Metal Ions and Complexes in Organic Reactions. Part XIII.[1] Oxidative Effects of Silver(II) Complexes of Pyridinecarboxylic Acids

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Aldehydes or ketones were produced by reaction of silver(II) picolinate (pyridine-2-carboxylate) in aqueous suspension with some arylalkanes and arylalkanols; the response of substrates differed in certain respects from that reported when the oxidant was silver(II) oxide in phosphoric acid. The silver(II) complexes of pyridine-2-carboxylic, -3-carboxylic, -4-carboxylic, and -2,3-dicarboxylic acids exhibited only minor differences in efficiency when compared as oxidants for primary and secondary amines and other organic substrates.

SOME oxidative effects of silver(II) picolinate (pyridine-2-carboxylate) have been described,[2,3] in particular with primary and secondary amines as substrates. Another account of oxidation by this reagent has since appeared,[4] dealing mainly with alcohols, monosaccharide derivatives, and olefins as substrates. All these reactions resemble oxidations effected by some transition-metal oxides [5] in being heterogeneous; *i.e.* the process involves metal ions in a solid phase and organic solutes in a liquid phase. On occasions when silver(II) oxide has been tested as an oxidant for organic compounds, little effect has been found, except in an investigation [6] involving strongly acidic conditions, which were provided by the presence of phosphoric or nitric acids in the liquid phase;

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[1] Part XII, R. G. R. Bacon and D. J. Maitland, preceding paper.

[2] R. G. R. Bacon and W. J. W. Hanna, *Proc. Chem. Soc.*, 1959, 305.

[3] R. G. R. Bacon and W. J. W. Hanna, *J. Chem. Soc.*, 1965, 4962.

[4] J. B. Lee and T. G. Clarke, *Tetrahedron Letters*, 1967, 415.

[5] W. F. Pickering, *Rev. Pure Appl. Chem.* (*Australia*), 1966, **16**, 185.

[6] L. Syper, *Tetrahedron Letters*, 1967, 4193.

conversion of arylalkanes and arylalkanols into aldehydes or ketones then occurred, attended by dissolution of the oxide. In the present paper we illustrate (*a*) oxidation of arylalkanes and arylalkanols by silver(II) picolinate (Table 1), and (*b*) a comparison of the picolinate with related silver(II) pyridinecarboxylates as oxidants for organic compounds (Table 2).

Under the conditions shown in Table 1 (the supply of oxidant being arbitrarily restricted to 2 mol.), oxidations involved the steps $>CH_2 \longrightarrow >CH\cdot OH \longrightarrow >CO$ at a benzylic carbon atom, or fission of the C–C bond in bibenzyl, which may occur *via* the glycol[3] or *via* deoxybenzoin. Response of the *ortho*-substituted compounds appears to be affected by steric hindrance, as was noted also when silver(II) oxide in phosphoric acid was investigated.[6] The latter reagent oxidised toluene but not diphenylmethane. The reverse effect was found with silver(II) picolinate, which does however react sluggishly with ethylbenzene in water[2] and with toluene in dimethyl sulphoxide.[4]

TABLE 1

Oxidation of arylalkanes and arylalkanols (0·01 mole) by stirred suspensions of silver(II) picolinate (0·02 mole) in water (200 ml.) at 80°

Substrate	Reaction time (hr.)	Product	Amount of oxidant theoretically required (mole)	Yield (%)
CH_2Ph_2	12	$COPh_2$	0·04	43
$o\text{-}MeC_6H_4\cdot CH_2Ph$	12	$o\text{-}MeC_6H_4\cdot COPh$	0·04	26
$p\text{-}MeC_6H_4\cdot CH_2Ph$	12	$p\text{-}MeC_6H_4\cdot COPh$	0·04	46
$CHPh_2\cdot OH$	2	$COPh_2$	0·02	65
$o\text{-}MeC_6H_4\cdot CHPh\cdot OH$	4 [a]	$o\text{-}MeC_6H_4\cdot COPh$	0·02	36
$m\text{-}MeC_6H_4\cdot CHPh\cdot OH$	6	$m\text{-}MeC_6H_4\cdot COPh$	0·02	54
$p\text{-}MeC_6H_4\cdot CHPh\cdot OH$	12	$p\text{-}MeC_6H_4\cdot COPh$	0·02	53
$CH_2Ph\cdot CH_2Ph$	8	PhCHO	0·06	34
$CH_2Ph\cdot COPh$	1	PhCHO	0·02	40

[a] At 98°.

TABLE 2

Oxidation of organic substrates (0·01 mole) by stirred suspensions of silver(II) complexes of pyridinecarboxylic acids (0·02 mole) in water (150 ml.) at 70°

	Yield of carbonyl compound (%) from oxidation by:			
Substrate	Ag^{II} picolinate [a]	Ag^{II} nicotinate	Ag^{II} isonicotinate	Ag^{II} quinolinate
Isopropylamine	16	28	31	32
n-Butylamine	14	16	22	
Isobutylamine	9	13	21	18
s-Butylamine	27	28	25	
Cyclohexylamine	41	34	42	
Benzylamine	51	30	35	
Di-isopropylamine	31	50	42	50
Di-n-butylamine	67	46	35	
Di-isobutylamine	73	55	40	72
Di-s-butylamine	62	46		
Dicyclohexylamine	61	54	56	
Dibenzylamine	76	70	77	
Benzyl alcohol [b]	53	49	49	
Phenylacetic acid [c]	30	20	31	
2,6-Dimethylphenol [d]	30	19	17	

[a] These figures are quoted from refs. 2 and 3; equal or greater yields were obtained in check experiments. [b] At 85°. [c] At 85°, producing benzaldehyde; 0·04 mole of oxidant used. [d] At 20°, producing 3,3′,5,5′-tetramethyldiphenoquinone (R. G. R. Bacon and A. R. Izzat, *J. Chem. Soc* (*C*), 1966, 791).

The silver(II) complexes (Table 2) are obtained by oxidising silver nitrate with aqueous persulphate in the presence of the pyridinecarboxylic acids; the picolinate and quinolinate are probably monomeric and contain chelate ligands, whilst the nicotinate and isonicotinate are probably polymeric and may contain multi-membered rings.[7] An alternative preparative method was found, involving oxidation of the methyl group of α-picoline, theoretically in accordance with the equation:

$$4C_5H_4NMe + 13S_2O_8^{2-} + 2Ag^+ + 8H_2O \longrightarrow 2(C_5H_4N\cdot CO_2)_2Ag + 26SO_4^{2-} + 28H^+$$

Corresponding reaction at the methyl group of toluene gives benzaldehyde and bibenzyl.[8]

Investigation of comparative oxidising efficiency was prompted, in part, by current interest in the influence of ligands on electron-transfer processes in transition-metal complexes.[9] The responses of the series of substrates were fairly similar towards each oxidant. In the case of particular substrates, the yields were often somewhat better if silver(II) picolinate or quinolinate was chosen.

EXPERIMENTAL

Preparation of Silver(II) *Complexes*.—The nicotinate,[10] isonicotinate,[10] and picolinate[3] were prepared by mixing silver nitrate (0·1 mole) with an excess of the pyridinecarboxylic acid (0·3 mole) in aqueous solution (final vol. 2 l.), treating the resulting suspension of white silver(I) salt with a large excess of aqueous sodium persulphate (0·3 mole) at ambient temperature, stirring for 4 hr., filtering off the red silver(II) complex, washing thoroughly with water, vacuum drying, and storing in the dark. A modified procedure,[11] involving stronger solutions, and addition of persulphate to the silver nitrate before the pyridinedicarboxylic acid, was used for the quinolinate. Yields were 90—95% (based on $AgNO_3$) for the picolinate, nicotinate, and quinolinate, but considerably lower for the isonicotinate (Found for the picolinate: C, 41·0; H, 2·4; N, 8·1; for the nicotin-

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[7] J. A. McMillan, *Chem. Rev.*, 1962, **62**, 65.

[8] R. G. R. Bacon and J. R. Doggart, *J. Chem. Soc.*, 1960, 1332.

[9] *E.g.*, A. G. Sykes, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 153.

[10] B. Banerjee and P. Ray, *J. Indian Chem. Soc.*, 1956, **33**, 503.

[11] B. Banerjee and P. Ray, *J. Indian Chem. Soc.*, 1957, **34**, 207.

ate: C, 40·6; H, 2·3; N, 8·3; for the isonicotinate: C, 40·6; H, 2·4; N, 7·7. Calc. for $C_{12}H_8AgN_2O_4$: C, 40·9; H, 2·3; N, 8·0%. Found for the quinolinate: C, 35·6; H, 2·5; N, 6·1. Calc. for $C_{14}H_8AgN_2O_8,2H_2O$: C, 35·3; H, 2·5; N, 5·9%). Determination of the oxidising power of the reagents [3] gave *ca.* 98% of the theoretical value in all cases.

For an alternative method of preparation, a solution of 2-picoline (0·2 mole), in water (500 ml.) containing sodium persulphate (0·75 mole) and silver nitrate (0·1 mole), was stirred for 7 hr. at 50°. The resulting precipitate of red crystalline silver(II) picolinate was filtered off and an additional quantity was obtained by treatment of the filtrate with further persulphate (0·2 mole). The total precipitate, after being washed and dried, amounted to 26·8 g. (76%).

Oxidation of Arylalkanes and Arylalkanols by Silver(II) *Picolinate.*—Pure samples of the phenyltolylmethanes (liquids) and the phenyltolylmethanols (m.p.s of *ortho-*, *meta-*, and *para*-isomers, 91, 61, and 57°, respectively) were available by synthesis. Samples of synthesised phenyl tolyl ketones were available for comparison with those obtained by oxidation. All the substrates formed liquid layers under the conditions of reaction (Table 1). After the red silver(II) picolinate had been converted into the white silver(I) salt, the product was isolated by extraction with ether. Benzaldehyde was determined as its 2,4-dinitrophenylhydrazone. The ketonic content of crude products containing benzophenone or phenyl tolyl ketones was determined by an i.r. analytical method based on the intensity of the carbonyl absorption band. Also, the oxidation products were separated chromatographically on alumina and fractions were identified spectroscopically; unchanged hydrocarbons were eluted by light petroleum and derived ketones by ether; in the case of alcohol oxidations, successive reinforcement of light petroleum by ether led to elution of the ketone, followed by unchanged alcohol.

Oxidation of Amines etc. *by Silver*(II) *Complexes.*—Procedures previously described in the case of the picolinate [3] were used to effect oxidations by stirred aqueous suspensions of the silver(II) complexes at *ca.* 70° (Table 2) and to determine the resulting aldehyde or ketone as its 2,4-dinitrophenylhydrazone. To check the analytical method, it was applied to an aqueous acetone solution of known concentration. The weight of precipitate was greater than the theoretical (*ca.* 105%) and the m.p. was too low, owing to occlusion of excess of the reagent. Two recrystallisations, from the minimum of ethanol, raised the m.p. to its correct value and lowered the yield to *ca.* 94%. Similar purification was applied to derivatives of the oxidation products, the stated yields of which (Table 2) are therefore a little below the correct values. Reactions were carried out until the deep red silver(II) complex was replaced by the white silver(I) salt. The times required, varying with the substrate, were: for the nicotinate, 0·5—4 hr.; for the isonicotinate, 0·2—0·6 hr.; for the quinolinate, 0·5—0·8 hr.; for the picolinate,[3] 0·1—3 hr. Yields showed adequate reproducibility in duplicate experiments.

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