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SYNTHESIS OF PYRIDINE N-OXIDE–SbCl$_5$ COMPLEXES AND THEIR INTRAMOLECULAR AND OXYGEN-TRANSFER REACTION

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Abstract—Mixing with equimolar solutions of pyridine N-oxide or its homologs and SbCl$_5$ in CCl$_4$ deposited 1:1 complexes as colorless crystals in high yield. On thermolysis, these complexes underwent intramolecular oxygen transfer to give selectively the corresponding 2-pyridone derivatives. N,N-Dimethylaniline N-oxide and SbCl$_5$ also gave a crystalline 1:1 complex which on thermolysis yield *o*-dimethylaminophenol in good yield.

In the course of our studies on the Wallach rearrangement of azoxybenzenes, 1:1 complexes between azoxybenzenes and SbCl$_5$ were shown to undergo selective ortho-Wallach rearrangement on thermolysis to give 2-hydroxyazobenzenes.[1,2] It was also shown that 2-pyridone is selectively formed by thermolysis of pyridine N-oxide-SbCl$_5$ complex.[1] In view of the importance of the N-oxide of pyridines and other N-heteroaromatics in intra[3–9] and intermolecular oxygen transfer reaction,[3–10] the SbCl$_5$ complexes of substituted pyridine N-oxides and several other N-oxide were prepared and their thermolysis was investigated.

RESULTS AND DISCUSSION

Mixing with equimolar solution of pyridine N-oxide 1 and SbCl$_5$ in carbon tetrachloride immediately deposited a colorless crystalline complex in essentially quantitative yield. The complex has a sharp m.p., and its elemental analysis showed that is a 1:1 complex. Similar complexes were obtained from other N-oxides in high yield. Table 1 lists their spectral data which show characteristic IR bands around 1600 cm^{-1} and strong UV max around 260 nm. These complexes are assumed to have an ionic structure such as 2 by analogy with the ionic or highly polarized structure of acetyl halides with antimony pentachloride: RCO$^+$SbCX$_6^-$ or RCO$^+\cdots$SbCX$_6^-$, where X = F or Cl.[11,12]

Thermolysis of the N-oxide–SbCl$_5$ complexes in nitromethane or nitrobenzene was shown to give the corresponding 2-pyridone derivatives 3 selectively. The results summarized in Table 2 indicated that the yield of 2-pyridones generally increases with reaction time, whereas in the case of SbCl$_5$ complex of N,N-dimethylaniline N-oxide the production of tarry materials increases with increased reaction time, probably due to thermal instability of the primary product under the reaction conditions. It is noteworthy that the complexes of 3-methylpyridine N-oxide and isoquinoline N-oxide gave 3-methyl-2-pyridone and 1-isoquinoline respectively in a highly selective manner. In the case of rearrangement of 3-methylpyridine, N-oxide, 3-methyl-2-pyridone seems to be formed selectively because a resonance structure having O$^{-\sigma}$ in N–O group and C$^{+\sigma}$ on 2-position in pyridine ring take part strongly in this reaction.

This reaction provides a more convenient method for synthesizing 2-pyridone derivatives than the previously reported methods involving multistep synthesis.[14,15] Several workers have reported reactions on those pyridine N-oxides with acetic anhydride leading to acetoxy pyridines which can be hydrolysed into 2-pyridones.[5–9] However, the migration of the O atom does not always occur selectively: for example, 3-methylpyridine N-oxide gave rise to 3- and 5-methyl-2-pyridones and 4-methylpyridine N-oxide gave 4-(acetoxymethyl) pyridine and 3-acetoxy-4-methylpyridine.[8] A similar result has been reported for the reaction of N,N-dimethylaniline N-oxide with acetic anhydride giving rise to *o*-dimethylaminophenol but being accompanied with several by-products.[15] Although the mechanism of the selective O-transfer is obscure, the 2-pyridone formation appears to have some analogy to the reaction of pyridine N-oxide with acetic anhydride which also leads to an O transfer to the ring C atom. This has been suggested to occur via an ionic mechanisms.[8] Additionally, the thermolysis of the pyridine N-oxide–SbCl$_5$ complex was carried out in boiling benzene and toluene, in a hope of the occurrence of an intermolecular O-transfer to the solvent molecule. Under these conditions, no phenolic product originated from the solvents was detected—2-pyridone was the sole product.

Furthermore, styrene added to the reaction system with the pyridine N-oxide–SbCl$_5$ complex did not undergo polymerization. The results suggest that the 2-pyridone formation occurs via an intramolecular ionic migration of the O–Sb group (Scheme 1) similar to the mechanism proposed for the 2-hydroxyazobenzene formation in the thermolysis of azoxybenzene-SbCl$_5$ complexes.[2]

Table 1. SbCl$_5$ complexes of pyridine N-oxides

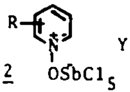
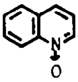
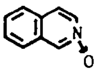
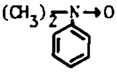
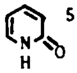
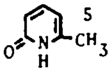
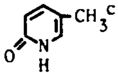
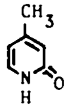
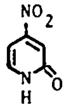
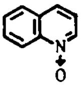
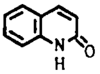
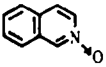
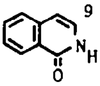
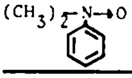
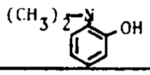
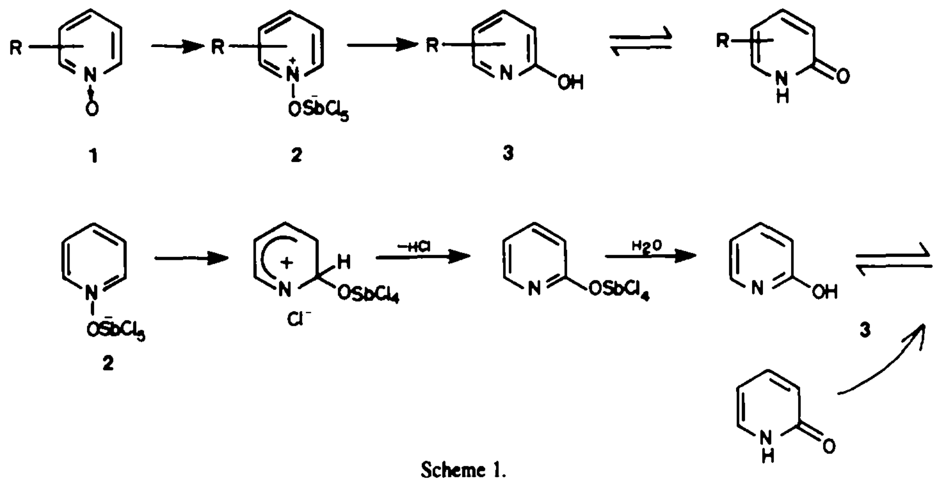
 $\underline{2}$	Yield (%)	m p (°C)	Analysis, Found(Calcd.) % C	H	N	I R (cm^{-1})	U V $\lambda_{max.}^{CHCl_3}(\varepsilon)$
H	94.5	194	15.12(15.22)	1.27(1.24)	3.50(3.55)	1615,1470,1200	259(14100)
2-CH$_3$	93.7	105	16.67(17.63)	1.78(1.71)	3.43(3.42)	1610,1260,1185, 1170	260(9400)
3-CH$_3$	98.0	110	18.22(17.63)	1.80(1.71)	3.46(3.42)	1610,1490,1245, 1100	260(11200)
4-CH$_3$	94.3	225-227	17.22(17.63)	1.90(1.71)	3.57(3.42)	1630,1270,1200	261(12400)
4-NO$_2$	99.0	252	13.56(14.20)	0.98(0.92)	5.40(5.92)	1600,1460,1040	241(8900) 339(14600)
	95.0	219	24.55(25.30)	1.65(1.66)	2.98(3.30)	1615,1315,1270, 1200	246(12500)
	85.0	196-197	23.68(25.30)	1.61(1.66)	2.63(3.30)	1620,990	255(16300) 305(8900)
	90.3	112	19.95(21.91)	2.80(2.52)	2.96(3.19)	2800,1600,1440, 960	274(11900)

Table 2. Thermal reaction of 1 : 1 complexes of pyridine N-oxides with SbCl$_5$

$\underline{2}$	Reaction conditions$^{a)}$		Reaction products	
SbCl$_5$ Complexes	Time (hr)	Temp. (°C)	Yield (%)	Literature of previous works
H	5.0	reflux	81.1	 5
	5.0	85-90$^{b)}$	40.0	
2-CH$_3$	5.0	reflux	44.1	 5
	10.0	reflux	70.4	
3-CH$_3$	2.0	180$^{b)}$	29.8	 c) 6
	10.0	reflux	81.0	
4-CH$_3$	6.0	reflux	78.1	 8
4-NO$_2$	3.0	reflux	60.0	 13
	10.0	reflux	85.5	
	3.0	75-80$^{b)}$	30.0	 14
	10.0	reflux	71.7	
	5.0	reflux	89.0	 9
	7.0	reflux	93.5	
	1/3	reflux	71.4	 15
	1.0	reflux	33.3	

a) Nitromethane (b.p lol,3°C) was used as the solvent unless otherwise stated. b) Nitrobenzene was enployed as the solvent. c) 2-Hydroxy-5-methylpyridine was not detected.



Scheme 1.

In the formation process of 2-pyridone, elimination of one Cl atom on the O–$SbCl_5$ group and rearrangement of $SbCl_4$ group to 2-position of pyridine ring take place in the complex at almost same time. As a matter of fact, hydrogen chloride evolves violentry with proceedingly of the reaction. Finally, 2-pyridone is formed by treatment of water from rearrangement product containing O–$SbCl_4$ group.

EXPERIMENTAL

Preparation of N-*oxides*. Pyridine and its homologs were oxidized with H_2O_2 in AcOH.[14] The same method was used to prepare N,N-dimethylaniline N-oxide.[15]

Preparation of the complexes of pyridine N-oxides with $SbCl_5$ (table 1): Colorless crystals were deposited immediately from solns prepared by mixing 0.95 g (10 mmol) pyridine N-oxide and 3.0 g (10 mmol) $SbCl_5$ in CCl_4 (5 ml and 10 ml respectively). The mixture was allowed to stand for several hours and the deposited crystals were collected by filtration. The crystals were thoroughly washed with CCl_4 and then with petroleum ether. The yield was 3.37 g (94.5%). The complexes of pyridine N-oxide homologs and that of N,N-dimethylaniline N-oxide were prepared by the same procedure. The m.p. of the complexes were measured in a sealed tube.

Thermal reaction of the complex of pyridine N-*oxide with* $SbCl_5$ (Table 2). Pyridine N-oxide-$SbCl_5$ complex (1 g; 3.4 mmol) in nitromethane (10 ml) was heated at reflux temp for 5 hr in a flask equipped with a $CaCl_2$ tube and then the mixture was poured into water. A white ppt of Sb_2O_5 was filtered off and washed with water and ether. The combined filtrate was separated and the etheral layer was extracted with 3% NaOHaq. The alkaline soln was acidified with HCl and then extracted with ether. After the etheral extracts were dried, 2-pyridone was obtained by evaporation of ether. The yield was 163 mg (81.5%). The complexes of pyridine N-oxide homologs and N,N-dimethylaniline N-oxide were treated by the same procedure to give the corresponding 2-pyridones. The authentic samples of the products were prepared by Sandmeyer reaction of 2-aminopyridines[8] and used for identification. The authentic sample of *o*-dimethylaminophenol N-oxide with Ac_2O.[15]

Thermolysis of the complex of pyridine N-*oxide with* $SbCl_5$ *in benzene*. The pyridine N-oxide–$SbCl_5$ complex (0.5 g, 1.7 mmol) was heated at reflux temp in 20 ml benzene for 7 hr and the mixture then poured into water. No phenol was detected in both the aqueous and benzene layers by TLC, using the color producing reagent of phenols (3-methyl-2-benzo-thiazoline hydrazone hydrachloride). Phenolic products were not detected either in the reaction of the complex with toluene.

The reaction of the complex of pyridine N-*oxide with styrene*. A mixture of the complex (0.5 g; 1.7 mmol) and styrene (1 g; 10 mmol) in nitromethane (10 ml) was warmed at 80° for 2 hr. The mixture was poured into water and the organic layer separated from water was dried and then divided into two portions. When excess MeOH was added to the one portion, no polystyrene was deposited. The red color of bromine (0.3 g, 2 mmol) added to the other portion disappeared immediately. On the other hand, pyridine N-oxide did not react with bromine in nitromethane on standing overnight.

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