Tetrahedron Letters No.42, pp. 4193-4198, 1967. Pergamon Press Ltd. Printed in Great Britain.

SILVER (II) AS AN OXIDANT FOR ORGANIC COMPOUNDS

Ludwik Syper
Department of Organic Chemistry
Technical University, Wrocław, Poland

(Received in UK 21 June 1967)

Silver (II) ion is one of the strongest oxidants in acidic media (1,2). In our previous work (3), dealing with oxidation of organic compounds with cerium (IV) , we have shown that strong oxidant does not necessarily have to be unselective in its action upon organic compounds. The principal matter there is a selection of the proper reaction conditions.

For the same reasons as in the case of cerium (IV) we have undertaken an investigation of silver (II) as an oxidant in organic chemistry. Lee and Clarke (4) have reported, a few months ago, their preliminary results on the oxidation of various organic compounds with silver (II) complexes in basic media. Now we report the results of our investigation on the application of silver (II) as an oxidant for alcohols and aromatic hydrocarbons. We were interested only in the oxidation of these compounds to aldehydes and ketones. All our experiments were carried out in acidic media. Silver (II) was used in the form of silver (II) oxide (5). Four procedures were applied in our experiments :

Procedure A. Organic compounds 1 mM in 10 ml of an appropriate acid and silver (II) oxide (2 mM for alcohols, 4 mM for hydrocarbons) were stirred, first at a lower temperature then at higher. The end of reaction was indicated by disappearance of black silver (II) oxide. Then the mixture was diluted with water and extracted with ether. The further procedure is as described (3) in the experiments with cerium (IV).

Procedure B. The reaction is carried out as in the procedure A. The carbonyl compound is converted to its 2,4-dinitrophenylhydrazone without prior extraction with ether from the reaction mixture. Inorganic ions present in the mixture do not interfere in the determination.

Procedure C. A solution of AgO in 5 ml of cold HNO_3 was added dropwise to a stirred and cooled solution of organic compound in 5 ml of the same acid. The further procedure is as in A.

Procedure D. In this procedure silver(II) oxide is added in small portions during the reaction.

It has been found that silver (II) in acidic media is a very specific oxidant of organic compounds. The results on the oxidation of alcohols are summarized in Table 1. Benzylic alcohols are oxidized to benzaldehydes in good yields. Allylic alcohols are oxidized to the corresponding unsaturated aldehydes in satisfactory yields also. Secondary aliphatic alcohols are oxidized to ketones. This reaction cannot be accomplished with cerium (IV) in good yield. Primary aliphatic alcohols are oxidized to aldehydes in poor yields. Tertiary aliphatic alcohols are resistant towards silver (II) under mild conditions. The oxidation of benzyl alcohol and o-chlorobenzyl alcohol was carried out in nitric acid. We have proved that under the indicated conditions these alcohols are not oxidized by nitric acid. When benzyl alcohols are oxidized by silver (II) to aldehydes the observed stoichiometry is 1:2, whereas in the case of cerium (IV) the observed stoichiometry is 1:1.

Our results dealing with the oxidation of aromatic hydrocarbons are summarized in Table 2. A methyl group attached to an aromatic ring is oxidized to an aldehyde group. When the benzene ring bears an activating substituent the yields are good. When more then one methyl group is present only one is oxidized. The method cannot be applied to benzene derivatives with deactivating substituents, such as $Cl, NO_2, OS_2C_6H_5$. The reaction is very sensitive to steric hindrance. The oxidation of p-phthalimidotoluene by silver(II) gives the corresponding aldehyde in 96% yield, whereas o-phthalimidotoluene is completely resistant towards oxidation. The same effects have been observed in the oxidation of these compounds by cerium (IV). The para compound

TABLE 1

Oxidation of Alcohols to Aldehydes and Ketones by Silver (II)

Alcohol	Procedure	Reaction Conditions		Yield
		Solvent[a]	Temp. °C (Time, min)	%
$C_6H_5CH_2OH$	A	AcOH + H_3PO_4 85% (10 : 1)	20 (120), 40 (120), 60 (20)	65
	C	HNO_3 10 M	–10 (3)	71
p-$O_2NC_6H_4CH_2OH$	A	H_3PO_4 1 M	20 (60), 40 (20), 60 (10)	87
m-$O_2NC_6H_4CH_2OH$	A	H_3PO_4 1 M	20 (60), 40 (20), 60 (10)	85
o-$O_2NC_6H_4CH_2OH$	A	H_3PO_4 1 M	20 (60), 40 (20), 60 (30)	79
o-$ClC_6H_4CH_2OH$	C	HNO_3 65%	–10 (3)	65
p-$H_3COC_6H_4CH_2OH$	A	H_3PO_4 1M	5 (25)	93
p-isopropylbenzyl alcohol	A	AcOH + H_3PO_4 85% (10 : 1)	20 (120), 40 (60)	71
$CH_2 = CHCH_2OH$	B	H_3PO_4 2M	20 (7)	70
$CH_3CH = CHCH_2OH$	B	H_3PO_4 1M	20 (40)	73
$C_6H_5CH = CHCH_2OH$	A	AcOH	20 (180), 40 (100)	75
cyclohexanol	A	H_3PO_4 4M	20 (8)	55
i-C_3H_7OH	B	H_3PO_4 2M	20 (60)	75
$C_6H_5CH_2CH_2OH$	A	AcOH + H_3PO_4 85% (10 : 1)	20 (60), 40 (60), 60 (60)	44
$(CH_3)_2CHCH_2OH$	B	AcOH + H_3PO_4 85% (10 : 1)	20 (60), 40 (90)	30

[a] The volume ratios are given

TABLE 2

Silver (II) Oxidation of Aromatic hadrocarbons to Aldehydes and Ketones

Starting compound	Procedure	Reaction Conditions: Solvent[a]	Reaction Conditions: Temp. °C (Time, min)	Yield %
$C_6H_5CH_3$	D	H_3PO_4 85%	-10 (30)	54
$p-C_6H_4(CH_3)_2$	A	AcOH 60% + H_3PO_4 85% (10 : 0.5)	20 (80), 40 (40)	60
$m-C_6H_4(CH_3)_2$	A	AcOH 60% + H_3PO_4 85% (10 : 0.5)	20 (60), 40 (60)	75
$o-C_6H_4(CH_3)_2$	A	AcOH 60% + H_3PO_4 85% (10 : 0.5)	20 (60), 40 (80)	49
$1,3,5-C_6H_3(CH_3)_3$	A	AcOH 60% + H_3PO_4 85% (10 : 0.5)	20 (60), 40 (30)	71
	A	dioxan + H_3PO_4 85% (10 : 1)	20 (60), 40 (120), 60 (60)	63
p-cymene	A	AcOH 60% + H_3PO_4 85% (10 : 0.5)	20 (60), 40 (30)	63
$p-H_3COC_6H_4CH_3$	A	dioxan + H_3PO_4 85% (10 : 0.5)	20 (30)	90
$o-H_3COC_6H_4CH_3$	A	dioxan + H_3PO_4 85% (10 : 0.5)	20 (60), 40 (60)	84
$p-AcHNC_6H_4CH_3$	A	dioxan + H_3PO_4 85% (10 : 0.5)	20 (60), 40 (120)	51

TABLE 2

(Continued)

Starting compound	Procedure	Reaction Conditions		Yield %
		Solvent [a]	Temp. °C Time, min	
o-Phthalimidotoluene	A	AcOH + H_3PO_4 85% (10 : 1)	20(60), 40(60), 60(90)	96
o-Phthalimidotoluene	A	AcOH + H_3PO_4 85% (10 : 1)	20(60), 40(60), 60(90)	0.0
m-$ClC_6H_4CH_3$	D	H_3PO_4 85%	-10(60)	19
2-Methylnaphthalene	A	dioxan + H_3PO_4 85% (10 : 1)	20(60), 40(120), 60(60)	63
2,3-Dimethylnaphthalene	A	dioxan + H_3PO_4 85% (10 : 1)	20(60), 40(120), 60(90)	64
2,6-Dimethylnaphthalene	A	dioxan + H_3PO_4 85% (10 : 1)	20(60), 40(120), 60(60)	70
$C_6H_5CH_2CH_3$	D	H_3PO_4 85%	-10(60)	65
$(C_6H_5)_2CH_2$	D	H_3PO_4 85%	-10(100)	0.0
Tetralin	A	AcOH 60% + H_3PO_4 85% (10 : 0.5)	20(60), 40(40)	52
Indane	A	AcOH 60% + H_3PO_4 85% (10 : 0.5)	20(60), 40(60)	60
C_6H_6	D	HNO_3 6M	5(10)	33[b]
	D	$HClO_4$ 6M	7(7)	34[b]

[a] The volume ratios are given

[b] p-Benzoquinone is formed

can be converted to the aldehyde by ceric ammonium nitrate in 50% acetic acid in 77% yield, but the ortho compound is not oxidized. p-Cymene is oxidized by silver (II) to cuminaldehyde. There is formed only one carbonyl compound, otherwise as in the case of cerium (IV). Methylnaphthalenes are oxidized to the corresponding monoaldehydes in satisfactory yields. This reaction could not be accomplished by cerium (IV). We were not able oxidize o-and m-acetyltoluidine to aldehydes or cyclohexene to cyclohexenone. Diphenylmethane was not oxidized by silver (II). Ethylbenzene with silver (II) gives acetophenone, tetralin gives 1-tetralone and indane gives 1-indanone. It should be emphasized that benzene itself can be oxidized by silver (II) to p-benzoquinone. The conversion of benzene into quinone takes place in nitric, perchloric and phosphoric (85%) acid. Ceric ammonium nitrate in 6M $HClO_4$ oxidizes benzene to p--benzoquinone in 20% yield. 6 Moles of the oxidants for 1 mole of benzene was used. p-Benzoquinone was isolated and characterized as its reaction product with 2,4-dinitrophenylhydrazine.

REFERENCES

1. J.J. Lingane and D.G. Davis, Anal.Chim.Acta **15**, 201 (1956).
2. D.G. Davis and J.J.Lingane, Anal.Chim.Acta **18**, 245 (1958).
3. L.Syper, Tetrahedron Letters 4493 (1966).
4. J.B. Lee and T.G.Clarke, Tetrahedron Letters 415 (1967).
5. R.N. Hammer and J.Kleinberg, Inorg.Syn. **4**, 12