

OXIDATION OF METHYLPYRIDINES WITH SOME ARGENTOUS COMPOUNDS

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Summary

The applicability in syntheses of the oxidation of picolines, lutidines and sym-collidine with argentous sulfate and argentous oxide was investigated. Reaction of these pyridine bases carried out in autoclaves resulted in precipitation of silver powder usually with excellent yield in every case. Methyl groups of methylpyridines are oxidized partly to carboxylic groups which are removed under the experimental conditions to form pyridine or lower methylpyridines, respectively. However, principally tars are formed.

Introduction

In our recent patents [1—3] and papers [4—6] we presented results of the reaction of copper sulfate with pyridine and its methyl homologues. In all reactions carried out at elevated temperature in steel vessels copper powder precipitates and pyridine bases undergo well defined oxidation processes. Thus pyridine, all the 3-picoline and 3,5-lutidine form corresponding 1-*H*-pyridine-2-one-s in an assumedly intramolecular reaction of the relevant σ -coordination compounds. Methylpyridines bearing methyl groups in the α and/or γ -positions of the pyridine ring undergo oxidation predominantly to carboxylic acids which decarboxylate under reaction conditions. this turns the overall process into a demethylation of pyridine bases.

Our attempts to carry out similar oxidations of pyridine and its methyl derivatives with argentous salts [7] have revealed powdered metal silver to precipitate. The much lower selectivity of the reaction accompanied by a significantly higher yield of precipitated silver in comparison with the yield of precipitated copper in former experiments with copper sulfate allow to assume

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both a different course and mechanism of such oxidations. At the same time the applicability of the reaction with argentous compounds in syntheses attracts attention.

The results of our investigation into this problem are presented in this paper. Thus, both argentous sulfate and oxide are subject to the reaction with pyridine, all three isomeric picolines, 2,3-, 2,4-, 2,6- and 3,5-lutidines and 2,4,6-collidine.

Experimental

A pyridine base, the argentous compound and water were heated to the elevated temperature in a 5×10^{-2} dm³ steel autoclave with glass lining. The amounts of reagents and the reaction conditions are specified in Tables I and II. The powder precipitated at the bottom of the autoclave was separated with a centrifuge, washed with distilled water and dried. Its identity was proven by the reaction with ammonium hydroxide followed by the oxidation with potassium chromate (positive reaction for argentous oxide and negative for metal silver). The isolation of the products of reaction of pyridine origin was carried out following the procedure described earlier [6]. Chromatographic quantitative analysis of their benzene extracts was carried out using a CHROM-5 apparatus (Czechoslovakia) with $1 \times 4 \times 10^{-3}$ m TENAX GC column. The temperature was programmed (8.5×10^{-2} K/s) in the range of 403—433 K. The flow rate of nitrogen was 2.5×10^{-4} dm³/s.

The lack of pyridinols and 1-*H*-pyridones was postulated after negative reaction with ferric chloride carried out on fractions of particular reaction mixtures.

Results and discussion

The experiments carried out with argentous compounds have revealed essential differences in the course of the reactions in comparison with similar reactions of the bases studied with cupric sulfate. Contrary to the complex of copper sulfate with pyridine which reacted to 1-*H*-pyridine-2-one, sulfur dioxide and copper powder, the complex of argentous sulfate with pyridine appeared to be entirely passive to both elevated temperature and pressure. These reaction conditions which are suitable for the transformation of cupric complexes with 3-picoline and 3,5-lutidine into 1-*H*-3- and 5-methylpyridine-2-one-s as well as 1-*H*-3,5-dimethylpyridine-2-one, respectively, and copper powder caused in every case precipitation of silver powder from the relevant argentous complexes but pyridones were not formed.

In the case of reactions with copper sulfate it has been found that copper powder was formed directly from the complexes and its amount was dependent

Table I
Results of the Reaction of Pyridine Bases with Argentous Sulfate

Base	Ag ₂ SO ₄ , g	H ₂ O, cm ³	Temp., K	Reaction time, h	Products				
					Ag		Ag ₂ O		Demethylated Compounds, Yield, %
					mg	%	mg	%	
2-Picoline	2	3	423	1	21	1.5	248	17.9	pyridine, 1.22%
				2	87	6.3	207	13.0	
				4	531	38.4	40	2.7	
				6	746	53.9	38	2.4	
				6	1,378	99.6	3	0.2	
	0.33	3	453	8	211	92.3	9	3.3	
	0.03	3	453	8	20	95.7	0	0.0	
	0.05	10	453	8	34	99.4	0	0.0	
	0.025	10	453	8	15	86.7	1	5.2	
3-Picoline	2	3	423	4	45	3.2	95	6.0	pyridine, 0.82%
				6	36	2.6	13	0.8	
				6	131	9.5	200	12.6	
4-Picoline	2	3	453	8	1,382	99.7	5	0.3	pyridine, 0.94%
2,3-Lutidine	2	3	453	6	1,317	95.1	8	0.5	pyridine, 0.39%, 2-picoline, traces
2,4-Lutidine	2	3	423	4	146	10.6	196	12.3	pyridine, 0.46%, 2-picoline, 0.49%
				8	1,326	95.8	6	0.4	
2,6-Lutidine	2	3	453	6	1,329	96.1	55	3.7	pyridine, 0.25%, 2-picoline, traces
3,5-Lutidine	2	3	453	6	149	10.8	224	15.1	pyridine, 0.31%
2,4,6-Collidine	2	3	423	4	65	4.7	168	11.3	pyridine, 0.52%, 2,4-lutidine, 0.2%
				6	227	16.4	127	8.5	
				6	1,371	99.0	6	0.4	

Table II
Reaction of Pyridine Bases with Argentous Oxide^{a)}

Base	Metallic Silver precipitated		Products of demethylation, %
	g	%	
2-Picoline	1.302	93.2	pyridine, 0.63%
3-Picoline	0.899	64.4	pyridine, 0.41%
4-Picoline	1.264	90.5	pyridine, 0.41%
2,3-Lutidine	1.337	95.7	pyridine, 0.33%, 2-picoline, traces
2,4-Lutidine	1.335	95.6	pyridine, 0.29%, 2-picoline, 0.15%
2,6-Lutidine	1.276	91.4	pyridine, 0.18%, 2-picoline, traces
3,5-Lutidine	0.830	59.4	pyridine, 0.31%
2,4,6-Collidine	1.327	95.0	pyridine, 0.26%, 2-picoline, 0.13%, 2,4-lutidine, 1.97%, 2,6-lutidine, 0.24%

^{a)} 3×10^{-3} kg of each pyridine base, 3×10^{-3} dm³ of water and 1.5×10^{-3} kg of argentous oxide were reacted in every case at 423 K for 4 h.

on the reaction time. Present studies on the behaviour of complexes with argentous sulfate show that silver powder is formed indirectly from the corresponding complexes. In the first stage of the reaction, argentous oxide precipitates which quite readily oxidizes methylpyridines. This has been also proven by the experiments run with methylpyridines and argentous oxide instead of argentous sulfate. The results of the reactions are shown in Tables I and II.

The oxidizing ability of argentous oxide depends on the pH of the medium. In acidic medium resulting from the reactions run with silver sulfate the rate of oxidation is reduced. Further differences noted between the behaviour of cupric and argentous complexes are related to the transformation of the ligands. Only minute amounts of demethylated products are formed from argentous complexes contrary to cupric complexes. Unidentified tarryproducts containing $-\text{CH}=\text{CH}-$ bonds as proven by IR spectra ($\nu_{\text{CH}=\text{CH}}$ in the region of 1620 cm^{-1}) are principal products. Methylpyridines exhibit evident selectivity towards oxidation with cupric ion. α -Methyl groups are most readily oxidized followed by the γ - and β -methyl groups. The yield of precipitated silver powder points to the lower selectivity of these groups toward the oxidation with argentous compounds. Simultaneously, the pathway of the oxidation favours the formation of tars. This fact can be interpreted in terms of the ability of the proton abstraction from the methyl group by argentous oxide in an intermolecular process and the addition of carbanion to pyridine aldehydes formed in parallel. Finkelstein and Elderfield [8] did not observe such reactions in the case of the oxidation of 2-picoline with argentous acetate in glacial acetic acid. Pyridine, but not tars and silver powder have been the only reaction products identified, because the solvent prevented

the formation of argentous oxide in the course of the reaction. Some complications of the reactions studied in this paper could be anticipated in view of the results patented by Pearlman [9]. This author has shown that some aromatic carboxylic acids, among them both nicotinic and isonicotinic acid, are hydroxylated by argentous oxide in the positions vicinal to the carboxylic group. The latter are decarboxylated in this one-step reaction. Any possibility of the hydroxylation of the pyridine ring in the course of our experiments may be ruled out on the basis of the analysis of the IR spectra of the tarry products (lack of bands in the region of $3200\text{--}3500\text{ cm}^{-1}$) and a negative spot test with ferric chloride for the hydroxy group.

As a conclusion, the reaction under study can be solely useful for the precipitation of metal silver from aqueous solutions of its sulfate and suspensions of its oxide.

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