Pergamon

Tetrahedron 55 (1999) 4071–4076

TETRAHEDRON

Clay-Supported Tetrabutylammonium Periodate as a Versatile Oxidant for Alcohols and Sulfides

C.Venkatachalapathy, M.Rajarajan, H.Shayira Banu[†] and K.Pitchumani*

School of Chemistry, Madurai Kamaraj University, Madurai-625 021, INDIA

Received 29 September 1998; revised 12 January 1999; accepted 28 January 1999

Abstract - Clay-supported tetrabutylammonium periodate is found to oxidise efficiently benzylic alcohols to the corresponding aldehydes without overoxidation to acids. It also oxidises aryl sulfides selectively to the corresponding sulfoxides. © 1999 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

Supported reagents[1,2] based on inorganic materials have been widely employed in organic syntheses. Ease of handling, good dispersion of active sites leading to improved reactivity, safer and milder reaction conditions and reusability are a few advantages of using these supported reagents. They are also "environmentally friendly" as their use leads to minimal pollution and waste. Solid oxidants based on silica, alumina and other porous materials are an important class of supported reagents[3-5] used for the chemoselective oxidation of organic substrates. Solid acids, used as more environmentally acceptable replacements for conventional Brönsted and Lewis acids, have also gained attention in recent years and K10-montmorillonite, an inexpensive acidic industrial catalyst, has been the support of choice.

Clay-supported potassium permanganate[6] (for the selective oxidation of allylic alcohols into α,β-unsaturated ketones without affecting the double bond), thallium (III) nitrate supported on K10-montmorillonite[7-9] (for effective oxidative rearrangement of alkyl aryl ketones into alkyl arylcarboxylates), anhydrous iron(III) nitrate supported on K10- montmorillonite (clayfen,[10] for the oxidation of alcohols to the corresponding aldehydes), clay-supported copper(II) nitrate (claycop,[11] for aromatization of 1,4-dihydropyridines) and clay-supported zinc chloride (clayzic, as an environmentally friendly alternative[12-14] to the hazardous aluminium chloride in Friedel-Crafts reactions) are a few common clay-based reagents. Oxidation of sulfides with oxone in dichloromethane in the presence of wet-montmorillonite or kaoline clays,[15-17] alcohol oxidation with *in situ* generated montmorillonite K10-supported ferric nitrate[18] and oxidation of cyclohexanones using magnesium monoperoxyphthalate[19] in the presence of bentonite clays have also been reported. There are also other examples of clay based oxidants[20-22] employed recently. In many cases, a deeper understanding of the clay-oxidant interaction and the mechanism is desirable.

[†]Department of Materials Science, Madurai Kamaraj University, Madurai - 625 021, INDIA

0040-4020/99/$ - see front matter © 1999 Elsevier Science Ltd. All rights reserved.

PII: S0040-4020(99)00101-5

In recent years, much attention has been paid to the use of quaternary ammonium salts for a wide range of reactions[23-28] in homogeneous phase in non-aqueous solvents. The solubility of quaternary ammonium salts in several solvents provides advantages in terms of high reaction rates, low reaction temperatures and absence of side reactions. However, some of them need catalysts for activation. For example, tetrabutylammonium periodate (TBAPI) alone is not able to transform hydroxyl groups to the corresponding carbonyl compounds in aprotic solvents. However in the presence of a Lewis acid ($AlCl_3$ or BF_3-Et_2O) as catalyst,[29] TBAPI is able to oxidise alcohols to the carbonyl compounds, thiols to disulfides, thioethers to sulfoxides in $CHCl_3$ and CH_3CN as solvents. This prompted us to prepare clay-supported TBAPI and to study the oxidation of alcohols and sulfides. The emphasis will be on simplicity of the method, selectivity with regard to overoxidation, efficiency and mildness of conditions.

RESULTS AND DISCUSSION

The data presented in Table 1 amply demonstrate the efficiency of clay-supported TBAPI towards the oxidation of benzylic alcohols to the corresponding carbonyl compounds in good yield. Substituted benzyl alcohols react less efficiently and a poor correlation between availability of electron density and reactivity is observed. With a *para*-nitro group there is no oxidation at all. Similarly, bulkier alcohols like piperonyl alcohol and adamantanol do not react. However, bulkier alcohols which have a planar geometry and are able to retain it in the transition state undergo efficient oxidation. This observation prompted us to propose that the presence of a hydroxyl group in the substrate leads to partial swelling of the clay interlayer, between which the substrate penetrates and is oxidised by the active form of the oxidant (Figure 1).

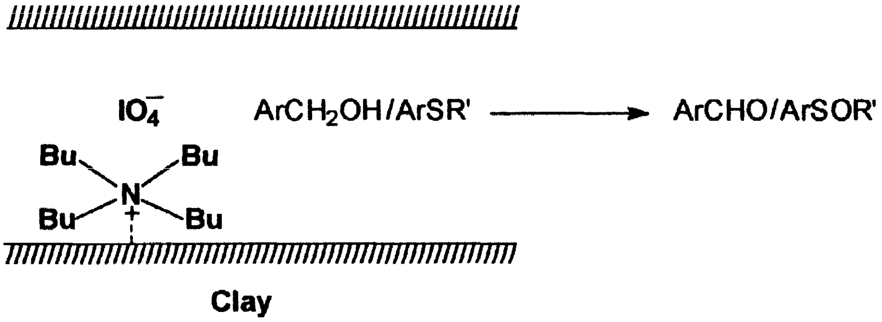

Figure 1. Oxidation of benzyl alcohols and sulfides by clay-supported TBAPI

The reaction is facile and general to other primary, secondary as well as aliphatic alcohols demonstrating the versatility of the oxidant. Both the Brönsted and Lewis acidic sites of clay are involved in the generation of active species of periodate,[30] which may be either IO_4^- or H_5IO_6 depending on the interlayer acidity. The likelihood of the active oxidant leaching out of the clay on becoming neutral i.e., H_5IO_6 may be ruled out since it contains electron-deficient iodine which may still be attracted towards the interlayer.

Table 1. Oxidation of alcohols to carbonyl compounds[a] with clay supported TBAPI

substrate	reaction time (hours)	Yield (%)	substrate	reaction time (hours)	Yield (%)
Benzyl alcohol	1.5	98	Adamantanol	4.0	0
4-Methoxybenzyl alcohol	3.0	61	Diphenylmethanol	3.0	70
4-Methoxybenzyl alcohol	4.0	92	Diphenylmethanol	4.0	98
2-Methoxybenzyl alcohol	3.0	62	Hydroquinol	4.0	70
2-Methoxybenzyl alcohol	4.0	93	Benzoin[b]	5.0	99
N,N-dimethyl-4-benzyl alcohol	4.0	70	Cyclohexanol[b]	4.0	70
3-Nitrobenzyl alcohol	4.0	0	Benzyl alcohol[c]	4.0	10
1-Naphthalenemethanol	3.0	57	4-Methoxybenzyl alcohol[c]	4.0	5
1-Naphthalenemethanol	4.0	89	2-Methoxybenzyl alcohol[c]	4.0	4
2-Naphthalenemethanol	4.0	87	Diphenylmethanol[c]	4.0	2
Piperonyl alcohol	4.0	0			

[a] 0.115 mmol alcohol, 2 ml isooctane and 100 mg clay - supported TBAPI (0.115 mmol) were stirred under reflux conditions. [b] In an oil bath at 120 °C. [c] In the absence of clay.

The mildness of the reagent has been shown by the facile oxidation of sulfides to sulfoxides in water. The reaction, however, is inefficient in isooctane and chloroform. Absence of significant swelling of the clay interlayer in these solvents may be responsible for this. However, when placed in water, the layers swell apart resulting in penetration of substrate followed by oxidation. It is interesting to note that the oxidation of sulfides to sulfoxides is much more efficient and faster (Table 2) when compared to the corresponding oxidation by periodate,[31] and a TBAPI /$AlCl_3$ mixture.[29] It is also considerably faster than the oxidation with alumina-supported sodium metaperiodate.[5,32] It is likely that the intercalation of the quaternary ammonium group in clay leaves the periodate ion more free for attack on sulfides. The results of oxidation of various sulfides to sulfoxides are presented in the Table 2.

The advantages of this oxidant are manifold. It does not require the polar medium and protic acid catalysis needed for periodate oxidation which puts severe restrictions on its use with acid-sensitive and easily hydrolysable molecules. TBAPI alone is not able to transform hydroxyl groups to the corresponding carbonyl compounds in aprotic solvents. However, in the presence of K10-montmorillonite clay, TBAPI can act as a strong oxidising agent. Though oxidation is observed with TBAPI in the presence of Lewis acid[32] in aprotic polar solvents, the clay-TBAPI composite is superior due to a much simpler work-up. A hydrocarbon solvent is sufficient for the oxidation of alcohol. It is significant to note that the oxidation proceeds with equal efficiency in the presence of clay instead of Lewis acids.

Thus the present work amply demonstrates the multifunctional nature of clays: as an efficient catalyst (activating TBAPI by generating the active species of periodate utilising the Brönsted and Lewis acidic sites) and as a good support (combining with the tetrabutylammonium group, thus leaving the periodate group free and ready for attack). This clay-TBAPI composite is a more efficient, simple, "environmentally friendly" and cleaner oxidant than conventional reagents.

Table 2. Oxidation of sulfides to the corresponding sulfoxides[a] with clay-supported TBAPI

Substrate	Reaction time (minutes)	Yield (%)	Substrate	Reaction time (minutes)	Yield (%)
PhSMe	15	98	4-$MeOC_6H_4SMe$	15	94
$PhSCH_2CH_3$	15	98	4-$HOOCC_6H_4SMe$	15	79
$PhSCH(CH_3)_2$	15	95	4-MeC_6H_4SMe[b]	15	52
$PhSC_3H_7$	15	96	4-$MeOC_6H_4SMe$[b]	15	51
$PhSC_4H_9$	15	89	PhSMe[c]	240	70
4-MeC_6H_4SMe	15	85	PhSMe[d]	300	88

[a] 0.115 mmol sulphide, 1.5 ml water and 100 mg clay - supported TBAPI (0.115 mmol) were mixed and stirred under reflux condition for 15 minutes.[b] Absence of clay. [c] TBAPI / $AlCl_3$ mixture in refluxing acetonitrile.[29] [d] Alumina-supported sodium metaperiodate.[5,32]

EXPERIMENTAL

TBAPI[4,33] is prepared easily from an aqueous solution of sodium metaperiodate and tetrabutylammonium bromide in quantitative yield at room temperature. This oxidising agent is a white, stable solid which can be stored in darkness for several days without losing its activity. Substituted benzyl alcohols were prepared[34] from the sodium borohydride reduction of the corresponding aldehydes. Other alcohols are commercially available and are used after purification. Sulfides[35] were prepared by standard procedures.

Preparation of clay-supported tetrabutylammonium periodate

To 1 g of tetrabutylammonium periodate dissolved in 10 ml of acetone, 1 g of K10-montmorillonite was added slowly with stirring for 1h. Acetone was removed by rotary evaporation. The supported reagent was collected as a free flowing powder and stored in a black coloured bottle. It is found to be stable and retains its white colour for a long time.

Oxidation of benzyl alcohols with clay-supported TBAPI in isooctane

In a round-bottomed flask (25 ml), equipped with a condenser and a magnetic stirrer, a solution of alcohol (0.115 mmol) in isooctane (2 ml) was prepared. Clay-supported TBAPI (100 mg) was added to the solution and the reaction mixture was stirred under reflux conditions for 4h. The reaction mixture was then extracted thrice (3x10 ml) with ether . The ether solution was treated with sodium thiosulphate (20%, 10 ml). The aqueous layer was separated and the ethereal solution was washed with water. The organic layer was dried over anhydrous Na_2SO_4 and the ether was evaporated. The residue was dissolved in methanol and analysed by HPLC. Oxidised products[36] were identified by comparing with authentic samples and also by their characteristic $\nu_{C=O}$ in IR.

Oxidation of sulfides with clay-supported TBAPI in water

In a round-bottomed flask (25 ml), equipped with a condenser and a magnetic stirrer were placed 0.115 mmol sulfide in dichloromethane (2 ml) and 1.5 ml water. Clay-supported TBAPI (100 mg) was added to the solution and the reaction mixture was stirred under reflux conditions for 15 minutes. The reaction mixture was then extracted thrice (3x10 ml) with ether. The ether solution was treated with sodium thiosulphate (20%,10 ml) in order to reduce the liberated iodine. The aqueous layer was separated and the ether solution was washed with water. The organic layer was dried over anhydrous Na_2SO_4 and ether was evaporated. The residue was dissolved in methanol and analysed by HPLC. Oxidised products were identified by coinjection with authentic samples prepared by known methods.[36]

ACKNOWLEDGEMENTS

The authors thank Prof.C.Srinivasan and Prof. S.Sivasubramanian for helpful discussions. Financial assistance from CSIR (CV) is gratefully acknowledged.

REFERENCES

1. Laszlo, P. (ed.), "*Preparative Chemistry using Supported Reagents*", Academic Press, San Diego, **1987**.
2. Clark, J. H.; Kybett, A. P.; Macquarrie, D. J. "*Supported Reagents: Preparation,Analysis and Applications*", VCH, New York, **1992**.
3. Savoia, D.; Trombini, C.; Umani-Ronchi, A. *J.Org.Chem.* **1982**, *47*, 564.
4. Santaniello, E.; Ferraboschi, P. *Nouv.J.Chim.* **1980**, *4*, 279; Santaniello, E.; Manzocchi, A.; Farachi, C. *Synthesis*, **1980**, 563; Santaniello, E.; Ponti, F.; Manzocchi, A. *Tetrahedron Lett.*, **1980**, *21*, 2655.
5. Liu, K. T.; Tong, Y. C. *J.Org.Chem.*, **1978**, *43*, 2717.
6. Lee, D. G.; Noureldin, N. A. *Tetrahedron Lett.*, **1981**, *22*, 4889.
7. Chiang, C. S.; McKillop, A.; Taylor, E. C.; White, J. F. *J.Am.Chem.Soc.*, **1976**, *98*, 6750.
8. McKillop, A.; Young, D. W. *Synthesis*, **1979**, 401.
9. McKillop, A.; Young, D. W. *Synthesis*, **1979**, 481.
10. Cornelis, A.; Laszlo, P. *Synthesis*, **1980**, 849.
11. Balogh, M.; Hermecz, I.; Meszaros, Z.; Laszlo, P. *Helv.Chim.Acta.*, **1984**, *67*, 2270.

12. Rhodes, C. N.; Franks, M.; Parkes, G. M. B.; Brown, D. R. *J.Chem.Soc.*, *Chem.Commun.*, **1991**, 804.
13. Clark, J. H.; Cullen, S. R. (in part); Barlow, S. J.; Bastock, T. W. *J.Chem.Soc.*, *Perkin Trans.*2, **1994**, 1117.
14. Barlow, S. J.; Bastock, T. W.; Clark, J. H.; Cullen, S. R. *J.Chem.Soc.*, *Perkin Trans.*2, **1994**, 411.
15. Hirano, M.; Tomaru, J.; Morimoto, T. *Chemistry Lett.*, **1991**, 523.
16. Hirano, M.; Tomaru, J.; Morimoto, T. *Bull.Chem.Soc.Jpn.*, **1991**, *64*, 3752.
17. Hirano, M., Kudo, H.; Morimoto, T. *Bull.Chem.Soc.Jpn.*, **1992**, *65*, 1744.
18. Hirano, M.; Komiyay, K.; Morimoto, T. *Organic Prep.Proced.Internat.*, **1995**, *27*, 703.
19. Hirano, M.; Ueno, Y.; Morimoto, T. *Synth.Commun.*, **1995**, *25*, 3765.
20. Tateiwa, J.; Horiuchi, H.; Uemura, S. *J.Chem.Soc.*, *Chem.Commun.*, **1994**, 2567.
21. Sharma, G. V. M.; Venkata Ramanaiah, K. C.; Krishnudu, K. *Tetrahedron Asymmetry*, **1994**, *5*, 1905.
22. Delaude, L.; Laszlo, P.; Lehance, P. *Tetrahedron Lett.*, **1995**, *36*, 8505.
23. Keller, W. E. (ed.) "*Compendium of Phase-Transfer Reactions and Related Synthetic Methods*", Fluka AG, CH-9470 Buchs, Switzerland, 15, **1979**.
24. Raber, D. J.; Guida, W. C. *J.Org.Chem.*, **1976**, *41*, 690.
25. Hutchins, R. O.; Kandasamy, D. *J.Am.Chem.Soc.*, **1973**, *95*, 6131.
26. Sala, T.; Sargents, M. V. *J.Chem.Soc.*, *Chem.Commun.*, **1978**, 253.
27. Landini, D.; Rolla, G. *Chem. Ind.*, **1979**, 213.
28. Schmidt, H. J.; Schaefer, H. J. *Angew.Chem.Int.Ed.Engl.*, **1979**, *18*, 78.
29. Firouzabadi, H.; Sardarian, A.; Badparva, H. *Bull.Chem.Soc.Jpn.*, **1996**, *69*, 685.
30. Crouthamel, C. E.; Meek, H. V.; Martin, D. S.; Banks, C. V. *J.Am.Chem.Soc.*, **1949**, *71*, 3031.
31. Ruff, F.; Kucsman, A. *J.Chem.Soc.*, *Perkin Trans.* 2, **1985**, 683.
32. Villemin, D.; Ricard, M. *Nouv.J.Chim.*, **1980**, *6*, 605.
33. Ferraboschi, P.; Azadani, M. S., Santaniello, E.; Trave, S. *Synth.Commun.*, **1986**, *16*, 43.
34. Vogel, A. I. "*A Text book of Practical Organic Chemistry*", ELBS, Longman Group UK Ltd., (5th edn.), **1989**, 524.
35. Oberneyer, J. *Ber.*, **1887**, *20*, 2918; Fehnel, C. A.; Carmackm, M. *J. Am. Chem. Soc.*, **1949**, *79*, 84; de la Mare, P. B. D.; Vernon, C. A. *J. Am. Chem. Soc.*, **1956**, *78*, 41; Price, C. C.; Stacy, G. W. *J. Am. Chem. Soc.*, **1946**, *68*, 498; Mauthner, F. *Ber.*, **1906**, *39*, 3594; Kannan, P.; Pitchumani, K.; Rajagopal, S.; Srinivasan, C. *J. Chem. Soc.*, *Chem. Commun.*, **1996**, 369.
36. Price, C. C.; Hydock, J. J. *J. Am. Chem. Soc.*, **1952**, *74*, 1943; Leandri, G.; Mangini, A.; Passerini, R. *J.Chem. Soc.*, **1957**, 1386.