Meso-ionic Compounds of the 1, 3-Dithiole Ring System[1]

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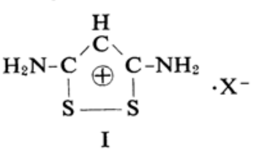
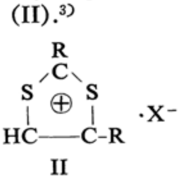
In connection with the research on the 1, 2- and 1, 3-dithiole ring systems, it has been reported that the oxidation of dithiomalonamide with hydrogen peroxide in the presence of the appropriate acid gives 3, 4-diamino-1, 2-dithiolyl salt (I)[2] and that the dehydration of phenacyl or acetonyl carbodithioate with hydrogen chloride gives 1, 3-dithiolium salts (II).[3]



I



II

In a previous paper,[4] we reported that a new type of meso-ionic compounds containing two sulfur atoms in a ring, which were referred to as dithiolone imine salts, was prepared by the action of hydrogen chloride or acyl chlorides on cyanomethyl dithiobenzoate. The object of this paper is to describe the synthesis of dithiolone, which has an exocyclic oxygen atom instead of a nitrogen atom of dithiolone imine salts, and the properties of dithiolone imine salts.

It has been reported that *N*-thiobenzoylsarcosine under goes ring closure in hot acid anhydrides to give meso-ionic compounds, ψ-4-acyl-3-methyl-2-phenylthiazol-5-one.[5] As the

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1) This paper is Part XX of Studies on Meso-ionic Compounds.

2) K. A. Jensen, H. R. Baccaro and O. Buchardt, *Acta Chem. Scand.*, **71**, 163 (1963).

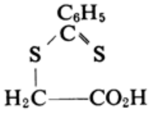
3) D. Leaver and W. A. H. Robertson, *Proc. Chem. Soc.*, **1960**, 252.

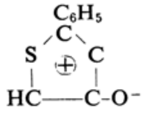
4) M. Ohta and M. Sugiyama, This Bulletin, **36**, 1437 (1963).

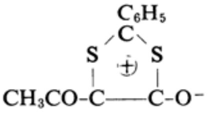
5) A. Lawson and C. E. Searle, *J. Chem. Soc.*, **1957**, 1556.

formation of a meso-ionic ring occurred between thiocarbonyl and carboxyl groups, a ring closure may be expected with carboxymethyl dithiobenzoate. Carboxymethyl dithiobenzoate was prepared by the action of chloroacetic acid upon potassium dithiobenzoate prepared from benzotrichloride and potassium sulfide by the elimination of potassium chloride.[6]

When carboxymethyl dithiobenzoate (III) was heated in acetic anhydride for several hours, a pale red substance which could not be purified was isolated. The treatment of III with acetic anhydride in the presence of triethylamine or pyridine led to tar formation.

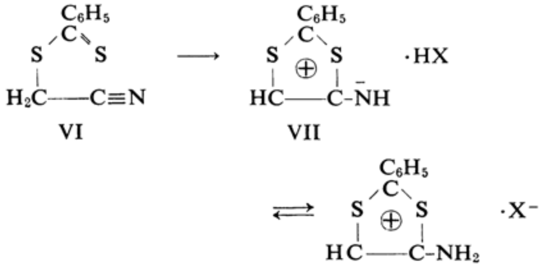

III


IV


V

It is well known that acetic anhydride, in the presence of boron trifluoride, is a strong acetylating agent,[7] but the formation of a meso-ionic ring with this reagent has not been reported.

When carboxymethyl dithiobenzoate (III) was treated with acetic anhydride at 60°C in the presence of a catalytic amount of boron trifluoride etherate, a red substance with an empirical formula, $C_9H_6OS_2$, was isolated. The compound was unchanged on treatment with hot acid or cold alkali, but when treated with hot alkali it decomposed to give a substance of an unknown structure. The analytical results and the infrared spectrum of the compound suggested that it was not acetylated 2-phenyldithiolone (V), but 2-phenyldithiolone (IV). Attempts to prepare the corresponding 2-benzyl derivative were unsuccessful. The treatment of *S*-thiophenacyl thioglycolic acid with acetic anhydride, or with acetic anhydride and boron trifluoride etherate, led to tar formation. It has been expected that an increased charge distribution provided by the phenyl substituent would stabilize the dithiolone ring.


VI VII VIII

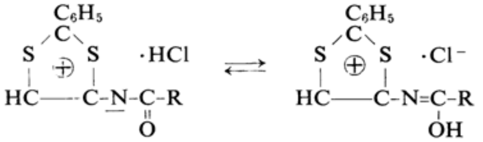
VIIa, $X=NO_3$
VIIb, $X=HSO_4$

The preparations of cyanomethyl dithiobenzoate and of 2-phenyldithiolone imine picrate, *N*-acetyl- and *N*-benzoyl-2-phenyldithiolone imine hydrochlorides were reported in a previous paper.[4]

When a benzene solution of cyanomethyl dithiobenzoate (VI) was treated with an excess of nitric acid and sulfuric acid, the nitrate (VIIa) and the hydrogen sulfate (VIIb) of 2-phenyldithiolone imine crystallized out in 50% and 60% yields respectively. The nitrate is in the form of orange plates and is slightly soluble in water, alcohol and acetone, but insoluble in benzene, ether and chloroform. Dithiolone imine salts are stable towards acids, but a trace amount of even a weak base causes its instant decomposition. An attempt to prepare the corresponding 2-benzyl derivative was unsuccessful owing to the failure to obtain cyanomethyl dithiophenylacetate.

Infrared spectra show that the cation (VII) may be considered to be an amino derivative of the pseudoaromatic ring system isosteric with the dithiolyl cation, it is probable that the phenyl substituent stabilizes the dithiolone imine salts.

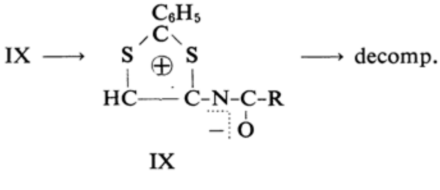
By the action of acyl chlorides, e.g., propionyl chloride, (β-carbomethoxy)propionyl chloride and (δ-carbomethoxy)valerianyl chloride, upon VI, the corresponding *N*-acyl derivatives crystallized out, as in the case of benzoyl and acetyl chlorides.[4]


IX X

IXa, $R=CH_2CH_3$
IXb, $R=(CH_2)_2CO_2CH_3$
IXc, $R=(CH_2)_4CO_2CH_3$

The infrared spectrum indicates that they exist, at least in part, in the enolic forms (X).

When the *N*-acyl salts (IX) were treated with a weak base, e.g., sodium hydrogen carbonate or ammonia, free bases (XI) were formed, but when they were treated with a strong base, decomposition occurred.


IX

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[6] J. C. Crawholl and D. F. Elliott, ibid., **1951**, 2071.
[7] V. G. Yashunskii and V. F. Vasil'eva, *Doklady Akad. Nauk. U. S. S. R.*, **130**, 350; *Chem. Abstr.*, **54**, 10999 (1960).

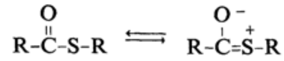
TABLE I. CHARACTERISTIC INFRARED SPECTRA OF DITHIOLONE AND DITHIOLONE IMINE SALTS*

2-Phenyldithiolone	3050w, 1690s, 1590s, 1570s, 1490m, 1450m, 1135m, 1045m, 755m, 735m, 695m, 685m.
2-Phenyldithiolone imine picrate	3350s, 3100s, 1635s, 1600m, 1560s, 1515s, 1500s, 1465m, 1360s, 1335s, 1240s, 1080m, 775m, 710m.
2-Phenyldithiolone imine nitrate	3210s, 3100s, 2920w, 1615s, 1595m, 1520s, 1390s 1295s, 770s, 765s, 750m.
2-Phenyldithiolone imine hydrogen sulfate	3210s, 3100s, 3050w, 2920w, 1615m, 1595w, 1520s, 1455m, 1295m, 1225s, 1195s, 770s, 765s.
N-Acetyl-2-phenyldithiolone imine hydrochloride	3400m br, 3075m, 3050m, 2780s, 2700s, 1670s, 1585m, 1545s, 1475s, 1450s, 1370s, 1285m, 1230m, 1010m, 765s, 680m.
N-Propionyl-2-phenyldithiolone imine hydrochloride	3400m br, 3050m, 2780s, 2650s, 1675s 1590w, 1550s, 1470s, 1460s, 1450m, 1370s, 1280s 1195s, 1170s, 760s, 675s.
N-Benzoyl-2-phenyldithiolone imine hydrochloride	3400m br, 3050s, 2825s, 2670s, 1645s, 1540s, 1540s, 1507s, 1468s, 1450s, 1305s, 1290s, 1240m, 1190m, 1175m, 835s, 760s, 710s, 670s.
N-(β-Carbomethoxy) propionyl-2-phenyldithiolone imine hydrochloride	3400m br, 3050, 2800s, 2675s, 1725s, 1675s, 1585w, 1540s, 1470s, 1280s, 1215s, 1155s, 765m, 680m.
N-(δ-Carbomethoxy) valerianyl-2-phenyldithiolone imine hydrochloride	3400m br, 3020m, 2900w, 2775m, 2600s, 1715s, 1670s, 1580w, 1435s, 1270s, 1150s, 760m, 670m.

* Taken on an EPI-S2 Model manufactured by Hitachi Ltd. by KBr tablets and are reported in wave numbers.

s: strong, m: middle, w: weak, br: broad

The frequencies of the infrared absorption bands of the dithiolone imine salts, related compounds and the dithiolone (IV) are shown in Table I. The spectrum of the dithiolone (IV) shows the characteristic strong bands at 1690, 1590 and 1570 cm^{-1} and differs from the spectrum of carboxymethyl dithiobenzoate. The absorptions, ranging between 3000 and 2500 cm^{-1}, and 1710 cm^{-1}, due to the COOH stretching and deformation, disappear in the spectrum of the dithiolone. Bellamy suggested[8] that the C=O absorption of thiols appeared at 1680 ± 10 cm^{-1} as a result of the resonance, as is shown below:



$$R-\overset{O}{\overset{\|}{C}}-S-R \rightleftharpoons R-\overset{O^-}{\overset{|}{C}}=\overset{+}{S}-R$$

Accordingly, the absorption of the dithiolone (IV) at 1690 cm^{-1} may, with great certainty, be assigned to the polarized C=O band. The strong band at 1590 cm^{-1} in the spectrum of carboxymethyl dithiobenzoate is assigned to a phenyl absorption. The strong band at 1570 cm^{-1} may be ascribed to a vibration of the aromatic ring system which disappears in the spectrum of the dithiobenzoate (III) and is comparable with the absorption at 1520 cm^{-1} in the spectra of dithiolone imine salts.

The spectra of the picrate, nitrate and hydrogen sulfate are practically identical, they all show a very strong band at ca. 1520 cm^{-1}. This band may be ascribed to the vibrations of the aromatic ring system and should be compared with the two strong bands of the dithiolyl cation at 1515 and 1530 cm^{-1}. The absorptions at 3210, 3100 and 1615—35 cm^{-1} are assigned to NH_2 stretching and deformation frequencies, they are very similar to the absorptions of the dithiolyl salts. A characteristic feature of the spectra of *N*-acyl hydrochlorides is the appearance of broad bands at ca. 3400 cm^{-1} and at 1150—75 cm^{-1}. These absorptions are assigned to the OH group and show that acylamino groups are present in part in the enolic form, R-C(OH)=N-. The spectra of *N*-acyl hydrochlorides also show a very strong band due to C=O stretching at 1645—75 cm^{-1}. The spectra of the *N*-(β-carbomethoxy)propionyl and *N*-(δ-carbomethoxy)valerianyl hydrochlorides, show in addition, strong ester absorptions at 1725 and 1715 cm^{-1} respectively.

Experimental

2-Phenyldithiolone (IV).—In 100 ml. of acetic anhydride, 12.75 g. of carboxymethyl dithiobenzoate (III) was dissolved with heat; then 5 ml. of boron trifluoride etherate was added to the mixture, and the resulting mixture, was stirred for an hour below 60°C. After it had cooled, the mixture was poured onto 500 g. of ice, and the precipitate which separated out was collected, washed with water and dried. Recrystallization of the precipitate from chloroform-ether gave red needles (4.9 g., 42%), m. p. 185—186°C (decomp.).

Found: C, 55.68; H, 3.30; S, 32.73. Calcd. For $C_9H_6OS_2$: C, 55.67: H, 3.09: S, 32.91%.

2-Phenyldithiolone Imine Nitrate (VIIa).—The preparation of cyanomethyl dithiobenzoate was described in a previous paper.[4] Forty-eight grams of

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[8] L. J. Bellamy and P. E. Rogasch, *J. Chem. Soc.*, **1960**, 2218.

crude cyanomethyl dithiobenzoate was dissolved in 100 ml. of benzene to a total volume of 160 ml. (solution A), and the solution was then dried over anhydrous sodium sulfate. A solution of 3.5 g. of nitric acid (65% conc.) in 10 ml. of ethanol was vigorously stirred, drop by drop, into 20 ml. of solution A while the mixture was being cooled with an ice bath, orange plates (3.9 g., 50%) crystallized out. Recrystallization from ethanol - ethyl acetate gave orange plates, m. p. 130.5°C (decomp.).

Found: C, 41.86; H, 3.18; N, 10.75. Calcd. for $C_9H_8N_2O_3S_2$: C, 42.19; H, 3.13; N, 10.94%.

2-Phenyldithiolone Imine Hydrogen Sulfate (VIIb).—To 20 ml. of solution A, a solution of 4.5 g. of sulfuric acid in 20 ml. of ethanol was added with vigorous shaking, the temperature of the mixture rose gradually and gave a red oil which, on cooling, gave a red precipitate. The recrystallization of the separated precipitate (5.5 g., 62%) from ethanol gave red-orange needles, m. p. 152—154°C (decomp.).

Found: C, 37.07; H, 3.52; N, 4.81. Calcd. for $C_9H_9NO_4S_3$: C, 37.11; H, 3.19; N, 4.81%.

***N*-Propionyl-2-phenyldithiolone Imine Hydrochloride (IXa).**—To 20 ml. of solution A, 4.6 g. of propionyl chloride was added drop by drop while the solution was cooled and shaken; the mixture was then kept standing for a day. The recrystallization from ethanol of the precipitate (4.7 g., 59%) gave yellow needles, m. p. 215—216°C (decomp.).

Found: C, 50.67; H, 4.28; N, 5.12. Calcd. for $C_{12}H_{12}NOS_2Cl$: C, 50.35; H, 4.20; N, 4.90%.

***N*-(β-Carbomethoxy)propionyl-2-phenyldithiolone Imine Hydrochloride (IXb).**—The treatment of 20 ml. of (β-carbomethoxy)propionyl chloride by a procedure similar to thas described above gave a yellow precipitiate (4.6 g., 49%). The recrystallization of the precipitate from ethanol gave yellow needles, m. p. 186°C (decomp.).

Found: C, 48.83; H, 4.97; N, 3.98. Calcd. for $C_{14}H_{14}NOS_2Cl$: C, 48.84; H, 4.07; N, 4.07%.

***N*-(δ-Carbomethoxy)valerianyl-2-phenyldithiolone Imine Hydrochloride (IXc).**—The recrystallization from ethanol of the yellow precipitate (3.7 g., 36%) obtained from the treatment of 20 ml. of solution A with 6.5 g. of (δ-carbomethoxy)valerianyl chloride in a procedure similar to that used in the experiment with IXa, gave yellow needles, m. p. 196°C (decomp.).

Found: C, 51.27; H, 4.84; N, 4.05. Calcd. for $C_{16}H_{18}NO_3S_2Cl$: C, 51.61; H, 4.84; N, 3.76%.

The preparations of 2-phenyldithiolone imine picrate, *N*-acetyl-2-phenyldithiolone imine and *N*-benzoyl-2-phenyldithiolone imine hydrochlorides were reported in a previous paper.4)

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