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Synthesis of DMSO-SbCl5 (1:1) Complex and Its Oxidizing Action toward Alcohols

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From an equimolar mixture of DMSO and $SbCl_5$ in carbon tetrachloride, a DMSO-$SbCl_5$(1:1) complex (**1**) was formed as a white precipitate in a quantitative yield. The structure of **1** was determined by X-ray crystallographic analysis. Butyraldehydes, para-substituted benzaldehydes and benzils were obtained by the oxidation of butylalcohols, para-substituted benzylalcohols and benzoins using **1** as an oxidizing agent.

In a series of investigations of synthetic reactions using $SbCl_5$ complexes with organic compounds having an oxygen atom, a new compound **1** was synthesized from DMSO and $SbCl_5$ and used as an oxidizing agent toward some alcohols. Benzils were formed in high yield on the oxidation of the corresponding benzoins by **1**. It was found that an oxygen and two chlorine atoms of **1** were used as the real reagents on the oxidation of benzoins.

Experimental

Synthesis of DMSO-$SbCl_5$ (1:1) Complex 1. A white precipitate was deposited immediately from the solution prepared by mixing 1.1 g (14 mmol) DMSO and 4.7 g (14 mmol) $SbCl_5$ in carbon tetrachloride (10 ml and 20 ml respectively) under cooling. The mixture was allowed to stand overnight. The products were collected by filtration, throughly washed with carbon tetrachloride followed by petroleum ether. The yield was 5.2 g (98.7%); mp 153 °C. IR (KBr) 1420, 1400,1320, 1035, 980, 875, 500, and 300 cm^{-1}. UV ($CHCl_3$) 278 nm (ε 800). Found: C, 6.23%, H, 1.64%. Calcd for C_2H_5SO-$SbCl_5$: C, 6.37%; H, 1.60%.

Crystal Structure Analysis of the DMSO-$SbCl_5$ (1:1) Complex 1. The thin plate crystals grown from a benzene solution of **1** were orthorhobic, a=23.418(8) Å, b=13.517(5) Å, c=10.529 Å, $\alpha=\beta=\gamma=90°$, and space group Iba2. Intensity data were collected on a Rigaku four circle diffractometer with a Zr-filtered Mo-$K\alpha$ radiation, λ=0.7107 Å. A crystal was sealed in a glass capillary containing mother liquid to avoid deterioration of crystallinity during the intensity data collection. A total of 1588 non-zero unique intensity data up to $2\theta=54°$ were measured by the θ—2θ scan technique.

The Patterson function followed by a minimum function, and successive Fourier and difference Fourier methods showed a disordered DMSO-$SbCl_5$ (1:1) complex together with a solvent molecule of benzene in an asymmetric unit. The initial structure was refined to an R-factor of 0.13, $R=\sum||F_o|-|F_c||/\sum|F_o|$, by the least squares method with an isotropic temperature factor for all the non-hydrogen atoms of the complex and the benzene molecule. Further refinement with an anisotropic temperature factor for the non-hydrogen atoms of **1** gave no appreciable improvement in the crystal structure. The reasons for the failure of the refinement may be because the intensity data have systematic errors from X-ray absorption by the crystal, the capillary and the mother liquid, and the benzene molecule loosely packed in the crystal. As a difference Fourier synthesis did not give any reasonable residual density, the structual analysis of the crystal was terminated at this stage. The atomic scattering factors were taken from the International Table for X-ray crystallography.[1] All the caluculations were carried out at the Computer Center of Tottori University. The final positional and thermal parameters with their estimated standard deviations are listed in Table 1.

Preparation of 2,2′-Dinitrobenzoin 5d. Crude **5d** was prepared by mixing both EtOH solution of *o*-nitrobenzaldehyde and KCN aqueous solution. Pure **5d** was obtained by crystallization with acetone-water (1:1) solution, mp 164—165 °C(lit,[2] 168—169 °C). *p*-Toluoin was also prepared in the same way, mp 86—87 °C (lit,[3] 88—89 °C). The commercially available benzoins, butyl alcohols and benzyl alcohols were used as received.

Oxidation of Benzoin 5a with DMSO-$SbCl_5$ (1:1) Complex 1. A mixture of **5a** (1.0 g, 4.7 mmol) and **1** (1.8 g, 4.7 mmol) was kept in nitromethane (5 ml) for 5 h at 40 °C. The reaction mixture was poured into ice-water and filtered. The filtrate was extracted with ether and the solution was dried with Na_2SO_4. After evaporation, the residue was separated by column chromatography (benzene-silicagel) to give benzil (**2**) (0.96 g, 96.8%). Dimethyl sulfide (**3**) was detected in the reaction mixture by gas chromatography (Injection: 170 °C, Column: 70 °C, N_2: 60 ml/min., Silicon SE 30). The reaction products were identified by comparison of their melting points and IR spectra with those of authentic samples.

Results and Discussion

The compound **1** immediately crystallized from an equimolar solution of DMSO and $SbCl_5$ in carbon

TABLE 1. POSITIONAL AND THERMAL PARAMETERS WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atoms	$x\times10^3$	$y\times10^3$	$z\times10^3$	$B_{eq}/Å^2$
Complex (**1**)				
Sb	128(3)	175(2)	0	3.71(0.03)
Cl(1)	59(10)	163(10)	160(10)	4.7 (0.2)
Cl(2)	202(11)	170(11)	153(11)	5.5 (0.2)
Cl(3)	61(12)	128(11)	−150(14)	6.3 (0.2)
Cl(4)	196(10)	199(10)	−160(12)	5.3 (0.2)
Cl(5)	117(13)	343(12)	18(23)	8.1 (0.3)
S(1)	143(17)	−56(17)	60(18)	3.6 (0.3)
S(2)	150(19)	−53(19)	−61(20)	4.3 (0.3)
O(1)	148(52)	32(52)	−48(53)	5.7 (1.3)
O(2)	140(37)	24(36)	41(36)	3.1 (0.8)
C(1)	92(35)	−135(36)	−5(94)	5.8 (0.8)
C(2)	208(37)	−116(38)	15(67)	5.9 (0.9)
Benzene				
C(3)	44(42)	390(42)	539(44)	6.0 (1.0)
C(4)	79(55)	389(55)	631(61)	7.9 (1.3)
C(5)	138(49)	397(47)	595(50)	6.5 (1.0)
C(6)	159(41)	395(41)	469(49)	6.2 (1.1)
C(7)	116(65)	396(61)	373(68)	9.2 (1.6)
C(8)	57(64)	396(63)	417(65)	9.4 (1.6)

tetrachloride in quantitative yield. The crystals **1** having a sharp mp were presumed to be DMSO–$SbCl_5$ (1:1), from the results of elemental analysis.

An X-ray crystallogrophic structure determination for **1** was undertaken. The structure **1** with bond lengths and their estimated standard deviations and the atomic numbering scheme are given in Fig. 1. The central metal atom exhibits a distorted octahedral coordination with five chlorine atoms and an oxygen atom of DMSO. The bond angles are listed inTable 2. The DMSO molecule is statistically disordered in the crystal. Two pairs of disordered positions were assigned for an oxygen and a sulfur atom. Each methyl carbon atom, however, was located at a single site. Consequently the methyl sites are shared with two disordered molecules. The bond distances of Sb–Cl for Cl(1), Cl(2), Cl(3), and Cl(5), 2.33 Å to 2.37 Å, are in good accord with those of $SbCl_5$–$PO(CH_3)_3$, 2.32 Å to 2.37 Å.[4] The Sb–Cl (5) bond is significantly shorter than the other Sb–Cl bonds. The bond angles for the two disordered oxygen, antimony and five chlorine atoms depart considerably from those of a regular octahedral structure. This distortion prevents the sulfur atom of DMSO from making abnormal short contacts with chlorine atoms.

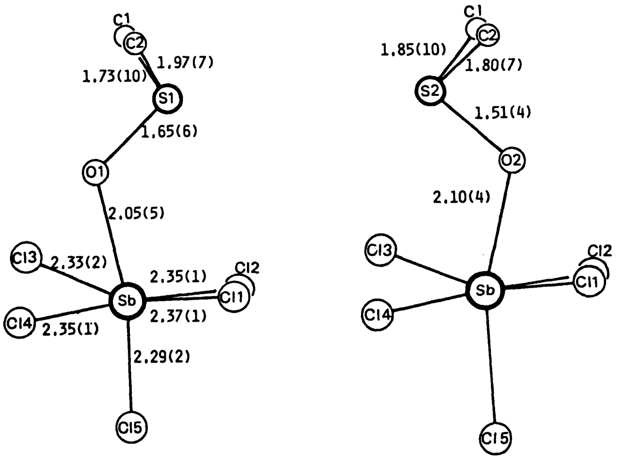


Fig. 1. Legand for Figure.
Molecular structure of DMSO-$SbCl_5$ (1:1) complex **1** together with bond length in Å and their estimated standard deviations in parentheses. Both $SbCl_5$ portions of two structures are common.

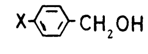
Table 2. Bond angles for DMSO-$SbCl_5$ complex(**1**) with their estimated standard deviations in parentheses

Bond angles	ϕ/°		ϕ/°
Cl(1)-Sb-Cl(2)	91.1(0.5)	Cl(1)-Sb-Cl(3)	162.6(0.6)
Cl(1)-Sb-Cl(4)	89.9(0.5)	Cl(1)-Sb-Cl(5)	93.0(0.7)
Cl(2)-Sb-Cl(3)	89.6(0.5)	Cl(2)-Sb-Cl(4)	175.0(0.5)
Cl(2)-Sb-Cl(5)	86.1(0.7)	Cl(3)-Sb-Cl(4)	90.7(0.5)
Cl(3)-Sb-Cl(5)	104.4(0.7)	Cl(4)-Sb-Cl(5)	89.8(0.7)
Cl(1)-Sb-O(1)	88.7(1.5)	Cl(1)-Sb-O(2)	74.9(1.0)
Cl(2)-Sb-O(1)	105.6(1.5)	Cl(2)-Sb-O(2)	83.0(1.1)
Cl(3)-Sb-O(1)	74.3(1.5)	Cl(3)-Sb-O(2)	87.9(1.1)
Cl(4)-Sb-O(1)	78.5(1.5)	Cl(4)-Sb-O(2)	101.2(1.1)
Cl(5)-Sb-O(1)	168.2(1.6)	Cl(5)-Sb-O(2)	163.5(1.2)
Sb-O(1)-S(1)	119.7(2.9)	Sb-O(2)-S(2)	122.6(2.3)
O(1)-S(1)-C(1)	103.2(3.7)	O(2)-S(2)-C(2)	97.2(2.8)
O(1)-S(1)-C(2)	94.8(3.0)	O(2)-S(2)-C(1)	94.2(3.4)
C(1)-S(1)-C(2)	100.4(3.8)	C(1)-S(2)-C(1)	96.4(3.7)

The oxidation of benzyl alcohol (**4a**) and its derivatives (methyl (**4b**), nitro (**4c**), and chloro (**4d**) in para-position) with equimolar **1** gave the corresponding benzaldehydes in moderate yields. The yield of benzaldehydes somewhat increased at reflux temperature in the cases of **4b**, **4c**, and **4d**. When air was conducted into the reaction mixture of **4a** and **1**, the yield of benzaldehyde (**5**) also increased (Table 3). The oxidation of butyl (**6a**), isobutyl (**6b**) and *s*-butyl alcohol (**6c**) with **1** also proceeded at room temperature to give butyraldehyde, isobutyraldehyde and ethyl methyl ketone respectively in moderate yields. When the reaction of the butyl alcohols (**6a**, **6b**, and **6c**) with **1** was carried out at 80 °C under air stream, the yield of carbonyl compounds increased. In the absence of **1**, the yield of **5** was only 2.5% even under aeration and refluxing conditions. Under similar conditions, butyl alcohols (**6a**, **6b**, and **6c**) were not oxidized at all.

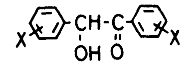
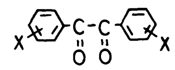
In the oxidation of benzoin (**7a**), *p*-toluoin (**7b**), *p*-anisoin (**7c**), 2,2′-dinitrobenzoin (**7d**) and furoin (**8**) with **1**,the corresponding benzils or furil were formed in high yields at room temperature (Table 4). When the reactions of **7a** and **7b** with 1 were carried out at elevated temperature, the yields of the corresponding benzils were further improved. A 98.7% yield of **2** was also obtained at a low molar ratio (**7a**/1=0.5)

Table 3. The oxidation of benzyl alcohols and butyl alcohols with DMSO-$SbCl_5$ (1:1) complex **1**

		Reaction conditions[a]			Yield of carbonyl compounds/%[b]
		Solvent	Temp °C	Time h	
H	**2a**	CH_3NO_2	60	3	57.4[c,d]
CH_3	**2b**	benzene	Reflux	2	55.8
NO_2	**2c**	CH_3NO_2	Reflux	7	42.9
Cl	**2d**	CH_3NO_2	Reflux	1	10.5
Butyl alc.	**4a**	CH_3NO_2	80	2	47.3[c]
Isobutyl alc.	**4b**	CH_3NO_2	80	2	41.0[c]
s-Butyl alc.	**4c**	CH_3NO_2	80	2	50.9[c]

a) Molar ratio (Complex/Alcohols): 1 b) Carbonyl compounds were isolated as 2,4-dinitrophenylhydrazone c) Air was passed in the reaction mixture during reaction d) Yellow crystals (mp 58.0—59.0 °C, 5.5 wt.%) were obtained as a by-product.

TABLE 4. THE OXIDATION OF BENZOINS WITH DMSO-$SbCl_5$ (1:1) COMPLEX **1**

		Reaction conditions[a]			Products yield/%		Recovered starting materials/%
		Molar ratio (1/benzoins)	Temp °C	Time h		Tarrry products/Wt.%	
		1.0	Room temp.	24	94.2	2.0	Not detected
H	**7a**	1.0	80[b]	2	97.6	1.3	Not detected
		0.5	Reflux[c]	2	98.7(77.0)[d]	trace	Not detected
4,4′-CH_3	**7b**	1.0	Room temp.	24	79.4	8.0	10.1
4,4′-OCH_3	**7c**	1.0	Room temp.	24	77.1	7.0	10.0
		1.0	40	1	98.0(88.0)[d]	1.3	Not detected
2,2′-NO_2	**7d**	1.0	Room temp.	24	91.0	2.1	1.4
Furoin	**8**	1.0	5	1	75.3(31.0)[d]	10.0	4.0

a) Nitromethane was used as a solvent in most runs. b) DMSO was used as a solvent. c) A mixed solvent (30 ml benzene and 5 ml nitromethane) was used. d) In parenthesis, the yield of benzils studied by Dyke and Pritchard[5] are given.

(Table 4). In the oxidation of **7b** and **7c** with **1**, the yield of the corresponding benzils was low in comparison with **7a** and **7d** under the same conditions (Table 4). It seems to depend on the electron donating character of the methyl and methoxy groups.

The complexes of $SbCl_5$ with trimethylamine oxide, pyridine *N*-oxide[5] and *N,N*-dimethylbenzylamine oxide[6] were used in the oxidation of both **7a** and **8**. Dyke and Pritchard[7] also carried out the oxidation of **7a**, **7c**, and **8** using a DMSO-acetic acid medium. But **1** is a better reagent to give benzils from the corresponding benzoins in comparison with the reagents described above.[5–7] In the reaction of **4a**, **5a**, or **7a** with $SbCl_5$, the corresponding carbonyl compounds were not detected under the present mild conditions.

Increasing the ratio of **1** to **7a** resulted in increasing yields of both **2** and concomitant **3**, as shown in Fig. 2. It is evident that an oxygen atom in **1** is consumed in the oxidation of **7a**. In order to estimate the amount of chlorine which was consumed in the reaction of **7a** with **1** (10 h at 40 °C), the hydrogen chloride generated was transfered into aqueous silver nitrate solution by bubbling nitrogen gas through the reaction mixture. The oxidation of **7a** with **1** under these conditions should proceed essentially to completion (Table 4). The precipitated silver chloride corresponded to 88.6% of the expected value based on the assumption that two of the chlorine atoms in **1** are consumed as the oxidizing agent. Therefore, the present reaction may be shown by the following stoichiometry [Equation (a)].

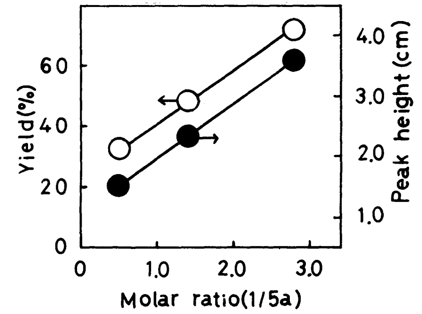
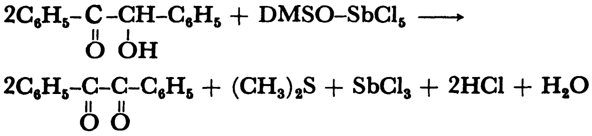


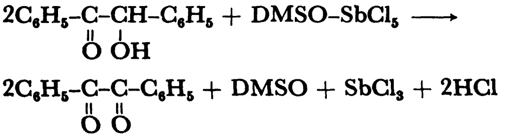
Fig. 2. The oxidation of benzoin **5a** with DMSO-$SbCl_5$ (1:1) complex **1**.
Reaction conditions: Benzoin 1.0 g (4.7 mmol) in nitromethane (10 ml) at 50 °C for 2 h.
○: Benzil, ●: $(CH_3)_2S$



$$2C_6H_5-\underset{\underset{O}{\|}}{C}-\underset{\underset{OH}{|}}{CH}-C_6H_5 + DMSO\text{-}SbCl_5 \longrightarrow$$

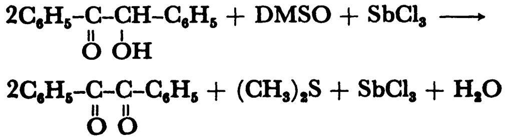
$$2C_6H_5-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-C_6H_5 + (CH_3)_2S + SbCl_3 + 2HCl + H_2O \qquad (a)$$

When **7a** was allowed to stand with an equimolar combination of DMSO and $SbCl_3$ in nitromethane for 24 h at room temperature,the compound **2** was obtained in a 48% yield with **3**, but no hydrogen chloride was generated. Thus, the reaction of benzoins with **1** seems to proceed in the following two steps. When **1** was mixed with **7a** in nitromethane, hydrogen chloride generated immediately. Therefore, two chlorine atoms in **1** first react with **7a** to form **2** [Equation (b)] and subsequently another molecule of **7a** was also oxidized to **2** by the interaction of both DMSO and $SbCl_3$ [Equation (c)].



$$2C_6H_5-\underset{\underset{O}{\|}}{C}-\underset{\underset{OH}{|}}{CH}-C_6H_5 + DMSO\text{-}SbCl_5 \longrightarrow$$

$$2C_6H_5-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-C_6H_5 + DMSO + SbCl_3 + 2HCl \qquad (b)$$



$$2C_6H_5-\underset{\underset{O}{\|}}{C}-\underset{\underset{OH}{|}}{CH}-C_6H_5 + DMSO + SbCl_3 \longrightarrow$$

$$2C_6H_5-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-C_6H_5 + (CH_3)_2S + SbCl_3 + H_2O \qquad (c)$$

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