XCII.—*Thiocyanoacetone and its Derivatives and Isomerides.*

By JOSEPH TCHERNIAC.

THIOCYANOACETONE, $\text{SCN}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$, was first obtained by the action of monochloroacetone on barium thiocyanate in alcoholic solution (Helson and Tcherniac, *Ber.*, 1883, **16**, 349). Later it was found that the reaction takes place in the absence of alcohol when the crystallised barium salt is intimately mixed with monochloroacetone (Tcherniac, *Ber.*, 1892, **25**, 2623). Further investigation has shown that an aqueous solution of any thiocyanate of the alkalis (except that of ammonia) or of the alkaline earths can be used with advantage. As an example, the preparation by means of the sodium salt may be described.

To 92.5 grams (1 mol.) of monochloroacetone,* 191.4 c.c. (1.1 mols.) of a 46.55 per cent. solution of sodium thiocyanate were added, and the mixture was stirred for ten hours. The temperature rose about 25° , and a brown oil gradually separated. The whole product, oil and aqueous solution, was completely extracted with ether. The ethereal extract, which contained an appreciable quantity of dissolved thiocyanate, was shaken with successive quantities (10 c.c.) of water until the wash-water gave only a slight reaction with ferric chloride. The united washings, which contained some thiocyanoacetone, were reserved for addition to the following preparation before the ether extraction.

The ether was distilled off from a water-bath at the lowest temperature possible. Fifty c.c. of distilled water were added to the residue, and the whole was heated in a water-bath to $40\text{--}50^\circ$ under 14 mm. pressure. The water distilled over, carrying with it some chloroacetone and its impurities, together with a very small quantity of thiocyanoacetone (0.35 gram).

The residue was dried in a vacuum over sulphuric acid, and analysis showed it to be nearly pure thiocyanoacetone (108—109 grams = 95 per cent. yield).

Purification of Thiocyanoacetone.—Thiocyanoacetone cannot be distilled without decomposition in the ordinary vacuum of the water-pump—about 14 mm. (Tcherniac, *Ber.*, 1892, **25**, 2625). It distils, however, unaltered under a pressure of about 1 mm. A portion of the thiocyanoacetone prepared as above was placed in an Anschütz distillation flask with collar and sealed-on receiver.

* Prepared by Fritsch's method (*Ber.*, 1893, **26**, 597), using magnesia instead of marble, and carefully fractionated. It contained traces only of dichloroacetone.

Ground in the neck of the receiver were a U-tube filled with calcium chloride and potassium hydroxide, and a Hittorf tube. The apparatus was exhausted by means of a mercury pump, the flask being heated in a water-bath. With purple light in the Hittorf tube, most of the oil, evaporating from the surface without visible boiling, passed over at $73.5-74.5^{\circ}$, and was collected separately. The distillate was a highly refracting, colourless oil having D_{20}^{25} 1.1892. Analysis gave results showing close agreement with the formula C_4H_5ONS .

On keeping, especially in the light, the oil gradually became yellow, and finally dark-coloured.

Action of Hydrochloric Acid on Thiocyanacetone.

It has already been shown that dilute aqueous hydrochloric acid does not produce any great alteration in thiocyanacetone (Tcherniac, *Ber.*, 1892, **25**, 2618).

When 5 per cent. of its weight of hydrogen chloride is led into thiocyanacetone, kept cool, a crystalline magma is formed which liquefies on keeping. On extraction with ether, the thiocyanacetone is recovered apparently unaltered. A quite different result is obtained when the substance is saturated with hydrogen chloride.

Thiocyanacetone (115 grams:1 mol.) was saturated with hydrogen chloride (70 grams), the whole being cooled with running water. After the resulting magma had completely liquefied, the syrup was dissolved in 500 c.c. of water, and the solution extracted with ether. The latter left on distillation 70 grams of a pale brown oil, which was distilled under 14 mm. pressure from a water-bath, and gave 40 grams of a colourless distillate passing over at 69° .

In another preparation the solution was distilled in a current of steam instead of being extracted with ether, and gave half the weight of the thiocyanacetone taken.

The oil was washed with dilute sodium hydroxide solution, dried over calcium chloride, and distilled. By far the greater part passed over at $167-167.5^{\circ}/754.4$ mm.

Found: C=35.99; H=3.2; N=10.22; Cl=26.43. S=24.38.

C_4H_4NClS requires C=35.95; H=2.99; N=10.48; Cl=26.59; S=23.97 per cent.

Apparently this substance is 2-chloro-4-methylthiazole (I), a

homologue of 2-chlorothiazole (II) (Schatzmann, *Annalen*, 1891, **261**, 10), the boiling point of which is 144—144.5°

2-Chloro-4-methylthiazole is a colourless oil boiling at 167—167.5°/754.4 mm. and 69°/14 mm.; it has D_{15}^{15} 1.2992. It possesses a characteristic odour resembling that of pyridine, and slightly alkaline properties; thus, it dissolves in concentrated hydrochloric acid, but not in the dilute acid. It is comparatively stable; after boiling for twelve hours with a methyl-alcoholic solution of sodium methoxide, only one-twentieth of its chlorine was removed, and the bulk of the oil remained unaltered. In this respect it differs from chlorothiazole, which is said to retain the chlorine very loosely. This is not an isolated fact. The chemical behaviour of the members of the thiazole group is often so radically different from that of their methylated homologues (see Schatzmann, *loc. cit.*) that serious doubts must arise as to their analogy of structure.

It was found that of the 70 grams of hydrogen chloride absorbed by the thiocyanacetone, 14 grams had been consumed in the reaction

The residue from the distillation of the ethereal extract, together with the aqueous solution from which the oil had been extracted, after neutralisation with sodium carbonate and further extraction with ether, yielded 25 grams of "hydroxymethylthiazole" (after purification by crystallisation).

The action of alcoholic hydrogen chloride on thiocyanacetone will be described later.

Thiocyanacetone and Ammonia.

The so-called hydroxymethylthiazole, which was obtained accidentally by Hantzsch and Weber (*Ber.*, 1887, **20**, 3127) in an attempt to prepare thiocyanacetone, owed its formation to the circumstance that they had used sodium carbonate for salting out the thiocyanacetone. As has been shown (*Ber.*, 1892, **25**, 2619), all alkaline substances possess the power of converting thiocyanacetone into its isomeride. Aqueous ammonia produces exactly the same result. Hantzsch's statement (*Annalen*, 1888, **249**, 7) that the chief product of the action of ammonia on thiocyanacetone is aminomethylthiazole (thiocyanopropimine) is devoid of all foundation, as may be seen from the following experiments.

Thiocyanacetone (115 grams:1 mol.) was dissolved in 1500 grams of water, the solution cooled, and 50 c.c. of 20 per cent.

ammonia were added. Heat was evolved, and a yellow resin separated. After forty hours, the solution was filtered, and to the filtrate 172 c.c. of 25 per cent. hydrochloric acid were added, much carbon dioxide being evolved.

The acid solution was extracted with ether in the author's automatic apparatus (this vol., p. 1090), and the ethereal extract evaporated in the water-bath. The brown, syrupy residue was heated in a vacuum on the water-bath, when some water possessing the pungent odour of thiocyanic acid distilled over. The distillate gave the thiocyanate reaction and gradually deposited a small quantity of radially grouped yellow needles, which became dark at about 150° and decomposed at about 200° (perthiocyanogen?).

The residue from the distillation (63.5 grams) was boiled for some time with ether under a reflux condenser. After repeated crystallisations, about 25 grams of pure "hydroxymethylthiazole" were obtained from the solution, together with a small quantity of the yellow substance above-mentioned.

If any aminomethylthiazole had been formed, it must have remained in the hydrochloric acid solution which had been extracted with ether. This solution was therefore rendered alkaline with sodium hydroxide and completely extracted in the apparatus. The ethereal extract left on distillation 1.732 grams of a dark syrup only partly soluble in hydrochloric acid. The hydrochloric acid solution was filtered, warmed with animal charcoal to 50°, and again filtered. After several days, a black mud was deposited, which was filtered off. The filtrate was warmed with charcoal (0.5 gram) and again filtered. To the filtrate, hydrochloric acid was added, together with platinic chloride in excess, and the whole left to remain overnight, when the yellow precipitate was collected. When dry, it weighed 1.040 grams, proved insoluble in water or alcohol, and melted at about 220°. (Found: $\text{Pt}=30.36$. $(\text{C}_4\text{H}_6\text{N}_2\text{S}, \text{HCl})_2\text{PtCl}_4$ requires $\text{Pt}=30.34$ per cent.)

Assuming this to be pure double salt, it corresponds with 0.477 gram of aminomethylthiazole from 115 grams of thiocyanacetone. Moreover, as thiocyanate is formed in the reaction, there is no reason to think that even this minute quantity of the base owes its origin to anything more than the well-known action of ammonium thiocyanate on thiocyanacetone (Norton and Tcherniac, *Ber.*, 1883, **16**, 345).

In view of the foregoing results, Hantzsch's explanation (*loc. cit.*, p. 26; compare Beilstein, "Handbuch der organischen Chemie," IV, 518) of the formation of aminomethylthiazole (thiocyanopropimine), namely, that by the action of ammonium thiocyanate on chloroacetone, thiocyanacetone is first formed, and is

then converted by combination with free (!) ammonia into aminomethylthiazole, must be regarded as invalid.

The Isomerides of Thiocyanacetone: Hydroxymethylthiazole, or α -Methylrhodim.

For reasons to be stated later, the so-called hydroxymethylthiazole will henceforth be known as α -methylrhodim.

The author has shown (*Ber.*, 1892, **25**, 3648) how α -methylrhodim is best prepared from thiocyanacetone. The same method may be used for its preparation direct from chloroacetone.

To 92.5 grams of monochloroacetone, 1500 grams of water, 125 grams of potassium thiocyanate (or the equivalent amount of the sodium salt), and 30 grams of sodium hydrogen carbonate are added. The mixture is shaken from time to time and allowed to remain for ten days. A brown resin is gradually deposited, and the aqueous solution is filtered off and warmed to 45°. Twenty grams of animal charcoal are then added, and the mixture is left to remain for two hours and shaken from time to time. It is then filtered, and the filtrate extracted with ether in the apparatus. On an average, there accumulated in the flask containing the ether 33 grams of white needles, which, after being washed with ether, melted at 102–103°. From the ethereal solution, a further 14 grams were obtained, making in all 47 grams, that is, approximately 41 per cent. of the theoretical yield.

Instead of extracting with ether, a tedious operation in the absence of an automatically working apparatus, the aqueous solution can be evaporated in a vacuum from a water-bath, care being taken to keep the temperature of the bath below 60° until there remain about five parts of water for one of α -methylrhodim. On cooling, 75–80 per cent. of the substance will crystallise out, and the mother liquor may be further concentrated.

When less water or sodium hydrogen carbonate is used in the preparation, the yield is smaller.

Impure α -methylrhodim is best purified by recrystallisation from five times its weight of water at 55–60°. Thus, 41 grams of the crude product were dissolved in 205 grams of water, the solution being shaken with charcoal and filtered warm. The first crop yielded 32 grams of needles melting at 102–103°.

By utilising the mode of formation from ammonium thio-carbamate (observed by Marchesini, *Gazzetta*, 1893, **23**, ii, 442), the preparation of α -methylrhodim can be much more satisfactorily accomplished than by the above method. The way there followed, namely, heating in an alcoholic solution, is unsuitable as a method

of preparation. It required thorough modification to obtain from it a simple and practical method.

Ammonium thiocarbamate, $\text{NH}_2\cdot\text{CO}\cdot\text{S}\cdot\text{NH}_4$, is easily obtained pure by leading carbonyl sulphide into alcoholic ammonia cooled with ice. The gas is readily absorbed, and a white, crystalline powder is soon deposited, which is rapidly collected, washed with alcohol, and dried in a vacuum over sulphuric acid. Two hundred and fifty c.c. of 4.14 per cent. alcoholic ammonia yielded 18.82 grams of the dry salt.

The thiocarbamate (14.3 grams: about 0.15 mol.) was dissolved in a little water, ice added, and 12 c.c. of monochloroacetone (13.95 grams = 0.15 mol.) were mixed with the solution, and the flask was imbedded in ice. Soon a violent reaction took place, when the chloroacetone dissolved, the ice melting within the flask. The slightly yellow liquid was filtered, and the filtrate (74 grams) left to remain overnight. It set to a paste of yellowish needles (12.85 grams, dry) melting at $101\text{--}102^\circ$. From the filtrate 3.2 grams were obtained, the total of more than 16 grams representing a yield of 93 per cent. The product was easily purified by one crystallisation from water.

This result, compared with the complications attending the preparation from thiocycanoacetone, renders highly improbable the intermediate phase

suggested by Hantzsch and Weber (*Ber.*, 1887, **20**, 3128) as part of the mechanism of the isomerisation.

α -Methylrhodim and Methyl Sulphate: Dimethylrhodim.

α -Methylrhodim (115 grams: 1 mol.) was dissolved in 500 c.c. of 2*N*-sodium hydroxide, and 95 c.c. of methyl sulphate (1 mol.) were gradually added, cooling with water. The solution was extracted with ether in the apparatus. The ether left 122.6 grams of a yellow oil, which solidified on cooling. When dissolved in its own volume of water, it showed a lower critical solution temperature. The slightest warmth, even that of the hand, induced separation into two layers, which mixed again on cooling. The solution was shaken with 10 grams of charcoal, filtered, the turbid filtrate concentrated in a vacuum at 35° , when it became clear again, and the concentration continued until the solution in the distillation flask weighed 145 grams. (A small quantity of oil distilled over with the water.) To the cold solution a tiny crystal from a previous preparation was added, and the whole left over sulphuric acid in a vacuum. Large crystals were gradually formed and removed

from time to time. In all, 65 grams were collected and recrystallised from a small quantity of water.

In another preparation, the crude product remaining after the distillation of the ether was drained on the vacuum pump from the oil which it contained, and was then washed with ether.

A quantity of crude product (20 grams) which had been kept for two years and had become brown and viscid was purified in the following manner. It was dissolved in water with the addition of 20 c.c. of *N*-sodium hydroxide and extracted with ether. The extract was almost colourless, and the aqueous solution yellowish-brown. The ether was evaporated, and left 17.322 grams of oil which soon solidified, the temperature rising to 46°. The substance was dissolved in its own weight of water at 25°, and when the solution assumed the ordinary temperature (17°), a fragment of a crystal was added. Overnight, large crystals separated (10.359 grams, m. p. 48–49°), and from the mother liquor a further crop was obtained (5.4 grams).

The original yellowish-brown solution which had been extracted with ether was acidified with hydrochloric acid and again extracted. The ether left 1.442 grams of a yellowish-brown oil which did not crystallise.

It appears from the foregoing that it will simplify the purification to add sodium hydroxide to the aqueous solution containing the product of the interaction of the sodium salt of α -methylrhodim and methyl sulphate before extracting with ether.

The substance after repeated crystallisations reached a maximum melting point, and was then analysed.

Found: C=46.22; H=5.81; N=10.52; S=25.20.

C_5H_7ONS requires C=46.51; H=5.43; N=10.85; S=24.80 per cent.

The substance is therefore dimethylrhodim,

It is very readily soluble in water or ether, and crystallises from the former in large, transparent prisms or plates melting at 49–50°.

The strong tendency of this substance to form large, well-defined crystals created a desire for the determination of its crystallographic characteristics.

This work has been kindly undertaken for me by Mr. G. M. Bennett, to whom I tender my warmest thanks. His report is as follows:

“Crystallographic examination of dimethylrhodim.
Crystal system: monoclinic; holohedral class. Habit:

R R*

prismatic, with elongation parallel to the *c*-axis. Axial angle = $98^{\circ}11'$. Axial ratios : $a:b:c = 2.580:1:1.874$. Forms observed : (100), (110), (001), ($10\bar{1}$). There is a well-marked cleavage in the plane (100).

"The following are the regular measurements:

	Observed.	Calculated.
100-110	$68^{\circ}37'$	—
110- $\bar{1}10$	42 51	$42^{\circ}46'$
100-001	81 49	—
001- $\bar{1}01$	38 40	38 43
100- $10\bar{1}$	59 28	—
001-110	86 58	87 1
$\bar{1}01$ -110	79 11	79 20

"The faces of the crystals were rather dull through abrasion, particularly the small ones, so that some of the values are a little uncertain."

Hydrolysis of Dimethylrhodim.

The substance (2.58 grams) was heated with 10 c.c. of hydrochloric acid (D 1.19) for two hours at 140° in a sealed tube. There was considerable pressure on opening the tube, and the escaping gas had an odour of hydrogen sulphide and mercaptan. The contents of the tube were washed out with water and distilled, when some oil, apparently chloromethylthiazole, passed over with the water. The residual liquid was rendered alkaline and distilled into hydrochloric acid so long as the evolved vapours gave an alkaline reaction.

Part of the hydrochloride was obtained as such. After crystallisation, it gave $\text{Cl} = 52.26$, whilst $\text{CH}_3\cdot\text{NH}_2\cdot\text{HCl}$ requires $\text{Cl} = 52.29$ per cent. The remainder was converted into the platinichloride, which contained $\text{Pt} = 41.12$, whilst $(\text{CH}_3\cdot\text{NH}_2\cdot\text{HCl})_2\text{PtCl}_4$ requires $\text{Pt} = 41.32$ per cent.

No other base than methylamine was observed, and the total amount represented more than 90 per cent. of the theoretical.

It appears, therefore, that the methyl group introduced into the molecule of α -methylrhodim is attached to the nitrogen atom.

An attempt to prepare an *O*-ether from α -methylrhodim by the action of methyl iodide on the silver salt was unsuccessful. The alkaline solution is, indeed, precipitated by silver nitrate, but the precipitate consists chiefly of silver sulphide, part of the substance being destroyed.

α -Methylrhodim and Phosphorus Pentachloride.

α -Methylrhodim, which can be crystallised from warm phosphoryl chloride without any alteration, was dissolved in that solvent, a little more than the equivalent quantity (1 mol.) of phosphorus

pentachloride added, and the mixture heated to 50°. Hydrogen chloride was evolved, and a product was formed which was purified by repeated crystallisation from benzene.

Found: S=21.74.

C_4H_4ONClS requires S=21.40 per cent.

The chloride consists of pale brown, radially grouped acicular crystals melting and decomposing at 144°. It dissolves in dilute sodium hydroxide solution with a slight evolution of heat and the loss of the whole of its chlorine. On saturating the alkaline solution with carbon dioxide, a fine mud is deposited, which shrinks on drying to brown, brittle nodules (about 70 per cent. of the weight of the chloride) not melting at 220°.

The constitution of this product will be considered later.

Thiocyanoacetone and Alcoholic Hydrogen Chloride:
 β -Methylrhodim.

Hydrogen chloride (75 grams) was led into a mixture of thiocyanoacetone (115 grams:1 mol.), alcohol (115 grams), and water (18 grams). On the following day, the mixture was placed in a vacuum over sulphuric acid and sodium hydroxide, and allowed to remain for several days. The brown residue (162 grams), containing a few crystals, was removed with water and extracted in the automatic apparatus. After some time, crystals began to appear both in the flask of boiling ether and in that of the aqueous solution. The extraction was continued for eight days until the crystals in the latter had disappeared. By that time, an abundance of crystals had accumulated in the ether flask, along with some brown oil. The latter was decanted with the ether, and the crystals were washed with ether and alcohol. The crystals (38 grams, dry) were dissolved under a reflux condenser in 760 grams of boiling water, charcoal was added, and the solution filtered hot. On cooling, white crystals were gradually deposited (33 grams).*

The same substance was formed when α -methylrhodim was left to remain for a long time in contact with concentrated hydrochloric acid, preferably in the presence of alcohol. A mixture of 11.5 grams of α -methylrhodim, 50 grams of hydrochloric acid (D 1.19), and 25 c.c. of alcohol yielded more than 3 grams of the substance.

Found: C=41.41; H=4.54; N=11.93; S=28.11.

C_4H_5ONS requires C=41.74; H=4.35; N=12.17; S=27.83 per cent.

* From the mother liquors chloromethylthiazole (18 grams) and α -methylrhodim (25 grams after purification) were obtained.

The substance, another isomeride of thiocyanacetone, is named β -methylrhodim.

β -Methylrhodim is deposited from hot water as a white, crystalline powder; from alcohol by slow crystallisation in stout, colourless, quadratic plates melting at 183—184°. It dissolves in about 20 parts of boiling water and in about 475 parts at 15°. It is fairly readily soluble in boiling alcohol, less so in cold, and sparingly so in ether. When submitted to prolonged extraction in the apparatus with a relatively small quantity of ether, it accumulates in the boiling solvent and separates gradually in fine, colourless, transparent plates.

It is readily soluble in alkalis, and is precipitated therefrom by acetic acid.

β -Methylrhodim and Hydrochloric Acid.

β -Methylrhodim (3.45 grams) was heated with 30 c.c. of hydrochloric acid (D 1.19) for two hours at 100° in a sealed tube. There was no pressure on opening the tube, and the yellow solution yielded 3 grams of α -methylrhodim, together with a minute quantity (0.045 gram) of white crystals, which separated from the ethereal extract. They shrank, became brown at 250°, and did not melt at 265°. Whilst, therefore, β -methylrhodim is formed from α -rhodim under the influence of cold hydrochloric acid, the inverse conversion takes place almost completely at a higher temperature.

*Thiocyanacetone and Sodium Hydrogen Sulphite:
isoMethylrhodim.*

After prolonged heating of thiocyanacetone on the water-bath, it was found to contain a crystalline substance, different from the then known derivatives. The same substance was obtained by the action of alkali hydrogen sulphites on thiocyanacetone, and, after many attempts, a method was perfected which allowed it to be prepared with certainty and in a state of purity.

The action of free sulphur dioxide may be described first.

A solution of thiocyanacetone (11.5 grams) in 150 grams of water absorbed 37 grams of sulphur dioxide, of which 26 grams were lost when the solution was left in a vacuum at the ordinary temperature. The solution was then extracted with ether, and yielded only 0.45 gram of a yellow oil. The extracted solution was concentrated to 20 c.c. in a vacuum on a water-bath at 40°. The residue, which still had the odour of sulphur dioxide, was again treated with ether, and yielded 8.24 grams of fairly pure thiocyanacetone.

It would appear, therefore, that a sulphonic acid possessing a certain degree of stability is formed.

Quite different is the behaviour of thiocyanoacetone towards alkali hydrogen sulphites when they contain no free sulphur dioxide.

Thiocyanoacetone (230 grams:2 mols.) was added to a mixture of 2150 c.c. of water and 360 c.c. of a 27·8 per cent. solution of sodium hydrogen sulphite, which was neutral towards methyl-orange. The temperature rose 11°. The solution was shaken with charcoal and filtered rapidly through a folded filter. After two days there was an abundant crystallisation. The crystals were collected (72 grams, dry) and recrystallised (66·5 grams, dry) from 1450 grams of boiling alcohol.

Found: C=41·70; H=4·29; N=12·05; S=27·66.

C_4H_5ONS requires C=41·74; H=4·35; N=12·17; S=27·83 per cent.

The substance has therefore the composition of thiocyanoacetone, and is a third isomeride of that compound; it will be named *isomethylrhodim*.

isoMethylrhodim is remarkable for its great power of crystallisation and sparing solubility in cold water or alcohol. It requires 16 parts of boiling and 400 parts of cold alcohol. It crystallises from alcohol in white, long, brilliant, interwoven needles melting at 127—128°.

It dissolves slowly in dilute sodium hydroxide solution, but with decomposition. When the orange-coloured solution is treated with carbon dioxide, it evolves hydrogen sulphide and deposits after a time a sparingly soluble salt (sodium cyanurate?).

The sodium hydrogen sulphite used for the preparation of *isomethylrhodim* does not act solely as a catalyst. Part of the aqueous mother liquor from which the *isomethylrhodim* had been separated, and containing a trace only of sulphuric acid, was distilled with hydrochloric acid, and the distillate collected in a receiver containing water and sodium hydrogen carbonate. A portion of the distillate was oxidised with bromine, and the sulphuric acid produced was estimated gravimetrically. The result revealed the consumption of 56·13 grams of sodium hydrogen sulphite, a little more than one molecule for four molecules of thiocyanoacetone.

Preparation of isoMethylrhodim from Chloroacetone.

Monochloroacetone (92·5 grams:1 mol.) was stirred for two and a-half hours with 190 c.c. of a 47 per cent. solution of sodium

thiocyanate, cooling with water, when sodium chloride began to be deposited. A solution of 60 grams of crystallised potassium hydrogen sulphite in 300 c.c. of water was added, when nearly all dissolved, and the stirring was continued for half an hour. After two days, the yellow needles (44.27 grams, dry, m. p. 124—125°), containing some oil, were separated and recrystallised twice from 700 and 500 grams, respectively, of boiling alcohol, yielding, finally, 34.285 grams of white needles melting at 127—128°.

When sodium hydrogen sulphite solution was used instead of the crystallised potassium salt, the yield was much lower.

The various quantities of oil obtained in the different preparations were found to consist chiefly of thiocyanacetone.

isoMethylrhodim and Hydrochloric Acid: Dithiazylamine.

Concentrated hydrochloric acid acts slowly on *isomethylrhodim* at the ordinary temperature, but rapidly on heating. *isoMethylrhodim* (23 grams) was boiled with 200 c.c. of concentrated hydrochloric acid and 66 c.c. of water under reflux for twenty minutes, when some hydrogen chloride was evolved. About half the liquid was then distilled off, a yellow oil passing over with the distillate. From the latter, ether extracted 1.5 grams of oil.

To the orange residue in the distillation flask, 300 grams of water were added, the whole was boiled for some time, filtered from a yellow resin, the solution treated with charcoal, and filtered hot. On cooling, faint yellow, efflorescent needles were deposited (10.2 grams, anhydrous), which were dissolved in 115 c.c. of boiling 8 per cent. hydrochloric acid, the solution being shaken with charcoal and filtered hot. On cooling, long, yellow, prismatic needles separated, which were collected and washed with the same dilute acid. After being pressed between filter paper, they weighed 13.1 grams; they contained water of crystallisation, as well as some hygroscopic moisture. In a vacuum over sulphuric acid and sodium hydroxide, they effloresced to a powder and lost about 27 per cent. of their original weight. For analysis, some of the substance was recrystallised as above.

Found: C=39.09; H=4.53; N=16.69; Cl=14.57; S=26.09.

$C_8H_9N_3S_2 \cdot HCl$ requires C=38.79; H=4.04; N=16.97; Cl=14.34; S=25.86 per cent.

Found: H_2O =27.00.

$C_8H_9N_3S_2 \cdot HCl \cdot 5H_2O$ requires H_2O =26.67 per cent.

The substance is a hydrochloride, the acid of which can be estimated by titration.

The compound crystallises in pale yellow needles which easily

lose their water of crystallisation, crumbling to a fine, yellow powder which does not melt at 250° , but appears to sublime and decompose.

One part of the anhydrous salt is soluble in 46.25 parts of water at 26° and in 3—4 parts of hot water. The hydrate is fairly soluble in concentrated and sparingly so in dilute hydrochloric acid. The latter is a very convenient solvent for its purification; thus, one part of the hydrate (equal to 0.733 part of the anhydrous salt) dissolves in about 9 parts of hot 10 per cent. hydrochloric acid, whilst it requires more than 130 parts of the cold acid of the same strength. It separates from alcohol as a yellow, crystalline powder.

The Base, $C_8H_9N_3S_2$.

The aqueous solution of the hydrochloride is precipitated by alkali hydroxides, when these are not in excess, or by alkali carbonates.

The hydrochloride (57 grams) was dissolved in 2600 grams of water, the slightly turbid solution filtered, 115 c.c. of 2*N*-sodium hydroxide were added to the filtrate, and the white, voluminous, caseous precipitate was collected (48 grams, dry, instead of the theoretical 48.6 grams, m. p. $148-150^{\circ}$).

The 48 grams were recrystallised from 340 grams of hot alcohol. On cooling, yellowish, asbestos-like needles were deposited (38.4 grams, dry, m. p. $150-151^{\circ}$). The mother liquor yielded a further quantity (8.8 grams).

For analysis, the substance was twice recrystallised from a mixture of benzene and light petroleum.

Found: C=45.37; H=4.57; N=19.69, 19.74.

$C_8H_9N_3S_2$ requires C=45.49; H=4.27; N=19.90 per cent.

The base crystallises from the above solvent in almost white, spherical clusters of needles; from alcohol, in felt-like aggregates of long, silky needles melting at $153-154^{\circ}$. It dissolves in about 5 parts of hot and 37 parts of cold alcohol. It is insoluble in water or alkali carbonates, but soluble in alkali hydroxides.

Determination of Molecular Weight by the Cryoscopic Method.

Weight of solute. Gram.	Weight of of solvent. Grams.	Nature of solvent.	Δ .	M.W.
0.1077	12.945	Benzene	0.13°	313.6
0.1659	"	"	0.20	313.8
0.1107	19.630	Nitrobenzene	0.105	351.6
0.1674	"	"	0.172	357.5

Average 334.0

$C_8H_9N_3S_2$ requires M.W. = 211.

Determination of Molecular Weight by the Ebullioscopic Method.

0.1939 Gram of substance in alcohol. Constant for 100 c.c. = 15.6.

Rise in temperature.	Grams in 100 c.c.	M.W.
0.110°	2.938	416.7 (?)
0.137	2.620	298.3
0.120	2.365	307.4
0.107	2.154	314.0
	Average	334.0

The average happens to be the same by both methods, but the individual results are too divergent to make the average appear conclusive; it corresponds approximately with 1.5 times the simple formula $C_8H_9N_3S_2$. Since this formula cannot be multiplied by 1.5, the only recourse is to double it, unless, indeed, we admit molecular aggregation in solution, a phenomenon which does not appear uncommon in the case of complicated compounds.

A determination by Zerewitinov's method (*Ber.*, 1907, **40**, 2023; 1908, **41**, 2233) of the active hydrogen in the base, in pyridine solution, cold or hot, gave respectively 1.274 and 1.476 atoms of hydrogen per molecule of the formula $C_8H_9N_3S_2$. Of course, it is not impossible that the substance undergoes a far-reaching change under the influence of magnesium methyl iodide.

As will be seen later, when the structure of the group C_4H_4NS is discussed, the base is probably *dithiazylamine*, $(C_4H_4NS)_2NH$.

Examination of the Oil.

The oil, the second product of the action of hydrochloric acid on *isomethylrhodim*, was distilled under 14 mm. pressure several times, when it passed over at 94—97° (mostly at 96—97°), each time leaving a residue and undergoing slight decomposition. It would no doubt distil unchanged under still lower pressure.

As was to be expected, the results of the analysis were only approximate.

Found: C = 49.14; H = 5.67; S = 45.24.

C_8H_4S requires C = 50.00; H = 5.55; S = 44.44 per cent.

*Determination of Molecular Weight by the Cryoscopic Method.**In Glacial Acetic Acid.*

Weight of solute.	Weight of solvent.		
Gram.	Grams.	Δ .	M.W.
0.1530	20.91	0.205°	139.2
0.3792	,,	0.515	136.3
0.5322		0.720°	137.8

$C_6H_8S_2$ requires M.W. = 144.

The formula, C_3H_4S , has therefore to be doubled. A determination by the ebullioscopic method gave the number 188.

The compound is a colourless, highly refractive oil having a characteristic odour reminiscent of turpentine. It dissolves in concentrated sulphuric acid, yielding an orange-coloured solution which is not precipitated by water.

The formation of this substance, jointly with that of the base, may be accounted for as follows:

About two-thirds of the quantity of the base to be expected from this equation is obtained and one-third of the amount indicated for the compound, $C_6H_8S_2$.

The structural formula of $C_6H_8S_2$ may be represented by I, and

if the ring (II) be termed thiën, the compound, $C_6H_8S_2$, will be 2:5-*dimethylthiën*.

isoMethylrhodim and Methyl Iodide.

Five sealed tubes each containing 7 grams of *isomethylrhodim*, 10 grams of methyl iodide, and 20 grams of methyl alcohol were heated for three hours at 125° . On opening the tubes, the escaping gas had a fishy odour and contained carbon dioxide. The brown liquid, containing needle-shaped crystals, was removed with methyl alcohol and distilled from a water-bath. The residue (53.75 grams) was boiled with 750 c.c. of water, the solution filtered from a black tar, and boiled with charcoal. On cooling, a mixture (3.835 grams) of compact crystals (A) and of fine needles was deposited and separated mechanically; the latter proved to be unaltered *isomethylrhodim*.

The mother liquor was reduced by distillation to about 250 c.c. Along with the water, a small quantity of a malodorous oil and some solid matter passed over, which gave an ethereal extract of 0.622 gram.

The aqueous residue from the distillation was boiled with animal charcoal and filtered hot. On cooling, crystals (1.4 grams) similar to (A) were deposited.

The filtrate was now concentrated to 50 c.c., and yielded a further quantity (2.67 grams) of the same substance. The final mother liquor (B) will be mentioned later.

The three crystallisations of (A), together weighing about 7 grams, were dissolved in 400 grams of boiling water, the solution treated with charcoal, and filtered hot. The crystalline deposit (4.405 grams, dry) was recrystallised from 135 grams of water, and yielded 3.467 grams of long, colourless, massive crystals not melting at 265°. When heated on platinum, they sublimed without melting (Found: C=27.80; H=2.53; N=33.09. CHON requires C=27.90; H=2.33; N=32.72 per cent.).

The substance has therefore the composition of cyanuric acid, the properties of which it possesses. Thus, it gives Hofmann's reaction with sodium hydroxide and Wöhler's with copper sulphate.

The final mother liquor (B) was distilled in a vacuum to dryness, and the residue (23.51 grams) crystallised from alcohol. White plates (13.07 grams) were obtained which volatilised completely at about 220° with the evolution of iodine (Found: C=18.15; H=4.54; S=15.47; I=61.54, 62.13. C₃H₉Si requires C=17.65; H=4.41; S=15.68; I=62.25 per cent.).

The compound is therefore trimethylsulphine iodide.

It thus appears that under the influence of methyl iodide at a comparatively low temperature, isomethylrhodim undergoes complete disruption.

Comparative Examination of the Three Rhodims.

Determination of Molecular Weight by the Cryoscopic Method.

α-Methylrhodim, m. p. 103—104°.

Weight of solute. Gram.	Weight of solvent. Grams.	Nature of solvent.	Δ.	M.W.	Average.
0.1342	21.385	Nitrobenzene	0.26°	173.8	—
0.0845	"	"	0.14	183.8	178.8
0.3380	27.925	Glacial acetic acid	0.405	114.1	—
0.3412	"	"	0.40	117.1	115.6

β-Methylrhodim, m. p. 183—184°.

0.094	22.005	Glacial acetic acid	0.110°	151.4	—
0.1604	"	"	0.14	203.0	177.0

isoMethylrhodim, m. p. 127—128°.

0.1080	19.57	Nitrobenzene	0.105°	378.0	—
0.079	"	"	0.065	404.7	391.35

Determination of Molecular Weight by the Ebullioscopic Method.

In alcohol: constant for 100 c.c., 15·6.

Preliminary tests with acetanilide gave an average M.W.=157 instead of 135.

α-Methylrhodim, m. p. 103—104°:0·3312 gram.

Rise in temperature.	Grams in 100 c.c.	M.W.	Average.
0·620°	5·018	126·2	—
0·554	4·476	126·0	—
0·496	4·039	127·0	—
0·440	3·680	130·5	127·4

β-Methylrhodim, m. p. 183—184°:0·2175 gram.

0·155°	3·295	331·6	—
0·137	2·939	334·7	—
0·125	2·652	331·0	—
0·110	2·417	342·7	336·66

isoMethylrhodim, m. p. 127—128°:0·1732 gram.

0·078°	2·624	524·8	—
0·070	2·340	522·0	—
0·060	2·112	549·1	—
0·052	1·924	577·2	543·1

C_4H_5ONS requires M.W.=115.

Owing evidently to anomalies of aggregation, the results are not so conclusive as might be desired. *α*-Methylrhodim has certainly the simple molecule C_4H_5ONS , whereas there is some uncertainty concerning the two other isomerides. The author is inclined to regard *β*-methylrhodim as $2(C_4H_5ONS)$ and *isomethylrhodim* as $4(C_4H_5ONS)$, the structure of the ring, C_4H_5ONS , not being necessarily the same in the three isomerides.

Constitution of the Three Methylrhodims.

The so-called *meso*-hydroxymethylthiazole has, according to Hantzsch and Weber (*Ber.*, 1887, **20**, 3127), the structural formula I, which is that of a tertiary alcohol or phenol. The only fact

adduced by Hantzsch and Weber in favour of this formula was the alleged formation of *meso*-aminothiazoles by the action of ammonia

or primary bases. Later, however, Hantzsch had to admit the complete indifference of that compound towards ammonia or organic bases, having discovered that the reacting substance was thiocycanoacetone alone. This, and similar facts which were gradually evolved in the study of the aminothiazoles, led to these substances being represented as perfect models of tautomerism, hydroxymethylthiazole being endowed with a ketonic double (II), in spite of the absence of properties commonly possessed by ketones, as had been pointed out by Hantzsch and Weber themselves.

The author's long acquaintance with hydroxymethylthiazole has failed to reveal to him a single fact pointing to the presence of either a hydroxyl or a carbonyl group in that compound. It behaves neither as an alcohol nor as a ketone, and it affords no justification whatever for the assumption of tautomerism, that last resort of a formula in difficulties. Furthermore, the action of phosphorus pentachloride, which, as has been shown, leaves the oxygen intact, whilst it introduces chlorine into the molecule, makes the presence of either a hydroxyl or a carbonyl group at least improbable. The two formulæ (I and II) are, however, not only improbable, but impossible, as is proved by the study of the hydrolysis of the methylated derivative, $\text{CH}_3 \cdot \text{C}_4\text{H}_4\text{ONS}$, which the author has succeeded in obtaining in a state of purity. Indeed, this substance would have to be represented as

The first of these formulæ is that of an *O*-ether which can give no methylamine on hydrolysis; neither can a substance possessing the second formula, since the $\text{N} \cdot \text{CH}_3$ group is in the position 3, which, as Traumann (*Annalen*, 1888, **249**, 44) has shown in the case of 2-imino-3:4-dimethyl-2:3-dihydrothiazole (III), yields ammonia on hydrolysis, but no methylamine.

The compound, $\text{CH}_3 \cdot \text{C}_4\text{H}_4\text{ONS}$, on the contrary, gives a quantitative yield of methylamine.

We are thus led to the conclusion that the group $\text{N} \cdot \text{CH}_3$ occupies the position 2, which brings us to the formula IV for "hydroxy-

methylthiazole." A compound of this structure may be derived from thiocyanacetone if it is assumed that the latter passes into the enolic form, that a hydrogen atom then migrates, and, finally, that the chain is closed,

It appears, therefore, that the substance which has been known since 1887 as hydroxymethylthiazole is not a thiazole at all. It might be called 2-imino-4-methylthioxole, but for the sake of simplicity, and in view of the now proved existence of two other isomerides of thiocyanacetone, it seems preferable to adopt the generic name *rhodim* for this class of compounds.

Thus, hydroxymethylthiazole becomes α -methylrhodim; the isomeride melting at 183—184°, β -methylrhodim; the isomeride melting at 127—128°, *isomethylrhodim*.

It has been shown that the first two can be easily converted into one another. They stand, therefore, in the closest connexion and have to be considered as structurally analogous, the only difference being in the size of the molecule, that of the β -isomeride being probably double.

The same cannot be said of *isomethylrhodim*; its chemical behaviour, which is quite different, goes to show that it possesses one of the formulæ formerly claimed by α -methylrhodim,

more likely the latter. A glance at it shows pre-existing the fragments, $\text{CH}_3 \cdot \text{C} \cdot \text{CH} \cdot \text{S}$, $\cdot \text{CO} \cdot \text{NH} \cdot$, etc., into which the compound can be made to decompose. The formula is, of course, not simple; it would have to be multiplied probably by 4, which could cause it to rank with cyanuric acid, the identity of which with tetra-carbamide has been recently demonstrated (Walters and Wise, *J. Amer. Chem. Soc.*, 1917, **39**, 2472).

The base, dithiazylamine, $\text{C}_8\text{H}_9\text{N}_3\text{S}_2$, which is formed from *isomethylrhodim* by the action of hydrochloric acid, may be represented by the formula V, which makes it appear as the parent sub-

stance of the ammonium hydriodide, $C_{10}H_{14}N_3IS_2$, obtained by Hantzsch and Weber (*Ber.*, 1887, **20**, 3131) in small quantity by the action of methyl iodide on aminomethylthiazole, to which, starting from another direction, they assigned the structural formula VI.

The chlorinated derivative of α -methylrhodim, C_4H_4ONClS , may be

more likely the first.

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