Ameri

Chemistry Department, Shahid Beheshti University, P.O. Box 19396-4716, Tehran, Iran

$NaBrO_3$ combined with NH_4Cl is found to be an efficient reagent for the conversion, in aqueous acetonitrile and under mild conditions, of benzylic and secondary alcohols into aldehydes and ketones, respectively.

The oxidation of alcohols to carbonyl compounds is a fundamental transformation of organic chemistry which is attracting much current interest.[1–4] A great number of oxidizing agents can effect the conversion of alcohols into carbonyl compounds, and synthetic chemists are faced with an wide choice of methods for this reaction. However, the susceptibility of aldehydes to further oxidation narrows the choice of reagents for the oxidation of primary alcohols to aldehydes in good yield, and if the alcohol group is part of a complex molecule that is sensitive to acidic or basic reagents then the choice of effective oxidants is narrowed still further. The discovery of new oxidants for the transformation of alcohols to carbonyl compounds under mild conditions with a variety of alcohols is of prime importance in synthetic organic chemistry. Oxidations of alcohols by $NaBrO_3$ in the presence of cerium(IV) ammonium nitrate (CAN),[5] bromine,[6] $NaHSO_3$,[7] HBr,[8] H_2SO_4,[9] $HClO_4$[10] and HOAc,[11] have been reported, most of the reactions having occurred in relatively strong acidic solutions. We report here the oxidation of benzylic and secondary alcohols with $NaBrO_3$–NH_4Cl into the corresponding aldehydes and ketones.

We have found that this method of oxidation is very convenient for the conversion of alcohols into carbonyl compounds because of its simplicity and use of mild reaction conditions. Furthermore, NH_4Cl and $NaBrO_3$ are both cheap and easily available compared to most other oxidizing agents that have so far been employed. As shown in Table 1, a wide variety of secondary alcohols and some benzylic alcohols could be easily oxidized to the corresponding carbonyl compounds. However, other primary alcohols (Table 1, entries 3–5) were recovered practically unchanged.

In order to obtain some information about the reaction pathway, cyclohexanol was allowed to react with (a) $NaBrO_3$–NH_4OAc [5 mmol $NaBrO_3$ and 7 mmol NH_4OAc in 10 ml solvent mixture (acetonitrile–water 7:3)] and (b) $NaBrO_3$ (5 mmol $NaBrO_3$ in 10 ml same solvent mixture) in the absence of NH_4Cl. Neither $NaBrO_3$–NH_4OAc nor bromate ion alone was capable of oxidizing cyclohexanol. This fact excludes the possibility of the alcohols being oxidized with just BrO_3^- ion and also when bromate ion exists in the presence of NH_4^+ ion in a solution which does not have any acidic property (the pH of 5 mmol $NaBrO_3$ and 7 mmol NH_4OAc in 3 ml of H_2O is 7.20). However, in a solution in which both bromate and NH_4^+ ions co-exist, NH_4^+ ion hydrolysis gives an acidic solution (the pH of 5 mmol $NaBrO_3$ and 7 mmol NH_4Cl in 3 ml of H_2O is 4.00) while the BrO_3^- ions are capable of oxidizing the alcohols. In order to illustrate the role of NH_4Cl in providing an acidic solution, we performed experiments in various buffer solutions in the absence of chloride ion. Thus we repeated the oxidation of cyclohexanol in HOAc–NaOAc (7 ml CH_3CN + 3 ml buffer solution with pH = 4.62), potassium hydrogen phthalate (7 ml CH_3CN + 3 ml buffer solution with pH = 3.99) and NaH_2PO_4 (7 ml CH_3CN + 3 ml buffer solution with pH = 3.86). No reaction occurred in any of these experiments after 3 h at 80 °C. These experiments showed that the reaction is not only pH-dependent, but also requires the definite presence of Cl^- from NH_4Cl in order to proceed. The chloride ion mentioned above is suggested to generate bromine and chlorine *via* the following reaction:[12]

$$2BrO_3^- + 2X^- + 12H^+ \rightarrow Br_2 + X_2 + 6H_2O \qquad X = Cl,\ Br$$

and can in turn oxidize alcohols.[13]

We have found that Br_2 is generated after *ca.* 2.5 h when $NaBrO_3$ (5 mmol) is added to a solution of NH_4Cl (7 mmol, in 7 ml CH_3CN + 3 ml H_2O) at room temperature.

Also, a of NH_4Br–$NaBrO_3$ mixture was observed to release bromine and we suggest that this system could be a good candidate for the oxidation of alcohols or as a brominating agent of alkenes.

In conclusion, $NaBrO_3$–NH_4Cl is an excellent oxidizing agent which promises to be economical with high yields, employs simple and mild reaction conditions, and is thus a convenient reagent for selective oxidation of secondary and benzylic alcohols.

Experimental

All products are known compounds and were identified by comparison of their physical and spectral data with those of authentic samples. Melting points were determined in open capillaries using an oil-bath and are uncorrected. IR spectra were recorded as neat films or as KBr pellets on a Shimadzu 470 spectrometer. ^1H NMR spectra were recorded at 90 MHz on a JEOL EX-90 instrument with $CDCl_3$ as solvent and Me_4Si as an internal standard. pH Measurements were carried out with a Schott CG model 825 pH meter equipped with a combined glass–calomel electrode; all the pH measurements were performed in aqueous solution. All alcohols are commercial materials and were purchased from Fluka, Aldrich or Merck. Reagent-quality solvents were used without further purification. Yields reported refer to isolated products or 2,4-dinitrophenylhydrazone derivatives (2,4-DNP)[14,15] of the carbonyl compounds.

General Procedure.—Alcohol (5 mmol) was added to a mixture of $NaBrO_3$ (0.755 g, 5 mmol) and NH_4Cl (0.4 g, 7.5 mmol) in aqueous acetonitrile (CH_3CN–H_2O = 7/3 v/v; 10 ml). The mixture was stirred at 80 °C for 1–3 h. When the reaction was complete, the resulting solution was extracted with methylene dichloride (20 ml × 2). The combined organic layers were washed with a saturated aqueous solution of $NaHCO_3$ and dried over $MgSO_4$. After filtration, the solution was concentrated to afford the crude carbonyl compound, which was frequently of good purity without further treatment, although, if necessary, it could be purified by distillation, crystallization or chromatography, as appropriate.

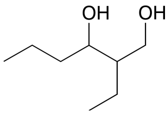
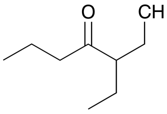
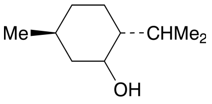
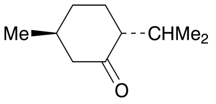
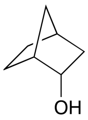
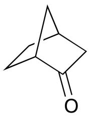
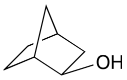
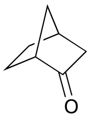
Financial support by the Research Council of Shahid Beheshti University is gratefully acknowledged.

---

*To receive any correspondence.

†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1998, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

Table 1 Oxidation of alcohols to carbonyl compounds by $NaBrO_3$–NH_4Cl in acetonitrile–water (7:3 v/v) at 80 °C

Entry	Reactant	Product	Reaction time (t/h)	Yield (%)		Bp of carbonyl product at 760 Torr (T/ °C)	Mp of carbonyl product (T/ °C)	Mp of 2,4-DNP (T/ °C)
				2,4-DNP	Isolated			
1	$CH_3CH_2CH_2CH(OH)CH_3$	$CH_3CH_2CH_2COCH_3$	3.0	75	80	102 (100–101[a])	—	142 (144[b])
2	$(CH_3)_2CHCH(OH)CH_3$	$(CH_3)_2CHCOCH_3$	3.30	90	88	94 (94–95[a])	—	120 (117[b])
3			2.30	50	49	—	—	118 (118.5–119.5[c])
4	Octan-1-ol	No reaction	6.0					
5	Hexan-1-ol	No reaction	6.0					
6	Cyclopentanol	Cyclopentanone	1.0	90	85	127–139 (131[a])	—	144 (142[b])
7	Cyclooctanol	Cyclooctanone	3.0	90	83	185–193 (195[a])	—	162 (163[b])
8	Cyclohexanol	Cyclohexanone	2.0	90	91	150–155 (155[a])	—	160–161 (162[b])
9[d]	4-*tert*-Butylcyclohexanol	4-*tert*-Butylcyclohexanone	3.0	70	72	—	48–49(47–50[c])	
10[d]	2-*tert*-Butylcyclohexanol	2-*tert*-Butylcyclohexanone	3.0	50	53	62[f]		
11[g]			4.0	80	81	202–203 (207[a])	—	146 (146[b])
12	$PhCH_2OH$	PhCHO	2.0	86	80	175 (179[a])	—	230 (237[b])
13	PhCH(OH)Me	PhCOMe	2.0	95	88	199–201 (202[a])	—	240 (250[b])
14	$4\text{-}O_2NC_6H_4CH_2OH$	$4\text{-}O_2NC_6H_4CHO$	2.0	80	78	—	104–105 (106[b])	315 dec (320 dec[b])
15[h]			1.0	60	62	—	93–95 (94–96[e])	125 (125–126[i])
16[j]			1.0	60	61	—	93–95 (94–96[e])	—
17	Me_3COH	No reaction						
19[k]	Cyclohexanol	No reaction						

[a] From ref. 16 at 760 Torr (≈101080 Pa). [b] From ref. 16. [c] From ref. 17. [d] *cis* and *trans* isomers. [e] From ref. 18. [f] At 5 Torr (≈665 Pa) (lit.,[15] 62.5, 4 Torr ≈532 Pa). [g] (–)-Menthol. [h] (+)-*endo*-Norborneol. [i] From ref. 4. [j] (+)-*exo*-Norborneol. [k] In the absence of NH_4Cl.

Received, 10th March 1997; Accepted, 28th October 1997
Paper E/7/01647F

References

1 R. C. Larock, *Comprehensive Organic Transformation*, VCH, Weinheim, 1989.
2 M. Hudlicky, *Oxidation in Organic Chemistry* (*ACS Monograph 186*), American Chemical Society, Washington, DC, 1990.
3 A. H. Haines, *Methods for Oxidation of Organic Compounds: Alcohols, Alcohol Derivatives, Alkyl Halides, Nitroalkanes, Alkyl Azides, Carbonyl Compounds, Hydroxy Arenes and Aminoarenes*, Academic Press, London, 1988.
4 I. Yavari and A. Shaabani, *J. Chem. Res. (S)*, 1994, 274.
5 (*a*) T-L. Ho, *Synthesis.*, 1978, 936; (*b*) H. Tomidca, K. Oshima and H. Nozaki, *Tetrahedron Lett.*, 1982, **23**, 539.
6 L. Farkas and O. Schachter, *J. Am. Chem. Soc.*, 1949, **71**, 2827.
7 K. Takase, H. Masuda, O. Kaf, Y. Nishiyama, S. Sakaguchi and Y. Ishii, *Chem. Lett.*, 1995, 871.
8 S. Kajigaeshi, T. Nakayama, N. Nagasaki, H. Yamasaki and S. Fujisaki, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 747.
9 G. Hoist, *Kgl. Fysiogrof. Sallskap. Lund*, 1940, **10**, 63 (*Chem. Abstr.*, 1941, **35**, 7808[9]).
10 A. C. Chatterji and S. K. Roy, *Z. Phys. Chem. (Leipzig)* 1972, **250**, 137 (*Chem. Abstr.*, 1972, **77**, 139201z).
11 Vijayalaxmi and E. V. Sundaram, *J. Indian Chem. Soc.*, 1978, **55**, 567.
12 N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements.*, Pergamon Press, Oxford, 1984, p. 1012.
13 For an excellent review of the oxidizing power of bromine in aqueous solution, see: J. Palou, *Chem. Soc. Rev.*, 1994, 357.
14 R. M. Roberts, J. C. Gilbert, L. B. Rodwald and A. S. Wingrove, *Modern Experimental Organic Chemistry*, Saunders, Philadelphia, 4th edn., 1985, pp. 700–701.
15 J. Zhang, R. L. Hertzler and E. J. Eisenbraun, *J. Chem. Educ.*, 1992, **69**, 1037.
16 W. J. Criddle and G. P. Ellis, *Spectral and Chemical Characterization of Organic Compounds: A Laboratory Handbook*, Wiley, Chichester, 3rd edn., 1990.
17 R. L. Wear, *J. Am. Chem. Soc.*, 1951, **73**, 2390.
18 Aldrich Catalogue/Handbook of Fine Chemicals, 1994–1995.