XCIV.—*The Action of Lead Thiocyanate on the Chlorocarbonates. Part II. Carboxymethyl- and Carboxyamyl-thiocarbimides and their Derivatives.*

By ROBERT ELLIOTT DORAN.

IN the Society's Transactions for 1896 (p. 324, *et seq.*), the author described the preparation and properties of carboxyethylthiocarbimide, and dealt with the further proof which it afforded of the generic character of the interaction, discovered by Miquel, which occurs when certain of the acidic chlorides are heated under suitable conditions with lead thiocyanate. The present communication is chiefly concerned with the homologous methyl compound, and as the methods of preparation were usually carried out in the same way as those described in Part I., briefer details will be sufficient.

Preliminary experiments showed that there was no apparent sign of interaction when methyl chlorocarbonate alone was heated with lead thiocyanate, and only traces of a thiocarbimide could be detected when the mixture was diluted with benzene and again heated. When, however, a mixture of benzene and toluene was used as solvent for the chlorocarbonate, interaction took place fairly readily on heating, and was completed, as a rule, after ten to twenty minutes' boiling. Working on a larger scale, 20 grams of methyl chlorocarbonate were dissolved in a mixture of equal volumes of benzene and toluene, and added, in a flask, to a quantity of dry lead thiocyanate about one and a-half times that required by the equation :

The flask was connected with a reflux apparatus, and the mixture, with frequent shaking, cautiously heated to boiling. Interaction set in rapidly, as was indicated by a change of colour in the liquid and in the lead salt, but brisk ebullition had to be maintained for upwards of twenty minutes before the liquid (now bright yellow), when cooled and allowed to clear by subsidence, was found to be free from chlorine. The lead chloride and unchanged thiocyanate were removed by filtration, washed with benzene, and the filtrate further diluted with this solvent until, assuming an approximately quantitative yield, each c.c. should contain 0.5 gram of the thiocarbimide. From this solution, some of the derivatives to be described presently were prepared. It is desirable to note here that the yields of the thiocarbimide, as estimated from the yields of its derivatives, only approached that theoretically obtainable on one or two occasions. Much greater difficulty has, in fact, been experienced in getting complete interaction

between methyl chlorocarbonate and lead thiocyanate than between its ethyl homologue and the same salt. So far, the cause of this has not been ascertained, but it has been noticed occasionally that the formation of the thiocarbimide apparently stopped when rather less than half the chlorocarbonate taken had undergone change. No variation in the amount of solvent used, or in the relative proportions of its constituents, or the use of toluene alone, with the object of getting a higher temperature, appeared to have any appreciable effect in completing the interaction; whilst the possible influence of mass and of surface coating of the thiocyanate was eliminated as far as possible, both by the use of a very large excess of the lead salt and by filtering off that partly acted on, replacing it by a fresh charge and reheating. An extended series of experiments was made with several of the other thiocyanates, those of silver, mercury, ammonium, and potassium being tried, and the last-named was the only one that gave anything like satisfactory results. It has been found that when methyl, ethyl, or amyl chlorocarbonate is diluted with dry benzene and allowed to stand in contact with dry, finely-powdered potassium thiocyanate, interaction commences at the ordinary temperature on the third or fourth day (when the clear liquid becomes faintly yellow and gives a slight but distinct black precipitate with ammoniacal silver nitrate), and continues until, after a period of two to three months, it *approaches* completion. Unfortunately, however, whilst there is still unchanged chlorocarbonate present, decomposition sets in, accompanied by the formation of mercaptans, chlorides, carbon dioxide, and an amorphous, orange-yellow solid, insoluble in water, which has not yet been examined; nevertheless the greater part of the chlorocarbonate used undergoes change in accordance with the equation:

Solutions of carboxymethylthiocarbimide obtained in this way have been used in the preparation of some of the derivatives to be described later. The action of heat appears to have little effect in increasing the rate at which the change takes place, unless the operation is conducted under pressure, when, in two experiments made at the temperature of the water-bath, it resulted in decomposition with explosive violence.

On account of the poor yields, and partly on account of the fairly complete examination of the corresponding ethyl compound (*loc. cit.*), no attempt was made to isolate carboxymethylthiocarbimide. Its properties, as determined in solution, in respect to its action on desulphurising agents, and lack of any action on ferric chloride, are identical in every way with those of its homologue, $\text{EtO} \cdot \text{CO} \cdot \text{NCS}$. It

was found that the presence of upwards of 50 per cent. of unchanged chlorocarbonate did not affect the preparation of the derivatives described, although of course it resulted in the simultaneous formation of the urethanes and hydrochlorides corresponding to the individual amines used, as well as the required sulphuretted compound, in accordance with the general equation,

As the hydrochlorides thus formed are practically insoluble, and the urethanes usually freely soluble in benzene, whilst the thiocarbamides and thioureas as a rule occupy a conveniently intermediate position, the separation and purification of the last, when obtained in sufficient quantity, were readily effected.

Turning now to the derivatives themselves, it will prevent unnecessary repetition to state beforehand that they were all prepared in the same way, by adding the bases, dissolved in benzene or alcohol, to the benzene or benzene-toluene solution of the thiocarbimide, in the proportions required by the equation,

Interaction occurred immediately with development of heat, and usually with separation of a solid consisting of the required thiocarbamide or thiourea, or mixtures of them with the hydrochloride of the base used, in those cases where the parent substance was not obtained free from unchanged chlorocarbonate. In all instances where no definite yield is mentioned, this condition prevailed in a greater or less degree.

Aromatic Derivatives.

ab-Carboxymethylphenylthiocarbamide, $\text{CH}_3\text{O}\cdot\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$.

—This substance was obtained from aniline and the thiocarbimide. When recrystallised from alcohol, it formed long, white needles melting at 158° without decomposition. On analysis :

0.2008 gave 0.2248 BaSO_4 . S = 15.39.

$\text{C}_9\text{H}_{10}\text{O}_2\text{N}_2\text{S}$ requires S = 15.25 per cent.

The compound is freely soluble in hot, but only sparingly so in cold, alcohol or benzene, and is sparingly soluble in hot water. In alcoholic solution, it is readily desulphurised on warming with neutral silver nitrate, or on boiling with alkaline lead tartrate, and at once in the cold with alkaline silver nitrate.

ab-Carboxymethylbenzylthiocarbamide,

—Only a very poor yield of this derivative was obtained, and when

recrystallised from aqueous alcohol, from which it separated in tufts of needles, it melted at 134° without decomposition.

0.124 gave 0.130 BaSO_4 . $S = 14.41$.

$\text{C}_{10}\text{H}_{12}\text{O}_2\text{N}_2\text{S}$ requires $S = 14.3$ per cent.

It is freely soluble in hot, and moderately so in cold, alcohol or benzene, but is insoluble in water. Its alcoholic solution gives a white precipitate, blackening on heating, with neutral silver nitrate, an immediate black precipitate with the ammoniacal nitrate, and is slowly desulphurised on boiling with alkaline lead solution.

ab-Carboxymethyl-o-tolylthiocarbamide,

—The yield of the crude product amounted to 96 per cent. of the theoretical. The pure substance melted at 172° without decomposition.

0.1999 gave 0.2092 BaSO_4 . $S = 14.38$.

$\text{C}_{10}\text{H}_{12}\text{O}_2\text{N}_2\text{S}$ requires $S = 14.30$ per cent.

The compound is moderately soluble in hot, and sparingly so in cold, benzene or alcohol, separating from the former in needles and from the latter in feathery plates. It is insoluble in water. With desulphurising agents, it behaves like the phenyl derivative.

ab-Carboxymethyl-p-tolylthiocarbamide,

—A 35 per cent. yield was obtained in the form of thick, short prisms melting at 158° without decomposition.

0.20 gave 0.2101 BaSO_4 . $S = 14.44$.

$\text{C}_{10}\text{H}_{12}\text{O}_2\text{N}_2\text{S}$ requires $S = 14.30$ per cent.

For all practical purposes, the properties of this compound are identical with those of the *o*-derivative.

ab-Carboxymethyl- α -naphthylthiocarbamide,

—This compound crystallises from alcohol in tufts of long, flexible needles melting at 193° with copious effervescence.

0.2212 gave 0.20 BaSO_4 . $S = 12.43$.

$\text{C}_{13}\text{H}_{12}\text{O}_2\text{N}_2\text{S}$ requires $S = 12.32$ per cent.

The substance is moderately soluble in hot, and sparingly so in cold, benzene, rather sparingly soluble in hot, and nearly insoluble in cold, alcohol, and is insoluble in water. The behaviour of this and the following compound, with the usual reagents for the removal of sulphur, is practically the same as that of the tolyl derivatives.

ab-Carboxymethyl- β -naphthylthiocarbamide,

—By recrystallisation from mixed alcohol and benzene, this compound

was obtained in microscopic needles melting at 184° with decomposition.

0.2014 gave 0.1822 BaSO_4 . $\text{S} = 12.43$ per cent.

It is freely soluble in hot, and moderately so in cold, benzene, sparingly soluble in hot, and nearly insoluble in cold, alcohol, and very sparingly soluble in hot-water.

Fatty Derivatives.

ab-Carboxymethylmethylthiocarbamide, $\text{CH}_3\text{O}\cdot\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{CH}_3$.—This compound was obtained in the form of fine, white needles melting at 146° without decomposition.

0.2028 gave 0.3219 BaSO_4 . $\text{S} = 21.8$.

$\text{C}_4\text{H}_8\text{O}_2\text{N}_2\text{S}$ requires $\text{S} = 21.63$ per cent.

It is moderately soluble in hot, and sparingly so in cold, alcohol, benzene, or water. Its alcoholic solution gives a white precipitate with neutral silver nitrate, which blackens on heating; it is at once desulphurised by the ammoniacal nitrate, but only darkens slightly on prolonged boiling with alkaline lead solution.

ab-Carboxymethylethylthiocarbamide, $\text{CH}_3\text{O}\cdot\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_2\text{H}_5$, occurs in tufts of white, feathery needles melting at 86° without decomposition.

0.203 gave 0.295 BaSO_4 . $\text{S} = 19.9$.

$\text{C}_5\text{H}_{10}\text{O}_2\text{N}_2\text{S}$ requires $\text{S} = 19.76$ per cent.

The compound is freely soluble in hot or cold alcohol or benzene, moderately so in hot, but sparingly so in cold, water, and is nearly insoluble in cold light petroleum. With desulphurising agents, it reacts like the preceding compound.

ab-Carboxymethylisobutylthiocarbamide, $\text{CH}_3\text{O}\cdot\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_4\text{H}_9$.—This substance, of which only a very poor yield was obtained, crystallises from light petroleum in long prisms melting at 83° without decomposition.

0.153 gave 0.1895 BaSO_4 . $\text{S} = 17.02$.

$\text{C}_7\text{H}_{14}\text{O}_2\text{N}_2\text{S}$ requires $\text{S} = 16.85$ per cent.

It is freely soluble in hot or cold alcohol or benzene, moderately so in hot, and only sparingly so in cold, light petroleum. It behaves like the methyl and ethyl derivatives with lead and silver salts.

Carboxymethylthiourea, $\text{CH}_3\text{O}\cdot\text{CO}\cdot\text{N}:\text{C}(\text{NH}_2)\cdot\text{SH}$.—On passing a stream of ammonia through a quantity of the benzene-toluene solution of the thiocarbimide, vigorous action occurred, accompanied by the evolution of heat and traces of hydrogen sulphide. A little solid

separated while the liquid was still hot, and on cooling a considerable crop of crystals was obtained which, when collected, washed with benzene and recrystallised, first from water and then from alcohol, from which it separated in short prisms, melted at 166° with copious effervescence, the gas evolved being apparently methyl mercaptan.

0.20 gave 0.348 BaSO_4 . $S = 23.92$.

$\text{C}_3\text{H}_6\text{O}_2\text{N}_2\text{S}$ requires $S = 23.89$ per cent.

The substance is moderately soluble in hot, sparingly so in cold, benzene, freely but slowly soluble in hot, and sparingly so in cold, alcohol, moderately so in hot, and nearly insoluble in cold, water. Its aqueous solution is readily desulphurised by the usual reagents, and gives a very fine mirror of lead sulphide with alkaline lead tartrate.

Trisubstituted Thioureas.

Of these, three were prepared, from piperidine, and methyl- and benzyl-anilines, but only one of them, that derived from the first-named base, was obtained in quantity sufficient for satisfactory identification.

Carboxymethylpiperidylthiourea, $\text{CH}_3\text{O}\cdot\text{CO}\cdot\text{N}:\text{C}(\text{SH})\cdot\text{NC}_5\text{H}_{10}$. — The yield of the crude substance amounted to 11 per cent. of the theoretical. When purified by recrystallisation, firstly from mixed benzene and light petroleum, secondly from the latter solvent alone, and thirdly from water, it melted at 97° .

0.205 gave 0.2355 BaSO_4 . $S = 15.8$.

$\text{C}_8\text{H}_{14}\text{O}_2\text{N}_2\text{S}$ requires $S = 15.77$ per cent.

It is very freely soluble in benzene, alcohol, ether, chloroform, or acetone; but only sparingly so in hot, and nearly insoluble in cold, water or light petroleum. Its alcoholic solution is not visibly affected by prolonged boiling with alkaline lead solution, and only darkens slightly under the same conditions with ammoniacal silver nitrate.

Carboxymethylphenylsemithiocarbamide,

$\text{CH}_3\text{O}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}(\text{SH})\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$.

—Vigorous action occurred when phenylhydrazine, dissolved in alcohol, was added to a benzene-toluene solution of carboxymethylthiocarbimide. A solid separated almost at once, and by recrystallisation from alcohol was eventually obtained pure in the form of white, glistening plates melting at 180° , and remelting at the same temperature.

0.2078 gave 0.215 BaSO_4 . $S = 14.22$

$\text{C}_9\text{H}_{11}\text{O}_2\text{N}_3\text{S}$ requires $S = 14.23$ per cent.

The substance is moderately freely but slowly soluble in hot, and

is nearly insoluble in cold, alcohol, sparingly so in hot benzene, and insoluble in water. Its alcoholic solution, with neutral silver nitrate, gives a white silver salt which blackens slowly on heating, and shows the usual reactions characteristic of a hydrazine derivative with copper sulphate and ferric chloride.

Thiocarbamates.

Three of these were prepared by mixing an excess of the corresponding alcohols with a benzene solution of the thiocarbimide. They were obtained by allowing the benzene and excess of alcohol to evaporate spontaneously, and were purified by recrystallisation from light petroleum in the case of the first two, and from aqueous alcohol in the case of the benzyl compound. In alcoholic solution, they all gave white silver salts, which blackened at once on heating, after the addition of ammonia.

Methyl Carboxymethylthiocarbamate, $\text{CH}_3\text{O}\cdot\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{O}\cdot\text{CH}_3$.—White, feathery needles melting at 46° .

0.2042 gave 0.3198 BaSO_4 . $\text{S} = 21.53$.

$\text{C}_4\text{H}_7\text{O}_3\text{NS}$ requires $\text{S} = 21.49$ per cent.

Ethyl Carboxymethylthiocarbamate, $\text{CH}_3\text{O}\cdot\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{O}\cdot\text{C}_2\text{H}_5$.—Long needles melting at 83° .

0.205 gave 0.296 BaSO_4 . $\text{S} = 19.85$.

$\text{C}_5\text{H}_9\text{O}_3\text{NS}$ requires $\text{S} = 19.65$ per cent.

Benzyl Carboxymethylthiocarbamate, $\text{CH}_3\text{O}\cdot\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{O}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5$.—Tufts of fine, creamy-white needles melting at 103° .

0.2084 gave 0.220 BaSO_4 . $\text{S} = 14.51$.

$\text{C}_{10}\text{H}_{11}\text{O}_3\text{NS}$ requires 14.24 per cent.

In Part I of this communication, to which reference has already been made, it was shown, when dealing with the "constitution of nitrogen bases and isomerism," that Seidel's so-called "ethyl isophenylthioallophanate" (*J. pr. Chem.*, 1885, [ii], 32, 261) was identical with the author's *s*-carboxyethylphenylthiocarbamide, and that Seidel's statement that the group $\text{RO}\cdot\text{CO}\cdot$ was "negative" to $\text{R}'\text{CO}$, and could be expelled by it from compounds of the type specified, was incorrect. In fact, the very opposite was established in the case then under investigation, since it was found that carboxyethylphenylthiocarbamide remained unchanged after heating with a large excess of acetyl chloride, whilst the converse change was readily effected by heating acetylphenylthiocarbamide with ethyl chlorocarbonate,

the product being in every respect identical with that obtained by the direct union of aniline with carboxyethylthiocarbimide. Since this result was published, the author has prepared several other carboxyethyl derivatives by heating various acetylthioureas with $\text{EtO}\cdot\text{COCl}$, and, in the course of the present investigation, has further established the *positive* character of the group $\text{R}'\text{O}\cdot\text{CO}$, so far as the group $\text{CH}_3\cdot\text{CO}\cdot$ is concerned, by the following experiment. Five grams of methyl chlorocarbonate were added to 3 grams of acetylphenylthiocarbamide in a flask and the mixture heated on the water-bath under a reflux condenser for 20 minutes, until all solid had disappeared. Acetyl chloride, hydrogen chloride, and traces of hydrogen sulphide were evolved just as in the experiment made with ethyl chlorocarbonate. The contents of the flask solidified on pouring out into a dish, and the solid matter, when freed as far as possible from a rather sticky mother liquor (containing acetyl chloride, methyl acetate, and unchanged chlorocarbonate), and purified by recrystallisation from alcohol, was obtained in fine, white needles melting at $157\text{--}158^\circ$, and giving on analysis, $\text{S} = 15\cdot34$ per cent. (calc. $\text{S} = 15\cdot25$ per cent.). The interaction is represented by the equation :

Acetyl-*o*- and -*p*-tolylthiocarbamides give identical results under similar treatment; in fact, the method is probably a generic one, whereby thiocarbamides and thioureas containing the group $\text{R}'\text{O}\cdot\text{CO}\cdot$ may be obtained from the corresponding acetyl compounds.

As disposing of all the work which he intends doing for the present with thiocarbimides derived from the chlorocarbonates of the *fatty* series, the author would briefly describe here the preparation and properties of certain derivatives of carboxyamylthiocarbimide.

The parent substance was obtained by slow interaction, at the ordinary temperature, between finely-powdered and well-dried potassium thiocyanate and carboxyamylchlorocarbonate dissolved in pure anhydrous benzene. The experiment extended over three months, air having access all the time through a capillary opening to the vessel in which it was made; but the admission of moisture was prevented, as far as possible, by a long column of calcium chloride in a drying tube.

At the end of this time, the clear solution (which left no appreciable solid residue on evaporation to dryness), whilst desulphurising copiously with alkaline lead and silver solutions, still reacted rather strongly for chlorine; but as there were obvious indications that decomposition had commenced, the experiment was stopped, the liquid filtered from the potassium chloride (formed in accordance with the

general equation already given) and excess of unchanged potassium thiocyanate. It was then divided into equal parts, and the following derivatives were prepared by adding the corresponding amines, in alcoholic solution, until no further sign of interaction was observed. Very poor yields were obtained, but these were quite sufficient for satisfactory identification :

ab-Carboxyamylphenylthiocarbamide, $C_5H_{11}O \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_6H_5$.
—Fine white needles from light petroleum, melting at $97-98^\circ$, without decomposition.

0.2036 gave 0.1790 $BaSO_4$. $S = 12.08$.

$C_{13}H_{18}O_2N_2S$ requires $S = 12.04$ per cent.

ab-Carboxyamyl-o-tolylthiocarbamide, $C_5H_{11}O \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_7H_7$.
—This compound also crystallises in fine, white needles, closely resembling the phenyl derivative and melting at $96-97^\circ$ without decomposition.

0.2082 gave 0.1734 $BaSO_4$. $S = 11.45$.

$C_{14}H_{20}O_2N_2S$ requires $S = 11.44$ per cent.

Both these compounds gave the usual reactions with lead and silver salts characteristic of the class they represent. They are very freely soluble in benzene or hot alcohol, and moderately so in cold alcohol, from which they separate as oils on the addition of water, but are practically insoluble in cold light petroleum.

An attempt was made to prepare carboxyamylthiourea by passing dry ammonia through another portion of the solution, and a white, crystalline product was obtained melting at $56-57^\circ$, which in alcoholic solution desulphurised with neutral and ammoniacal silver nitrate, and gave a mirror of lead sulphide on boiling with alkaline lead tartrate. The mean of two sulphur determinations was, however, $S = 9.702$ per cent., as against 16.85 required for $CSN_2H_3 \cdot CO_2 \cdot C_5H_{11}$. The product is probably a mixture of this compound with amyl carbamate, resulting from interaction between ammonia and the unchanged amyl chlorocarbonate present, but the quantity obtained was too small to permit of their separation.

The two fully identified derivatives furnish an interesting example of the effect of the introduction of the higher alkyl group (C_5H_{11} in place of C_2H_5 or CH_3) on the melting point, for whilst the differences between the melting points of the phenyl and *o*-tolyl derivatives of carboxymethylthiocarbimide and carboxyethylthiocarbimide are 14° and 22° respectively, in the present case there is only a difference of 1° . They are sufficiently close, in fact, to suggest, if without analytical data, the barely possible accident of using the same amine for both preparations. When mixed, however, in equal portions, the melting

point of the two compounds (96—97° and 97—98°) drops smartly to 84°.

An attempt has been made to tabulate the melting points of the compounds described in this and the previous communication, and some interesting relationships have been observed, particularly amongst the isomeric thiocarbamides and thiocarbamates.

The author does not intend to deal with this portion of his subject at present, but hopes shortly to lay before the Society an account of some derivatives of ethoxalylthiocarbimide which have been prepared, and to extend the present research to the action of lead or other thiocyanates on phenyl chlorocarbonate.

CHEMICAL DEPARTMENT,
QUEEN'S COLLEGE, CORK.