On Carbolthionic Acids and Their Esters. Part I.

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ABSTRACT

According to the method of Prof. M. Matsui the following carbolthionic esters, acids and salts were prepared, and their physical constants were determined:

Thionbenzoic ethylester, Thionbenzoic acid, Silver thionbenzoate, Thionacetic ethylester, Thionacetic amylester, Thionacetic phenylester Thionphenylacetic ethylester, Thionpropionic ethylester, Thionparatoluic amylester Thionparatoluic ethylester, Thion-β-naphtoic ethylester.

A general mode of formation for the esters of the carbolthionic acids of the formula RC : S. OH was first found out in this laboratory by Prof. M. Matsui,[1] who also succeeded in isolating the free acids by saponifying the esters with alkali at ordinary temperature. As his work was, however, interrupted since that time, the thionic acids and esters hitherto prepared by him are very limited in number, and even those already isolated have been but insufficiently studied. So at the suggestion of Prof. M. Matsui, a repetition and extension of the work were undertaken by the present writer in order to complete the study on the new sulphur compounds.

Thionbenzoic Ethylester

$C_6H_5CSOC_2H_5$

This was prepared from benziminoethylester by treating its ethereal solution with dry hydrogen sulphide gas. It is a yellowish liquid boiling at 124°–127° under 3–5 mm pressure. When heated under an atmospheric pressure, it boils at about 240° with partial decomposition. The results of analysis were found as follows:

1 Mem. Coll. Sci. Eng. Kyoto, **1**, 286 (1908), **3**, 247 (1912); Beilstein, 4 Aufl., I, 182, 232, 245.

0·1894 grm. substance gave 0·2829 grm. Ag_2S.

	Calc. from $C_6H_5CSOC_2H_5$.	Found.
S.	19·29	19·32 %

The following physical constants were determined:

Specific gravity, $d\left(\frac{20^\circ}{4^\circ}\right) = 1{\cdot}0452$; Specific refractivity, $\left(\frac{n-1}{d}\right)_D = 0{\cdot}5570$; Viscosity, $1{\cdot}8169\ (27^\circ)$.

As was pointed out by Prof. M. Matsui[1] the ester reacts upon ammonia in two different ways, that is, in an alcoholic solution the sulphur group in the ester is replaced by the imino group and thus an iminoester is formed as the main product, while in an ethereal solution the ester behaves toward ammonia so as to yield the corresponding amide just as the ordinary ester does. Now it was ascertained that similar reactions generally take place between the ester and amines or hydrazines.

Thionbenzoic acid

C_6H_5CSOH

By saponifying thionbenzoic ester with an aqueous potash solution at ordinary temperature, Prof. Matsui isolated the free acid only in a very impure state and could therefore not examine its properties satisfactorily. When an alcoholic potash solution was used, the saponification was found to take place more smoothly, precipitating the acid as its potassium salt. The precipitated salt was collected and dissolved in water, and the aqueous solution, cooled with ice, was made acidic by cautiously adding dilute hydrochlóric acid, whereupon a yellowish crystalline substance separated out. The yellow substance was extracted with ether, and into the ethereal extract, which was well dehydrated with fused calcium chloride, a current of dry air was passed to drive off the ether. When nearly all the ether had evaporated the residue was placed in a vacuum desiccator and left to stand till the ether had completely evaporated.

Thionbenzoic acid is a yellow crystalline substance soluble in ordinary organic solvents. Its solution is coloured a yellowish green. It is exceedingly unstable and quickly changes into benzoic acid evolving hydrogen sulphide. Even in a dry ether solution it undergoes decomposition gradually at ordinary temperature, and quickly at a higher. A high temperature must, therefore, be avoided in every stage of its preparation. Its sulphur content was determined with the following results:

0·1095 grm. substance gave 0·1840 grm. $BaSO_4$.

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2 Mem. Coll. Sci. Eng. Kyoto, **3**, 248 (1912).

	Calc. from C_6H_5CSOH.	Found.
S.	23·21	23·08%.

The silver salt was prepared by shaking an ethereal solution of the acid with an aqueous solution of silver nitrate, when it formed as a white precipitate which soon became greyish. The precipitate after having been purified and dried was analysed with the following results:

0·1103 grm. substance gave 0·0481 grm. Ag.

	Calc. from C_6H_5CSOAg	Found
Ag	44·03	43·61%

Lead and barium salts were also prepared as yellow crystalline substance, but copper and iron salts could not be isolated.

Thionacetic Esters

1. Thionacetic Ethylester $CH_3CSOC_2H_5$

This was prepared by treating an ethereal solution of acetiminoethylester with dry hydrogen sulphide, according to the method described by Prof. Matsui, and the portion boiling at 105°–107° (atmospheric pressure) was collected.

It is a mobile liquid of pale yellowish colour whose physical constants were determined as follows:

Specific gravity $d\left(\frac{17^\circ}{4^\circ}\right)=0·8980$; Specific refractivity, $\left(\frac{n-1}{d}\right)_D=0·5002$; Viscosity, 0·7167 (17°).

The ester is more readily saponificable than the corresponding benzoic ester, but as the free acid is very unstable indeed it could by no means be obtained in such a pure state that its physical constants might accurately be determined. The quantity of sulphur in the ester was determined as follows:

0·1021 grm. substance gave 0·2424 grm. Ag_2S.

	Calc.	Found
S.	30·79	30·71 %

2. Thionacetic Amylester. $CH_3CSOC_5H_{11}$

A pale yellow liquid boiling at 72°–74° under 55 mm pressure, $d\left(\frac{23^\circ}{4^\circ}\right)=0·8639$, $\left(\frac{n-1}{d}\right)=0·4977$, Viscosity at 23°=0·8592.

The results of analysis were as follows:

0.0992 grm. substance gave 0.1686 grm. Ag_2S.

	Calc.	Found
S.	21·93	21·99%

3. Thionacetic Phenylester. $CH_3CSOC_6H_5$.

A yellow liquid boiling at 90°–94° under 38 mm pressure.

$d\left(\frac{20°}{4°}\right)=0.9914$, $\left(\frac{n-1}{d}\right)=0.5008$.

It was analysed with the following results:

0.1028 grm. substance gave 0.1658 grm. Ag_2S.

	Calc.	Found.
S.	21.06	20.87 %

4. Thionphenylacetic Ethylester $C_6H_5CH_2CSOC_2H_5$

A yellow liquid boiling at 170° under 99 mm pressure.

$d\left(\frac{12°}{4°}\right)=1.0142$, $\left(\frac{n-1}{d}\right)=0.5317$, Viscosity $=1.9276$ (12°). The results of analysis were as follows:

0.1341 grm. substance gave 0.1800 grm. Ag_2S.

	Calc.	Found.
S.	17.79	17.36 %

Thionpropionic Esters

1. Thionpropionic Ethylester. $C_2H_5CSOC_2H_5$.

This was prepared from propioiminoethylester and hydrogen sulphide, and the portion distilling at 125°–129° (atmospheric pressure) was collected.

$d\left(\frac{20°}{4°}\right)=0.8912$, $\left(\frac{n-1}{d}\right)=0.4844$, Viscosity $=0.6519$ (20°). The results of analysis were as follows:

0.2123 grm. substance gave 0.4454 grm. Ag_2S.

	Calc.	Found.
S.	27.13	27.14 %

The thionpropionic acid prepared from the ester by saponification was also found to be very unstable indeed, and instantly to change into propionic acid even in a dry ether solution. It was observed to form a white lead salt, but no further properties could be examined.

2. Thionpropionic Amylester $C_2H_5CSOC_5H_{11}$.

A pale yellow liquid boiling at 84°–86° under 30 mm pressure.

$d\left(\frac{22°}{4°}\right)=0.8595$, $\left(\frac{n-1}{d}\right)=0.5050$, Viscosity $=0.8784$ (22°).

The results of analysis were as follows:

0.1432 grm. substance gave 0.2278 grm. Ag_2S.

	Calc.	Found.
S.	20.01	20.58 %

Thionparatoluic Ethylester. $C_7H_7CSOC_2H_5$.

A yellow liquid boiling at 140°–145° under 70 mm pressure.

$d\left(\frac{20^\circ}{4^\circ}\right)=0.9992$, $\left(\frac{n-1}{d}\right)=0.5527$, Viscosity$=2.1141(20^\circ)$. It was analysed with the following results:

0.1564 grm. substance gave 0.2195 grm Ag_2S.

	Calc.	Found.
S.	17.79	18.16 %

Thion-β-naphtoic Ethylester $C_{10}H_7CSOC_2H_5$.

This is a yellow solid substance. It reacts upon a concentrated nitric acid not so violently as in the case of the lower thionic esters. The results of analysis are shown below:

0.0972 grm. substance gave 0.1109 grm Ag_2S.

	Calc.	Found.
S.	14.83	14.76 %

Its boiling point was observed to be 188°–194° under 30 mm pressure.

The writer takes this opportunity of warmly thanking Professor M. Matsui for kind assistance and encouragement in carrying out the work which was undertaken at his suggestion.