[Chem. Pharm. Bull. 17(4) 661—668 (1969)]

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# Studies on Thiohydroxamic Acids and Their Metal Chelates. VII.[1] Syntheses of Some Compounds Possessing Mercapto and Hydroxyimino Groups and Their Reactivities with Metal Ions

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Several compounds possessing both mercapto and hydroxyimino groups, such as 2-mercaptoacetophenone oxime, 3-mercaptopropiophenone oxime and 5-nitro-2-mercaptobenzaldehyde oxime, were prepared, and their reactivities with metal ions were compared with those of the corresponding ketones or aldehyde and those of thiohydroxamic acids. It was found that these compounds did not show any sensitive color reactions with $Fe^{3+}$, $Ti^{4+}$, $UO_2^{2+}$ and $VO^{2+}$ and did not form stable $Fe^{3+}$ and $Cu^{2+}$ complexes, differing from thiohydroxamic acids, and that the conversions of the compounds possessing both carbonyl and mercapto group to the corresponding oximes did not give any effect on the sensitivities and selectivities.

It has been revealed that thiohydroxamic acids form five-membered metal chelates, coordinated with mercapto and hydroxyimino groups simultaneously, and that they display characteristic coloration with $Fe^{3+}$, $Ti^{4+}$, $UO_2^{2+}$ and $VO^{2+}$, being different from usual organic reagents possessing mercapto group.[1,3] This paper deals with the preparation of several compounds possessing both mercapto and hydroxyimino groups in the favorable position for coordination, such as 2-mercaptoacetophenone oxime, 3-mercaptopropiophenone oxime and 5-nitro-2-mercaptobenzaldehyde oxime. The reactivities of these compounds with metal ions were compared with those of thiohydroxamic acid, and their possibilities as organic reagents were evaluated.

## (A) Syntheses of Ligands

(i) 2-Mercaptoacetophenone Oxime and Analogous Compounds (V): Since the preparative methods of 2-mercaptoacetophenone (II, $R=C_6H_5$) reported by Groth[4] or Kretov[5] were ineffective and rather complicated, we treated 2-bromoacetophenone with hydrogen sulfide in pyridine. The analogous compounds listed in Table I were prepared in the same manner, but 1-naphthyl, 2-furyl, and 2-thienyl mercaptomethyl ketone were decomposed to the corresponding methyl ketones (IV) during the purification. 2-Mercaptoacetophenone oxime and its analogous compounds (V) summarized in Table II were obtained by treating II with hydroxylamine in neutral solution. The disulfides (VII) obtained by oxidation of V with iodine were identical in every respect with the oxime of VI obtained by iodine oxidation of II.

(ii) 3-Mercaptopropiophenone Oxime and Analogous Compounds (IX): Preparation of 3-mercaptopropiophenone (VIIIa) was accomplished by the reaction of 3-bromoacetophenone and sodium thiosulfate in ethanol, followed by the hydrolysis of the products, while 3-phenyl-

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[1] Part VI: K. Nagata, *Chem. Pharm. Bull.* (Tokyo), 17, 653 (1969).

[2] Location: *Sagisukami, Fukushima-ku, Osaka.*

[3] K. Nagata and S. Mizukami, *Chem. Pharm. Bull.* (Tokyo), 15, 61, 70 (1967).

[4] B. Groth, *Arkiv. Kemi Mineral. Geol.*, 9, 63 (1924) [*C.A.*, 18, 1280 (1924)].

[5] A.E. Kretov, A.N. Panchenko and A. Konovalchik, *J. Gen. Chem.* (U.S.S.R.), 1, 396 (1931) [*C.A.*, 26, 2442 (1932)].

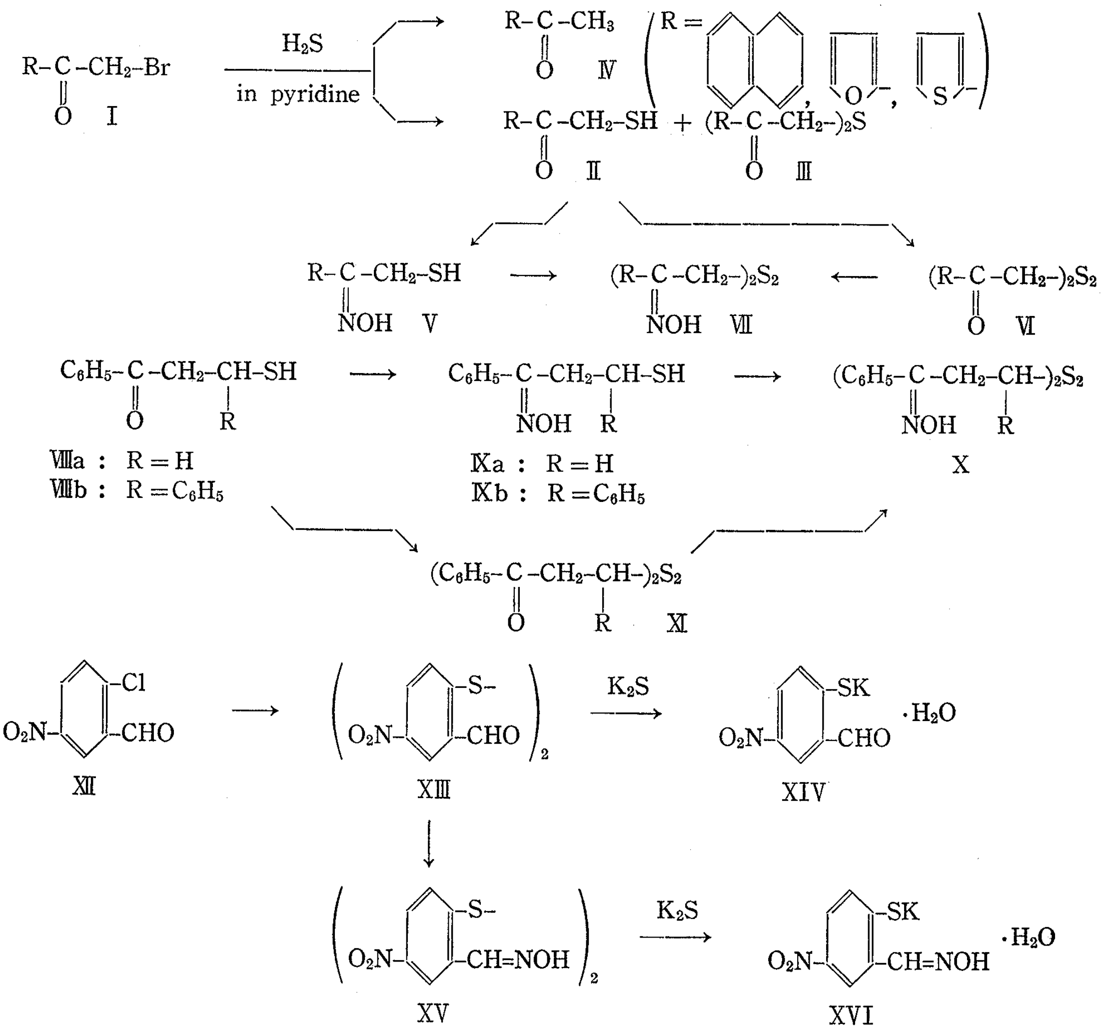

Chart 1

3-mercaptopropiophenone (VIIIb) was synthesized by the procedure of Fromm.[6] 3-Bromopropiophenone gave only 3,3″-thiodipropiophenone by the reaction with potassium sulfhydrate or sodium disulfide, and its bromo group could not be replaced by hydrogen sulfide even under more rigorous conditions than those for the preparation of II. The reactions of VIII with hydroxylamine were carried out in dilute acetic acid because of the instability of VIII in alkaline solution.

(iii) 5-Nitro-2-mercaptobenzaldehyde Oxime (XVI): Even though it was reported that 2-mercaptobenzaldehyde was isolated as 2,4-dinitrophenylhydrazone by Weygand,[7] and as sodium salt by Friedländer,[8] we were not successful to obtain either 2-mercaptobenzaldehyde or its salt in practical yields by these methods. On the other hand, the direct replacement of the chloro group in 2-chlorobenzaldehyde was not taken place by treating with sodium sulfide, sodium disulfide or sodium sulfhydrate. Thus, only 5-nitro-2-mercaptobenzaldehyde (XIV) and its oxime (XVI) were prepared as potassium salts by the reaction of the corresponding disulfides, XIII and XV, with potassium sulfide.

### (B) Reactivities with Metal Ions

Typical reactivities of those compounds with metal ions are summarized in Table III. These compounds show sensitive coloration with $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$ and $Pd^{2+}$, but the colora-

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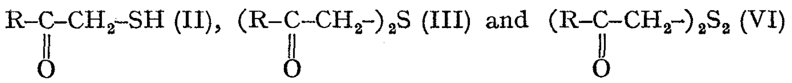
[6] E. Fromm, *Ann.*, **394**, 301 (1912).
[7] F. Weygand, *Angew. Chem.*, **65**, 525 (1953).
[8] P. Friedländer and E. Lenk, *Chem. Ber.*, **45**, 2083 (1912).

TABLE I.

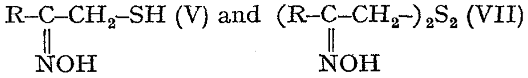


$\mathrm{R{-}\underset{\overset{\|}{O}}{C}{-}CH_2{-}SH}$ (II), $\mathrm{(R{-}\underset{\overset{\|}{O}}{C}{-}CH_2{-})_2S}$ (III) and $\mathrm{(R{-}\underset{\overset{\|}{O}}{C}{-}CH_2{-})_2S_2}$ (VI)

| R | Appearance | mp (°C) | Yield (%) | Formula | Analysis (%) Calcd. C | Calcd. H | Calcd. S | Found C | Found H | Found S | mp of III (°C) | mp of VI (°C) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_6H_5$ | scale | 23—24[a)]<br>(bp 126—127/6 mmHg) | 60 | $C_8H_8OS$ | 63.13 | 5.30 | 21.07 | 62.92 | 5.39 | 20.66 | 77—78 | 79—80 |
| $p$-$CH_3$–$C_6H_4$ | needle | 41<br>(bp 112/2 mmHg) | 61 | $C_9H_{10}OS$ | 65.03 | 6.06 | 19.29 | 64.98 | 6.13 | 19.21 | 89 | 83 |
| $p$-Cl–$C_6H_4$ | needle | 72 | 70 | $C_8H_7OSCl$ | 51.48 | 3.78 | 17.18 | 51.46 | 3.88 | 17.25 | 121 | 125 |
| $p$-HO–$C_6H_4$ | amorph. | 133—134 | 62 | $C_8H_8O_2S$ | 57.22 | 4.99 | 19.06 | 57.12 | 4.79 | 18.72 | 192 (decomp.) | 208 (decomp.) |
| 2-$C_{10}H_7$ | amorph. | 59 | 51 | $C_{12}H_{10}OS$ | 71.26 | 4.98 | 15.85 | 70.92 | 5.05 | 15.58 | 109 | 103—104 |

a) ref. mp 23—24°[1)]

TABLE II.

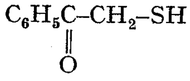
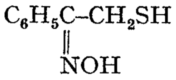
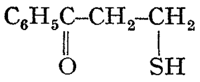
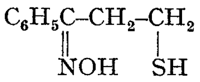


$\mathrm{R{-}\underset{\overset{\|}{NOH}}{C}{-}CH_2{-}SH}$ (V) and $\mathrm{(R{-}\underset{\overset{\|}{NOH}}{C}{-}CH_2{-})_2S_2}$ (VII)

| R | Appearance | mp (°C) | Formula | Analysis (%) Calcd. C | Calcd. H | Calcd. N | Calcd. S | Found C | Found H | Found N | Found S | mp of VII (°C) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_6H_5$ | prism | 70—71[a)] | $C_8H_9ONS$ | 57.46 | 5.42 | 8.38 | 19.17 | 57.24 | 5.49 | 8.08 | 19.01 | 146—148 |
| $p$-$CH_3$–$C_6H_4$ | prism | 90 | $C_9H_{11}ONS$ | 59.64 | 6.12 | 7.73 | 17.69 | 59.45 | 6.34 | 8.11 | 17.62 | 157—158 |
| $p$-Cl–$C_6H_4$ | prism | 87—89 | $C_8H_8ONSCl$ | 47.64 | 4.00 | 6.94 | 15.90 | 47.36 | 4.11 | 7.24 | 15.77 | 179—181 |
| 2-$C_{10}H_7$ | needle | 130 | $C_{12}H_{11}ONS$ | 66.33 | 5.10 | 6.45 | 14.76 | 66.68 | 5.39 | 6.37 | 14.43 | 176 |

a) ref. mp 70°[1)]

Table III. Comparison of

| Metal ion |  $C_6H_5C(=O)-CH_2-SH$ | |  $C_6H_5C(=NOH)-CH_2SH$ | |  $C_6H_5C(=O)-CH_2-CH_2SH$ | |  $C_6H_5C(=NOH)-CH_2-CH_2SH$ | |
|---|---|---|---|---|---|---|---|---|
| | Appearance | L.C. | Appearance | L.C. | Appearance | L.C. | Appearance | L.C. |
| Ag (I) | yellow ppt. | | yellow ppt. | | yellow ppt. | | white ppt. | |
| Mn (II) | —— | | —— | | —— | | —— | |
| Fe (II) | —— | | —— | | —— | | —— | |
| Co (II) | d.violet ppt. | 0.5 | v. brown ppt. | 0.5 | r. violet oil | 2 | v. brown ppt. | 2 |
| Ni (II) | brown ppt. | 1 | g. brown ppt. | 2 | brown oil | 10 | brown ppt. | 2 |
| Pd (II) | orange ppt. | 2 | orange ppt. | 2 | yellow ppt. | 0.1 | yellow ppt. | 0.5 |
| Cu (II) | o. yellow ppt. | 5 | d. violet ppt. | 3 | yellow ppt. | 2 | d. green ppt. | 2 |
| Zn (II) | white ppt. | | white ppt. | | white ppt. | | white ppt. | |
| Cd (II) | white ppt. | | white ppt. | | white ppt. | | white ppt. | |
| Hg (II) | white ppt. | | white ppt. | | white ppt. | | —— | |
| Sn (II) | yellow ppt. | | white ppt. | | white ppt. | | —— | |
| Pb (II) | yellow ppt. | | p. yellow ppt. | | white ppt. | | p. yellow ppt. | |
| $UO_2$ (II) | —— | | —— | | —— | | —— | |
| VO (II) | —— | | —— | | —— | | —— | |
| Al (III) | —— | | —— | | —— | | —— | |
| Bi (III) | yellow ppt. | | yellow ppt. | | yellow ppt. | | yellow ppt. | |
| Cr (III) | —— | | —— | | —— | | —— | |
| Fe (III) | green ppt. (unstable) | | green ppt. (transient) | | —— | | —— | |
| Ti (IV) | —— | | —— | | —— | | —— | |
| Pt (IV) | —— | | —— | | —— | | —— | |

——; Apparent change was not observed. L.C.; recognizable limit concentration ($\gamma$/0.05 ml)

tion and the limit of identification with oximes was found to be nearly the same as those with the corresponding ketones or aldehydes.

Metal complexes isolated are summarized in Table IV. From the analytical data, all the copper complexes obtained by the reaction with cupric acetate are supposed to be in cuprous form. Similar results were reported also for the other reagents including mercapto group.[9] The metal complexes of 2-mercaptoacetophenone and its oxime are soluble in organic solvents, such as ethylacetate and chloroform, but the solubilities of the oxime complexes are lower than those of the former because of the hydrophilic character of hydroxyimino group. The complexes of the former display some characteristics of chelate compounds, such as the relatively low melting points and the shift of the C=O stretching band of the ligand to a lower frequency by the coordination with metal ion. Although the direct proofs of the chelation could not be obtained for the latter oxime complexes, their ultraviolet spectra (Fig. 1) resemble to those of the former complexes in the positions and intensities. Metal complexes of VIII, IX and XIV, XVI are precipitated gela-

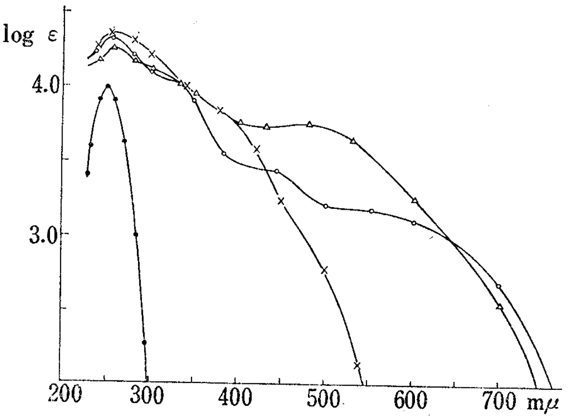


Fig. 1. Absorption Spectra of Metal Chelates of 2-Mercaptoacetophenone Oxime (V) in EtOH

●—●—● ligand ○—○—○ M=Ni
△—△—△ M=Co ×—×—× M=Pd

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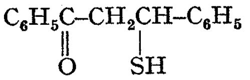
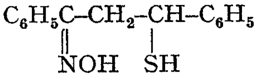
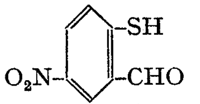
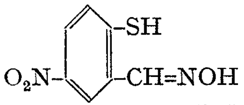
9) S.B. Sant, *Anal. Chem.*, **31**, 1879 (1959); I.M. Klotz and G.H. Czerlinski, *J. Am. Chem. Soc.*, **80**, 2920 (1958); H. Tanaka and A. Yokoyama, *Chem. Pharm. Bull.* (Tokyo), **8**, 1012 (1960).

Reactivity with Metal Ions

|  $C_6H_5C(=O)-CH_2CH(SH)-C_6H_5$ | |  $C_6H_5C(=NOH)-CH_2-CH(SH)-C_6H_5$ | |  | |  | |
|---|---|---|---|---|---|---|---|
| Appearance | L.C. | Appearance | L.C. | Appearance | L.C. | Appearance | L.C. |
| white ppt. | | white ppt. | | orange ppt. | | r. orange ppt. | |
| —— | | —— | | —— | | —— | |
| —— | | —— | | yellow ppt. | | g. brown ppt. | |
| y. brown ppt. | 2 | brown oil | 2 | brown ppt. | 50 | d. brown ppt. | 50 |
| r. brown ppt. | 5 | brown oil | 2 | r. brown ppt. | 15 | v. brown ppt. | 7 |
| orange ppt. | 0.5 | yellow ppt. | 0.5 | brown ppt. | 10 | r. brown ppt. | 10 |
| p. green ppt. | 5 | p. blue ppt. | 3 | brown ppt. | 10 | d. green ppt. | 25 |
| white ppt. | | white ppt. | | —— | | —— | |
| white ppt. | | white ppt. | | orange ppt. | | yellow ppt. | |
| white ppt. | | white ppt. | | orange ppt. | | yellow ppt. | |
| —— | | white ppt. | | orange ppt. | | yellow ppt. | |
| p. yellow ppt. | | p. yellow ppt. | | orange ppt. | | yellow ppt. | |
| —— | | —— | | —— | | —— | |
| —— | | —— | | orange ppt. | | g. green ppt. | |
| —— | | —— | | —— | | —— | |
| yellow ppt. | | p. yellow ppt. | | orange ppt. | | orange ppt. | |
| —— | | —— | | o. brown ppt. | | yellow ppt. | |
| —— | | —— | | y. brown ppt. | | d. brown ppt. (unstable) | |
| —— | | —— | | orange ppt. | | orange ppt. | |
| white ppt. | | white ppt. | | orange ppt. | | orange ppt. | |

d.; dark v.; violet r.; reddish y.; yellow g.; greyish o.; orange p.; pale

tinously, so that the pure complexes could not be obtained except some kinds of nickel and cupric complexes.

Furthermore, it should be pointed out that all the oximes investigated in this work do not show generally any appreciable coloration with $Fe^{3+}$, $Ti^{4+}$, $UO_2^{2+}$ and $VO^{2+}$. Although XVI gives colored precipitates with $Fe^{3+}$, $Ti^{4+}$ and $VO^{2+}$, differing from V and IX, the colorations are quite different from those of thiohydroxamic acids and the sensitivities are also very low. In addition, the fact that the color of $Fe^{3+}$ salt is identical with that of $Fe^{2+}$ salt may indicate the reduction of $Fe^{3+}$ to $Fe^{2+}$ during the course of reaction. These results show that the characteristic behaviors of thiohydroxamic acids, the sensitive coloration with $Fe^{3+}$, $Ti^{4+}$, $UO_2^{2+}$ and $VO^{2+}$, and the formation of stable $Fe^{3+}$ or $Cu^{2+}$ salts, are not general for the other compounds possessing both mercapto and hydroxyimino groups.

In general, it seems that the ketones or aldehydes as described in this paper are not recommendable as an organic reagent, and that their conversions to the corresponding oximes do not give any effect on the sensitivities and selectivities, but reduce solubilities of their metal complexes in nonpolar solvents. Tanaka[10] has also gave the similar comment for the analytical applications of the ketones possessing mercapto groups which form S,O-coordinated six-membered metal chelates.

## Experimental

Ultraviolet and visible spectra were measured with a Hitachi spectrometer model EPS-2U. Infrared spectra were measured with a Nippon Bunkō double-beam spectrometer model DS 201B. All melting points described in this paper were uncorrected.

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[10] H. Tanaka and A. Yokoyama, *Chem. Pharm. Bull.* (Tokyo), **10**, 1133 (1962).

Table IV. Metal Salts of II, V, VIII, IX, XIV, XVI: $(\text{Ligand})_n\text{M}\cdot\text{XH}_2\text{O}$ (M=Metal Ion)

| Ligand | M | $n$ | X | Appearance (recrystn. solvent) | mp (decomp.) | Formula | Analysis (%) Calcd. C | Calcd. H | Calcd. N | Calcd. M | Found C | Found H | Found N | Found M |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| II | Cu (I) | 1 | 0 | yellow powder ($CHCl_3$–ether) | 114—116 | $C_8H_7OSCu$ | 44.74 | 3.29 | | 29.59 | 44.75 | 2.99 | | 29.16 |
| | Zn (II) | 2 | 0 | p. yellow powder | 165—167 | $C_{16}H_{14}O_2S_2$-Zn | 52.25 | 3.84 | | 17.77 | 52.28 | 3.82 | | 17.77 |
| | Cd (II) | 2 | 0 | white powder | 106—110 | $C_{16}H_{14}O_2S_2$-Cd | 46.33 | 3.40 | | 27.10 | 46.05 | 3.46 | | 27.52 |
| | Pd (II) | 2 | 0 | o. brown powder | 110—130 (obscure) | $C_{16}H_{14}O_2S_2$-Pd | 47.01 | 3.45 | | 26.03 | 47.02 | 3.34 | | 26.02 |
| | Co (II) | 2 | 0 | d. brown powder | 206—207 | $C_{16}H_{14}O_2S_2$-Co | 53.18 | 3.91 | | 16.31 | 53.08 | 3.86 | | 16.70 |
| V | Cu (I) | 1 | 0 | yellow powder | 130 | $C_8H_8ONSCu$ | 41.82 | 3.51 | 6.10 | 27.65 | 41.73 | 3.58 | 6.04 | 27.44 |
| | Zn (II) | 2 | 0 | white powder | >250 | $C_{16}H_{16}O_2N_2$-$S_2Zn$ | 48.31 | 4.05 | 7.04 | 16.43 | 48.73 | 3.87 | 6.78 | 16.25 |
| | Ni (II) | 2 | 0 | brown powder | 118—119 | $C_{16}H_{16}O_2N_2$-$S_2Ni$ | 49.13 | 4.12 | 7.16 | 15.01 | 49.20 | 4.19 | 6.95 | 15.72 |
| | Pd (II) | 2 | 1 | yellow powder | >250 | $C_{16}H_{16}O_2N_2$-$S_2Pd\cdot H_2O$ | 42.06 | 3.96 | 6.13 | 23.29 | 41.90 | 3.63 | 5.91 | 24.01 |
| | Co (II) | 2 | 1.5 | d. brown powder | 220 (decomp.) | $C_{16}H_{16}O_2N_2$-$S_2Co\cdot 1.5H_2O$ | 45.93 | 4.58 | 6.70 | 14.09 | 45.90 | 4.19 | 6.60 | 14.77 |
| VIIIb | Cu (I) | 1 | 0 | orange powder (MeOH) | 113[a] | $C_{15}H_{13}OSCu$ | 59.09 | 4.30 | | 20.84 | 58.94 | 4.33 | | 21.45 |
| | Ni (II) | 2 | 0 | r. brown powder ($CHCl_3$–EtOH) | 127—128 | $C_{30}H_{26}O_2S_2Ni$ | 66.56 | 4.84 | | 10.84 | 66.50 | 5.01 | | 10.09 |
| IXb | Ni (II) | 2 | 1.5 | brown powder | 161—162 | $C_{30}H_{28}O_2N_2$-$S_2Ni\cdot 1.5H_2O$ | 60.21 | 5.22 | 4.68 | 9.81 | 60.08 | 4.84 | 4.70 | 9.75 |
| XIV | Ni (II) | 2 | 0 | r. brown powder | >270 | $C_{14}H_8O_6N_2$-$S_2Ni$ | 39.75 | 1.91 | 6.62 | 13.87 | 39.52 | 2.00 | 6.70 | 13.50 |
| XVI | Ni (II) | 2 | 0.5 | brown powder (EtOH) | >270 | $C_{14}H_{10}O_6N_4$-$S_2Ni\cdot 0.5H_2O$ | 36.39 | 2.40 | 12.13 | 12.70 | 36.35 | 2.46 | 11.93 | 11.90 |

a) ref. mp 111°[8]

p.; pale o.; orange d.; dark r.; reddish

**2-Mercaptoacetophenone and Analogous Compounds (II)**——An ether solution of 2-bromoacetophenone or its analogous compounds was added dropwise under stirring into the $H_2S$ saturated pyridine in a cold bath, and the reaction mixtures were agitated under introduction of $H_2S$ for another 2 hr, then poured into ice cold HCl and extracted with ether. The ether extracts were dried and evaporated to get oily residues which were partly solidified at 0°. After filtration, recrystallization of the residue from EtOH gave (III). Recrystallization of the filtrate from petroleum or distillation at reduced pressure gave (II). Reinbold's test; reddish orange, IR $\text{cm}^{-1}$; $\nu_{SH}$ 2570±10 (Nujol), $\nu_{C=O}$ 1675±10 (Nujol).

To an ether solution of (II) was added 0.1 N $I_2$ untill the color of $I_2$ did not disappear, and the solution was extracted with ether. The ether extracts, after washing successively with 0.1 N $Na_2S_2O_3$ and water, was dried and evaporated. The disulfide (VI) was yielded from the residue, which was recrystallized from AcOEt or petroleum. IR $\text{cm}^{-1}$; $\nu_{C=O}$ 1665±5 (Nujol).

**2-Mercaptoacetophenone Oxime and Analogous Compounds (V)**——An equimolar mixture of II in EtOH and $NH_2OH$ in water was allowed to stand for a few days in an atmosphere of nitrogen. Then, EtOH was evaporated *in vacuo*, and a small amount of water was added into the residue to afford the precipitate, which was extracted with hot $CCl_4$. V was precipitated as colorless crystalls from the $CCl_4$ extracts by adding petroleum. IR $\text{cm}^{-1}$; $\nu_{SH}$ 2750±15 (Nujol), $\nu_{OH}$ 3230±10 (Nujol), Reinboldt's test; reddish orange.

V was oxidized to the corresponding disulfide (VII) with 0.1 N $I_2$. $Na_2S_2O_3$ solution, 16.6 g in 15 ml of water, was added to hot EtOH (40 ml) under vigorous stirring. To this solution was added slowly 3-bromopropiophenone (XVII, 17 g) dissolved in EtOH (100 ml) and the mixtures were agitated for another few hours, during which time the mixtures became homogeneous. After allowing to stand overnight at room temperature, the solvent was evaporated to dryness under reduced pressure. The residues was once extracted with 200 ml of ether and filtered. The residues (15 g) was then dissolved in 30 ml of HCl (1:1) and heated on a steam bath for 1 hr in a nitrogen atmosphere, and the separated oil was extracted with ether. Evaporation of ether gave 5 g of pale yellow oil, which was distilled at 142—143° at 17 mmHg to yield 1.5 g of pure VIIIa, mp 35—37°. Reinboldt's test; pink, IR cm$^{-1}$; $\nu_{SH}$ 2540 ($CCl_4$), $\nu_{C=O}$ 1686 ($CCl_4$), *Anal.* Calcd. for $C_9H_{10}OS$: C, 65.03; H, 6.06; S, 19.29. Found: C, 65.41; H, 6.14; S, 18.95. By addition of ether solution of XVII into the alcoholic KOH which was saturated with $H_2S$ at room temperature or by treatment of XVII with $Na_2S$ in refluxing EtOH for 0.5 hr, was produced almost quantitatively 3,3″-thiodipropiophenone (XVIII), which was recrystallized from EtOH, colorless needles, mp 103—104°. IR cm$^{-1}$: $\nu_{C=O}$ 1679 (Nujol). *Anal.* Calcd. for $C_{18}H_{10}O_2S$: C, 72.45; H, 6.08; S, 10.75. Found: C, 72.53; H, 6.18; S, 11.07.

**3-Mercaptopropiophenone Oxime and Analogous Compounds (IX)**——a) 3-Mercaptopropiophenone Oxime (IXa): To a mixture of (VIIIa) and a little excess of $NH_2OH \cdot HCl$ in EtOH was added to one equivalent of AcONa powder, the solution was refluxed for 3 hr in a nitrogen atmosphere, and evaporated under reduced pressure to leave oil. By addition of pieces of metal sodium to an ether solution of the oil, sodium salt of IXa was precipitated as colorless needles, which was recrystallized from EtOH–ether. The sodium salt was very hydroscopic and decomposed slowly. Addition of 0.1 N $I_2$ to an aqueous solution of the sodium salt afforded 3,3″-dithiodipropiophenone dioxime (X, R=H) as colorless powder, which was recrystallized from ether–petroleum, mp 145—146°. *Anal.* Calcd. for $C_{18}H_{20}O_2N_2S_2$: C, 59.97, H, 5.59; N, 7.77; S, 17.79. Found: C, 60.25; H, 5.92; N, 7.44; S, 17.67. X was also prepared by treating (XI, R=H) in EtOH with a neutral solution of $NH_2OH$ for a few days at room temperature.

b) 3-Phenyl-3-mercaptopropiophenone Oxime (IXb): 3-Phenyl-3-mercaptopropiophenone[6] was treated with $NH_2OH \cdot HCl$ as described above. Evaporation of the solvent gave IXb, which was recrystallized from $CCl_4$ as colorless needles, mp 111°. Rheinbold's test; orange, IR cm$^{-1}$: $\nu_{SH}$ 2580 (Nujol); $\nu_{OH}$ 3200 (Nujol). *Anal.* Calcd. for $C_{15}H_{15}ONS$: C, 70.01; H, 5.88; N, 5.44; S, 12.46. Found: C, 69.91; H, 5.98; N, 5.19; S, 12.32. IXb in ether was oxidized with 0.1 N $I_2$ to yield the corresponding disulfide (X; $R=C_6H_5$), which was recrystallized from $CCl_4$ as colorless amorphous powder, mp 171—172°. *Anal.* Calcd. for $C_{30}H_{28}O_2N_2S_2$: C, 70.28; H, 5.50; N, 5.46; S, 12.51. Found: C, 70.16; H, 5.64; N, 5.54; S, 12.30.

**Potassium Salt of 5-Nitro-2-mercaptobenzaldehyde (XIV)**——For the preparation of 5,5′-dinitro-2,2′-dithiodibenzaldehyde, the procedures of Fries and Hodgson were modified.[12,13] The mixtures of $Na_2S \cdot 9H_2O$ (16 g) and sulfur powder (2.2 g) in a small amount of water were added under reflux into an alcohol solution of 5-nitro-2-chlorobenzaldehyde (25 g in 300 ml). After refluxing for 2 hr, the hot reaction mixtures were filtered and the residues were washed with hot water and then three times with each 50 ml portion of nitrobenzene. From the combined nitrobenzene extracts, 5,5′-dinitro-2,2′-thiobenzaldehyde was afforded as pale yellow powder, mp 226—230° (decomp.). *Anal.* Calcd. for $C_{14}H_8O_6N_2S$: C, 50.60; H, 2.43; N, 8.43; S, 9.65. Found: C, 50.60; H, 2.57; N, 8.38; S, 9.84. The residue left after extraction with nitrobenzene contained XIII, which was washed successively with hot EtOH, $CS_2$ and ether and dried at 110° for 2 hr. pale yellow powders, mp 273—274° (decomp.). *Anal.* Calcd. for $C_{14}H_8O_6N_2S_2$: C, 46.15; H, 2.21; N, 7.69; S, 17.60. Found: C, 46.28; H, 2.34; N, 7.59; S, 17.45. The conc. solution of $K_2S$ (5 g in water) was added into a suspension of XIII (6 g) in EtOH (100 ml), and the mixtures were stirred at 40—50° in a nitrogen atmosphere until the homogeneous reddish solution was obtained. After filtration, the mother liquor was evaporated to dryness under reduced pressure, and the residue dried overnight in a vacuum deciccator was dissolved in 25 ml of anhydrous acetone and filtered through charcoal. To the filtrate was added about 300 ml of ether, and the resulting precipitates of XIV was collected by filtration. XIV was then recrystallized from EtOH–ether and dried in vacuum. mp 216—217° (decomp.). *Anal.* Calcd. for $C_7H_4O_3NSK \cdot H_2O$: C, 35.13; H, 2.53; N, 5.85; K, 16.34. Found: C, 34.82; H, 2.80; N, 6.14; K, 15.78.

An aqueous solution of XIV was acidified with dil. HCl and the separated oil was extracted with ether. After drying the ether extracts over $Na_2SO_4$, a small amount of $CH_3ONa$ in MeOH was added to afford the precipitate of the sodium salt, which was recrystallized from EtOH–ether as red powders. mp 205—208°. *Anal.* Calcd. for $C_7H_4O_3NSNa \cdot H_2O$: C, 37.67; H, 2.71; N, 6.28; Na, 10.30. Found: C, 37.66; H, 2.88; N, 6.30; Na, 10.20.

100 mg of XIV was treated under reflux with $CH_3I$ (60 mg) in EtOH for 1.5 hr, and was yielded 30 mg of 5-nitro-2-methylthiobenzaldehyde, which was recrystallized from EtOH as yellow needles. mp 163—164°. IR cm$^{-1}$: $\nu_{C=O}$ 1688 (Nujol). *Anal.* Calcd. for $C_8H_7O_3NS$: C, 48.72; H, 3.58; N, 7.10; S, 16.26. Found: C, 48.97; H, 3.81; N, 7.74; S, 16.43. Treatment of XIV with acetyl chloride under reflux in anhydrous benzene for 1 hr gave 5-nitro-2-acetylthiobenzaldehyde, which was recrystallized from ether as pale yellow flakes, mp 88°. IR cm$^{-1}$: $\nu_{C=O}$ 1708, 1697 (shoulder) (Nujol). *Anal.* Calcd. for $C_9H_7O_4NS$: C, 48.00; H, 3.13; N, 6.22; S, 14.24. Found: C, 48.27; H, 3.12; N, 6.15; S, 13.77.

**Potassium Salt of 5-Nitro-2-mercaptobenzaldehyde Oxime (XVI)**——A mixture of $NH_2OH \cdot HCl$ (3.1 g) and AcONa (3.6 g) in 12 ml of water, being heated on a steam bath, was added dropwise into a suspension of XIII (7.2 g) in 120 ml of 95% EtOH, and the solution was refluxed for another 1 hr. The resulting pale yellow precipitates (5.2 g), which was sparingly soluble in various solvents, was gathered and washed

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12) K. Fries and G. Brothuhn, *Chem. Ber.*, 56, 1630 (1923).

13) H.H. Hodgson and H.G. Beard, *J. Chem. Soc.*, 1927, 2423.

with water and EtOH. Recrystallization of the precipitate from large amount of MeOH gave 5,5′-dinitro-2,2′-dithiodibenzaldehyde dioxime (XV), mp 161—164° (decomp.). *Anal.* Calcd. for $C_{14}H_{10}O_6N_4S_2$: C, 42.64; H, 2.56; N, 14.21; S, 16.26. Found: C, 43.09; H, 2.53; N, 14.19; S, 16.38. Treatment of the crude XV with $K_2S$ as described in XIII gave XVI, mp 80—81°, yellow color of XVI thus obtained turned reddish-brown on drying at 40—50° *in vacuo*. *Anal.* Calcd. for $C_7H_5O_3N_2SK \cdot H_2O$: C, 32.80; H, 3.54; N, 10.93; K, 15.25. Found: C, 33.10; H, 3.39; N, 10.59; K, 14.53. Acidification of an aqueous solution of XVI gave XV again. Treatment of XVI with $CH_3I$ gave 5-nitro-2-methylthiobenzaldehyde oxime, which was recrystallized from ether-petroleum as yellow needles, mp 186—188°. *Anal.* Calcd. for $C_8H_8O_4N_2S$: C, 45.27; H, 3.80; N, 13.20; S, 15.11. Found: C, 45.50; H, 3.99; N, 12.91; S, 14.83.

**Preparation of Metal Salt and Complex**——Transition metal complexes of II, V, VIII, XIV and XVI were prepared directly by mixing an aqueous solution of metal salt with EtOH solution of the ligands. The resulting precipitates were filtered and washed successively with water, EtOH and ether. If necessary, the crude complex was recrystallized from $CHCl_3$ or MeOH. For the preparation of copper complex, the mixture of the ligand and $(AcO)_2Cu$ in EtOH was warmed on a steam bath for a few minutes. The reactivities of those ligands against metal ions were examined in a test tube by mixing both compounds in buffer solution. Limit of the identification was examined on a spot plate by adding ligand solution to various concentrations of metal ion.

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