UDC 547.569-386

# 5. Hisashi Tanaka and Akira Yokoyama : Studies on Sulfur-containing Chelating Agents. IX.*1 Syntheses of Alkyl or Aryl *o*-Mercaptophenyl Ketones, Esters of *o*-Mercaptobenzoic Acid, S-Esters of *o*-Mercaptothiobenzoic Acid, and their Metal Chelates.

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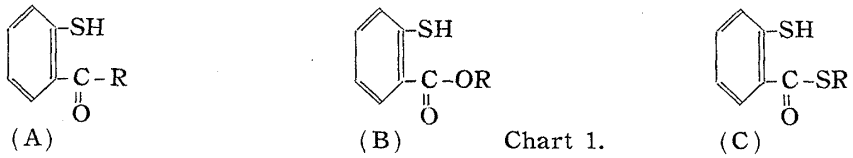
In the previous papers, β-mercaptoketones,[1] β-mercapto-acid esters,[2] β-mercaptothiolic acid esters,[3] and α,β-unsaturated β-mercapto-acid esters,*1 and metal chelates of these ligands were reported. All of these ligands involve aliphatic mercapto group and carbonyl group. Comparing the chelating ability of these ligands, it was found that α,β-unsaturated β-mercapto-acid esters in whose chelate ring conjugated double bond is present, and β-mercaptothiolic acid esters are strong chelating agents.

This paper deals with the syntheses of alkyl or aryl *o*-mercaptophenyl ketones (A), and esters of *o*-mercaptobenzoic acid (B) and S-esters of *o*-mercaptothiobenzoic acid (C), and their metal chelates. As in these ligands, double bond of benzene ring conjugates with carbonyl group in the chelate ring, and aromatic mercapto group is present at the position *ortho* to the carbonyl group, these ligands are expected to be a very strong chelating agent. From the results obtained in the carbonyl compounds with aliphatic mercapto group at β-position, (C), which involves conjugated double bond and thiolic acid ester group, would be expected to have a strong chelating ability.




(A) (B) Chart 1. (C)

*o*-Mercaptoacetophenone (I) and *o*-mercaptobenzophenone (II) were prepared as (A). (I) was reported in the course of the synthesis of thioindigo[4] but it was not described in detail. (I) was prepared from *o*-aminoacetophenone by the procedure shown in Chart 2. However, (I) was unstable in the air and gradually oxidized to its disulfide and thioindigo-type compound. (II) was prepared from *o*-benzoylbenzoic acid by the procedure shown in Chart 2. (II) is not oxidized to thioindigo-type but is not stable in the air.

Ethyl (III), isopentyl (IV) and phenyl *o*-mercaptobenzoate (V) were prepared as (B) by the usual esterification of *o*-mercaptobenzoic acid. S-Ethyl (VI), S-isopropyl (VII), S-isopentyl (VIII), and S-phenyl *o*-mercaptothiobenzoate (IX) were prepared as (C), from *o*,*o*'-dithiodibenzoic acid by the procedure shown in Chart 2.

The reaction of these ligands with metal ions was tested by a spot test in acidic (acetic acid), neutral, and alkaline (ammonium hydroxide and sodium carbonate) solution. The results are shown in Table I. A marked difference in selectivity was found in these different types of ligand. Iron reacted only with (C) and cobalt reacted with (B) and (C). (A), (B), and (C) which are carbonyl compounds with aromatic mercapto group are reactive with larger member of metals. Nickel did not react with β-mercaptoketones involving aliphatic mercapto group,[1] but (A) produced red precipitate with nickel. (B) and (C)

*1 Part VII. H. Tanaka, A. Yokoyama : This Bulletin, **10**, 19 (1962).
*2 Yoshida, Sakyo-ku, Kyoto (田中 久, 横山 陽).
1) Part I. H. Tanaka, A. Yokoyama : This Bulletin, 8, 275 (1960).
2) Part V. *Idem* : *Ibid.*, **9**, 66 (1961).
3) Part VI. *Idem* : *Ibid.*, **10**, 13 (1962).
4) Höchster Farbw. : D. R. P. 198,509 (Frdl., **9**, 577 (1908)).

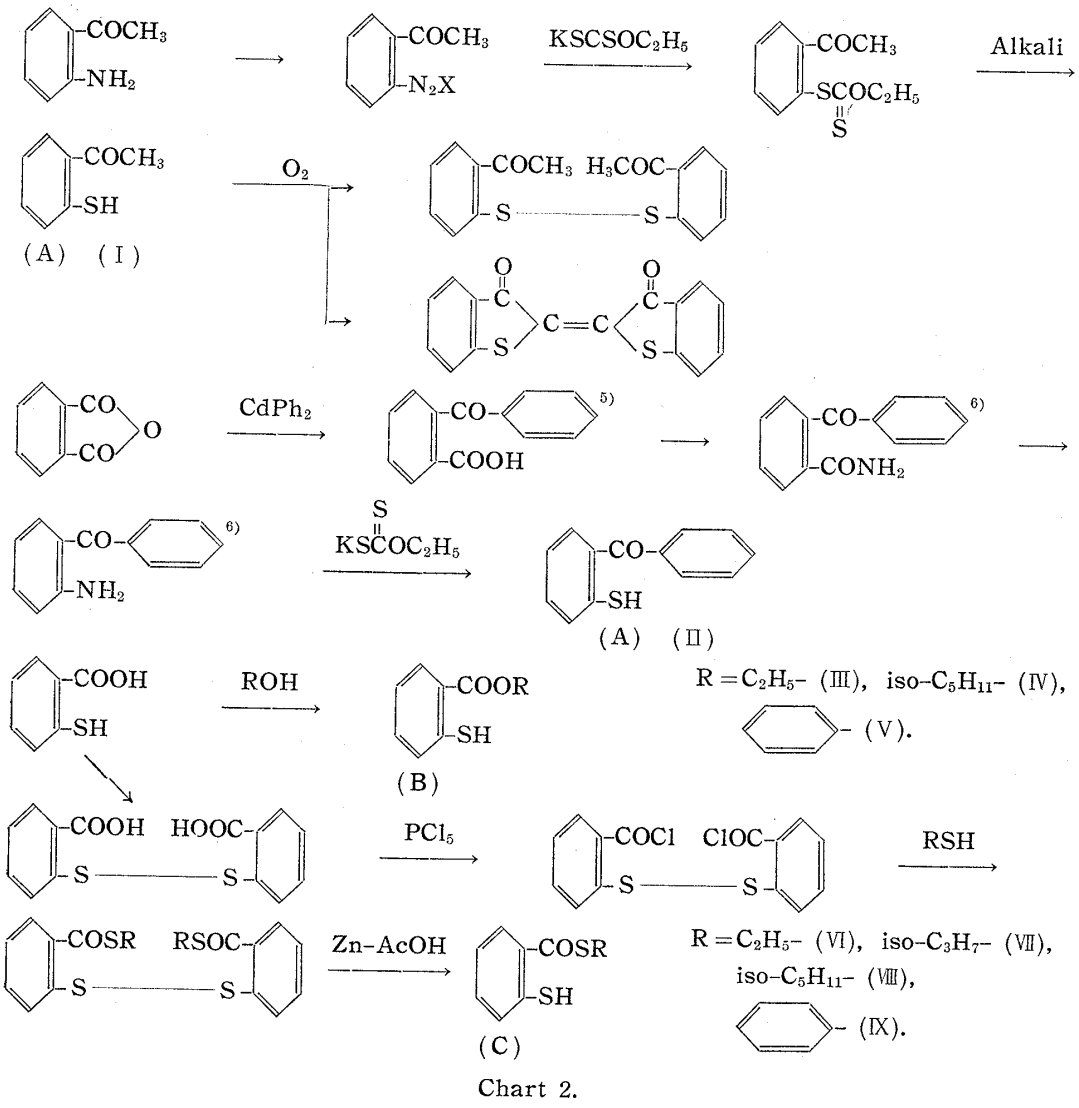



Chart 2.

Table I. Spot Test (in neutral solution)

| Metal | Alkyl or aryl *o*-mercaptophenyl ketone (A) | Ester of *o*-mercaptobenzoic acid (B) | S-Ester of *o*-mercaptothiobenzoic acid (C) |
|---|---|---|---|
| $Fe^{2+}$ | | | Green |
| $Co^{2+}$ | | Green ppt. | Brown ppt. |
| $Ni^{2+}$ | Orange ppt. | Orange-red ppt. | Orange-red ppt. |
| $Cu^{2+}$ | Brown ppt. | Yellow ppt. | Orange-yellow ppt. |
| $Pd^{2+}$ | Red ppt. | Red ppt. | Orange ppt. |
| $Ag^{+}$ | Yellow ppt. | Yellow ppt. | Yellow ppt. |
| $Cd^{2+}$ | | | 〃 |
| $Pt^{4+}$ | Yellow | Orange | Orange ppt. |
| $Au^{3+}$ | Brown | Brown | Brown |
| $Hg^{2+}$ | White ppt. | White ppt. | White ppt. |
| $Pb^{2+}$ | Yellow ppt. | Yellow ppt. | Yellow ppt. |
| $Bi^{3+}$ | 〃 | 〃 | 〃 |
| $UO_2^{2+}$ | Pale yellow | Pale yellow | Pale yellow |

Reagent: 5% EtOH solution of (A), (B), or (C).

5) P. L. Benneville: J. Org. Chem., **6**, 462 (1941).
6) C. L. Hewett: J. Chem. Soc., **1948**, 293.

reacted with cobalt and iron, but β-mercapto-acid esters[2] and β-mercaptothiolic acid esters[3] involving aliphatic mercapto group did not. From these results it is presumed that (B) and (C) have stronger chelating ability than the corresponding aliphatic compounds. The order of the chelating ability of these various types of ligands will be reported and discussed in detail in a later paper of this series.

The chelates produced from iron, cobalt, nickel, copper, palladium, platinum, gold, bismuth, and uranyl were soluble in organic solvents, such as ethyl acetate, chloroform, and benzene. The recognizable limits of iron, cobalt, nickel, palladium, and bismuth were measured and are listed in Table II. These ligands were especially sensitive to nickel and palladium so that they would be applicable as the analytical reagent for these metals.

Table II. Recognizable Limit of Metals

| Ligand | | Recognizable limit (γ/0.05 cc.) | | | | | |
|---|---|---|---|---|---|---|---|
| | | $Fe^{3+}$ | $Co^{2+}$ | $Ni^{2+}$ | $Cu^{2+}$ | $Pd^{2+}$ | $Bi^{3+}$ |
| (A) | (I) | | | 1 | 10 | 1 | 5 |
| | (II) | | | 1 | 15 | 1 | 5 |
| (B) | (III) | | 3* | 1 | 3 | 0.5 | 3 |
| | (IV) | | 1* | 0.5 | 1 | 0.05 | 5 |
| | (V) | | 5* | 5 | 5 | 1 | 10 |
| (C) | (VI) | 1 | 5* | 0.5 | 1 | 0.1 | 0.5 |
| | (VII) | 3 | 5* | 0.5 | 2 | 0.2 | 0.5 |
| | (VIII) | 1 | 5* | 0.5 | 1 | 0.1 | 1 |
| | (IX) | 10 | 10* | 0.5 | 5 | 0.2 | 1 |

Reagent: 5% EtOH solution.
* Measured in $Na_2CO_3$ solution. Others were measured in neutral solution.

As to the reactions of these ligands with copper, nickel, and cobalt, a considerable difference was observed according to the difference in the type of these ligands.

**1) Alkyl or Aryl *o*-Mercaptophenyl Ketones (A)**

(I) was so unstable that its metal chelate could not be isolated. Copper chelate of (II) was obtained as a brown crystalline powder with the ratio of one mole of the ligand to one atom of copper. Nickel chelate of (II) could not be obtained as a crystal, but its absorption curve in chloroform solution was as shown in Fig. 1.

**2) Esters of *o*-Mercaptobenzoic Acid (B)**

When an ethanolic solution of the ligand (B) and cupric acetate in aqueous solution were mixed, yellow crystals which were extractable into chloroform and ethyl acetate precipitated. However, these yellow crystals became immediately insoluble in such organic solvents and copper chelate could not be separated. Nickel chelates of (B) were separated as orange-red crystals. They melted sharply with decomposition and the ratio of the ligand to the metal was 2:1. Cobalt chelates were separated as green crystals. They melted sharply and the ratio of the ligand to the metal was 3:1. These cobalt chelates were considered to be cobalt(III) chelates similar to the case of β-mercaptothiolic acid esters[3] and α,β-unsaturated β-mercapto-acid esters.*[1]

**3) S-Esters of *o*-Mercaptothiobenzoic Acid (C)**

Copper chelates of the ligand (C) were separated as orange-yellow crystals. They melted with decomposition at a high temperature and the ratio of the ligand to the metal was 1:1. Nickel chelates were separated as an orange-red crystalline powder and the ratio was 2:1. Cobalt chelates were separated as yellow-green crystals but purification was difficult. Microanalytical data indicated that the ratio was 3:1. The properties of the ligand (C) were almost analogous to those of the chelates from β-mercaptothiolic acid esters.[3]

Infrared spectra of ethyl *o*-mercaptobenzoate (III), S-ethyl *o*-mercaptothiobenzoate (VI), and their metal chelates in chloroform solution were measured. In the case of (III), the absorption maxima of mercapto group and ester group were observed at 2560 and 1700 $cm^{-1}$, respectively. In the case of their metal chelates, the absorption band of mercapto group disappeared and considerable shift of the absorption maximum of the ester group to a lower frequency was observed. The absorption maximum of the ester group was observed at 1610 $cm^{-1}$ in nickel chelate and at 1620 $cm^{-1}$ in cobalt chelate. In the case of (VI), the absorption maxima of mercapto group and thiolic acid ester group were observed at 2570 and 1680 $cm^{-1}$ respectively. In the case of their metal chelates, the absorption of mercapto group disappeared and in some cases shift of the absorption of thiolic acid ester group to a lower frequency was observed. The absorption maximum of thiolic acid ester group was observed at 1680 $cm^{-1}$ in copper chelate, at 1575 $cm^{-1}$ in nickel chelate, and at 1580 $cm^{-1}$ in cobalt chelate. The shift of the absorption maxima of ester and thiolic acid ester group suggests that these chelates are considerably stable.

The absorption curves of the metal chelates of the ligands (III) and (VI) are shown in Figs. 2 and 3. No difference of absorption curve was observed by the effect of the alkyl group of ester and thiolic acid ester group.

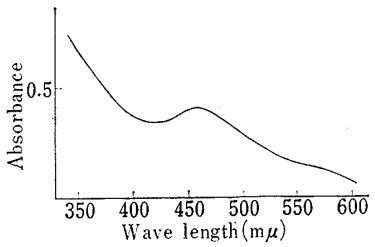
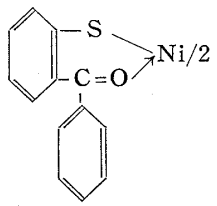



Fig. 1. Nickel Chelate of (II) (A)
($5\times10^{-5}$ mole in $CHCl_3$)



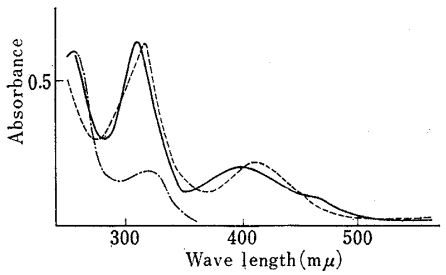




Fig. 2. Metal Chelates of (B)
——— Ni chelate of (III) ($2.5\times10^{-5}$ mole in $CHCl_3$)
--------- Co chelate of (III) ($1.2\times10^{-5}$ mole in $CHCl_3$)
– – – – – Ligand (III) ($5\times10^{-5}$ mole in $CHCl_3$)

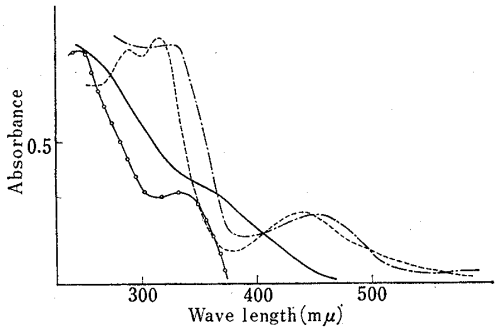



Fig. 3. Metal Chelates of (C)
——— Cu chelate of (VI) ($5\times10^{-5}$ mole in $CHCl_3$)
--------- Ni chelate of (VI) ($2.5\times10^{-5}$ mole in $CHCl_3$)
– – – – – Co chelate of (VI) ($1.2\times10^{-5}$ mole in $CHCl_3$)
—○—○ Ligand (VI) ($5\times10^{-5}$ mole in $CHCl_3$)

## Experimental

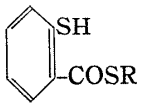
***o*-Mercaptoacetophenone (I)**——*o*-Aminoacetophenone hydrochloride (prepared from 10 g. of amine and 20 cc. of conc. HCl) in 200 cc. of ice-water was diazotized with 5.1 g. of $NaNO_2$ in 15 cc. of $H_2O$ at 0° to 1°. The solution of diazonium salt was added dropwise into 12 g. of K ethylxanthate in 15 cc. of $H_2O$ with stirring at 40~45° and stirring was continued for 30 min. The reaction mixture was extracted with $Et_2O$, which was washed with $H_2O$ and 10% NaOH, and dried over $CaCl_2$. After evaporation of the solvent, the residual oil was added to a solution of 17.5 g. of KOH in 50 cc. of EtOH and refluxed for 10 hr. The solvent was removed in a diminished pressure, 100 cc. of $H_2O$ was added to the residue and extracted witd $Et_2O$. Aqueous solution was acidified with 30% $H_2SO_4$ in a stream of $H_2$ gas and (I) separated out. This was extracted with $Et_2O$, which was washed with

$H_2O$ and dried over $CaCl_2$. After evaporation of the solvent, the residual oil (I) was distilled in a diminished pressure in $H_2$ stream. Yield, 1 g. $b.p_4$ 115～117°. Rheinboldt test, red. (I) became reddish oil immediately after distillation.

***o*-Mercaptobenzophenone (II)**——*o*-Aminobenzophenone hydrochloride[6] (prepared from 8.5 g. of amine and 8.5 cc. of conc. HCl) in 50 cc. of ice-water was diazotized with 3.1 g. $NaNO_2$ in 8 cc. $H_2O$ at 0° to 4°. To the solution of diazonium salt, 8 g. of K ethylxanthate in 10 cc. of $H_2O$ was added dropwise with stirring at 40～45° and stirring was continued for 1～1.5 hr. The reaction mixture was extracted with $Et_2O$, which was washed with $H_2O$, 10% NaOH, and $H_2O$, and dried over $CaCl_2$. After evaporation of the solvent, the residual oil was added to a solution of 15 g. of KOH in 50 cc. of EtOH and refluxed for 5 hr. The solvent was removed, 100 cc. of $H_2O$ was added to the residue, and extracted with $Et_2O$. Aqueous solution was acidified with 10% HCl. (II) that separated out was extracted with $Et_2O$, which was washed with $H_2O$, and dried over $Na_2SO_4$. After evaporation of the solvent, the residual oil was distilled in a diminished pressure to colorless oil, $b.p_{0.7}$ 160°. Yield, 0.6 g. Rheinboldt test, red. *Anal.* Calcd. for $C_{13}H_{10}OS$ : C, 72.89; H, 4.71. Found : C, 72.19; H, 5.10.

**Preparation of S-Esters of *o*-Mercaptothiobenzoic Acid (C)**——*o,o'*-Dithiodibenzoyl chloride (prepared from 0.01 mole of *o,o'*-dithiodibenzoic acid and $PCl_5$) in 80 cc. of benzene was added dropwise into 0.02 mole of thiol in 30 cc. of dehyd. pyridine with stirring under cooling with $H_2O$. Stirring was continued for 2 hr. and the mixture was allowed to stand overnight at room temperature. The reaction mixture was poured into 200 cc. of 10% HCl, the benzene layer was separated and washed with $H_2O$, saturated $NaHCO_3$ solution, and $H_2O$, and dried over $Na_2SO_4$. After evaporation of the solvent, the S-ester of *o,o'*-dithiobis (thiobenzoic acid) was obtained in a crude state. Without further purification, it was refluxed with 0.8 mole of Zn powder and 50 cc. of AcOH for 1 hr. After cool, the separated precipitate was collected and warmed on a water bath for 10 min. with 50 cc. of 10% $H_2SO_4$. This was extracted with $Et_2O$, which was washed with $H_2O$, saturated $NaHCO_3$ solution, and $H_2O$, and dried over $Na_2SO_4$. After evaporation of the solvent, the residual oil of S-ester of *o*-mercaptothiobenzoic acid was purified by distillation to pale yellow oil. Yield, 1～1.5 g. Rheinboldt test, red. Boiling point and microanalytical data are given in Table III.

Table III. S-Esters of *o*-Mercaptothiobenzoic Acid




| R | b.p. (°C/mm. Hg) | Formula | Analysis (%) Calcd. C | Calcd. H | Found C | Found H |
|---|---|---|---|---|---|---|
| $C_2H_5$– | 145～147/7 | $C_9H_{10}OS_2$ | 54.54 | 5.09 | 54.37 | 5.16 |
| iso-$C_3H_7$– | 125/4 | $C_{10}H_{12}OS_2$ | 56.60 | 5.70 | 56.33 | 5.65 |
| iso-$C_5H_{11}$– | 148～152/4 | $C_{12}H_{16}OS_2$ | 59.99 | 6.71 | 60.23 | 6.81 |
| $C_6H_5$– | * | $C_{13}H_{10}OS_2$ | 63.41 | 4.09 | 63.44 | 4.09 |

* As this thiolester decomposed by distillation, it was purified through Pb mercaptide.

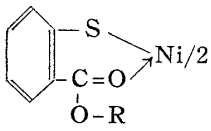
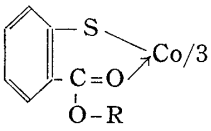
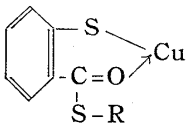
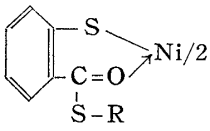
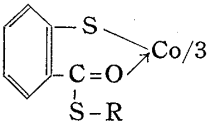
**Preparation of Copper Chelate of (II)**——EtOH solution of (II) and aqueous solution of excess $Cu(AcO)_2 \cdot H_2O$ were mixed and shaken for a few minutes on a water bath. Brown Cu chelate that separated out were collected, washed with EtOH and $H_2O$, and recrystallized from $Et_2O$. m.p. 117～118°. *Anal.* Calcd. for $C_{13}H_9OCuS$ : C, 56.43; H, 3.28; Cu, 22.95. Found : C, 56.59; H, 3.49; Cu, 22.97.

**Preparation of Nickel Chelate of (III) and (IV)**——EtOH solution of the ligand and aqueous solution of excess $Ni(AcO)_2 \cdot 4H_2O$ were mixed and shaken for a few minutes. An orange-red crystalline powder of Ni chelate was collected and washed with $H_2O$ and EtOH. Microanalytical data and m.p. are given in Table IV.

**Preparation of Cobalt Chelate of (III) and (IV)**——EtOH solution of the ligand and aqueous solution of excess $Co(AcO)_2 \cdot 4H_2O$ were mixed and shaken for a few minutes. Green Co chelate separated out immediately and was extracted with $Et_2O$. The extract was washed with $H_2O$ and the solvent was evaporated in a diminished pressure at room temperature. The residual Co chelate was purified by reprecipitation from EtOH-petr. ether to green needles. Microanalytical data and melting point are given in Table IV.

**Preparation of Copper Chelates of (VI), (VII), and (VIII)**——EtOH solution of the ligand and aqueous solution of excess $Cu(AcO)_2 \cdot H_2O$ were mixed and shaken for a few minutes on a water bath. The reaction mixture was extracted with $CHCl_3$, which was washed with $H_2O$ and the solvent was evaporated in a diminished pressure at room temperature. The oily residue solidified on addition

Table IV. Metal Chelates

| R | m.p. (°C) (decomp.) | Formula | Analysis (%) Calcd. C | Calcd. H | Calcd. Metal | Found C | Found H | Found Metal |
|---|---|---|---|---|---|---|---|---|
|  | | | | | | | | |
| $C_2H_5$– | 198 | $C_{18}H_{18}O_4S_2Ni$ | 51.34 | 4.28 | 13.95 | 51.55 | 4.54 | 14.25 |
| iso-$C_5H_{11}$– | 168～169 | $C_{24}H_{30}O_4S_2Ni$ | 57.06 | 5.99 | 11.62 | 56.83 | 5.98 | 11.77 |
|  | | | | | | | | |
| $C_2H_5$– | 110[a] | $C_{27}H_{27}O_6S_3Co$ | 53.83 | 4.49 | 9.79 | 54.02 | 4.75 | 9.93 |
| iso-$C_5H_{11}$– | 75～78[a] | $C_{36}H_{45}O_6S_3Co$ | 59.35 | 6.18 | 8.09 | 59.23 | 6.14 | 8.43 |
|  | | | | | | | | |
| $C_2H_5$– | 218～219 | $C_9H_9OS_2Cu$ | 41.46 | 3.48 | | 41.50 | 3.79 | [b] |
| iso-$C_3H_7$– | 222 | $C_{10}H_{11}OS_2Cu$ | 43.71 | 4.01 | 23.13 | 43.79 | 4.04 | 22.94 |
| iso-$C_5H_{11}$– | 175 | $C_{12}H_{15}OS_2Cu$ | 47.60 | 4.99 | 20.99 | 47.53 | 5.24 | 19.69 |
|  | | | | | | | | |
| $C_2H_5$– | 170 | $C_{18}H_{18}O_2S_4Ni$ | 47.71 | 3.98 | 12.96 | 47.72 | 4.08 | 12.40 |
| iso-$C_3H_7$– | 172 | $C_{20}H_{22}O_2S_4Ni$ | 49.93 | 4.58 | 12.21 | 49.64 | 4.59 | 13.19 |
| iso-$C_5H_{11}$– | 136～138 | $C_{24}H_{30}O_2S_4Ni$ | 53.66 | 5.59 | 10.94 | 53.06 | 5.52 | 10.28 |
|  | | | | | | | | |
| $C_2H_5$– | 138～140[a] | $C_{27}H_{27}O_3S_6Co$ | 49.86 | 4.15 | 9.06 | 49.04 | 4.15 | 10.44 |
| iso-$C_3H_7$– | 125～128[a] | $C_{30}H_{33}O_3S_6Co$ | 52.03 | 4.77 | 8.51 | 51.95 | 4.64 | 8.81 |
| iso-$C_5H_{11}$– | 113～116[a] | $C_{36}H_{45}O_3S_6Co$ | 55.68 | 5.80 | 7.59 | 55.06 | 5.50 | 8.23 |

*a*) melted without decomposition.
*b*) unreasonable value was obtained.

of $Et_2O$. Orange-yellow Cu chelate was purified by reprecipitation from $CHCl_3$–$Et_2O$ to a crystalline powder. Microanalytical data and melting point are shown in Table IV.

**Preparation of Nickel Chelate of (VI), (VII), and (VIII)**——EtOH solution of the ligand and EtOH solution of excess $Ni(AcO)_2 \cdot 4H_2O$ were mixed and shaken for a few minutes and allowed to stand for 2 hr. at room temperature. Orange-red crystalline powder of Ni chelate separated out, which was collected and washed with EtOH and $H_2O$. Microanalytical data and melting point are given in Table IV.

**Preparation of Cobalt Chelate of (VI), (VII), and (VIII)**——EtOH solution of the ligand and aqueous solution of excess $Co(AcO)_2 \cdot 4H_2O$ were mixed and shaken for a few minutes. Brown Co chelate that separated out was extracted with $CHCl_3$, which was washed with $H_2O$ and the solvent was evaporated in a diminished pressure at room temperature. The residual Co chelate was purified to yellow-green crystals by reprecipitation from $CHCl_3$–$Et_2O$. Yield was very poor. Microanalytical data and melting point are given in Table IV.

The authors express their gratitude to Prof. Toyozo Uno for his helpful advices. They are indebted to the members of the Microanalytical Center of the Kyoto University for the analytical data. The infrared spectra were determined by Mr. K. Machida and Mrs. I. Hamanaka of Kyoto University, to whom the authors are also grateful.

**Summary**

Alkyl or aryl *o*-mercaptophenyl ketones, esters of *o*-mercaptobenzoic acid and S-esters of *o*-mercaptothiobenzoic acid were synthesized, expecting their strong chelating ability due to the presence of aromatic mercapto group and double bond of benzene ring. Alkyl or aryl *o*-mercaptophenyl ketones were unstable and could not be investigated in detail. Esters of *o*-mercaptobenzoic acid and S-esters of *o*-mercaptothiobenzoic acid formed a chelate with cobalt, nickel, and copper in a ratio of 3:1, 2:1, and 1:1, respectively. These ligands were sensitive to nickel and palladium.

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## 6. Hideaki Shirai and Noriichi Oda: Studies on Phenanthrene Derivatives. IV.[1] Syntheses of 2,3:5,6-Bismethylenedioxy- and 2,3:6,7-Bismethylenedioxyphenanthrene and Ultraviolet Absorption Spectra of Certain Methylenedioxyphenanthrenes.

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In a continuation of studies on phenanthrene derivatives, several methylenedioxyphenanthrenes were synthesized. This paper deals with the syntheses of 2,3:5,6-bismethylenedioxy- and 2,3:6,7-bismethylenedioxyphenanthrene, and the analysis of the ultraviolet absorption spectra of these synthesized phenanthrenes to obtain some knowledge of relationship between the spectra and the positions of methylenedioxy and methoxyl groups in the phenanthrene ring.

**Syntheses of 2,3:5,6-Bismethylenedioxy- and 2,3:6,7-Bismethylenedioxyphenanthrene**

2,3:5,6-Bismethylenedioxy- and 2,3:6,7-bismethylenedioxyphenanthrene were synthesized by the Pschorr reaction, starting from 6-nitropiperonal (I) and homopiperonylic acid (II). Condensation of (I) with (II) by the Perkin-Oglialoro reaction gave a mixture of two stereoisomers of $\alpha$-(3,4-methylenedioxyphenyl)-2-nitro-4,5-methylenedioxycinnamic acid (III and IV). This mixture was submitted to silica-gel chromatography, and the high-melting form, assigned as *trans* (III), first eluted with ether. The lower-melting form, assigned as *cis* (IV), was obtained from the later eluate. On reduction, the *trans* isomer (III) gave the corresponding aminocinnamic acid (V), while the *cis* isomer (IV) gave the corresponding carbostyril (VI). (V) upon boiling in dehydrated ethanol produced the carbostyril (VI), as shown in Chart 1.

Aminocinnamic acid (V) was then submitted to the Pschorr reaction, from which three kinds of acidic materials, m.p. 243~244° (VII), 293~296° (decomp.) (VIII), and m.p. above 300° (IX) were obtained. (VIII) was proved to be $\alpha$-(3,4-methylenedioxyphenyl)-3,4-methylenedioxycinnamic acid from its ultraviolet absorption spectrum and mixed melting point determination with a specimen prepared from piperonal as will be described below. Such a side reaction i.e. elimination of the amino group, observed in Pschorr reaction, are well

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