

Studies of Thioacids and Their Derivatives

VIII. On Dithiolyl Salts and Related Compounds

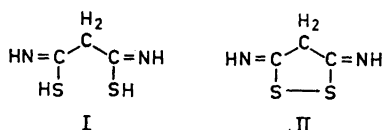
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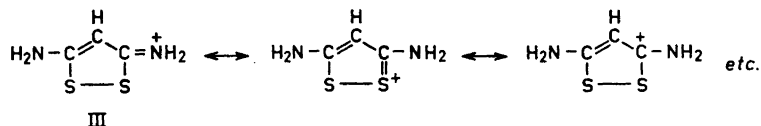
By the oxidation of dithiomalonamide and C-monoalkyldithiomalonamides ionic 3,4-diamino-1,2-dithiolyl salts are formed. From a consideration of the chemical properties and infrared spectra of these compounds it is concluded that these ions may be considered as pseudoaromatic structures. Analogous 3,5-diamino-1,2,4-dithiazolyl salts are formed by oxidation of dithiobiuret. The structures of some other compounds which may be considered as dithiolyl or dithiazolyl compounds have been discussed.

DITHIOLYL CATIONS

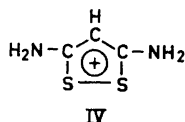
In connection with other researches on dithiocarboxylic acids it was attempted to oxidize dithiomalonamide (I) to a derivative of the heterocyclic ring dithiolane. The oxidation proceeded smoothly but the isolated compound had not the properties of a salt of diiminodithiolane (II):



This compound would be expected to form di-iminium salts with 2 equivalents of acid, but the isolated salt contained only one equivalent of acid and did not add more acid, even in the presence of excess of strong acids. The chemical properties of these salts and their infrared spectra suggest that the ion is derived not from dithiolane but from the unsaturated ring-system dithiole:



Accordingly the ion may in fact be considered as a diamino derivative of a pseudoaromatic ring-system, isosteric with the "tropylium" ion:



This result was communicated in a lecture to The Royal Danish Academy of Science in 1956¹. Independently Schmidt prepared the same ring-system. Since Schmidt has already published his results² we shall in the following mainly report on some results which supplement those of Schmidt.

We first called these salts dithiolonium salts. Schmidt calls them dithylium salts, but as the ions are not radicals with an odd number of electrons the ending "ylium" is misleading. According to a well established nomenclature rule the addition of a proton to a base is indicated by adding -ium to the name of the base (with elision of the final e); a cation derived by addition of a proton to the ring system dithiole should therefore be called the dithiolium ion, and the ion here discussed could be called the dehydrodithiolium ion or dithiolonium ion. However, after careful considerations of the general problem of the nomenclature of organic cations we have chosen the name dithiolylium cation as the most rational one. As expressed in the Report of the I.U.P.A.C. Commission on the Nomenclature of Inorganic Chemistry (Section 2) it seems impossible to introduce the distinction between ionic and covalent compounds into a consistent system of nomenclature, because the line of demarcation between the two categories is not sharp.

In a recent publication Klingsberg²² has reported on the preparation of salts of the parent dithiolylium cation. However, in this paper the ion has been called the dithiolium ion, although it is actually a dehydrodithiolium ion.

In the same way as Schmidt we first isolated the iodide by oxidation of dithiomalonamide with iodine. The corresponding chloride, bromide, nitrate and perchlorate were isolated by oxidation of dithiomalonamide with iron (III) chloride, bromide, nitrate, perchlorate, respectively, or by oxidation of dithiomalonamide with hydrogen peroxide in the presence of the appropriate acid.

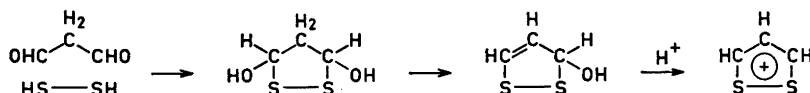
All these salts form colourless crystals, rather slightly soluble in water (1–3 g in 100 ml at room temperature) with neutral reaction. The electric conductivity of the aqueous solutions shows that they are completely dissociated strong electrolytes.

The structure proposed for the dithiolylium salts on the basis of these chemical properties is strongly supported by the infrared spectra discussed below.

By treatment of an aqueous solution of a dithiolylium salt with hydrogen sulfide it is smoothly reduced to dithiomalonamide, identified by analysis and infrared spectrum.

By addition of sodium hydroxide to an aqueous solution of a dithiolylium salt a precipitate is formed consisting of impure dithiomalonamide. On recrystallisation from ethanol pure dithiomalonamide was obtained, the infrared spectrum being identical in all details with that of an authentic sample of dithiomalonamide. Obviously a redox reaction takes place when the solution is made alkaline. It has not been possible to identify the other substances formed, but the infrared spectrum of the crude product shows the characteristic nitrile band at 2260 cm⁻¹, indicating that it also contains cyanothioacetamide.

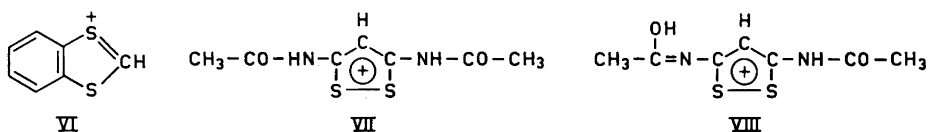
Several experiments were carried out to prepare salts of the basic dithiolyl ion by condensation of hydrogen disulfide with malonaldehyde diacetal in the presence of a strong acid. The reaction might be visualized to take the following course:



However, only sulfur and a polymeric substance could be isolated. Equally unsuccessful were attempts to prepare: 1) the dithiolyl ion by oxidation of propane-1,3-dithiol in the presence of a strong acid; 2) the corresponding dimethyldithiolyl salts from acetylacetone and hydrogen disulfide; 3) aminodithiolyl salts from propiolonitrile and hydrogen disulfide; 4) dihydroxydithiolyl salts from malonyl chloride and hydrogen disulfide, by oxidation of dithiomalonic acid, or by reaction of a diaminodithiolyl salt with nitrous acid. This may be taken as an indication that the iminium resonance structure (III) plays a rôle in stabilising the dithiolyl ion. However, the lack of success in the experiments with hydrogen disulfide may also be caused by the instability of this compound, since even malonodinitrile did not react with hydrogen disulfide with the formation of diaminodithiolyl salts.

The 1,3-dithiolyl ion is known in the form of a benzoderivative, prepared previously in 1926 by Hurltley and Smiles³ and formulated as a sulfonium ion (VI).

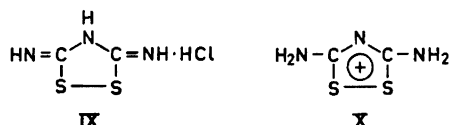
It is remarkable that the diaminodithiolyl ion can be diacetylated without losing its aromatic character. The chloride of the diacetylated ion (VII) is an ionic compound with similar properties to those of the diamino compound. Infrared spectra indicate that it is at least in part present in an enolic form (VIII).



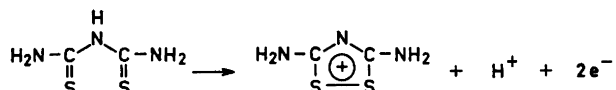
C-Monoalkyl- or arylthiomalonamides are oxidised in the same way as dithiomalonamide. We have prepared salts of the 4-ethyl-, 4-benzyl- and 4-phenyl-3,5-diaminodithiolyl ion. The phenyl derivative has also been described by Schmidt². The behaviour of a disubstituted dithiomalonamide is very different. Dimethyldithiomalonamide is oxidised by iodine or hydrogen peroxide with instantaneous formation of sulfur. From the filtrate dimethylmalonamide could be isolated in almost quantitative yield. This strongly supports the assumption that the diamino-1,2-dithiolyl ion has the structure IV and that the salts isolated are not simply salts of diiminodithiolane.

DITHIAZOLYL CATIONS

By oxidation of aryldithiobiurets dithiazole derivatives, known as "thiurets", were obtained a long time ago ⁴. Preisler and Bateman ⁵, in 1947, prepared the unsubstituted compound by oxidation of dithiobiuret with hydrogen peroxide and formulated it as the hydrochloride of diiminodithiazole (IX).

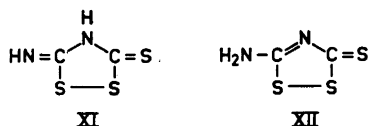


However, this compound and the thiurets form salts with only one equivalent of acid, and it therefore seems plausible that the basic ion is rather the diaminodithiazolyl ion (X), formed by the reaction:



Actually the chloride has properties quite similar to the dithiolyl salts and its infrared spectrum is only compatible with the formulation of the ion as the diaminodithiazolyl ion. That the ion (X) has the diamino and not an amino-imino structure has already been shown by Foss and Tjomsland ²³ who determined the crystal structure of the iodide by X-ray methods. We have only investigated the unsubstituted ion, but there seems to be no reason to doubt that the thiurets should be formulated in a similar way.

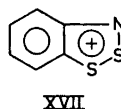
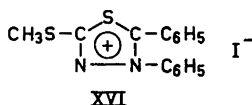
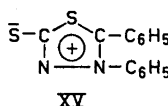
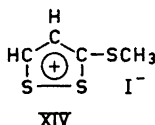
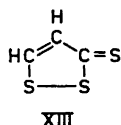
A related substance is the solid compound formed by decomposition of thiocyanic acid and known by the old name "xanthane hydride" ⁶. It has been formulated as an iminodithiazolinethion (XI), but here again the infrared spectrum is in accordance with the pseudoaromatic structure (XII).



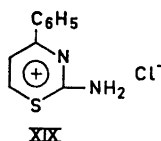
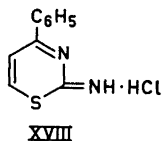
Accordingly "xanthane hydride" is analogous to the "trithiones" of Böttcher and Lüttringhaus ⁷, derivatives of dithiolethion (XIII), which recently have been studied extensively by various authors ⁸⁻¹². From considerations of the dipole moments and infrared spectra Mecke and Lüttringhaus ¹³ concluded that the basic ring-system has a decidedly aromatic character. The trithiones readily add methyl iodide and although the compounds so formed have been described simply as methyl iodide adducts, it is evident that they are actually methylmercapto-1,2-dithiolyl salts (XIV); Böttcher has also formulated them in a similar way. Contrary to our expectation xanthane hydride did not combine with methyl iodide.

There is no fundamental difference between the trithiones or xanthane hydride and the thiadiazole and triazole derivatives which were earlier considered to be "endo-compounds", but which were shown by measurement of their dipole moments to have a mesoionic structure (Jensen and Friediger¹⁴). These compounds add methyl iodide forming thiadiazolyl and triazolyl ions, *e.g.* "endothio-diphenylthiadiazoline" (XV) forms methylmercaptodiphenylthiadiazolyl iodide (XVI).

Derivatives of a 1,2,3-dithiazolyl ion are the so-called "Herz compounds"¹⁵. The ionic character of these compounds is well known, but they have been considered either as "benzo-1,3-thiaza-2-thionium" or "benzo-2,3-thiaza-1-thionium" ions¹⁶. There is, however, no reason to think that the charge should be located on one of the sulfur atoms, so the correct name would seem to be benzo-1,2,3-dithiazolyl ion (XVII).



Finally it should be mentioned that Cavallito, Martini and Nachod¹⁷ have prepared a substance to which they assign the structure of 2-imino-1,3-thiazine hydrochloride (XVIII), but which we would consider as a salt of the pseudo-aromatic thiazinyl ion (XIX). A study of other compounds of this type is in progress.



DISCUSSION OF THE INFRARED SPECTRA

The frequencies of the infrared bands of the dithiolyl salts and related compounds are shown in Table 1. The spectra are remarkably simple, showing only a few strong bands. They all show a very strong band with two peaks at 1515 and 1530 cm^{-1} . This band may be ascribed to vibrations of the aromatic ring system and should be compared with the strong band of the "tropylium" ion¹⁸ at 1477 cm^{-1} and the benzene band at 1485 cm^{-1} . Saturated solutions of the chloride in water and deuterium oxide show a very pronounced single band at 1530 and 1535 cm^{-1} , respectively, when the absorption of the solvent is compensated by the double beam technique.

This band does not appear in the spectrum of dithiomalonamide, but this shows a strong band at 1445 cm^{-1} which is practically missing in the spectra of the dithiolyl salts. Nor do the latter contain bands which could be ascribed to aliphatic $\text{C}=\text{C}$ or $\text{C}=\text{N}$ groups. The infrared spectra of dithiomalonamide and other thioamides will be discussed in another paper²⁴.

The spectra of the chloride, bromide, nitrate and perchlorate are practically identical. Most bands listed in Table 1 are strong bands. The weak band at 1430 cm^{-1} may be ascribed to the tautomeric dithiolanyliminium ion or to traces of dithiomalonamide formed by reduction of the dithiolyl salt. The absorptions at 3280, 3140, 1650, and 1625 cm^{-1} which occur at almost the same place in the spectrum of dithiomalonamide are assigned to NH_2 stretching and deformation frequencies.

The strong band at 1370 cm^{-1} in the spectra of the dithiolyl salts corresponds to a band at $1330\text{--}1360\text{ cm}^{-1}$ in the spectrum of dithiomalonamide and may with great certainty be assigned to $\text{C}-\text{N}$ vibration. A rather pronounced band at 1263 cm^{-1} in the spectra of the unsubstituted ion is missing in the spectra of the ions substituted in the 4-position. Its origin may be a ring-CH deformation. The strong band at 775 cm^{-1} is probably due to the symmetric wagging of the NH_2 groups.

The spectrum of the dithiolyl iodide differs a little from the spectra of the other salts, the bands at 775, 1370, 1430, 1625, and 1650 cm^{-1} being shifted to 793, 1350, 1400, 1590, and 1612 cm^{-1} ; further it contains a sharp band at 3360 cm^{-1} which is only indicated as a shoulder in the spectra of the other salts. These shifts are probably due to an electrostatic interaction between the dithiolyl ion and the large iodide ion, by which especially the NH frequencies are influenced. The bands at $1515\text{--}1530\text{ cm}^{-1}$ and 1263 cm^{-1} are unchanged.

The spectra of the 3,5-diamino-4-ethyl-1,2-dithiolyl ion and the 3,5-diamino-1,2,4-dithiazolyl ion are very similar to the spectrum of the 3,5-diamino-1,2-dithiolyl ion, showing very strong bands near 1600 and 1500 cm^{-1} and a rather strong band near 1370 cm^{-1} . The spectra of 3,5-diacetyldithiolyl and 3,5-diacetylamino-4-ethyldithiolyl ions also show the very strong "aromatic" band at ca. 1500 cm^{-1} and a $\text{C}-\text{N}$ band at 1370 cm^{-1} , but here, of course, the strong band due to NH_2 deformation is missing and instead the spectra show strong $\text{C}=\text{O}$ absorption at $1680\text{--}1690\text{ cm}^{-1}$. A characteristic feature of the spectra of the diacetylated ions is the appearance of a strong band at ca. 1200 cm^{-1} and a broad band at 3400 cm^{-1} . These are assigned to an OH group and show that one of the acetylamino groups is present in the enolic form, $\text{CH}_3\text{C}(\text{OH})=\text{N}-$. Accordingly the spectrum should also show $\text{C}=\text{N}$ absorption and this is probably indicated by a shoulder at 1625 cm^{-1} on the strong $\text{C}=\text{O}$ band.

The spectrum of dithiobiuret displays two $\text{C}-\text{N}$ bands (at 1340 and 1400 cm^{-1}) because the molecule contains two different $\text{C}-\text{N}$ bonds, and it shows two "thioamide bands" (*cf.* the forthcoming paper¹⁹) at 1560 and 1485 cm^{-1} , in addition to the NH_2 bands at 1651 and 1630 cm^{-1} . On oxidation to the dithiazolyl ion the two "thioamide bands" and one of the CN bands disappear and are replaced by the strong "aromatic" band in accordance with the postulated structural change.

The infrared spectrum of 3-amino-1,2,4-dithiazole-5-thion ("xanthane hydride") is very similar to the spectrum of the dithiolyl ion. It shows an intense "aromatic" band at 1510 cm^{-1} and a strong band at 1630 cm^{-1} , which proves that this compound contains an $-\text{NH}_2$ group; two weak bands at 2680 cm^{-1} and 1695 cm^{-1} seem, however, to indicate that the tautomer 3-imino-5-mercapto-1,2,4-dithiazole is present to a certain extent. A very strong band at 1315 cm^{-1} correspond to a similar band in the spectra of the dithiolyl and dithiazolyl ions and is assigned to C—N vibration.

Table 1. Infrared spectra of dithiolyl and dithiazolyl salts.

3,5-Diamino-1,2-dithiolyl chloride	3280 s, 3140 s, 1650 m sh, 1625 s, 1530 s, 1515 vs, 1430 w, 1370 m, 1263 m, 1105 w, 773 m.
3,5-Diacetylamino-1,2-dithiolyl chloride	3400 m, 3130 sh, 3060 m, 3000 m, 2860 s, 2760 s, 2680 sh, 1685 s, 1615 w sh, 1565 m, 1490 vs, 1425 w sh, 1405 m, 1365 s, 1285 vs, 1235 m, 1183 s, 1037 w, 1000 m, 973 w, 950 w, 870 m, 855 m, 845 m, 783 w, 737 m, 678 s.
3,5-Diamino-4-ethyl-1,2-dithiolyl chloride	3260 s, 3120 vs, 1620 vs, 1485 vs, 1450 s, 1383 m, 1370 w, 1310 w, 1245 w, 1155 w br, 1065 vw, 853 w, 730 w,
3,5-Diacetylamino-4-ethyl-1,2-dithiolyl chloride	3400 m, 3130 m, 3050 s, 2900 s, 1690 vs, 1625 sh, 1475 vs, 1445 s sh, 1372 s, 1330 w, 1305 w, 1275 s, 1230 vs, 1205 s, 1115 m, 1073 w, 1035 w, 1000 m, 985 m, 895 w, 730 w, 673 m.
3,5-Diamino-4-phenyl-1,2-dithiolyl iodide	3250 s, 3120 s, 1600 vs, 1585 w, 1475 vs, 1437 s, 1390 m, 1320 w, 1070 w, 795 w, 745 m, 695 m.
3,5-Diamino-1,2,4-dithiazolyl chloride	3360 m, 3240 s, 3100 vs, 1635 s, 1610 s, 1535 w, 1490 vs, 1450 m sh, 1365 s, 1250 w br, 1035 s, 730 m.
3-Amino-1,2,4-dithiazole-5-thione	3210 s, 3040 s, 2690 w, 1630 s, 1510 s, 1315 vs br, 1235 m sh, 1150 w, 1085 m, 1005 s, 745 m.

EXPERIMENTAL

The infrared spectra were obtained with a Perkin-Elmer 21 B double beam spectrometer equipped with a rock-salt prism. In most cases the KBr disc technique was applied (300 mg KBr mixed with *ca.* 1 mg of the substance), but in some cases also the spectra of aqueous solutions of dithiolonium salts were investigated.

Dithiomalonamides

Dithiomalonamides were prepared as described by Lehr *et al.*¹⁹ In one case we obtained by this method a large yield (30 g from 32 g of malononitrile) of another substance with m.p. $118-119^\circ\text{C}$, after recrystallisation from water, and only a small amount (7 g) of dithiomalonamide. According to the infrared spectrum, which exhibits the characteristic nitrile band at 2260 cm^{-1} , and analysis this compound is cyanothioacetamide, $\text{NC-CH}_2\text{-CSNH}_2$. (Found: C 35.65; H 4.19. Calc. for $\text{C}_3\text{H}_4\text{N}_2\text{S}$: C 36.00; H 4.03. As shown by Schmidt the formation of cyanothioacetamide takes place when the solution is not sufficiently alkaline. The addition of pyridine and diethylaminoethanol as proposed by Schmidt represents without doubt an improvement of the method of Lehr *et al.*

Substituted dithiomalonamides were prepared from substituted malonodinitriles mainly by the same method as that used for the preparation of dithiomalonamide: 0.1 mole of the nitrile²⁰ was dissolved in 100–200 ml of anhydrous ethanol and *ca.* 0.01 mole of potassium ethoxide was added. Hydrogen sulfide was bubbled through the solution at a slight excess of pressure (at room temperature or, in the case of benzylmalononitrile, at 60°C) for 3–4 h. The solution was kept in a well closed bottle at room temperature for

12–24 h and the treatment was repeated once or twice. Finally the solution was cooled in a refrigerator and the crystals, which had separated, were filtered off.

Ethylthiomalonamide, $C_2H_5CH(CSNH_2)_2$. Yield 40 %. Recrystallised from water. M.p. 158–60°C. (Found: C 37.20; H 6.41; N 17.00; S 38.70. Calc. for $C_2H_5N_2S_2$: C 37.03; H 6.22; N 17.27; S 39.47).

Dimethyldithiomalonamide, $(CH_3)_2C(CSNH_2)_2$. Yield 45 %. Recrystallised from water. M.p. 188–90°C. (Found: C 37.00; H 6.28; N 17.03. Calc. for $C_3H_{10}N_4S_2$: C 37.03; H 6.22; N 17.27). On melting this compound splits off hydrogen sulfide and is transformed into *a-cyanothioisobutyramide*, $(CH_3)_2C(CN)CSNH_2$. M.p. 107.5–108.5 after two recrystallisations from heptane. (Found: N 22.06. Calc. for $C_5H_8N_2S$: N 21.87). The presence of a cyano group in this compound is shown by an infrared band at 2240 cm^{-1} .

Dimethyldithiomalonamide is oxidised by iodine or hydrogen peroxide with the formation of dimethylmalonamide: 0.8 g of the thioamide was suspended in 10 ml of 0.1 N hydrochloric acid and a slight excess of hydrogen peroxide was added. The oxidation proceeded with heat evolution and separation of elementary sulfur and the thioamide went into solution. The filtrate was evaporated to dryness and the residue was recrystallised from water. Yield 0.53 g = 82 %. M.p. 273–274°C (lit.²¹ 263°C). (Found: N 21.27. Calc. for $C_5H_{10}N_2O_2$: N 21.53).

Benzylthiomalonamide, $C_6H_5CH_2CH(CSNH_2)_2$. Yield 55 %. Recrystallised from ethanol. M.p. 197–200°C. (Found: C 53.30; H 5.31; N 12.56. Calc. for $C_{10}H_{12}N_2S_2$: C 53.57; H 5.39; N 12.50).

Phenylthiomalonamide, $C_6H_5CH(CSNH_2)_2$. Yield 80 %. Recrystallised from water. M.p. 166–68°C (decomp.). (Found: C 51.25; H 4.90; N 13.24. Calc. for $C_9H_{10}N_2S_2$: C 51.42; H 4.80; N 13.33).

1,2-Dithiolyl salts.

3,5-Diamino-1,2-dithiolyl iodide. Dithiomalonamide (1 g) was dissolved in hot water (150 ml) and at 70–80°C a solution of iodine (ca. 2 g) in ethanol (30 ml) was added until the solution was slightly yellow. A few drops of the solution of dithiomalonamide were added to give a colourless solution. The solution was concentrated *in vacuo* to 50 ml and cooled in ice. During the evaporation almost colourless crystals had separated. Yield almost quantitative. The salt was recrystallised from water. M.p. 185°C (decomp.). (Found: C 13.57; H 2.05. Calc. for $C_3H_5N_2S_2I$: C 13.86; H 1.94).

The following iodides were prepared in a similar way, only using ethanol as solvent for the thioamide:

3,5-Diamino-4-benzyl-1,2-dithiolyl iodide. Yield 5.4 g from 4.5 g of benzylthiomalonamide. Recrystallised from water. M.p. 262–63°C (decomp.). (Found: C 34.10; H 3.09; N 7.62. Calc. for $C_{10}H_{11}IN_2S_2$: C 34.23; H 2.86; N 8.00).

3,5-Diamino-4-phenyl-1,2-dithiolyl iodide. Yield 2.5 g from 2.1 g of phenylthiomalonamide. Recrystallised from water. M.p. 258–62°C (decomp.). (Found: C 32.15; H 2.82; N 8.48. Calc. for $C_8H_9IN_2S_2$: C 32.14; H 2.68; N 8.33).

3,5-Diamino-1,2-dithiolyl chloride.

(a) By oxidation with hydrogen peroxide: Dithiomalonamide (1 g) was shaken with 15 ml of hydrochloric acid and 1.5 ml of hydrogen peroxide (30 %). The thioamide dissolved after a short time and later colourless crystals of the chloride began to separate. Yield 1 g. Recrystallised from water. M.p.: decomposes at about 250°C. The salt contains water of crystallisation. (Found: C 19.07; H 3.76; Cl 34.70. Calc. for $C_3H_5ClN_2S_2 \cdot H_2O$: C 19.24; H 3.76; Cl 34.70).

(b) By oxidation with iron(III) chloride: To dithiomalonamide (1 g) dissolved in hot water (150 ml) an aqueous solution of the calculated amount of $FeCl_3 \cdot 6H_2O$ was added. The solution was concentrated *in vacuo* to 20 ml, filtered after addition of activated carbon and cooled in ice. Yield 1 g.

In the same way the bromide, nitrate and perchlorate were prepared from 1 g of dithiomalonamide and iron(III) bromide, nitrate and perchlorate, respectively.

Bromide: Yield 1.3 g, after recrystallisation from water 0.6 g. M.p. 190°C (decomp.). (Found: C 16.68; H 3.09. Calc. for $C_3H_5BrN_2S_2$: C 16.92; H 2.37).

Nitrate: Yield 1.4 g, after recrystallisation from water 0.8 g. M.p.: decomposes at about 230°C. (Found: C 18.20; H 2.64; S 32.80. Calc. for $C_3H_5N_3O_3S_2$: C 18.46; H 2.58; S 32.83).

Perchlorate: Yield 0.6 g after recrystallisation from water. M.p. 185–90°C (decomp.). (Found: N 12.02. Calc. for $C_5H_5ClN_2S_2O_4$: N 12.05).

These three salts were also prepared in the same way as the chloride, by oxidation of dithiomalonamide with hydrogen peroxide in the presence of the appropriate acid.

3,5-Diamino-4-ethyl-1,2-dithiolyl chloride. By oxidation of ethyl dithiomalonamide (1.6 g) with iron(III) chloride in the same way as the unsubstituted compound. Yield 1.6 g (80 %). M.p. 172–73°C. Recrystallised from water it contains water of crystallisation which is lost over P_2O_5 . (Found: C 30.55; H 4.50; N 14.08. Calc. for $C_5H_5ClN_2S_2$: C 30.52; H 4.58 N 14.25).

3,5-Diacetylamino-1,2-dithiolyl chloride. A suspension of the diamino compound (0.2 g) in acetic anhydride (1 ml) was refluxed for 1 h and after the addition of 1 ml ethanol and cooling the crystals were filtered off. Yield 0.23 g. Recrystallised from 80 % ethanol. Colourless crystals with m.p. 270°C (decomp.). (Found: C 33.55; H 3.93; N 11.25. Calc. for $C_7H_5ClN_2O_2S_2$: C 33.27; H 3.57; N 11.09).

In the same way was prepared:

3,5-Diacetylamino-4-ethyl-1,2-dithiolyl chloride. M.p. 270°C (decomp.). (Found: C 38.50; H 4.83; N 10.27; Cl 12.63. Calc. for $C_9H_{13}ClN_2O_2S_2$: C 38.50; H 4.63; N 9.99; Cl 12.61).

By addition of aqueous ammonia to a solution of this chloride in water a white solid separated. (100 mg from 150 mg of the chloride). It was collected and recrystallised from ethanol. According to the analysis it seems to be *3,5-Diacetylimino-4-ethyl-dithiolane*. (Found: C 44.40; H 5.02; N 11.31. Calc. for $C_9H_{12}N_2O_2S_2$: C 44.26; H 4.92; N 11.45).

Dithiazole derivatives.

3,5-Diamino-1,2,4-dithiazolyl chloride. Dithiobiuret (obtained through the courtesy of the American Cyanamid Company, New York) was recrystallised from 0.01 N hydrochloric acid and oxidised with hydrogen peroxide according to Preisler and Bateman⁵. Yield 9.8 g from 9 g dithiobiuret = 87 %. The product contains approximately 1/4 mole of water which is removed by heating at 110°C. (Found: C 13.80; H 2.62; N 24.01. Calc. for $C_2H_4N_3S_2 \cdot 1/4 H_2O$: C 13.79; H 2.59; N 24.14).

3-Amino-1,2,4-dithiazole-5-thione ("xanthane hydride") was prepared according to Klason⁶ and recrystallised twice from 60 % acetic acid. (Found: N 18.66. Calc. for $C_2H_2N_2S_3$: N 18.69). Decomposes at 247–255°C.

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