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On Carbolthionic Acids and Their Esters.
Part. III
Carbithioic Acids and Esters.

By

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ABSTRACT.

The only method hitherto known as a general mode of formation of the carbithioic acids RCS_2H has been that of Houben, which is to bring the Grignard reagent into reaction with carbon bisulphide.

Now it was found out by the writer of the present article that M. Matsui's method for the formation of carbolthionic acids may be well applicable for the preparation of the esters of carbithioic acid, and by saponifying these esters free acids may also be isolated.

The following esters and acids were experimentally confirmed to be thus prepared:

Esters:—Ethylester of methylbithioic acid, ethylbithioic acid, phenylbithioic acid, benzylbithioic acid, paratolylbithioic acid, β -Naphthylbithioic acid, and tetrathio-oxalic acid.

Acids:—Methylbithioic acid, ethylbithioic acid, phenylbithioic acid, paratolylbithioic acid and tetrathio-oxalic acid.

By using M. Matsui's¹ method for the preparation of carbolthionic esters the writer has succeeded in preparing thio-carbolthionic esters or esters of carbithioic acids which were for the first time prepared by Houben² and his collaborators. They prepared the acids first by the reaction³ between the Grignard reagent and carbon bisulphide, and then esterified those acids with dialkyl sulphate. In the writer's method the

(1) Mem. Coll. Sci. Eng. Kyoto, **1**, 285 (1908); **3**, 247 (1912).

(2) Ber. **43**, 2481 (1910), **44**, 3228 (1911).

(3) Ber. **39**, 3219 (1906), **40**, 1303, 1725 (1907).

order of preparation was just the reverse, that is, esters were first prepared from thioimino-esters by the action of hydrogen sulphide, and these esters were then saponified with an alcoholic potash solution.

The experiment was conducted exactly in the same manner as in the preparation of carbolthionic esters by passing dry hydrogen sulphide into an ethereal solution of thio-iminoesters. As carbithioic esters thus formed further react upon ammonia, and change into the corresponding thiamides and mercaptanes, it is necessary to wash the ethereal solution promptly as soon as the reaction is over.

Methyl-carbithioic Ethylester



Into an ethereal solution of thioacetiminoethylester prepared according to the method of Pinner,¹ dry hydrogen sulphide gas was passed. The solution quickly began to take on an orange hue and at the same time white crystals of ammonium sulphide separated out. After sufficient hydrogen sulphide was passed, the ethereal solution was repeatedly washed with water completely to get rid of the hydrogen sulphide, ammonia and ammonium sulphide, and dried with fused calcium chloride. A mobile orange liquid obtained on evaporation of the ether was distilled, and the portion boiling at $128^\circ\text{--}132^\circ$ was collected and analysed.

0.0852 gm. substance gave 0.3488 gm. Ag_2S

	Calc.	Found.	
S	53.34	52.96	%

The orange liquid left on evaporation of the ether was sometimes found to contain some crystals of thioacetamide. This would perhaps be the product of the reaction of the ester upon ammonia which might have still been contained in the ethereal solution without being thoroughly washed away.

The properties of the methylbithioic ethylester thus prepared were found mostly to agree with those described by Houben.² It does not fume in a moist atmosphere as some carbolthionic esters do. Its specific gravity³ and index of refraction were determined as follows:

$$d\left(\frac{28^\circ}{4}\right) = 0.9807, \quad n = 1.5303 (28^\circ)$$

Ethylcarbithioic Ethylester.



This was prepared from thiopropioiminoethylester by treating its

(1) Ber. **16**, 352 (1883).

(2) Loc. cit.

(3) Houben found it to be $d_{16}^{16} = 1.036$

ethereal solution with hydrogen sulphide. It is an orange-coloured mobile liquid boiling at 150°-155°. The following physical constants were determined :

$$d\left(\frac{27^{\circ}}{4}\right) = 0.9711, \quad n = 1.5259 (27^{\circ}) \quad \text{viscosity} = 2.1535 (27^{\circ}).$$

Analysis: 0.1481 grm. substance gave 0.5450 grm. Ag₂S

	Calc.	Found.	
S	47.77	47.61	%

Phenylcarbithioic Ethylester.



This was obtained from thiobenziminoethylester as a red liquid boiling at 122°-125° under 72 mm. pressure. It was analysed with the following results :

0.1427 grm. substance gave 0.3952 grm. Ag₂S

	Calc.	Found.	
S	35.18	35.83	%

Benzylcarbithioic Ethylester.



This is an orange-coloured liquid boiling at 140°-144° under 45 mm. pressure. Its specific gravity and viscosity were determined as follows :

$$d\left(\frac{29^{\circ}}{4}\right) = 1.0462 \quad \text{viscosity} = 2.9831 (29^{\circ}).$$

Paratolylcarbithioic Ethylester.



Collecting the portion distilled off at 160°-165° under 85 mm. pressure, the following physical properties were determined :

A liquid of a red colour, $d\left(\frac{27^{\circ}}{4}\right) = 1.0085$, viscosity = 2.3215 (27°)

Analysis: 0.1373 grm. substance gave 0.3487 grm. Ag₂S

	Calc.	Found.	
S	32.67	32.86	%

β -Naphthylcarbithioic Ethylester.

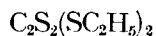


This was prepared from thio- β -naphthoiminoethylester as a thick liquid of a deep red colour boiling at 200°-205° under 45 mm. pressure.

Analysis: 0.1260 grm. substance gave 0.2622 grm. Ag₂S

	Calc.	Found.	
S	27.60	26.92	%

Tetrathio-oxalic Ethylester.



Thio-oxaliminoethylester prepared by passing cyanogen and hydrogen

chloride simultaneously into an ethereal solution of ethyl mercaptane was treated with hydrogen sulphide in the usual manner. The portion boiling at 90° - 93° under 43 mm. pressure was examined.

It is an orange-coloured liquid having a disagreeable odour and is insoluble in water. Its properties resemble those of the esters of monocarbitiolic acids in every respect.

The results of analysis were found as follows :

	0.0938 grm. substance gave 0.4390 grm. Ag_2S .		
	Calc.	Found.	
S	60.97	60.55	%

All the esters above described could without any difficulty be saponified with an alcoholic potash. It was, however, a very difficult task to collect them in a pure state and in quantities sufficient for close examination.

The following are the bithiolic acids thus isolated :

Methylbithiolic Acid. $\text{CH}_3\text{CS}_2\text{H}$

Methylbithiolic ethylester was mixed with an alcoholic potash solution and left to stand for a few days with an occasional shaking, when the acid formed by saponification precipitated as its potassium salt. The precipitates were collected, well washed with alcohol and then dissolved in water. On cooling the aqueous solution with ice it was acidified by adding dilute hydrochloric acid drop by drop. A yellow substance thus separated out in the solution was extracted with ether, and into the ether extract, after having been well dehydrated with fused calcium chloride, a current of dry air was passed to drive off the ether.

The bithiolic acid was obtained as an orange-coloured oily substance having a disagreeable penetrating odour. It is not so soluble in water as acetic acid.

For confirmation the quantity of sulphur was determined.

	0.0610 grm. substance gave 0.3270 grm. Ag_2S .		
	Calc.	Found.	
S	69.57	69.35	%
	Ethylbithiolic Acid $\text{C}_2\text{H}_5\text{CS}_2\text{H}$		

This was obtained as an orange-coloured oil by saponifying ethylbithiolic ethylester with alcoholic potash.

Analysis : 0.0112 grm. substance gave 0.0522 grm. Ag_2S

	Calc.	Found.	
S	60.39	60.29	%
	Phenylbithiolic Acid $\text{C}_6\text{H}_5\text{CS}_2\text{H}$		

This is a red-coloured thick oil having a penetrating odour. Its solution in organic solvents is also coloured red.

Analysis: 0.0252 gm. substance gave 0.0809 gm. Ag₂S.

	Calc.	Found.	
S	41.58	41.53	%

Benzylbithioic Acid C₅H₅CH₂CS₂H

A thick orange liquid having a penetrating odour.

Analysis: 0.0168 gm. substance gave 0.0491 gm. Ag₂S.

	Calc.	Found.	
S	38.12	37.81	%

Paratolylbithioic Acid C₇H₇CS₂H

This is a thick red liquid with a penetrating odour. It was analysed with the following results:

0.0229 gm. substance gave 0.0677 gm. Ag₂S.

	Calc.	Found.	
S	38.12	38.25	%

Tetrathio-oxalic Acid C₂S₂(SH)₂

This was isolated as an orange-coloured viscous liquid by saponifying its ethylester with alcoholic potash. Though it is only with difficulty soluble in water, it is very soluble in the ordinary organic solvents to which it imparts a yellow colour.

Analysis: 0.0151 gm. substance gave 0.0968 gm. Ag₂S.

	Calc.	Found.	
S	83.13	82.93	%

The writer wishes to express his hearty gratitude to Professor M. Matsui for his kind assistance and encouragement throughout the work.