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OBSERVATIONS ON THE CHEMISTRY OF THE IODOXY GROUP

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Abstract - In the presence of an appropriate catalyst, iodoxyarenes act as oxidants towards a variety of diverse functional groups.

Although many higher valent organoiodine compounds have been described in the literature over eighty years ago[1], interest in their use as oxidants for organic synthesis is of relatively recent vintage. Iodosobenzene, in particular, has been the subject of several communications within the past years[2]. By way of contrast, the chemistry of iodoxybenzenes has been little explored. We have recently used the efficient oxygen atom transfer from the iodoxy group to diphenyl diselenide as the basis of a catalytic method for dehydrogenation of steroidal-3-ketones and -3-ols to give the biologically important ring A 1,4-dien-3-one unit[3]. We envisage that for industrial oxidations using manganese, chromium and lead reagents, iodoxybenzenes, regenerated using commercial bleach[3], may well play an important role in reducing metal pollution.

The results of our preliminary studies with a variety of functional groups are presented in the Tables. From the data, it is apparent that the reactivity of iodoxybenzene, per se, is much less than would be predicted on purely thermodynamic grounds. Thus, although triphenylphosphine is readily oxidised, diphenyl sulphide is unreactive towards iodoxybenzene in dichloromethane at reflux. Consequently we reasoned that electrophilic complexation of the highly polarised iodine-oxygen bond would be expected to reduce the kinetic activation energy barrier. In practice, we have found that this may be accomplished by acid catalysis, Lewis acid catalysis, or by use of trichloroacetic anhydride.

TABLE 1

Oxidation of the Hydroxyl Group by Iodoxybenzene Derived Reagents

Substrate	Reagent (mols)	Catalyst	Solvent	Temp. (°C)	Time (h)	Product	Yield (%)
Benzylic							
Benzyl Alcohol	A (2.5)	–	Benzene	80	5	Benzaldehyde (isolated as 2,4-DNP)	81
para-Nitrobenzyl Alcohol	A (1.0)	–	Benzene	80	10	*para*-Nitrobenzaldehyde	87
para-tert-butylbenzyl Alcohol	A (2.5)	–	Benzene	80	5.5	*para*-tert-butylbenzaldehyde	76
"	A (1.0)	Acetic Acid	Acetic Acid	R.T	24	"	66
Glycols							
meso-Hydrobenzoin	A (0.75)	–	Dichloromethane	40	3	Benzaldehyde	89
	A (0.5)	Trichloroacetic Acid (0.05)	"	R.T	0.45	"	90
	B (0.75)	–	"	40	0.25	"	90
Benzpinacol	A (0.5)	–	"	40	20	Benzophenone	78
	A (0.5)	Trichloroacetic Acid (0.05)	"	R.T.	5	Benzophenone	97
1,2,5,6-Di-O-Isopropylidene-D-Mannitol	B (0.75)	–	"	40	2.5	2,3-Isopropylidene-D-glyceraldehyde	62
Phenols							
β-Naphthol	A (1.0)	Acetic Acid	Acetic Acid	R.T	0.10	1,2-Naphthoquinone	65
2,4-Di-*tert*-butyl *phenol*	A (1.0)	Acetic Acid	Acetic Acid	R.T	0.25	2,4-Di-*tert*-butyl-1,2-benzoquinone	82

Reagents A Iodoxybenzene

B -N-(*tert*-butyl)-N',N',N"N"-Tetramethylguanidinium *meta*-iodoxybenzoate

R.T Reaction performed at room temperature

Initially, we examined the oxidation of the hydroxyl group. (Table 1). Benzylic alcohols can be oxidised to the corresponding aldehyde under neutral conditions, but the reaction is strongly catalysed by acetic acid.

The cleavage of vicinal diols by these reagents is also a synthetically useful reaction which proceeds under neutral conditions but is subject to trichloroacetic acid catalysis. Unlike iodoxybenzene itself, the substituted guanidinium salt[4] of <u>meta</u>-iodoxybenzoic acid (<u>B</u>) is soluble in dichloromethane and possesses the practical advantage that <u>meta</u>-iodobenzoic acid may be simply recovered after reaction and recycled by hypochlorite oxidation. The salt, unlike periodate, is a chemospecific reagent since diphenyl sulphide, cholestanol and even diphenyl diselenide and triphenylphosphine are not oxidised.

Oxidation of the phenolic hydroxyl group in β-naphthol and 2,4-di-<u>tert</u>-butylphenol leads smoothly to the formation of the corresponding ortho-quinones.

Our results for a variety of organosulphur compounds are presented in Table 2.

TABLE 2

Oxidation of Organosulphur Compounds by Iodoxybenzene derived Reagents.

Substrate	Reagent (mols)	Catalyst (eq.)	Solvent	Temp. (°C)	Time (h)	Product	Yield (%)
<u>Thioacetals</u>							
Benzophenone-1,3-Dithiolan	A (1.7)	<u>p</u>-Toluene-sulphonic Acid (0.1)	Benzene	R.T.	2	Benzophenone	99
Benzaldehyde-1,3-Dithiolan		"	"	R.T.	0.75	Benzaldehyde	83
α-Tetralone-1,3-Dithiolan	A (1.7)	"	"	R.T.	0.75	α-Tetralone	53
<u>Sulphides</u>							
Diphenyl Sulphide	A (0.5)	–	Dichloromethane	40		–	–
	B (0.5)		"	40	1	–	–
	A (0.5)	Acetic Acid	Acetic Acid	R.T.	18	Diphenyl sulphoxide	81
	A (0.5)	Trityl Hexachloroantimonate (0.1)	"	40	2	" "	83
	A (1.0)	Trichloroacetic Anhydride (10)	"	R.T.	0.1	" "	80
	A (1.3)	" (0.1)	"	R.T.	2	" "	90
	A (1.0)	Titanium Tetrachloride (0.2)	"	R.T.	0.5	" "	86
Phenyl benzyl Sulphide	A (1.0)	Trichloroacetic Anhydride (10)	"	R.T.	0.1	Benzyl phenyl Sulphoxide	82
	A (2.4)	" (0.1)	"	R.T.	3	" "	79
Dibenzyl Sulphide	A (0.5)	Acetic Acid	Acetic Acid	R.T.	18	Dibenzyl Sulphoxide	94
	A (0.5)	Trichloroacetic Anhydride (1.0)	Dichloromethane	R.T.	1	" "	82
	A (1.0)	Cupric chloride (0.1)	Acetonitrile	R.T.	0.25	" "	79

The deprotection of thioacetal groups to the corresponding carbonyl compounds is an often encountered synthetic transformation[5], which can be accomplished at room temperature by use of iodoxybenzene and catalytic amounts of para-toluenesulphonic acid.

The controlled oxidation of dialkyl, diaryl, and alkyl-aryl sulphides to the corresponding sulphoxide can be readily achieved with a variety of catalysts. Over-oxidation is not normally observed even in the presence of an excess of iodoxybenzene. However, in the oxidation of diphenyl sulphide, use of the more powerful Lewis acid, titanium tetrachloride, leads smoothly and in high yield to the corresponding sulphone.

Clearly, the ready availability of inexpensive iodoxybenzene derived reagents[3], when coupled with the correct choice of catalyst as an ancillary control element, confers upon this system, the ability to develop a wide range of selective oxidants for organic synthesis.

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References

1 D.F. Banks, Chemical Reviews, 66, 243 (1966).

2 R.M. Moriarty, H. Hu and S.C. Gupta, Tetrahedron Letters, 22, 1283 (1981).
R.M. Moriarty, S.C. Gupta, H. Hu, D.R. Berenschot and K.B. White, J. Amer. Chem. Soc., 103, 686 (1981); J.T. Groves, W.J. Kruper Jr. and R.C. Haushalter, J. Amer. Chem. Soc., 102, 6377 (1980); J.T. Groves and W.J. Kruper Jr., J. Amer. Chem. Soc., 101, 7613 (1979); P. Müller and J. Godoy, Tetrahedron Letters, 22, 2361 (1981).

3 D.H.R. Barton, J.W. Morzycki, W.B. Motherwell and S.V. Ley, J. Chem. Soc. Chem. Commun., 1044 (1981).

4 For the preparation and use of strong hindered guanidine bases, see

5 D.H.R. Barton, J.D. Elliott and S.D. Géro, J. Chem. Soc. Chem. Commun.,000(1981).
N.J. Cussans, S.V. Ley and D.H.R. Barton, J.C.S. Perkin 1, 1654 (1980) and references therein.

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