J. Chem. Research (S), 1998, 120–121†

Selective Oxidations using Alumina-supported Iodobenzene Diacetate under Solvent-free Conditions†

Rajender S. Varma,* Rajesh K. Saini and Rajender Dahiya

Department of Chemistry and Texas Regional Institute for Environmental Studies (TRIES), Sam Houston State University, Huntsville, TX 77341-2117, USA

The solid reagent system iodobenzene diacetate–alumina expeditiously and selectively oxidises sulfides to sulfoxides and alcohols to carbonyl compounds in high yields under the influence of microwaves.

In recent years there has been considerable interest in the use of organohypervalent iodine reagents in organic synthesis.[1] Preparative conversion of sulfides into the corresponding sulfoxides[2] has been a challenging problem as these substrates commonly suffer from competitive overoxidation to sulfones. Among the polyvalent iodine reagents,[3] iodobenzene diacetate (IBD) has found usage for the oxidation of sulfides to sulfoxides although the conditions are rather stringent.[4] The relatively stronger oxidant bis(trifluoroacetoxy)iodobenzene (BTI)[5] oxidises aromatic sulfides to sulfoxides and/or sulfones but gives a mixture of products for aliphatic sulfides and normally requires longer time periods.

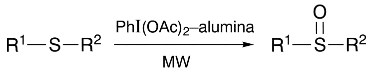
The oxidation of alcoholic groups to carbonyl functionalities continues to receive attention from chemists in search of newer and selective methods of oxidation.[6] Hypervalent iodine reagents such as iodoxybenzene,[3b] *o*-iodoxybenzoic acid (IBX),[7] bis(trifluoroacetoxy) iodobenzene (BTI)[8] and Dess–Martin periodinane[9] have been used for the oxidation of alcohols but the use of iodobenzene diacetate (IBD), in spite of its inexpensive nature, has not been explored except for a few examples of phenolic compounds.[10] The reactions with hypervalent iodine reagents, however, are usually conducted in solvents such as methanol, corrosive acetic acid or the irritant and high-boiling dimethyl sulfoxide (DMSO). Consequently, there is a need to develop a manipulatively easy and environmentally benign solvent-free protocol. In this context, organic reactions on solid supports[11,12] and those assisted by microwaves,[12–14] especially under solvent-free conditions,[12,13] have attracted attention because of their enhanced selectivity, milder reaction conditions and associated ease of manipulation.

In our program on new solvent-free reactions using microwaves (MW),[12] we have achieved the solvent-free and selective oxidation of sulfides to the corresponding sulfoxides and alcohols to carbonyl compounds in high yields using iodobenzene diacetate (IBD)–alumina, a reaction that is accelerated by microwaves.

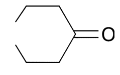
Oxidation of Sulfides.—The scope of the reaction using iodobenzene diacetate on alumina was explored with a variety of sulfides which are selectively oxidised to the corresponding sulfoxides in high yields. The reaction required only 40–90 s at 50% power for complete oxidation of the substrates (Table 1). The reactions of sulfides with neat IBD, in the absence of alumina, produced only *ca.* 10% of the sulfoxides. Presumably, the oxide and the hydroxide groups on the alumina surface or the associated water present therein assist in the formation of the sulfoxide. In this context, the suitability of various solid supports, ranging from acidic to basic surfaces, was examined and included neutral, acidic or basic alumina, silica, montmorillonite K 10 clay, bentonite clay and *p*-TSA-doped silica (3% on silica). Neutral alumina provided the best results in terms of high yields and formation of fewer by-products. The α-functionalization of the keto group, a typical reaction with IBD, was not observed in case of tetrahydrothiopyran-4-one (entry 9).[1] In addition to this favourable chemoselective aspect, the process was also applicable to long-chain aliphatic sulfides which are normally insoluble in polar solvents and are, therefore, difficult to oxidise (entry 7).

Oxidation of Alcohols.—The oxidation of neat alcohols with an equimolar amount of IBD afforded rapid formation of carbonyl compounds upon exposure to microwaves as summarized in Table 2. The alumina-supported IBD, however, appeared to be a better choice since the reactions of neat alcohols with IBD in the absence of alumina were relatively slow and resulted in lower yields (Table 2). This rapid

Table 1 Selective oxidation of sulfides to sulfoxides using alumina supported iodobenzene diacetate



$$R^1{-}S{-}R^2 \xrightarrow[\text{MW}]{\text{PhI(OAc)}_2\text{–alumina}} R^1{-}\overset{\overset{\text{O}}{||}}{S}{-}R^2$$

Entry	R^1	R^2	(t/s)	Yield[a] (%)	Mp (T/°C) or bp [(T/°C)/Torr] Found	Mp (T/°C) or bp [(T/°C)/Torr] Reported
1	Pr^i	Pr^i	40	80	62/3	87/15[b]
2	Bu^n	Bu^n	40	82	83/1	72/0.5[b]
3	Ph	Ph	90	88	69–70	69–71[c]
4	$PhCH_2$	Ph	90	86	123	117–121[b]
5	$PhCH_2$	$PhCH_2$	90	90	135	135–136[c]
6	Ph	Me	45	82	28–30	29–30[c]
7	n-$C_{12}H_{25}$	Me	90	88	62	[d]
8	—$[CH_2]_4$—		[f]	82	107–110/5	97–103/3[e]
9			90	85	108–109	109–110[c]

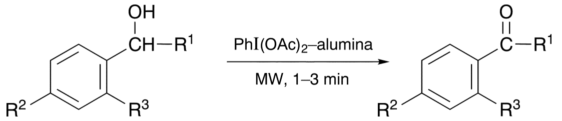
[a] Yields refer to pure isolated products. [b] K. Orito, T. Hatakeyama, M. Takeo and H. Suginome, *Synthesis*, 1995, 1357. [c] N. J. Leonard and C. R. Johnson, *J. Org. Chem.*, 1962, **27**, 282. [d] R. S. Varma, R. K. Saini and H. M. Meshram, *Tetrahedron Lett.*, 1997, **38**, 6525. [e] L.-T. Liu and Y.-C. Tong, *J. Org. Chem.*, 1978, **43**, 2717. [f] Reaction went to completion by simple admixing of the reactants at room temperature (*ca.* 10 min).

---

*To receive any correspondence (*e-mail:* CHM_RSV@SHSU.EDU).

†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 2 Oxidation of alcohols to carbonyl compounds using iodobenzene diacetate



				$PhI(OAc)_2$		Al_2O_3–$PhI(OAc)_2$		Mp (T/ °C) or bp [(T/ °C)/Torr]	
Entry	R^1	R^2	R^3	Time (t/min)	Yield (%)[a]	Time (t/min)	Yield (%)[a]	Observed	Reported
1	H	H	H	2.0	89	1.0	94	51–54/6	178.6/760[c]
2	H	p-Me	H	2.0	88	1.0	92	80–82/4	106/10[c]
3	H	p-OMe	H	1.5	91	2.0	95	92–95/3	83/2[c]
4	H	H	CH_2OH	1.5	81	1.5	86	72–73	72–74[d]
5	Et	H	H	2.0	83	2.0	89	64–65/2	91.6/10[c]
6	Bz	H	H	2.0	90	2.0	90	93–95	95–96[c]
7	p-$MeOC_6H_4CO$	p-OMe	H	—	[b]	3.0	96	131–132	132–134[d]
8	Hydroquinone			—	[b]	3.0	69	116	115–117[d]
9	Catechol			—	[b]	0.5	43	61–66[e]	60–70[c,e]

[a]Unoptimized yields refer to pure isolated products. [b]Mixture of products was formed. [c]*Handbook of Chemistry and Physics*, ed. R. C. West, CRC Press, Boca Raton, 67th edn., 1986. [d]*Aldrich Catalog Handbook of Fine Chemicals*, USA, 1996–1997. [e]Decomposed.

procedure was selective and avoided any over-oxidation to carboxylic acids. The protocol also eliminated the excessive use of corrosive solvents such as acetic acid, trifluoroacetic acid and high-boiling DMSO normally employed in reactions with relatively expensive hypervalent iodine reagents such as IBX and BTI.[3b,7,9a]

That the effect may not be purely thermal[15] is borne out by the fact that at *ca.* 85C in an oil-bath a relatively longer time (25–30 min) is required for complete oxidation of benzyl phenyl sulfide. Similarly, the oxidation of benzyl alcohol to benzaldehyde could be completed in 2 h in an oil-bath at a comparable temperature of 80C.

In conclusion, the new protocols with IBD on alumina are simple, rapid and high-yielding and avoid the drastic conditions normally employed. In addition, in a truly environmentally benign manner, the alumina support can be recovered and reused.

Experimental

A Sears Kenmore microwave (MW) oven operating at 2450 MHz (power 900 W) was used for all the experiments. Products were identified by comparison of their mps and IR and NMR spectra with those of authentic samples

General Procedure for Oxidation of Sulfides.—Neutral alumina (1.5 g) was thorougly mixed with IBD (532 mg, 1.65 mmol) and benzyl phenyl sulfide (300 mg, 1.5 mmol) using a pestle and mortar. The adsorbed material was placed in an alumina bath inside the microwave oven and irradiated at 50% power for two successive intervals of 45 s each (with time interval of 3–4 min; bath temperature rose to 80–85C). The progress of the reaction was monitored by TLC (hexane–ethyl acetate, 7:3 v/v). When the reaction was complete the whole material was directly charged onto a silica gel column which provided iodobenzene on elution with hexane (100 ml). The fractions eluted by chloroform–hexane (1:1 v/v) provided sulfone ($<$7% by NMR of crude product) and finally elution by chloroform afforded pure benzyl phenyl sulfoxide in 86% yield, mp 123 °C.

General Procedure for Oxidation of Alcohols.—Benzyl alcohol (108 mg, 1 mmol), IBD (355 mg, 1.1 mmol) and neutral alumina (1 g) were mixed using a pestle and mortar. The reaction mixture was placed in an alumina bath inside a microwave oven and irradiated for 1 min (bath temperature 80C). On completion of the reaction (TLC, hexane–ethyl acetate, 9:1 v/v), the crude product was directly charged onto a silica gel column. Elution with hexane (100 ml) provided iodobenzene. Subsequent use of hexane–ethyl acetate (9:1 v/v) as eluent afforded the pure carbonyl compounds in 94% yield.

We are grateful to the Texas Advanced Research Program (ARP) in chemistry (Grant no. 003606-023) and Office of Naval Research/SERDP (Grant no. N00014-96-1-1067) for financial support.

Received, 28th October 1997; Accepted, 12th November 1997
Paper E/7/07090J

References

1 (*a*) P. J. Stang and V. V. Zhdankin, *Chem. Rev.*, 1996, **96**, 1123; (*b*) O. Prakash, *Aldrichimica Acta*, 1995, **28**, 63; (*c*) A. Varvoglis, *The Organic Chemistry of Polycoordinated Iodine*, VCH, New York, 1992.

2 (*a*) J. B. Arterburn and S. L. Nelson, *J. Org. Chem.*, 1996, **61**, 2260; (*b*) R. Kakarla, R. G. Dulina, N. T. Hatzenbuhler, Y. W. Hui and M. J. Sofia, *J. Org. Chem.*, 1996, **61**, 8347; (*c*) R. Aldea and H. Alper, *J. Org. Chem.*, 1995, **60**, 8365.

3 (*a*) W. Ando, R. Tajima and T. Takata, *Tetrahedron Lett.*, 1982, **23**, 1685; (*b*) D. H. R. Barton, G. R. A. Godfrey, J. W. Morzycki, W. B. Motherwell and A. Stobie, *Tetrahedron Lett.*, 1982, **23**, 957.

4 (*a*) H. H. Szmant and G. Suld, *J. Am. Chem. Soc.*, 1956, **78**, 3400; (*b*) J. P. A. Castrillon and H. H. Szmant, *J. Org. Chem.*, 1967, **32**, 976.

5 D. Barbas, S. Spyroudis and A. Varvoglis, *J. Chem. Res. (S)*, 1985, *(S)* 196; *(M)* 2201.

6 I. E. Marko, P. R. Giles, M. Tsukazaki, S. M. Brown and C. J. Urch, *Science*, 1996, **274**, 2044.

7 (*a*) S. D. Munari, M. Frigerio and M. Santagostino, *J. Org. Chem.*, 1996, **61**, 9275; (*b*) M. Frigerio and M. Santagostino, *Tetrahedron Lett.*, 1994, **35**, 8019.

8 R. Barret and M. Daudon, *Tetrahedron Lett.*, 1990, **31**, 4871.

9 (*a*) D. B. Dess and J. C. Martin, *J. Org. Chem.*, 1983, **48**, 4155; (*b*) R. J. Linderman and D. M. Graves, *Tetrahedron Lett.*, 1987, **28**, 4259.

10 (*a*) A. McKillop, L. McLaren and R. J. K. Taylor, *J. Chem. Soc., Perkin Trans. 1*, 1994, 2047; (*b*) P. Wipf, Y. Kim and P. C. Fritch, *J. Org. Chem.*, 1993, **58**, 7195.

11 (*a*) J. H. Clark, *Catalysis of Organic Reactions by Supported Inorganic Reagents,* VCH, New York, 1994; (*b*) K. Smith, *Solid Supports and Catalysts in Organic Synthesis*, Ellis Horwood, Chichester, 1992; (*c*) P. Laszlo, *Preparative Chemistry Using Supported Reagents*, Academic Press, San Diego, 1987; (*d*) A. McKillop and D. W. Young, *Synthesis*, 1979, 401, 481.

12 (*a*) R. S. Varma and R. Dahiya, *Tetrahedron Lett.*, 1997, **38**, 2043; (*b*) R. S. Varma, R. Dahiya and S. Kumar, *Tetrahedron Lett.*, 1997, **38**, 2039; (*c*) R. S. Varma and R. K. Saini, *Tetrahedron Lett.*, 1997, **38**, 2623; (*d*) R. S. Varma and R. K. Saini, *Tetrahedron Lett.*, 1997, **38**, 4337; (*e*) R. S. Varma, R. Dahiya and S. Kumar, *Tetrahedron Lett.*, 1997, **38**, 5131; (*f*) R. S. Varma and H. M. Meshram, *Tetrahedron Lett.*, 1997, **38**, 5427; (*g*) R. S. Varma and R. K. Saini, *Synlett*, 1997, 857; (*h*) R. S. Varma, R. Dahiya and R. K. Saini, *Tetrahedron Lett.*, 1997, **38**, 8819 and references cited therein.

13 (*a*) A. Oussaid, L. N. Thach and A. Loupy, *Tetrahedron Lett.*, 1997, **38**, 2451; (*b*) D. Villemin and A. Benalloum, *Synth. Commun.*, 1991, **21**, 1, 63.

14 (*a*) S. Caddick, *Tetrahedron*, 1995, **51**, 10403; (*b*) C. R. Strauss and R. W. Trainor, *Aust. J. Chem.*, 1995, **48**, 1665.

15 K. D. Raner, C. R. Strauss, F. Vyskoc and L. Mokbel, *J. Org. Chem.*, 1993, **58**, 950.