January, 1982] © *1982 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, **55**, *345—346 (1982)* 345

$SbCl_5$ Complexes of Pyridine *N*-Oxide and Trimethylamine Oxide as the Oxidizing Agent

Jiro Yamamoto,* Mitushige Murakami, Noriaki Kameoka, Norio Otani,
Masahiro Umezu, and Teruo Matsuura†
Department of Industrial Chemistry, Faculty of Engineering, Tottori University, Tottori 680
† *Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606*

(Received April 25, 1981)

Synopsis. A 1:1 complex of pyridine *N*-oxide or trimethylamine oxide with $SbCl_5$ acted as an oxidizing agent to benzyl alcohol, bezoin, furoin, and thiophenols more easily than *via* the oxides to give benzaldehyde, benzil, furil, and the corresponding disulfides respectively. The trimethylamine oxide–$SbCl_5$ also oxidized *p*-xylene to *p*-tolualdehyde under nitrogen and to *p*-toluic acid under air.

We reported previously that α-pyridone is formed in a high yield by a thermally occurring intramolecular oxygen-transfer reaction of the pyridine *N*-oxide–$SbCl_5$ (1:1) complex (Complex A), and that the thermolysis of the *N*,*N*-dimethylaniline *N*-oxide–$SbCl_5$ (1:1) complex gives *o*-dimethylaminophenol.[1–2] We now find that Complex A and the trimethylamine oxide–$SbCl_5$ (1:1) complex (Complex B) can oxidized such organic compounds *i.e.* as benzyl alcohol, benzoin, furoin, thiophenols and *p*-xylene more easily than their parent oxides.

Results and Discussion

Complex B was prepared by the same procedure as has been reported for Complex A[2] (98.4%). Complex B is a white and hygroscopic solid: mp 98—100 °C (in a sealed capillary tube). Found: C, 9.73; H, 2.77; N, 3.71%. Calcd for $C_3H_9NOSbCl_5$: C, 9.66; H, 2.43; N, 3.74%. ν_{max}^{KBr}, 1610 cm^{-1}, 1470 cm^{-1}, 1440 cm^{-1}, 1230 cm^{-1}, 980 cm^{-1}; $\lambda_{max}^{CHCl_3}$ 270 nm (ε: 2400).

The thermolysis of Complex B in benzyl alcohol resulted in the formation of benzaldehyde in high yields (for example, a 63% yield in 300:1 (benzyl alc.:Complex B) at room temperature for 47 h and a 84.5% yield in 100:1 (benzyl alc.:Complex B) at 160 °C for 2 h), whereas trimethylamine oxide did not oxidize benzyl alcohol under similar conditions.

Thiophenols were more easily oxidized to give the corresponding diaryl disulfides in high yields with Complexes A and B than in the cases of oxidation using pyridine *N*-oxide and trimethylamine oxide (see Table 1). The effects of the para substituents on the oxidation rate of thiophenols were in the following order; $CH_3 > H > NO_2$. Benzoin and furoin were also oxidized with Complexes A and B to give benzil and furil respectively (see the table). *p*-Xylene was found to be oxidized with Complex B under aerial conditions to give *p*-toluic acid in a 35% yield, while *p*-tolualdehyde was obtained in a 27% yield under nitrogen.

The reaction of Complex A with thiophenols appears to proceed according to the following stoichiometry. Complex A may first oxidize a thiophenol

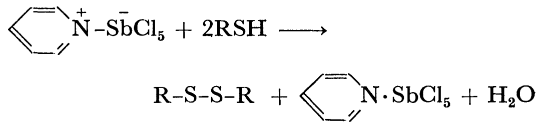
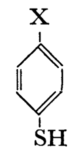
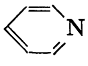
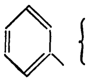
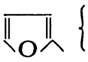
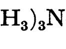
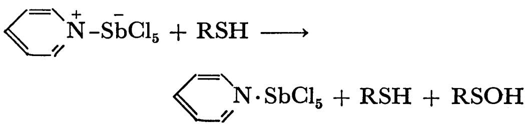


Table 1. The oxidation of thiophenols and benzoins by amine *N*-oxide–$SbCl_5$ (1:1) complexes

Substrates	X	Oxidants	Molar ratio (Substrates : Oxidants)	Temp/°C	Time/h	Solvents[c]	Yield/% of products[d]
	H	 N→O	1 : 1	50	2	C_6H_6	No detected
		Complex A[a]	1 : 1	50	2	C_6H_6	16.7
				Room temp	20	CH_3NO_2	77.5
		$(CH_3)_3N \to O$	1 : 1	Room temp	20	CH_3NO_2	55.3
		Complex B[b]	1 : 1	Room temp	20	CH_3NO_2	84.1
	CH_3	Complex B	1 : 1	Room temp	20	CH_3NO_2	92.7
	NO_2	Complex B	1 : 1	Room temp	20	CH_3NO_2	14.2
X C=O C-OH X		Complex A	1 : 2.1	40	5	CH_3NO_2	84.5
		Complex B	1 : 2.1	40	5	CH_3NO_2	66.0
		Complex A	1 : 1	40	0.5	CH_3NO_2	65.3
		Complex B	1 : 2	65	1.5	CH_3NO_2	60.5

In a typical run, a solution of thiophenol (4.3 g, 19.5 mmol) and Complex B (7.3 g, 19.5 mmol) in nitromethane (10 ml) was allowed to stand at room temperature for 20 h. The mixture was diluted with water and extracted with ether. The ethereal layer was washed with a 3% sodium hydroxide solution, water, dilute hydrochloric acid, and water successively and then dried. After the evaporation of the ether, the residue was practically distilled in a vacuum to give diphenyl disulfide (3.3 g, 77.5%). a)  N-O-$SbCl_5$. b) $(CH_3)_3N$-O-$SbCl_5$. c) The dessolved oxygen in these solvents did not affect any run. d) The oxidation products were identified by a comparison of their melting points and IR spectra with those of authentic samples.

to a sulfenic acid, similar to the formation of a sulfenic acid from $R_3\overset{+}{N}OH$ and RS^- ions.[3] The sulfenic acid thus reacts with a thiophenol to give a disulfide.[4]



$$RSOH + RSH \longrightarrow R\text{-}S\text{-}S\text{-}R + H_2O$$

Benzaldehyde, *p*-tolualdehyde, and cinnamaldehyde resist oxidation with Complexes A and B, probably because of the formation of a stable adduct between an aldehyde and $SbCl_5$[5–6].

References

1) J. Yamamoto, Y. Nishigaki, M. Imagawa, M. Umezu, and M. Matsuura, *Chem. Lett.*, **1976**, 261.

2) J. Yamamoto, M. Imagawa, S. Yamauchi, O. Nakazawa, M. Umezu, and T. Matsuura, *Tetrahedron*, **37**, 1871 (1981).

3) D. I. Relyea, P. O. Tawney, and A. R. Williams, *J. Org. Chem.*, **27**, 474 (1962).

4) E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Chemical Publishing Co., New York (1958), Vol. 1, p. 264.

5) F. Klaarges, H. Trages, and E. Muhlbauer, *Chem. Ber.*, **92**, 1819 (1959).

6) R. C. Paul, H. R. Singel, and S. L. Chadha, *J. Chem. Soc., A*, **1959**, 1819.