SHORT PAPER

J. Chem. Research (S),
2002, 270–271

Oxidation of alcohols with butyltriphenylphosphonium periodate under non-aqueous conditions[†]

Abdol Reza Hajipour*, Shadpour E. Mallakpour* and Heshmat A. Samimi

*Pharmaceutical Research Laboratory, College of Chemistry, Isfahan University of Technology,
Isfahan 84156, IR Iran*

The combination of butyltriphenylphosphonium periodate (BUTPPPI) and aluminum chloride in refluxing acetonitrile affords an efficient and mild system for the oxidation of a variety of alcohols, to the corresponding aldehydes and ketones. The experimental procedure is simple and the products are easily isolated in good yields.

Keywords: butyltriphenylphosphonium periodate oxidation of alcohols

The oxidation of alcohols into their corresponding aldehydes and ketones has significance in synthetic organic chemistry.[1-3] Many reagents for the oxidation of alcohol are known,[3] *e.g.* hypochlorite,[4] chromium (VI) oxides,[5] dichromate,[6] manganese (IV) oxide,[7] permanganate,[8] and ruthenium (VIII) oxide.[9] Unfortunately, one or more equivalents of these – often hazardous and toxic – oxidising agents are required to oxidise alcohols to the corresponding carbonyl derivatives under acid or base conditions in water. Because of the insolubility and sensitivity of alcohols, the quest for effective oxidants that use inexpensive and non-toxic reagents, which work under non-aqueous and neutral conditions for converting alcohols to carbonyl compounds, remains an important challenge.[10]

Sodium periodate is an inexpensive, water-soluble and stable oxidising reagent that is commercially available. This reagent is insoluble in non-aqueous solvents and this requirement for aqueous conditions has to be overcome. Very recently, we have introduced new reagents for the oxidation of alcohols under non-aqueous conditions.[11]

As part of our continued effort in this area, we now wish to report the synthesis of butyltriphenylphosphonium periodate **1** as an efficient and novel reagent for the oxidation of alcohols. Various alcohols have been successfully oxidised to afford the corresponding carbonyl compounds in good to excellent yields after 2–17 h. Using BUTPPPI **1** in the presence of 0.3 molar ratio of aluminum chloride, The reactions are performed in acetonitrile under reflux. It should be mentioned that aldehydes did not undergo further oxidation to their carboxylic acids under the reaction conditions.

The reagent is a white powder, which was prepared by the dropwise addition of an aqueous solution of $NaIO_4$ to an aqueous solution of butyltriphenylphosphonium bromide at room temperature. Filtration and drying of the precipitate produced a white powder which could be stored for months without losing its oxidation ability. This reagent is quite soluble in methylene chloride, chloroform, acetone, and acetonitrile and insoluble in non-polar solvents such as carbon tetrachloride, *n*-hexane, and diethyl ether.

In order to evaluate the effect of aluminum chloride in these reactions, we tried the reaction of 1-phenyl ethanol with **1** without using any aluminum chloride. Oxidation of 1-phenyl ethanol with **1** in the presence of various Lewis acids such as $ZnCl_2$, $FeCl_3$, $BiCl_3$ and $AlCl_3$ were also examined in acetonitrile under reflux conditions. Our observations showed that reaction time for oxidation of alcohols is effected the nature of the Lewis acids. Surprisingly only $AlCl_3$ was shown to be an effective catalyst for this purpose. (Table 1). The reaction in the presence of $ZnCl_2$, $FeCl_3$, and $BiCl_3$ (0.5 mmol) proceeds with lower efficiency even with a higher molar ratio of the oxidant (1.5 mmol) in comparison with the amount of oxidant used in the presence of $AlCl_3$ (0.3 mmol). This could be the effect of hardness and of the greater solubility of $AlCl_3$ in comparison with the other Lewis acids which have been used in these experiments. Alcohols **2** are oxidised to the corresponding carbonyl compounds **3** in acetonitrile under refluxing conditions in the presence of aluminum chloride in good to excellent yields. Benzoin was converted to benzil in quantitative yield after 150 min (Scheme 1 and Table 2). In comparison to benzylic alcohols, oxidation of aliphatic alcohols with this reagent occurs in lower yield and in a longer reaction time. When we tried to oxidise the allylic alcohols with this reagent several by-products was obtained. Therefore, this reagent is not suitable for oxidising allylic alcohols. The functional groups such as NO_2 and MeO decrease the rate of reaction. This could be the effect of these functional groups forming compleses with $AlCl_3$ (Table 2).

Table 1 Oxidation of 1-phenyl ethanol with reagent **1** with different Lewis acids in acetonitrile under refluxing conditions[a]

Entry	Lewis acid	Time/h	Yield/%
1	$ZnCl_2$[c]	3	30
2	$FeCl_3$[c]	3	30
3	$BiCl_3$[c]	3	50
4	$AlCl_3$[b]	3	90

[a]Monitored by TLC analysis. [b]Oxidant/alcohol/Lewis acid (1:1:0.3). [c]Oxidant/alcohol/Lewis acid (1.5:1:0.5).

In summary, in this study we have introduced a new reagent for the oxidation of different types of alcohols in acetonitrile in the presence of $AlCl_3$ under reflux. The stability, easy preparation, mildness of the reagent, and reaction conditions, easy work up and high yields of the products, under non-aqueous conditions make this method a useful one for oxidation of different alcohols to afford the corresponding carbonyl compounds.

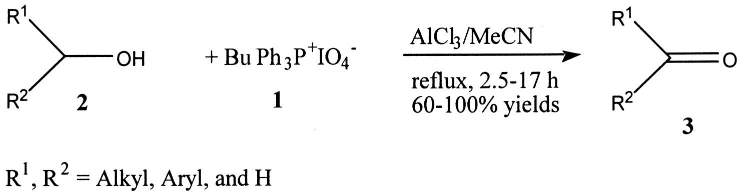
Experimental

General: All yields refer to isolated products. The products were characterised by comparison with authentic samples (IR and ^1H-NMR spectrum, melting and boiling points, TLC). All ^1H-NMR spectra were recorded at 90 and 500 MHz in $CDCl_3$ and CCl_4 relative to TMS (0.00ppm). The Research Institute of Petroleum Industry, Tehran, performed elemental analysis.

---

* To receive any correspondence. E-mail: haji@cc.iut.ac.ir

[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.



Scheme 1

Table 2 Oxidation of alcohols **2** with reagent **1** to carbonyl compounds **3** in refluxing acetonitrile [a, b]

Compound	R^1	R^2	Time/h	Yield[c]/%
2a	C_6H_5	H	7.0	90
2b	4-$NO_2C_6H_4$	H	11.0	90
2c	3,4-$(MeO)_2C_6H_3$	H	9.0	95
2d	4-PhC_6H_4	Me	9.00	99
2e	2-pyridyl	C_6H_5	6.0	90
2f	C_6H_5	Me	2.5	90
2g	4-$MeOC_6H_4$	H	10.0	100
2h	2-$MeOC_6H_4$	H	10.0	95
2i	C_6H_5	C_6H_5	6.0	100
2j	3-$MeOC_6H_4$	H	8	92
2k	4-ClC_6H_4	H	5.0	90
2l	2-ClC_6H_4	H	6.0	82
2m	C_6H_5	$C_6H_5CH_2$	4.5	90
2n	4-BrC_6H_4	Me	5.0	97
2o	4-ClC_6H_4	Me	2.5	89
2p	C_6H_5	C_6H_5CO	2.5	100
2q	2,3-$(MeO)_2C_6H_3$	H	5.0	91
2r	Cyclohexyl	-	12.0	95
2s	α-Tetralol	-	3.5	90
2t	$CH_5(CH_2)_6$	H	13.0	75
2u	$CH_5(CH_2)_4$	H	7.0	70
2v	$C_6H_5CH{=}CH$	H	3.0	nr
2w	$C_6H_5(CH_2)_2$	H	17.0	75
2x	$C_6H_5(CH_2)_3$	H	6.0	90

[a] Confirmed by comparison with authentic samples (IR, TLC and NMR).[10-11] [b] Oxidant/Alcohol/$AlCl_3$ (1.0:1.0:0.3). [c] Yield of isolated pure product after chromatography or distillation.

Preparation of butyltriphenylphosphonium periodate 1 (BUTPPPI): A solution of butyltriphenylphosphonium bromide (7.98 g, 20 mmol) in 50 ml of water was prepared, and then $NaIO_4$ (4.28 g, 20 mmol) in water (50 ml) was added dropwise to the above solution and stirred for 30 min at room temperature. The resulting white precipitate was filtered and washed with cooled distilled water (2×50 ml), and dried in a desiccator under vacuum over calcium chloride to afford a white powder (10.6 g, 98% yield), which decomposed at 240–243°C to a dark-brown material. H-NMR: 7.89–7.72 (m, 15 H), 3.23 (m, 2 H), 1.68 (m, 4 H), 0.92 (t, 3 H). ^{13}C-NMR: δ 136.03, 136.00, 134.62, 134.54, 131.27, 131.17, 119.72, 119.04, 118.26, 24.92 (d, *J* = 298.5 Hz, C-P). IR (KBr). Anal Calcd for $C_{22}H_{24}IO_4P$: C, 51.76; H 4.70%. Found: 52.00; H, 4.68%.

General procedure: oxidation of alcohols with BUTPPPI/$AlCl_3$: A solution of the alcohol (1 mmol) and $AlCl_3$ (0.04 g, 0.3 mmol) in acetonitrile was prepared. in a round-bottomed flask (25 ml) equipped with a reflux condenser and a magnetic stirrer, Buthyltriphenylphosphonium periodate (0.51 g, 1 mmol) was added to the solution and refluxed for .2.5–17 h. The reaction progress was followed by TLC (eluent: cyclohexane/EtOAc: 8:2) The reaction mixture was then cooled to room temperature and the solid was then separated through a thin pad of silica gel and washed with acetonitrile (15 ml). The filtrate was evaporated and the resulting crude material was purified by column chromatography on silica gel using a mixture of ethyl acetate and hexane as eluent (10:90). Pure carbonyl compounds were obtained in 60–100% yields (Table 2).

The authors thank the Isfahan University of Technology (IUT), IR Iran for financial support.

Received 27 October 2001; accepted 14 November 2001
Paper 01/1123

References

1 R.A. Sheldon and J.K. Kochi, *Metal-catalysed Oxidation of Organic Compounds:* Academic Press, New York, 1981.
2 S.V. Ley, J. Norman, W.P. Griffith and S.P. Marsden, *Synthesis*, 1994, 639.
3 M. Hudlicky, *Oxidation in Organic Chemistry*, American Chemical Society, Washington, DC, 1990.
4 R.V. Stevens, K.T. Chapman and H.N. Walter, *J. Org. Chem.*, 1980, **45**, 2030.
5 J.R. Holum, *J. Org. Chem.*, 1961, **26**, 4814.
6 D.G. Lee, *J. Org. Chem.*, 1970, **35**, 3589.
7 R.J. Highet and W.C. Wildman, *J. Am. Chem. Soc.*, 1955, **77**, 4399.
8 F.M. Manger and C. Lee, *Tetrahedron Lett.*, 1981, **22**, 1656.
9 L.M. Berkowitz and P.N. Rylander, *J. Am. Chem. Soc.*, 1958, **80**, 6682.
10 (a) A.R. Hajipour and N. Mahboubkhah, *J. Chem. Res. (S)*, 1998, 122; (b) A.R. Hajipour, S.E. Mallakpour and H. Adibi, *Chem. Lett.*, 2000, 460; (c) A.R. Hajipour, S.E. Mallakpour and S. Khoee, *Chem. Lett.*, 2000, 120; (d) A.R. Hajipour, S.E. Mallakpour and S. Khoee, *Synlett*, 2000, 740.
11 (a) I.M. Baltork, A.R. Hajipour and H. Mohammadi, *Bull. Chem. Soc. Jpn.*, 1998, **71,** 16; (b) A.R. Hajipour and N. Mahboobkhah, *Synth. Commun.*, 1988, **28,** 3143; (c) A.R. Hajipour and N. Mahboobkhah, *J. Chem. Res. (S),* 1998, 122; (d) A.R. Hajipour, I.M Baltork and G. Kianfar, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 2655; (e) A.R. Hajipour, I.M Baltork and G. Kianfar,. *Ind. J. Chem.*, 1998, **37B**, 607; (f) A.R. Hajipour and N. Mahboobkhah, *Org. Prep. Proced. Int.*, 1999, **31**, 112; (g) A.R. Hajipour, I.M Baltork and K. Niknam, *Org. Prep. Proced. Int.*, 1999, **31**, 335; (h) I.M. Baltork, A.R. Hajipour and R. Haddadi, *J. Chem. Res. (S)*, 1999, 102.