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OXIDATIONS INVOLVING SILVER–IX

OXIDATION OF PRIMARY AMINES BY SILVER(II) PICOLINATE.[1]

J. B. Lee,* C. Parkin and M. J. Shaw
Bayfordbury Research Laboratories, The Hatfield Polytechnic, Near Hertford, Herts

N. A. Hampson and K. I. MacDonald
Electrochemistry Laboratories, The University, Loughborough, Leics. LE11 3TU

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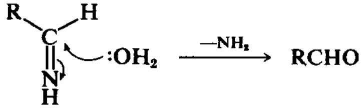
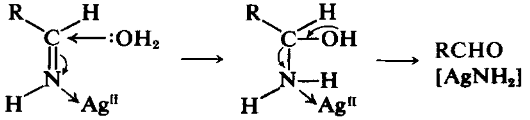
Abstract—A re-examination of the oxidation of primary amines of the type $R\cdot CH_2NH_2$ by silver(II) picolinate reveals that the major product is usually the nitrile RCN, rather than the aldehyde RCHO, as had been reported previously.[4]

As part of more extensive studies[2] on the synthetic applications of silver compounds, the behaviour of silver electrodes, and related topics, we have described the oxidation of primary amines at the silver electrode.[3] We have also studied the behaviour of amines both as substrates for oxidation, and as ligands, in non-electrochemical systems. In their paper on the oxidation of some amines with silver(II) picolinate, Bacon and Hanna[4] indicated that aldehyde was produced when amines of the type $R\cdot CH_2NH_2$ were oxidised by this reagent, although one isolated case of formation of nitrile was recorded; There was no indication of any product other than aldehyde in other cases. Aldehyde formation in these cases seems certain to proceed via an intermediate imine which undergoes hydrolysis *either* in the free state (Eq. A) *or* by a silver-assisted process (Eq. B).

A

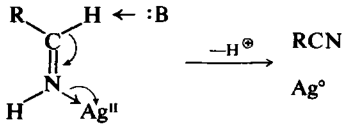


B



From our examination of some other systems it seemed reasonable that a third process should compete with this, namely oxidation to the nitrile (Eq. C) and the relative rates of the competing processes would determine the ratio of products.

C



In many of the oxidations described by Bacon, aldehyde was obtained in yields of less than 20%. In view of our previous results which indicated that reaction C proceeds rapidly and readily, we therefore re-examined the oxidation of primary amines under identical conditions to those reported to see if cyanides were also formed. In the oxidation of amines of the type $R\text{-}CH_2NH_2$ where R = alkyl we confirmed the formation of aldehyde in each case in low yield. However the major product in each case was the nitrile, and indeed for these amines the reaction represents a good method for the synthesis of nitrile. Table 1 summarises these results. Insofar as any pattern is observable, the greater the branching at the β-C atom, the greater the proportion of nitrile observed.

The results in the case of substituted benzylamines were even more interesting. For benzylamine itself almost equimolar proportions of benzaldehyde and benzonitrile were formed. Introduction of an electron-releasing group, such as a *p*-isopropyl group, into the nucleus led to formation of nitrile as the predominant reaction, whereas introduction of the electron-withdrawing nitro-group led to formation of aldehyde almost exclusively. The fortuitous balancing of the two competing reactions in the benzylamine case permits a clear observation of substituent effects, and hence permits a reasonable assumption concerning the reaction mechanisms.

In reaction C, if the *slow* step is attack by the

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*To whom communications should be addressed.

Table 1. Oxidation Products from the Reaction of RCH_2NH_2 with Silver(II) Picolinate*

Amine	Oxidation product ratio Nitrile	 Aldehyde
1-Aminobutane	77	23
1-Aminopentane	84	16
1-Amino-2-ethylbutane	90	10
1-Amino-2-ethyl hexane	92	8
1-Amino-3-methylbutane	76	24
1-Amino-dodecane	75	25
1-Amino-octane	68	32
Benzylamine	52	48
3,4-Methylenedioxy-benzylamine	84	16
p-Isopropyl-benzylamine	77	23
p-Nitro-benzylamine	12	88
1-Amino-2-methylpropane	60	40

*One mole amine: 4 mole oxidant. Essentially the same ratios are obtained with a 1:2 ratio, of amine: oxidant, but in this case about 40% of amine is recovered.

imine upon the positive silver of the complex, it would be anticipated that increased nucleophilicity of the imine nitrogen would increase the rate of reaction, the converse holding where the nucleophilicity is reduced. At the same time the change in the positive character of the imino carbon will directly influence its susceptibility to attack by water or hydroxyl (in the hydrolytic sequences A or B) in the opposite sense, that is the rate of reaction A or B (other things being equal) will be highest for the nitro-substituted imine. Thus the two effects reinforce each other, leading to the observed striking change in direction of reaction.

EXPERIMENTAL

UV and IR spectra were measured using Unicam SP 200, Perkin Elmer 237, Perkin Elmer 257, or Unicam SP 800 instruments as appropriate. ^{1}H·NMR spectra were recorded using Perkin Elmer R 10 or Varian A60 MHz instruments. Thin-layer analytical and thick-layer preparative chromatography used glass-supported silica or alumina eluted with benzene-MeOH, $CHCl_3$-MeOH, or petrol-benzene mixtures. Analytical GLC used Pye 104 instruments with PEGA, DNP, Apiezon L, silicone F, and carbowax columns. Organic materials were reagent grade materials redistilled or recrystallised as appropriate. Where available, Analar reagents were used. The improved preparation of silver(II) picolinate has been described previously.[5]

Some variation in scale and method of reaction and isolation of product was made as appropriate to the properties of substrate. The following is a typical experiment. Table 1 summarises this and other results.

Silver(II) picolinate oxidation of 1-amino-2-ethylhexane

To a stirred mixture of silver(II) picolinate (2 mole proportions 33·21 g) and water (140 ml) was added in three portions over 5 min 1-amino-2-ethyl-hexane (1 mole proportion, 6·1 g).

Vigorous stirring was continued, and the reaction monitored by removal of aliquots. Chloroform extracts and filtered aqueous layers of the aliquots were examined analytically by GLC and TLC. Only two products were observed in quantity, but traces of a third component (less than 2%) were found. Examination of a concentrated portion indicated the presence of nitrile (2230 cm^{-1}) and carbonyl (1708 cm^{-1}) groups. When reaction was complete the mixture was neutralised with dil HCl acid (5 mole equivs) and filtered. The residual solid was washed with chloroform (3 × 30 ml), and the washings used to extract the filtrate. GLC examination of the dried ($MgSO_4$) extract against appropriate standards indicated the presence of 2-ethylhexanonitrile (*ca* 91%). 2-ethylhexanal (*ca* 8%), and N-(2-ethylhexylidene)-1-amino-2-ethylhexane (*ca* 1%), the latter presumably arising as a byproduct by condensation of aldehyde and starting material. (In some experiments small traces of 1,1-bis(2′-ethylhexylamino-)-2-ethylhexane and 2-ethylhexyl-1-isonitrile were also obtained). The concentrated extract was fractionated under vacuum to give (a) 2-ethyl hexanonitrile (2·1 g) b.p. 208–211°. IR band at 2260 cm^{-1}; ^{1}H·NMR signals at 9·1 τ (m, 6 protons), 8·2–9·0 τ (m, 8 protons), 7·15 τ (m, 1 proton), (b) 2-ethylhexanal (0·13 g) b.p. 81°/40 mm, IR band 1708 cm^{-1} (s); ^{1}H·NMR signals at 9 τ (overlapping trs, 6 protons) 8·5–9·0 τ (m, 8 protons), 7·1 τ (m, 1 proton) 0·2 τ (d, 1 proton), (N.B. Since differential losses occur in the work up of the extract, the amounts produced as determined by GLC analysis are given in the Table), identical in IR, mass and ^{1}H·NMR spectra and GLC and TLC, with authentic materials. In a separate experiment a small amount of N-(2′-ethylhexylimine)-2-ethylhexane (identical in IR spectrum with authentic material) was isolated by preparative layer chromatography.

Preparation of authentic standards. A number of nitriles, aldehydes, and condensation products were not readily available. These were prepared by one of the standard methods, their identity and purity being checked by elemental analysis; GLC or TLC; mass, ^{1}H·NMR, and IR, spectroscopy.

Conversion of alcohols to aldehydes with silver(II) picolinate

n-Decanal. Silver picolinate (7·1 g) water (30 ml) and 1-decanol (3·2 g) were stirred together, and the temp slowly raised to 70°. Stirring was continued until the red coloration disappeared, and then dil HCl was added until no further precipitation of AgCl occurred. The soln was filtered, the residue washed with ether, and the ether washings used to extract the filtrate. Fractionation of the filtrate gave n-decanal (2·7 g), b.p. 105–108° (water pump) n_D^{17} 1·4281, 2,4-DNP, m.p. 100–101°, Dimedone derivative m.p. 93–94°.

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