contain a vinylidene group and a hemiketal system. The guaiane carbon skeleton has been established by its dehydrogenation giving S-guaiazulene (Ⅳ). Curcumol has been ozonized to give the norketone (Ⅸ) which has been converted into the acid (Ⅹ) and the lactone (Ⅻ). Spectroscopic study of these derivatives and other evidence show curcumol to be represented by formula I (R=H).

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170. Satoshi Mizukami and Kōichi Nagata: Studies on Thiohydroxamic Acids and Their Metal Chelates. I. Syntheses of Thiohydroxamic Acids and O-Methyl-thiohydroxamic Acids.

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The donor atoms which form metal chelates are restricted commonly to N, O and S. Of these, the sulfur atom only has 3p electrons so that the reagents including S atom must exhibit interesting selectivities and sensitivities, which differ from those of reagents including N or O atoms. However, studies on those compounds are lagging because of their instabilities and difficulties of synthesis even though further developments are expected.

It is well known that hydroxamic acids show characteristic color reactions with some transition metals. These reactions have been applied to the colorimetric determination of Fe^{3+}, Ti^{4+}, UO^{2+}, and especially the forming of red Fe^{3+} chelate has been very useful for the qualitative or quantitative assay of organic compounds which can be easily converted to hydroxamic acids, such as aldehyde, carboxylic acid, ester, anhydride and amide. There is too much literature on such analytical applications and the structures of their Fe^{3+} chelates to refer here in detail. We have also reported on the colorimetric determination of alcohols by hydroxamic acid method.[1] On the contrary, thiohydroxamic acids are very scarce in the literature except for a few reports on their synthesis.

From these standpoints we entered on this study in order to examine the chemical natures of thiohydroxamic acids more distinctly, and to investigate the roles of sulfur as ligand atom by comparative studies of the reactivities with metal ions and the structures of the metal chelates between thiohydroxamic acids and hydroxamic acids.

Some thiohydroxamic acids (Ⅳ) have been synthesized from dithioacids and hydroxylamine,[2~5] or hydroxamoyl chlorides and sodium hydrogen sulfide[6] by Cambi and Bacchetti, but these methods are not available for liquid thiohydroxamic acids

*1 Sagisukami, Fukushima-ku, Osaka (水上 聰, 永田耕一).

1) S. Mizukami, K. Nagata: Yakugaku Zasshi, **81**, 427 (1961).
2) L. Cambi: Atti. Acad. Lincei, **18**, I 687 (Chem. Abstr., **4**, 1738 (1910)).
3) *Idem*: Gazz. chim. ital., **41**, I 170 (Beilstein, **2**, I 39, **6**, I 228).
4) T. Bacchetti, A. Alemagna: Rend. Ist. Lombardo Sci. Lettere B., **91**, 30 (1957).
5) *Idem*: *Ibid.*, **91**, 574 (1957).
6) *Idem*: Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat., **24**, 161 (1958).

which are unstable and decomposed during the distillation, and some dithioacids are not always suitable as starting materials because of their instability.

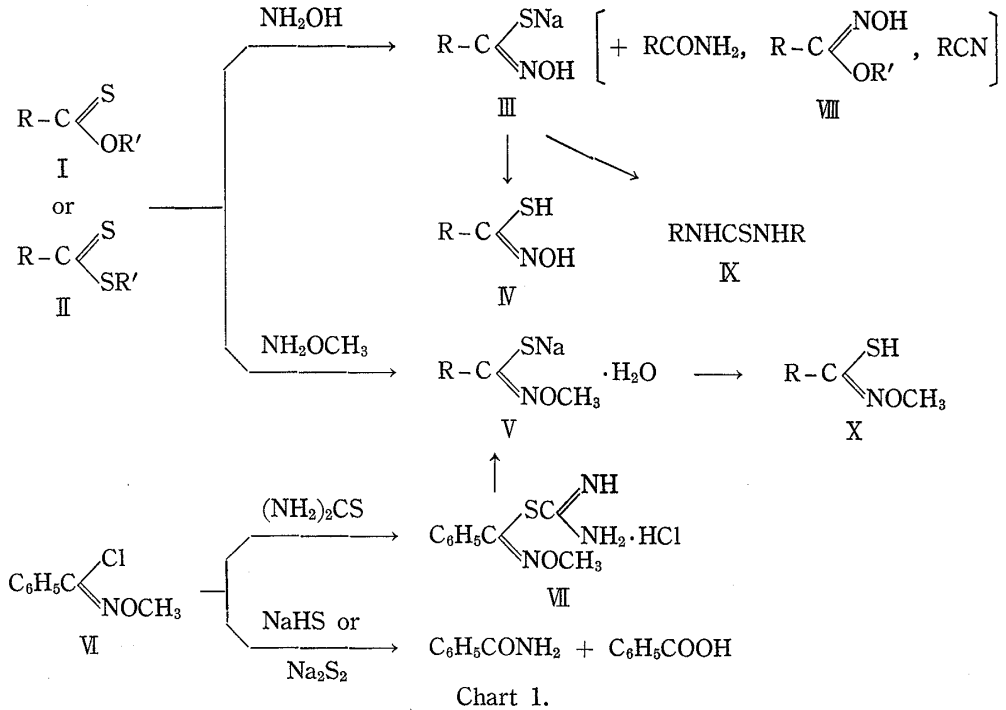

Chart 1.

As the first step of this series of work, this paper deals with a new method for the syntheses of thiohydroxamic acids as their sodium salts. Sodium salts of thiohydroxamic acids were prepared from esters of thionic acids (I) and hydroxylamine in the presence of sodium methylate with considerably good yield. This method is more advantageous than other methods reported before, because I are more stable and easier to refine than dithioacid. Sodium thiohydroxamates (III) are considerably stable and recrystallizable from acetone-ether.

The use of excess hydroxylamine did not affect the yield of III, while the use of excess sodium methylate produced the corresponding carboxylamide as the main product. The other by-products in this procedure were the corresponding nitriles, $Na_2S_2O_3$, etc., but the corresponding thiolic acids were not produced. The yields of III were not affected by the kind of the alcohol components in I. The esters of dithioacids (II) could be used also as the starting material in place of I. The obtained III are summarized in Table I.

The yields of III were about 70% for aromatic compounds with some exceptions, but for aliphatic ones the yields were considerably poor. *m*-, *p*-Hydroxy- or *p*-carboxy-benzothiohydroxamic acid were analyzed as nickel salts as shown in Table II, because their sodium salts could not be completely purified because they were hygroscopic and insoluble in acetone. In the case of the preparation of the sodium salts of isobutyro-thiohydroxamic acid, or *o*-methoxy- and *o*-hydroxy-benzothiohydroxamic acid, ethyl hydroxamate (VIII) was obtained as the main product and the obtained sodium salts were also so unstable that they decomposed during the recrystallization. These facts indicate that a steric hindrance between the sulfur atom and the substituted group facilitates the replacement of sulfur atom in the hydroxylaminolysis.

Some pure III were rearranged to the 1,3-disubstituted thiourea (IX) after long standing in the desiccator as reported by Ettlinger[7] for phenylacetothiohydroxamic acid. This rearrangement is likely to be increased by electron-releasing groups,

7) M. G. Ettlinger: J. Am. Chem. Soc., **79**, 1764 (1957).

Table I. $R-C(SNa)(NOH)\cdot XH_2O$

R	X	Appearance	Yield (%)	Formula	Analysis (%) Calcd. C	H	N	Na	Found C	H	N	Na
CH_3	2	white powder	40	$C_2H_8O_3NSNa$	16.11	5.41	9.39	15.41	16.45	5.41	9.28	15.36
C_2H_5	0	〃	7	C_3H_6ONSNa	28.34	4.76	11.02	18.08	28.17	4.85	11.21	17.98
C_3H_7	0	〃	16	C_4H_8ONSNa	34.03	5.71	9.92	16.26	33.90	5.74	9.75	16.56
C_6H_5	0	〃	72	C_7H_6ONSNa	47.99	3.45	8.00	13.13	47.91	3.76	7.76	13.14
p-CH_3-C_6H_4	0	〃	71	C_8H_8ONSNa	50.78	4.26	7.40	12.15	50.53	4.21	7.24	12.04
m-CH_3-C_6H_4	0	white powder (hygroscopic)	67	〃	50.78	4.26	7.40	12.15	50.58	4.24	7.34	12.37
p-Cl-C_6H_4	0	white powder	72	$C_7H_5ONClSNa$	40.11	2.40	6.68	10.97	39.81	2.68	6.62	10.93
m-Cl-C_6H_4	1	〃	72	$C_7H_7O_2NClSNa$	36.93	3.10	6.15	10.10	36.90	3.29	6.13	10.04
p-CH_3O-C_6H_4	0	〃	72	$C_8H_8O_2NSNa$	46.82	3.93	6.83	11.20	46.62	3.96	7.12	11.42
m-NO_2-C_6H_4	0	orange powder	80	$C_7H_5O_3N_2SNa$	38.19	2.29	12.72	10.44	38.31	2.45	12.80	10.51
β-$C_{10}H_7$	1	white powder	75	$C_{11}H_{10}O_2NSNa$	54.31	4.16	5.76	9.45	53.78	4.10	5.35	9.46
α-C_4H_3O	0	〃	76	$C_5H_4O_2NSNa$	36.36	2.44	8.48	13.92	35.84	2.58	8.14	13.43
α-C_4H_3S	0	〃	86	$C_5H_4ONS_2Na$	33.14	2.22	7.73	12.69	32.89	2.57	7.56	12.66

Table II. $\left(R-C(S-)(NOH)\right)_2Ni$

R	Appearance	Yield (%) (as sodium salt)	Formula	Analysis (%) Calcd. C	H	N	Ni	Found C	H	N	Ni
$(CH_3)_2CH$-	reddish brown needle	13	$C_8H_{16}O_2N_2S_2Ni$	32.56	5.47	9.49	19.90	32.75	5.63	9.82	19.83
p-OH-C_6H_4	reddish brown amorph.	15	$C_{14}H_{12}O_4N_2S_2Ni$	42.56	3.06	7.09	14.86	42.14	3.26	7.40	15.02
m-OH-C_6H_4	pale green leaflet	56	〃	42.56	3.06	7.09	14.86	42.28	3.21	7.26	14.59
o-OH-C_6H_4	orange yellow amorph.	20	〃	42.56	3.06	7.09	14.86	42.71	3.09	7.17	15.34
o-CH_3O-C_6H_4	orange brown amorph.	14	$C_{16}H_{16}O_4N_2S_2Ni$	45.42	3.81	6.62	13.87	45.18	3.97	6.40	13.78
p-HO_2C-C_6H_4	greenish yellow amorph.	80	$C_{16}H_{12}O_6N_2S_2Ni$	42.60	2.68	6.21	13.01	42.59	2.94	6.26	13.15

namely sodium *p*-methoxybenzothiohydroxamate rearranged more easily during a few months, whereas *m*-nitro compounds was very stable.

The crystalline thiohydroxamic acids (Ⅳ) were obtained by acidifying the solution of Ⅲ and recrystallization from adequate solvents, but the liquid one could not be distilled without decomposition even under high-vacuum. Table Ⅲ represents Ⅳ obtained.

Table Ⅲ. $R-C\begin{matrix}SH\\NOH\end{matrix}$

R	m.p. (°C)	Appearance	Formula	Analysis (%) Calcd. C	H	N	S	Found C	H	N	S
p-Cl-C_6H_4	99～100[a]	colorless needle	C_7H_6ONSCl	44.81	3.22	7.46	17.09	45.08	3.32	7.64	17.41
m-Cl-C_6H_4	47	〃	〃	44.81	3.22	7.46	17.09	44.75	3.29	7.96	17.59
p-CH_3O-C_6H_4	115～116[b]	colorless prism	$C_8H_9O_2NS$	52.44	4.95	7.64	17.46	52.12	5.31	7.26	17.09
m-NO_2-C_6H_4	105～106	yellow prism	$C_7H_6O_3N_2S$	42.42	3.05	14.13	16.18	42.54	3.18	13.89	16.23
β-$C_{10}H_7$	87	pale yellow leaflet	$C_{11}H_9ONS$	65.00	4.46	6.89	15.77	65.28	4.52	6.63	15.71

a) Ref. m.p. 93～94°[5] b) Ref. m.p. 122°[4]

Table Ⅳ. $R-C\begin{matrix}SNa\\NOCH_3\end{matrix}\cdot H_2O$

R	Appearance	Yield (%)	Formula	Analysis (%) Calcd. C	H	N	Na	Found C	H	N	Na
CH_3	white crystalline powder	52	$C_3H_8O_2NSNa$	24.82	5.56	9.65	15.84	24.69	5.72	9.37	16.20
C_6H_5	〃	62	$C_8H_{10}O_2NSNa$	46.37	4.86	6.76	11.09	46.51	4.88	6.72	11.23
p-CH_3-C_6H_4	white crystal	65	$C_9H_{12}O_2NSNa$	48.86	5.47	6.33	10.39	48.54	5.69	6.10	10.12
p-Cl-C_6H_4	〃	50	$C_8H_9O_2NSClNa$	39.76	3.75	5.80	9.51	39.34	3.91	5.67	9.90
p-CH_3O-C_6H_4	〃	57	$C_9H_{12}O_3NSNa$	45.56	5.10	5.90	9.69	45.82	5.18	5.85	9.94
m-NO_2-C_6H_4	yellow crystalline powder	67	$C_8H_9O_4N_2SNa$	38.10	3.60	11.11	9.11	38.16	3.70	11.20	8.82

Sodium O-methylthiohydroxamate (Ⅴ) summarized in Table Ⅳ were prepared by treating Ⅰ with O-methylhydroxylamine in the same way as the thiohydroxamic acids were. They could be also prepared by saponification of the corresponding isothiouronium salts (Ⅶ) with very poor yields, but treatment of O-methylbenzothiohydroxamoyl chloride (Ⅵ) with NaHS or Na_2S_2 yielded benzamide and benzoic acid as main products. On long standing, Ⅴ were very stable, but free O-methylthiohydroxamic acids (Ⅹ) were decomposed very slowly to give the corresponding thioamides as main product and small quantities of the corresponding nitriles.

Experimental*2

Esters of Thionic Acids (I) and Dithioacids (II)——According to the procedures of Matsui,[8,9] Sakurada[10,11] and Marvel,[12] I and II were prepared from HCl salts of imidate $\left(R-C\langle^{NH}_{OR'}\cdot HCl \text{ or } R-C\langle^{NH}_{SR'}\cdot HCl\right)$ and H_2S in pyridine, and they were purified by fractional distillation or by recrystallization from MeOH. Since HCl salts of ethyl ester of propion-, butyr- and isobutyr-imidic acid were not crystallized, the separated oil were used as they were. Esters of aliphatic thionic acids gave a weak C=O stretching band in their infrared spectra even though their analytical data were identical with theoretical values, but the band disappeared by repeating the distillation. The new compounds of I are summarized in Table V.

Table V. $R-C\langle^{S}_{OC_2H_5}$

R	Over-all yield from nitrile (%)	b.p./mm. Hg or m.p. (°C)	Formula	Analysis (%) Calcd. C	Calcd. H	Calcd. S	Found C	Found H	Found S
$(CH_3)_2CH-$	77	145/760	$C_6H_{12}OS$	54.50	9.15	24.25	54.68	9.12	24.33
m-CH_3-C_6H_4	86	138～140/70	$C_{10}H_{12}OS$	66.63	6.71	17.79	67.11	6.73	17.50
p-Cl-C_6H_4	45	36	C_9H_9OSCl	53.86	4.52	15.98	53.40	4.53	15.39
m-Cl-C_6H_4	57	117/14	〃	53.86	4.52	15.98	54.11	4.62	15.96
p-OH-C_6H_4	22	187～188/70 (48～50)	$C_9H_{10}O_2S$	59.32	5.53	17.59	59.88	5.66	17.05
m-OH-C_6H_4	61	166～168/17	〃	59.32	5.53	17.59	59.38	5.56	17.57
o-OH-C_6H_4	24	168～169/70	〃	59.32	5.53	17.59	59.53	5.57	17.24
o-CH_3O-C_6H_4	24	131～133/8	$C_{10}H_{12}O_2S$	61.20	6.16	16.34	61.52	6.23	16.05
m-NO_2-C_6H_4	69	63～ 65	$C_9H_9O_3NS$	51.17	4.29	15.18	50.75	4.32	15.60
p-HO_2C-C_6H_4	58	168～169	$C_{10}H_{10}O_3S$	57.13	4.79	15.25	57.59	4.80	14.66
	75	94～ 95/8	$C_7H_8O_2S$	53.82	5.16	20.53	53.99	5.26	20.63
	73	115～116/9	$C_7H_8OS_2$	48.80	4.68	37.23	48.97	4.73	36.87

Sodium Thiohydroxamate (III)——About 7% $NH_2OH\cdot HCl$ solution in MeOH and CH_3ONa solution (prepared by dissolving about 90 g. of sodium in 1 L. MeOH) were used after standardization by usual neutralimetry. To the filtrate of the mixture of 2 equivalent of $NH_2OH\cdot HCl$ solution and 2.9 equivalent of CH_3ONa solution was added an equivalent of I, and the reaction mixture was allowed to stand overnight at room temperature. The solvent was distilled at reduced pressure with an adequate evaporator. (The temperature of water bath should be kept bolow 40°, and not be evaporated to dryness.) After the resulting sirup was dissolved in a minimal amount of EtOH, small amount of insoluble material ($Na_2S_2O_3$ mainly) was removed by filtration, and washed with a small amount of EtOH until the residue did not show a permanent blue or green color with diluted hydrochloric acid solution of $FeCl_3$. Then ether was added to the adequately concentrated filtrate at reduced pressure with evaporator, and the resulting precipitate was filtered and washed with ether. (If a resinous compound was separated, the supernatant solvent was decanted and the residue was dried in a vacuum desiccator over P_2O_5). The residue was dissolved in acetone at room temperature, separated from small amount of insoluble materials (Na_2S and Na_2S_2) by filtration, and followed by the addition of ether. After filtration, the residue was washed with ether. Analytical sample was dried in a vacuum desiccator over P_2O_5 at room temperature, if necessary, after additional recrystallization from acetone-ether.

For synthesis of aliphatic sobium thiohydroxamate, the above mentioned procedure was modified slightly. To the ice-cold filtrate of the mixture of 1.0 equivalent of $NH_2OH\cdot HCl$ and 1.9 equivalent of CH_3ONa was added an equivalent of I. The mixture was kept first in an ice bath for 0.5 hr. and then at room tempera-

*2 All melting points were uncorrected.

8) M. Matsui: Mem. Coll. Sci. Kyōto, **1**, 285 (Chem. Abstr., **3**, 2697 (1909)).
9) *Idem*: *Ibid.*, **3**, 247 (Chem. Abstr., **6**, 1612 (1912)).
10) Y. Sakurada: *Ibid.*, **9**, 237 (1926) (Chem. Abstr., **21**, 2458 (1927)).
11) *Idem*: *Ibid.*, **10**, 79 (1926) (Chem. Abstr., **21**, 3609 (1927)).
12) C. S. Marvel, P. de Radzitzky, J. J. Brader: J. Am. Chem. Soc., **77**, 5997 (1955).

ture for about 3 hr. in a tightly stopped flask. After MeOH was removed in the manner previously described, the resulting sirup was taken up into acetone, and filtered. The precipitate which was obtained by addition of ether to the concentrated filtrate was collected by filtration, and recrystallized another two times from acetone–ether, if necessary, the acetone solution was treated with charcoal.

Because of the tendencies of sodium thiohydroxamates to decompose in solution, the procedures were desirable to be carried out in minimum period so that the use of about 2 g. of I presumed to be convenient. In above mentioned procedure, II could be used in place of I. The compounds which could not be refined as sodium salt because of their hygroscopic characters or their insolubilities in acetone, as shown in Table II, were identified as nickel salts. A portion of the sodium salts was dissolved in water and $(AcO)_2Ni$ solution was added. The precipitate was collected by filtration, washed with water, EtOH and ether in this order, and recrystallized from hot alcohol. Analytical samples were dried over P_2O_5 at reduced pressure.

Prior to determine the above mentioned procedures the effects of the amount of $NH_2OH \cdot HCl$ and CH_3ONa solution and reaction temperatures on the yields were examined as summarized in Table VI. It was obvious that the use of excess of CH_3OHa reduced the yielde of III.

Table VI. Effect of Reaction Conditions for Yield of Sodium Thiohydroxamate

$C_6H_5CSOC_2H_5$ (mole × 10^2)	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
$NH_2OH \cdot HCl$ (〃)	2.8	2.8	2.8	4.2	4.2	4.2	5.6	5.6	5.6	2.8	2.8	2.8	2.8
CH_3ONa (〃)	3.5	4.2	4.9	4.7	5.6	6.5	5.8	7.0	8.2	4.1	4.1	4.1	4.1
Time (hr.)	3	3	3	3	3	3	3	3	3	0.1	2	7	23
Yield (%)	23	63	31	38	70	2	26	71	14	42	72	70	72

$CH_3CSOC_2H_5$ (mole × 10^2)	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8
$NH_2OH \cdot HCl$ (〃)	1.3	1.7	1.8	2.4	6.8	1.8	1.8	1.8
CH_3ONa (〃)	2.6	3.3	3.5	4.8	13.5	3.5	3.5	3.5
Time (hr.)	20	20	20	20	20	0.7	4	18
Yield (%)	25	24	34	5	3	37	46	34

After long standing in a desiccator, III was dissolved in water, and filtered. The recrystallized residue was identical in all respects with the authentic 1,3-disubstituted-2-thiourea (IX) obtained from corresponding aniline and CS_2.

Thiohydroxamic Acids (IV)——To the aqueous solution of III was added diluted hydrochloric acid, and the precipitated solid was filtered, washed with water, and recrystallized from CCl_4, avoiding the long heating. The crystalline IV was remarkably stable when it was stored at 0° in non-polar solvents, but decomposed rapidly in polar solvent, such as alcohols. Although *m*-chlorobenzothiohydroxamic acid was separated oily, it was crystallized from petroleum ether at −20° after extraction with ether. Another liquid IV, such as aceto–, and benzothiohydroxamic acid, were distilled under high-vacuum, but the distillate was the corresponding nitrile.

Sodium O-Methylthiohydroxamate (V)——a) From I or II: By using $NH_2OCH_3 \cdot HCl$ in place of $NH_2OH \cdot HCl$, V was prepared in the same procedures as described for III. Recrystallization from acetone–ether and drying overnight at room temperatures over P_2O_5 gave an analytical samples. Addition of diluted hydrochloric acid to aqueous solution of V gave free O-methylthiohydroxamic acids (X), most of which were liquid. Only O-methyl-*m*-nitrobenzothiohydroxamic acid was obtained as solid, which was recrystallized from petroleum ether to give pale orange needles, m.p. 61°. *Anal.* Calcd. for $C_8H_8O_3N_2S$: C, 45.27; H, 3.80; N, 13.20; S, 15.11. Found: C, 45.46; H, 4.04; N, 13.27; S, 15.18.

b) Sodium O-methylbenzothiohydroxamate from O-methylbenzohydroxamoyl chloride (VI): A solution of 8.4 g. of VI (prepared according to Tieman's method[13]) in 30 ml. of EtOH was slowly added to the refluxing solution of 3.4 g. of thiourea in EtOH with stirring, and the refluxing was continued for another 6 hr. Removal of the solvent and recrystallization from acetone–ligroin mixture gave 7.5 g. of (N-methoxybenzimidoyl)isothiouronium chloride (VII) as colorless plates, m.p. 115~117°. *Anal.* Calcd. for $C_9H_{12}ON_3SCl$: C, 43.98; H, 4.92; N, 17.10; S, 13.05; Cl, 14.43. Found: C, 43.50; H, 5.03; N, 17.02; S, 12.73; Cl, 14.07.

To the solution of 2.2 g. of VII in EtOH was added 7 ml. of ethanolic potassium hydroxide (0.1 g./ml.), and the mixture was refluxed for 2 hr. After removal of the solvent to almost dryness, ether was added. The precipitated solid was recrystallized from acetone–ether to yield 0.3 g. of colorless powder, which was identical with sodium O-methylbenzothiohydroxamate prepared from method (a).

An attempt to obtain sodium O-methylbenzothiohydroxamate from VII and NaHS or Na_2S_2 was failed. To a solution of VII in EtOH was added an equivalent solution of NaHS in EtOH or Na_2S_2 in minimum water. The mixture was stirred for 3 hr. at room or boiling temperatures. After removal of the solvent, the residue was extracted with ether. Evaporation of ether afforded almost quantitative amount of benzamide and a little of benzoic acid.

13) F. Tiemann, P. Krüger: Chem. Ber., **18**, 732 (1885).

Summary

Nineteen kinds of sodium thiohydroxamate (I) were synthesized from hydroxylamine and esters of thionic acids or dithioacids in the presence of sodium methylate with about 40% yields for the aliphatic compounds and above 70% yields for the aromatic ones with some exceptions. A number of sodium O-methylthiohydroxamate (II) were also obtained by the analogous method using O-methylhydroxylamine. On long standing, I were apt to rearrange to the 1,3-disubstituted thiourea while II were very stable. Some crystalline thiohydroxamic acid and O-methylthiohydroxamic acids were prepared from I and II.

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171. Kōichi Nagata and Satoshi Mizukami: Studies on Thiohydroxamic Acids and Their Metal Chelates. II.*1 Structures of Thiohydroxamic Acids.

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For hydroxamic acids which are capable of tautomeric changes (IIIa, b) it has been established[1~4] that the keto-form exists predominantly both in the solid state and in solution, whereas there is no such reports of the structures and thiolthione tautomerisms of thiohydroxamic acids (Ia, b). In this paper some thiohydroxamic acids and O-methyl thiohydroxamic acids (IIa, b) which are reported in Part I*1 were examined by physical methods and their probable structures were discussed.

(a) (b) IIIa IIIb

I: R′=H II: R′=CH_3

A) Infrared Spectra

Some typical infrared spectra of II are shown in Fig. 1. No marked differences of the spectra are found between in carbon tetrachloride solution and in the solid or as the liquid film. The SH stretching frequencies at 2578±8 cm^{-1} are in a satisfactory agreement with those found for ordinary thiol group, 2600~2550 cm^{-1},[5] so that any hydrogen-bonding associated with thiol group is less likely. Furthermore, NH stretching bands are not found under any circumstances in the region 3400~3550 cm^{-1} (monomer) or 3300~3140 cm^{-1} (dimeric), in which those of secondary thioamides or

*1 Part I: This Bulletin, **14**, 1249 (1966).

*2 Sagisukami, Fukushima-ku, Oaska (永田耕一, 水上 聰).

1) D. Hadži, D. Prevoršek: Spectrochim. Acta, **10**, 38 (1957).
2) H. Lenormant: Bull. soc. chim. France, **1948**, 33.
3) F. Mathis: Compt. rend., **232**, 505 (1951).
4) W. J. Orville-Thomas, A. E. Parsons: J. Mol. Spectroscopy, **2**, 203 (1958).