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Studies of Organosulfur Compounds. VII. The Preparation and Reaction of Some Crystalline Piperidinium Salts of Aliphatic Dithio Acid

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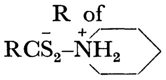
Although the syntheses of aliphatic dithio acid derivatives have been carried out, no isolation of the salts (almost entirely metal salts), which are very important as intermediates in the preparation of derivatives, have been reported as yet. In the course of the studies of the reactions bis(thioaroyl)disulfides with amines, it was found that the crystals of amine salts of aromatic dithio acid were very stable1) and could easily be obtained from the corresponding aromatic dithio acids and various secondary or tertiary amines.2) In this paper, we wish to report the successful preparation of some crystalline piperidinium salts of aliphatic dithio acid.

Results and Discussion

The reaction of dithiopropionic acid in ethyl acetate with an equimolar amount of piperidine gave piperidinium salts (IIa) of dithiopropionic acid in a 67% yield as glistering yellow crystals. The structure of IIa was identified by elemental analysis and by studying the IR and UV spectra. In the IR spectrum, strong broad absorption bands due to amine salts were observed in the range of 3000—2500 cm^{-1}, while the UV spectrum showed its maximum band at 455 mμ (ε 39). Furthermore, the structure of IIa was supported by the quantitative formation of the methylester through the action of methyl iodide. An analogous treatment of dithioisobutyric, dithiopentanoic, dithiohexanoic, and dithiocyclohexanecarboxylic acid with the piperidine gave the corresponding piperidinium salts (IIb—e) in good yields. The results are summarized in Table 1.

All the piperidinium salts obtained, except for that of dithiopropionic acid, were fairly stable in solid states at room temperature, and did not change when left standing for 3 days, but the salts gradually decomposed over 50°C, with the evolution of hydrogen sulfide. On the other hand, the salts of dithiopropionic acid

TABLE 1. PHYSICAL PROPERTIES AND ELEMENTAL ANALYSES OF THE AMINE SALTS OF ALIPHATIC DITHIO ACID

Comp	R of $R\text{C}\overset{-}{S}_2\text{-}\overset{+}{N}H_2$ 	Mp (°C)	Yield %	IR, KBr $\nu_{C=S}$ cm^{-1}	λ_{max}^{EtOH} (ε)		Color$^{a)}$	Formula	Found (Calcd), % C	H	S	N
IIa	C_2H_5	113—114	67	950 925	339 (17300)	455 (31)	Y	$C_8H_{17}NS_2$	50.83 (50.26)	8.63 (8.67)	33.33 (33.51)	7.10 (7.33)
IIb	*i*-C_3H_7	133—134	82	850	339 (16500)	455 (39)	Y	$C_9H_{19}NS_2$	52.83 (52.68)	9.18 (9.27)	31.12 (31.22)	6.91 (6.83)
IIc	*n*-C_4H_9	62—63	72	970	339 (17500)	455 (30)	OY	$C_{10}H_{12}NS_2$	54.88 (54.79)	9.63 (9.59)	29.83 (29.22)	6.28 (6.39)
IId	*n*-C_5H_{11}	92—93	84	1000	399 (17300)	455 (31)	OY	$C_{11}H_{23}NS_2$	56.98 (56.65)	9.91 (9.87)	28.09 (27.46)	6.22 (6.01)
IIe	*cyclo*-C_6H_{11}	131—132	79	990	339 (17700)	455 (39)	OY	$C_{12}H_{25}NS_2$	58.00 (58.53)	9.88 (9.76)	26.01 (26.02)	5.77 (5.69)

a) Y: Yellow, OY: Orange Yellow

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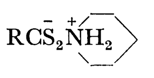
1) S. Kato and M. Mizuta, *Int. J. Sulfur Chem.*, in press.

2) S. Kato, T. Mitani, and M. Mizuta, unpublished data.

Table 2. Alkylation of the amine Salts (II)

R of 	RX	Solvent	Temp °C	Time hr	Products	Bp °C/mmHg	Yield %
C_2H_5	CH_3I	CH_2Cl_2	rt	3	$C_2H_5CS_2CH_3$	51/13	98
C_2H_5	C_2H_5I	CH_2Cl_2	rt	3	$C_2H_5CS_2C_2H_5$	65/13	97
i-C_3H_7	CH_3I	CH_2Cl_2	rt	4	i-$C_3H_7CS_2CH_3$[a]	70/ 8	97
n-C_4H_9	CH_3I	CH_2Cl_2	rt	5	n-$C_4H_9CS_2CH_3$[b]	84/ 9	96
C_6H_{11}	CH_3I	CH_2Cl_2	rt	5	$C_6H_{11}CS_2CH_3$	77/ 1	98

a) Found: C, 44.92; H, 7.22; S, 48.10%; (Calcd for $C_5H_{10}S_2$: C, 44.80; H, 7.12; S, 47.80%. b) Found: C, 48.76; H, 8.29; S, 43.36% (Calcd for $C_6H_{12}S_2$: C, 48.60; H, 8.12; S, 43.31%.

were unstable, and after one week even at 0°C completely changed from solid to oily material, with the evolution of hydrogen sulfide.

The salts were only slightly soluble in ether, benzene, and acetonitrile, but were easily soluble in dichloromethane, chloroform, acetone, and ethanol. The salts readily reacted with alkyl bromides or iodides in dichloromethane to give the corresponding alkyl esters in almost quantitative yields, but the reactions with t-butyl bromide or alkyl chlorides with no electron withdrawing group on their α-position did not occur, even under more severe conditions (Table 2).

Spectral Data. *a) IR Spectra*: Mecke and Spiesecke[3] assigned $\nu_{C=S}$ to 1216 cm^{-1} for dithioacetic acid. However, there has been only one recent report on the subject; in it Lindner and Kunze[4] assigned $\nu_{C=S}$ for 1242 cm^{-1} for silver and lead trifluorodithioacetates. We reported that $\nu_{C=S}$ for the amine salts of aromatic dithio acids was observed near 1000 cm^{-1}.[2] In the amine salts, very intensive absorption bands seemingly due to $\nu_{C=S}$ of the dithiocarboxylate group were observed in the 1000—925 cm^{-1} range without any exceptions (Table 1). This results fits with those of the amine salts of aromatic dithio acids, and also with the assignment given for metal salts of dialkyldithiocarbamates (near 982 cm^{-1})[5] and xanthates (1040 and 1080 cm^{-1}),[6] and for trialkylphosphonidithioformulate ($R_3P^+CSS^-$, near 1050 cm^{-1}).[7]

b) UV Spectra: Table 1 lists the absorption maxima (λ max) in mμ and the molecular extinction coefficients (ε) at each maximum. As is shown in Table 1, the amine salts (II) showed two characteristic maximum band, 339 (ε 16000—18000) and 455 mμ (ε 30—40), without any exceptions, indicating that the former bands are due to $\pi\rightarrow\pi^*$, and the latter, due to $n\rightarrow\pi^*$.

Attempts at the isolation of the amine salts of dithioacetic and dithio-2-methyl-isobutyric acids, and the crystallization of secondary or tertiary amine salts other than the piperidinium salts were unsuccessful.

Experimental[8]

Materials. Aliphatic dithio acids were prepared in dry THF by the method of Houben.[9]

Some typical procedures are shown, and the detailed data are summarized in Table 1.

Piperidinium Salts (IIb) of Dithioisobutyric Acid. A solution of 1.7 g (0.02 mol) of piperidine in ethyl acetate (2 ml) was added to ethyl acetate (10 ml) containing 4.1 g (0.02 mol) of dithioisobutyric acid at 5°C and allowed to stand for overnight below −20°C. The precipitates were filtered and recrystallized from dichloromethane–n-hexane to give 3.9 g of IIb as plate crystals.

Reaction of the Piperidinium Salts (IIa) of Dithiopropionic Acid with Methyl Iodide. A solution of IIa (0.03 mol) and methyl iodide (0.04 mol) in dichloromethane (10 ml) was stirred at room temperature for 1 hr. After evaporating the solvent and the excess of methyl iodide, a small portion of petroleum ether (bp below 40°C) was added to the residue and insoluble parts (piperidinium iodide) were filtered off. Vacuum distillation of the filtrate gave 3.4 g (94%) of methyl dithiopropionate: bp 46—47°C/10—11 mmHg; IR (neat): $\nu_{C=S}$ 1190 cm^{-1}. The boiling point, and the IR spectrum were identical with those of an authentic sample prepared by the method of Houben and Shultze.[9]

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[3] R. Mecke and H. Spiesecke, *Chem. Ber.*, **89**, 1110 (1956).

[4] E. Linder and U. Kunze, *Z. Anorg. Allg. Chem.*, **383**, 255 (1971).

[5] J. Chatt, L. A. Duncanson, and L. M. Venanzi, *Suomen Kemistilehti*, **29** *B*, 75 (1956) See Ref. 7).

[6] L. H. Little, G. W. Poling, and J. Leja, *Can. J. Chem.*, **39**, 745 (1961).

[7] K. A. Jensen and P. H. Nielsen, *Acta Chem Scand.*, **17**, 547 (1963).

[8] All melting points are uncorrected. The IR spectra were measured on a JASCO grating infrared spectrophotometer IR-G. The UV spectra were measured on a Hitachi 124 spectrophotometer.

[9] J. Houben and K. M. L. Schultze, *Ber.*, **43**, 2481 (1910).