[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

An Improved Preparation of Dithioesters and Some Reactions and Spectral Properties of These Compounds

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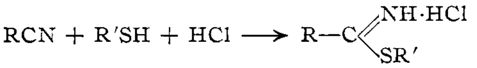
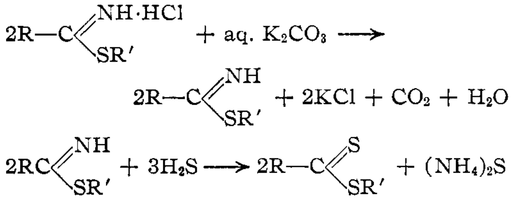
An improved procedure for making dithioesters from thioimidoesters has been developed and a few new dithioesters have been described. Some comparisons of reactions of esters, thiolesters and dithioesters have been reported. Some new thioamides have been prepared. The infrared absorption spectra of these compounds have been observed and tabulated. The ν(C═S) has been tentatively assigned to the 1170–1195 cm.$^{-1}$ region for dithioesters and to the 1180–1265 cm.$^{-1}$ region for thioamides.

Esters of dithioacids have been previously prepared in low yields by alkylating the salt of a dithioacid[1–6a,b] and from the nitrile by the method of Sakurada.[7] This latter method involves the steps



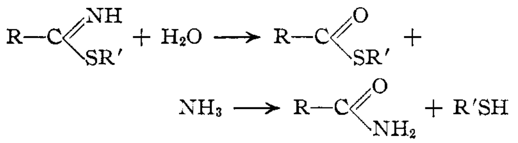
$$\mathrm{RCN + R'SH + HCl \longrightarrow R{-}C}\Big\langle{}^{\mathrm{NH\cdot HCl}}_{\mathrm{SR'}} \qquad \mathrm{(I)}$$



$$\mathrm{2R{-}C}\Big\langle{}^{\mathrm{NH\cdot HCl}}_{\mathrm{SR'}} + \mathrm{aq.\ K_2CO_3} \longrightarrow \mathrm{2R{-}C}\Big\langle{}^{\mathrm{NH}}_{\mathrm{SR'}} + \mathrm{2KCl + CO_2 + H_2O} \qquad \mathrm{(II)}$$

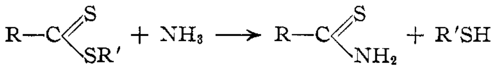
$$\mathrm{2RC}\Big\langle{}^{\mathrm{NH}}_{\mathrm{SR'}} + \mathrm{3H_2S} \longrightarrow \mathrm{2R{-}C}\Big\langle{}^{\mathrm{S}}_{\mathrm{SR'}} + \mathrm{(NH_4)_2S} \qquad \mathrm{(III)}$$

Reaction I has been shown to run well and give a near quantitative yield.[8,9] However, complications have been shown to arise in reaction II due to water hydrolyzing the thioimido ester[10] and the ammonia thus liberated further reacting to yield an amide.



$$\mathrm{R{-}C}\Big\langle{}^{\mathrm{NH}}_{\mathrm{SR'}} + \mathrm{H_2O} \longrightarrow \mathrm{R{-}C}\Big\langle{}^{\mathrm{O}}_{\mathrm{SR'}} + \mathrm{NH_3} \longrightarrow \mathrm{R{-}C}\Big\langle{}^{\mathrm{O}}_{\mathrm{NH_2}} + \mathrm{R'SH} \qquad \mathrm{(IV)}$$

We have observed another side reaction which occurs along with reaction III to produce the thioamide.



$$\mathrm{R{-}C}\Big\langle{}^{\mathrm{S}}_{\mathrm{SR'}} + \mathrm{NH_3} \longrightarrow \mathrm{R{-}C}\Big\langle{}^{\mathrm{S}}_{\mathrm{NH_2}} + \mathrm{R'SH} \qquad \mathrm{(V)}$$

The ammonia for this reaction may come from the hydrolysis of the thioimidoester or from the dissociation of ammonium sulfide. In one of our attempted preparations of ethyl dithiopropionate, the thiopropionamide was formed in 48% yield. This method is described in the Experimental part of this paper since the literature method of preparation claims only a 5–6% yield.[11]

To avoid these side reactions in the preparation of esters of dithioacids, we have developed a modification of Sakurada's method[7] in which the thioimidoester hydrochloride formed by reaction I is dissolved at 0° in a saturated solution of hydrogen sulfide in dry pyridine and an excess of hydrogen sulfide is added over a period of about six hours. The ester was then isolated by adding excess acid and extracting with ether. Distillation gave a 90% yield of product based on the thioimidoester salt used. Two new alkyl dithioesters have been prepared by essentially the same procedure. It was found that it was not essential to obtain a crystalline thioimido ester salt in order to obtain reasonably good yields of dithioester.

It has been found that the strongly basic amine, piperidine, reacts with ethyl dithioacetate at 0° to give the thioamide in 85–90% yield. *n*-Butylamine also reacts at 0° to give the amide but with less vigor. At room temperature these amines react violently with the dithioester. Aniline, however, does not yield an amide even at room temperature.

Ethyl thiolacetate will also react with piperidine to give N-acetylpiperidine, but the reagents can be mixed at room temperature without a vigorous reaction taking place. *n*-Butylamine also reacts with ethyl thiolacetate at room temperature but aniline does not appear to do so. Sakurada[12] has reported that the isoamyl ester of thionacetic acid ($CH_3CSOC_5H_{11}$) reacts with isobutylamine slowly in ether solutions to give the thioamide. Ahrens,[13] Auerbach and Wolffenstein[14] have reported that piperidine reacts with ethyl acetate only at 200°. This furnishes an interesting comparison between the amine reaction with esters, thioesters, thionesters and dithioesters.

We were unable to obtain condensation products of ethyl dithioacetate with benzaldehyde and formaldehyde indicating that the α-hydrogen atoms are probably less active in the dithioesters than in thiol esters[15] and thion esters.[16]

Infrared Studies of Dithioesters and Thioamides

The frequencies of the main infrared absorption bands and their relative intensities are listed in Table I. In the course of investigating the vibrational frequency assignments of dithioesters and thioam-

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[1] Belgian Government Postdoctorate Fellow, University of Illinois, 1954–1955.

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[7] Y. Sakurada, *Mem. Coll. Sci., Kyoto*, **10**, 79 (1926).

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ides, the ν(C=S) was observed to appear in the 1200 cm.$^{-1}$ region. Previously, the ν (C≡S) had been assigned to the range 1300–1400 cm.$^{-1}$ by Thompson,[17] *et al.*, and Colthup,[18] and to 1410–1550 cm.$^{-1}$ by Miller.[19] Bellamy[20] says that no adequate correlation has yet been devised for this vibration. Additional research necessary to complete this study is now in progress and will be published in the near future. However, we may tentatively assign the ν(C=S) to 1170–1195 cm.$^{-1}$ for dithioesters, and to 1180–1265 cm.$^{-1}$ for thioamides.

TABLE I

FREQUENCY OF MAJOR ABSORPTION BANDS[a] (CM.$^{-1}$) OF DITHIOESTERS AND THIOAMIDES

(vs, very strong; s, strong; ms, medium to strong; m, medium

Ethyl dithioacetate	Ethyl dithiopropionate	Isobutyl dithioacetate	*t*-Butyl dithiopropionate	Thiopropionamide	N-*n*-Butylthioacetamide	N-Thioacetylpiperidine
2955m	2960s	2955s	2955s	3375vs	3220vs	2930s
2910m	2920s	2865m	2915s	3171vs	3045m	2845m
1451m	2865m	1461m	1474m	2975s	2940vs	1504vs
1358m	1456s	1364m	1453s	1645s	2855m	1445vs
1195vs	1373m	1195vs	1363s	1453vs	1542vs	1363m
1099s	1256m	1097ms	1267m	1427m	1461s	1284vs
864vs	1187vs	865vs	1221m	1310s	1392s	1260vs
	968vs		1172vs	1232s	1336m	1172m
	901vs		1153vs	1070s	1305m	1157m
	777m		963vs	1009vs	1181s	1053m
			897vs	925vs	1110s	983s
				689s	930m	856s
					686s	

[a] The tabulated intensities are relative; all frequency values are corrected, the experimental error being ±10 cm.$^{-1}$ at 2000–4000 cm.$^{-1}$ and ±2 cm.$^{-1}$ at 650–2000 cm.$^{-1}$.

Experimental Part

Ethyl Dithioacetate.—Ethyl thioimidoacetate hydrochloride was prepared in 91% yield from acetonitrile and ethyl mercaptan by the procedure of Schmidt.[8]

In a large test-tube 100 cc. of dry pyridine was saturated with hydrogen sulfide by bubbling in the gas while maintaining the temperature at 0°. Then 45 g. of ethyl thioimidoacetate hydrochloride was added all at once and the flow of hydrogen sulfide was again started at 0°. Gas was passed in, rather rapidly at first and then more slowly for about six hours. The tube was shaken from time to time during the reaction. During this period the thioimidoester dissolved slowly, a large precipitate of ammonium chloride separated and the solution became orange in color. After about six hours, 50 cc. of ice-water was added with stirring. After about five minutes, this reaction mixture was poured into a mixture of 150 cc. of concentrated hydrochloric acid in 50 cc. of water and 150 g. of cracked ice. Then 150 cc. of ether was added. The mixture was shaken and the ether separated. The water layer was again extracted with 75 cc. of ether. The combined ether extracts were washed with a solution of 10 cc. of concentrated hydrochloric acid in 30 cc. of water, and then dried over anhydrous potassium carbonate. The ether was removed by distillation and the remaining ester distilled under reduced pressure. The yield was 34.8 g. (90%) of a pure yellow liquid boiling at 61° at 23 mm., n^{20}D 1.5700. Sakurada[7] gives the boiling point as 128–132° and Houben[1] gives it as 42–43° at 11 mm. Sakurada[7] lists n^{20}D 1.5303.

Anal. Calcd. for $C_4H_8S_2$: C, 39.96; H, 6.7; S, 53.34. Found: C, 39.97; H, 6.9; S, 53.27.

Isobutyl Dithioacetate. (a) **Isobutyl Thioimidoacetate Hydrochloride.**—Using the procedure of Schmidt[8] for the corresponding ethyl derivative 20.53 g. of acetonitrile and 45.1 g. of isobutyl mercaptan was dissolved in petroleum ether, cooled in ice and dry hydrogen chloride was passed in until about 20 g. had been absorbed (theory required 18.25 g.). The imidoester hydrochloride could not be crystallized even when the mixture was cooled to −70°. At this low temperature the petroleum ether was decanted from the heavy sirupy layer and the latter was dried overnight in a desiccator which contained both phosphorus pentoxide and solid sodium hydroxide. Finally the material was allowed to stand at about 1 mm. pressure for two hours. It was then used in the ester preparation.

(b) **Isobutyl Dithioacetate.**—The above sirup was added to 100 g. of dry pyridine saturated with hydrogen sulfide at 0° as described under the ethyl ester. In this case the hydrogen sulfide was passed in for 3 hours at 0–5°. Then the mixture was poured into a mixture of 260 cc. of concentrated hydrochloric acid, 250 g. of crushed ice and 150 cc. of ether. The ester was extracted, washed, dried and distilled as described before. The yield was 36.6 g. (49.2% calculated on the nitrile used) of an orange liquid boiling at 86–87° at 23 mm., n^{20}D 1.5400.

Anal. Calcd. for $C_6H_{12}S_2$: C, 48.6; H, 8.15; S, 43.35. Found: C, 48.90; H, 8.21; S, 42.06.

***t*-Butyl Thioimidopropionate Hydrochloride.**—The general procedure described by Pinner and Klein[10] for the preparation of thioimido chlorides was followed. Into 22.5 g. (0.25 mole) of *t*-butyl mercaptan, 13.75 g. (0.21 mole) of propionitrile in 35 cc. of ether was passed dry hydrogen chloride until 9.125 g. (0.25 mole) had been absorbed. No crystalline product separated at first but on adding more ether and cooling to 0°, crystallization occurred. The crystals were collected on a filter, washed with ether and dried overnight in a desiccator over solid phosphorus pentoxide and dry sodium hydroxide. The yield was 8.0 g. (17.5%).

***t*-Butyl Dithiopropionate.**—The product obtained above was dissolved in 30 cc. of dry pyridine and hydrogen sulfide passed into the mixture for 3 hours while cooling the mixture in running water. Ammonium chloride separated and was filtered off. In this first experiment the pyridine and ester were separated by distillation at ordinary temperatures. The ester boiled at 170° with some decomposition. Redistillation under reduced pressure gave about 5 g. (70%) of orange liquid boiling at 70° under 13 mm.

Anal. Calcd. for $C_7H_{14}S_2$: C, 51.8; H, 8.7; S, 39.5. Found: C, 52.16; H, 8.99; S, 38.74.

Ethyl Dithiopropionate.—Following the general procedure of Pinner and Klein[10] 57 g. (74%) of ethyl thioimidopropionate hydrochloride was prepared from 31 g. (0.5 mole) of ethyl mercaptan and 27.5 g. (0.5 mole) of propionitrile, m.p. 67°.

This 57 g. of salt was added to 80 cc. of dry pyridine and into the cooled mixture hydrogen sulfide was passed for two hours. Ammonium chloride separated and was filtered off. The pyridine was distilled and more ammonium chloride separated. The residual orange colored liquid was washed with dilute hydrochloric acid to remove any remaining pyridine and ammonium chloride, extracted in ether and distilled. There was obtained 25 g. (50%) of product boiling at 70–72° at 20 mm., n^{20}D 1.5542. Houben[1] reports the boiling point as 60–61° at 10 mm. and Sakurada[7] as 150–155°, n^{27}D 1.5259.

Anal. Calcd. for $C_5H_{10}S_2$: C, 44.73; H, 7.51; S, 47.76. Found: C, 44.46; H, 7.61; S, 47.71.

N-Thioacetylpiperidine.—In a three-necked flask fitted with a dropping funnel, thermometer and a tube leading to a cold trap (cooled in Dry Ice) was placed 12 g. (0.1 mole) of ethyl dithioacetate. The flask was flushed out with nitrogen cooled in an ice-bath and then 8.52 g. (0.1 mole) of piperidine was added slowly through the dropping funnel. Each drop of amine added caused a vigorous reaction. The color faded during the amine addition. At the end of the addition the mixture was warmed to about 80° to drive off the mercaptan and, to ensure complete removal, the flask was evacuated to about 1 mm. and heating continued for about 15 minutes. The material in the flask crystallized into a yellow mass which weighed 14.1 g. (98.5%). The material in the cold trap was ethyl mercaptan, b.p. 35°.

The crude N-thioacetylpiperidine was treated with char-

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[17] H. W. Thompson, D. L. Nicholson and L. N. Short, *Disc. Faraday Soc.*, **9**, 225 (1950).

[18] N. B. Colthup, *J. Opt. Soc. Amer.*, **40**, 397 (1950).

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[20] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 13–29.

coal in toluene solution but this did not remove the yellow color. However, two washings with low boiling petroleum ether did remove the color and the white crystals, m.p. 55–56°, weighed 11.5 g. Another 0.6 g. could be recovered from the petroleum ether.

Anal. Calcd. for $C_7H_{13}NS$: C, 58.62; H, 9.15; N, 9.77; S, 22.38. Found: C, 59.12; H, 9.13; N, 9.57.

Russell[21] prepared this thioamide from N-acetylpiperidine by the action of phosphorus pentasulfide and reported the melting point as 60–61°.

N-*n*-Butylthioacetamide.—In the same general manner for 12 g. of ethyl dithioacetate and 7.31 g. of *n*-butylamine, there was obtained a dark liquid which did not crystallize. On distillation there was obtained 11 g. (83.3%) of liquid boiling at 113° under 1 mm. pressure, n^{20}_D 1.5392.

Anal. Calcd. for $C_6H_{13}NS$: N, 10.67. Found: N, 10.50.

Attempts to Prepare N-Thioacetanilide.—Under the same general conditions no reaction was obtained between aniline and ethyl dithioacetate.

Reaction of Piperidine and Ethyl Thiolacetate.—When 12.75 g. of piperidine and 15.6 g. of ethyl thiolacetate were mixed at room temperature they reacted with the liberation of heat and some slight cooling was needed to keep the temperature below 60°. After about an hour at 60° the mixture was warmed to 100° to remove all of the mercaptan. The residual liquid was distilled to give 17.1 g. (89.8%) of product boiling at 224–225°, n^{20}_D 1.4815. Arens and Wibaut[22] report a boiling point of 220–230°.

Anal. Calcd. for $C_7H_{13}ON$: N, 11.00. Found: N, 11.03.

Thiopropionamide.—Pesina[11] has reported the preparation of this amide in 5–6% yield for the reaction of phosphorus pentasulfide on propionamide. In an attempt to convert ethyl thioimidopropionate hydrochloride to the dithioester in aqueous media we obtained the amide in 48% yield.

To an ice-cold 40% solution of potassium carbonate, 25 g. of ethyl thioimidopropionate hydrochloride was added. The free base was extracted in ether and the ether solution dried slightly over sodium sulfate and filtered. Hydrogen sulfide was passed into this solution at 0–5° for three hours. At first some solid ammonium sulfide separated and then disappeared as an aqueous layer separated. The reaction mixture was allowed to stand overnight, washed three times with water, dried over sodium sulfate and distilled. A very small amount of ethyl dithiopropionate distilled but the main portion boiled at 97° at 1–2 mm. and solidified on cooling. The yield was 7 g. (48%) of thiopropionamide, m.p. 41–42°. The literature[11] reports the melting point as 41–43°.

Anal. Calcd. for C_3H_7SN: N, 15.71. Found: N, 15.71.

This amide is soluble in water, ether, toluene and carbon tetrachloride. It is somewhat soluble in low boiling petroleum ether and cyclohexane.

Infrared Spectra.—The spectra were obtained employing a Perkin–Elmer model 21 double beam infrared spectrophotometer equipped with sodium chloride optics. All samples except thiopropionamide and thioacetylpiperidine were examined as liquid films; the latter were prepared by melting the solid between two sodium chloride plates and allowing the material to crystallize.

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[22] J. F. Arens and J. P. Wibaut, *Rec. trav. chim.*, **61**, 452 (1942).

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Triarylaminium Salt Free Radicals[1]

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A series of tri-*para*-substituted triarylamines has been prepared, and oxidized to the corresponding free radical triarylaminium ions. The products have been isolated as the perchlorates. Some properties of this family of stable free radicals are described.

Nearly 30 years ago, Weitz and Schwechten[2] reported the oxidation of solutions of tri-*p*-tolylamine to a deep blue product which they isolated as a perchlorate and a picrate. They also obtained a blue–green color on oxidation of tris-(*p*-aminophenyl)-amine, and a transient blue color with triphenylamine, but did not isolate reaction products in these cases. They suggested that their blue substances were free radical cations, and proposed the name aminium salt for compounds of this type. They also suggested that the blue tribromides prepared earlier by Wieland from tri-*p*-anisylamine[3a] and tri-*p*-tolylamine[3b] were aminium salt perbromides.

Their proposed structure for the blue oxidation product from tritolylamine has been verified by physical measurements. Walden and Birr[4] showed that the perchlorate in nitrobenzene has the conductivity of a strong electrolyte, with the blue ions migrating to the cathode. Katz[5] and Rumpf and Trombe[6] confirmed that the substance is a free radical by measurements of magnetic susceptibility. Finally, Granick and Michaelis[7] showed by potentiometric titration that conversion of amine to aminium ion involves loss of one electron.

More recently, the preparation of two other arylaminium perchlorates has been reported. Kuhn and Kainer[8] have made pentaphenylpyrrolium perchlorate, and Chu and Weissman[9] have prepared the triphenylaminium salt. Neither of these substances has been isolated in the pure state, and neither is stable in air. In contrast, tri-*p*-tolylaminium perchlorate was prepared using normal techniques which involved exposure to air, and was reported to be stable in the dry state "for several days." The research reported here was prompted by a need for a series of free radicals suitable for physical measurements. The available information suggested that such a series of tri-*para*-substituted amininium salts might be prepared, and might be sufficiently stable for convenient manipulation.

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[1] The major part of this work was carried out at Rutgers University with the support of the Office of Naval Research, under contract N7 onr 45403.

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