

LXII.—*Derivatives of Succinyl and Phthalyl Dithiocarbimides.*

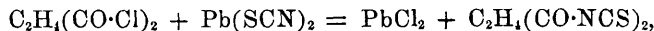
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NUMEROUS "mustard-oils" are known of the general type  $R'NCS$  (where  $R'$  is a monad hydrocarbon residue), and a few of the form  $R''(NCS)_2$ ,  $R''$  being a dyad residue of the same kind. Some three or four monacidyl thiocarbimides have also been obtained, notably  $CH_3CO \cdot NCS$  and  $C_6H_5 \cdot CO \cdot NCS$ ,\* but the existence of dithiocarbimides of the acid class appears not to have been hitherto recorded.

We have therefore commenced an investigation in the latter direction, and beg now to lay before the Society an account of the principal results hitherto obtained.

*Succinyl dithiocarbimide.*

Succinyl chloride and well-dried lead thiocyanate, in the proportions required by the equation



\* Obtained by Miquel (*Ann. Chim. Phys.*, 1877, [5], 11, 295; 300), from lead thiocyanate and the corresponding acid chlorides.

were mixed with anhydrous benzene, and heated on the water bath, shaking constantly. Before the boiling point was reached, action commenced with evolution of heat, and the solution became reddish-brown; the process was completed by adding a few more grams of lead thiocyanate, and heating for half an hour, using a reflux condenser. A brownish residue, consisting principally of lead chloride, was filtered off by means of the pump, and the filtrate, which was of a clear reddish-brown, was found to be free from chlorine, and possessed little odour save that of benzene; it gave, with alcohol and ammoniacal silver nitrate in the cold, a precipitate of silver sulphide, and was easily desulphurised by warming with alkaline lead tartrate, reactions indicating the presence of a thiocarbimide or one of its immediate derivatives.

By carefully evaporating most of the benzene at a gentle heat, a blackish oil was obtained, of pungent, tear-exciting odour, resembling that of acetylthiocarbimide, but it did not seem pure enough for analysis. Like the latter compound, it soon decomposes—even in the benzene solution—becoming dark coloured, and depositing a deep brown, pasty solid in small quantity.

An attempt was made to purify the substance by distillation in a vacuum, but it darkened considerably, and on raising the temperature slightly after the benzene had all come over, the mixture suddenly turned black, effervesced violently, and a sharp detonation occurred, shattering the distillation-flask. A strong odour of mushrooms was noticed.

Isolation by distilling in a steam current was out of the question, as the thiocarbimide proved to be decomposable by water; and after some further endeavours to precipitate it by means of light petroleum, which led to no definite result, an investigation of its derivatives was proceeded with.

In the experiments described below, the following method was generally adopted. A preliminary trial having shown that the yield amounted to over 90 per cent. of the theoretical, the product was further diluted with anhydrous benzene, so that every 5 c.c. should contain about 1 gram of succinyldithiocarbimide, and the freshly prepared solution was employed.

*Succinyldithiocarbimide and Aniline.* Succinyl-ab-diphenyldithioureä,  

$$\text{C}_2\text{H}_4(\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_6\text{H}_5)_2.$$

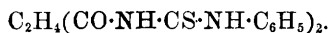
Nine grams (1 mol.) of the dithiocarbimide, in benzene, were carefully added to a cooled benzene solution containing 8.3 grams (2 mol.) of pure aniline. Interaction rapidly occurred, with evolution of heat, and in a very short time the contents of the vessel set to a paste. On

draining off the entangled benzene by means of the filter pump, and washing the residue with fresh benzene, a finely-divided, brownish, amorphous solid was obtained, amounting, when dry, to 15.5 grams, or about 90 per cent. of the weight of the materials employed.

The powder was digested with a little hot acetone, which removed most of the colouring matter, and the residue dissolved in (much) boiling acetone; on cooling, beautiful, silky needles were deposited, almost colourless, and melting at 207—208°. By adding water to the mother liquor, and recrystallising the precipitate from boiling glacial acetic acid, the compound was obtained in felted masses of pure, white, hair-like needles, melting, with effervescence, to a reddish-brown liquid, at 210—210.5° (corr.). A complete analysis was made, with the following results.

0.2993 gave 0.6086 CO<sub>2</sub> and 0.1331 H<sub>2</sub>O. C = 55.45 and H = 4.95.  
 0.1988 „ 24.8 c.c. moist nitrogen at 17° and 768 mm. N = 14.63.  
 0.2869 „ 0.3446 BaSO<sub>4</sub>. S = 16.5.

These figures are in accordance with the formula



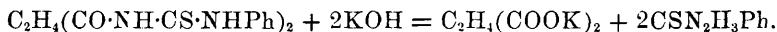
	Theory. C <sub>18</sub> H <sub>18</sub> N <sub>4</sub> S <sub>2</sub> O <sub>2</sub> .	Experiment.
C .....	55.90	55.45
H .....	4.67	4.95
N .....	14.54	14.63
S.....	16.59	16.51
O .....	8.30	(By diff.) 8.46

Succinyldiphenyldithiourea is very sparingly soluble in boiling alcohol, ether, or benzene, with difficulty in chloroform and ethylic acetate; more easily in boiling acetone or glacial acetic acid. It is insoluble in water and in boiling, concentrated hydrochloric acid, but dissolves freely in sulphuric acid or dilute caustic potash; the former solution is precipitated on adding water. If the latter be mixed with a few drops of lead solution, and heat applied, the tube becomes plated with a very brilliant galena speculum; the sulphur, also, is instantly withdrawn on adding silver nitrate to the warm alcoholic solution. Ferric chloride produces no colour change.

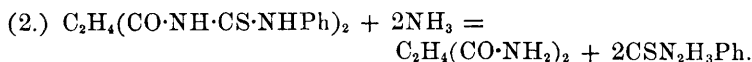
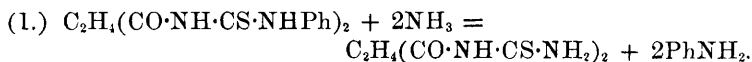
*Action of Caustic Alkali.*—A quantity of the pure dithiourea substance was dissolved, with gentle warming, in pure, dilute, caustic soda; on cooling, white prisms separated, which, after thorough washing with cold water, melted at 152—153° (uncorr.). Hydrochloric acid, when added, in very slight excess, to the clear filtrate from the crystals, threw down a copious precipitate of fine needles; these, when recrystallised from boiling water, occurred in well formed, pure white prisms, melting at nearly the same temperature as the former crop, namely,

154° (corr.). Both products were easily soluble in hot water, very sparingly in cold, freely in alcohol; the cold solution was blackened at once by ammoniacal silver nitrate, and yielded a fine mirror when heated with alkaline lead tartrate. These reactions, together with the appearance, intensely bitter taste, and melting point of the substance, characterise it as phenylthiourea (m. p. 154°).

When exactly neutralised, the hydrochloric acid filtrate gave, with ferric chloride, a reddish-brown precipitate, and with barium chloride, ammonia, and alcohol, a white, thereby showing the presence of a succinate. Caustic alkali therefore decomposes the phenylic derivative as follows.



*Action of Alcoholic Ammonia.*—Under the influence of this reagent, at a moderate temperature, a symmetrical disubstituted thiourea is converted, with loss of one of its radicles as amine, into a monosubstitution compound. Thus, from thiocarbanilide, Gebhardt obtained (*Ber.*, 1884, **17**, 3045) phenylthiourea and aniline; and from the dinaphthyl compound, similarly, naphthylthiourea and naphthylamine. Succinyldiphenyldithiourea, however, containing two different groups attached to the thiocarbonyl nuclei, might decompose in either (or possibly both) of the following ways.



that is, into succinyldithiourea and aniline, or into succinamide and phenylthiourea. An experiment was made as follows.

Another portion of the pure succinyldiphenyl compound was mixed with excess of alcoholic ammonia, and the turbid liquid heated for an hour at 120—130°; there was no pressure on opening the tube, and the contents had become almost perfectly clear. After standing for a short time, needles were deposited; these melted at 153°, and, after recrystallisation, at 154° (corr.), consisted, as shown by their properties, of phenylthiourea. A faint trace of thiocyanate was also found, due to partial attack of the phenylthiourea by the ammonia (*Claus, Ber.*, 1876, **9**, 694), and a barely detectable trace of aniline was present, due only to the decomposition in question,  $\text{CSN}_2\text{H}_3\text{Ph} + \text{NH}_3 = \text{NH}_4\cdot\text{SCN} + \text{NH}_2\text{Ph}$ . The action therefore appears to run according to equation (2) above, but the succinamide, unfortunately, was not isolated.

*Succinyl-ab-diorthotolylldithiourea*,  $C_2H_4(CO \cdot NH \cdot CS \cdot NH \cdot C_6H_4 \cdot CH_3)_2$ .

This compound was prepared in like manner to the preceding: 9 grams of succinyldithiocarbimide and 9.6 grams of orthotoluidine yielded 18 grams of dry product, or over 96 per cent. of the theoretical. The brownish, amorphous solid was dissolved in the least possible quantity (about a litre) of boiling glacial acetic acid, from which, on cooling, it separated in beautiful, sea-green prisms. By another recrystallisation from the same solvent, it was obtained in colourless, glassy needles, which melted, with copious effervescence, at the same temperature as the sea-green product, namely,  $217-218^\circ$  (corr.).

The formula was checked by a sulphur determination.

0.2074 gave 0.2290  $BaSO_4$ .  $S = 15.18$ .

$C_{20}H_{22}N_4S_2O_2$  requires  $S = 15.47$  per cent.

Silver sulphide is precipitated at once on adding silver nitrate to the warm alcoholic solution, and a brilliant mirror is formed by treatment with alkaline solution of lead. In its solubility relations, it closely resembles the corresponding phenyl derivative.

*Succinyl-ab-di- $\alpha$ -naphthylldithiourea*,  $C_2H_4(CO \cdot NH \cdot CS \cdot NH \cdot C_{10}H_7)_2$ .

The constituents in benzene solution at once united, with evolution of heat, forming a cream-coloured solid, which darkened superficially on exposure to air. It is practically insoluble in water, alcohol, chloroform, acetone, ethylic acetate, acetic acid, carbon bisulphide, benzene, toluene, cumene, and light petroleum; soluble in concentrated sulphuric acid; the last solution, when diluted with water, gave a jelly-like precipitate, which could not be filtered. The substance dissolved also in hot nitrobenzene, but did not separate on cooling. It was shaken up repeatedly with alcohol, filtered with the aid of the pump, well washed with more alcohol, and dried; as thus obtained, it was a pure white, fine powder, not affected by exposure to air, and melting to a black liquid at  $224-225^\circ$  (corr.). A determination of sulphur was made.

0.2 gave 0.1914  $BaSO_4$ .  $S = 13.15$ .

$C_{26}H_{22}N_4S_2O_2$  requires  $S = 13.18$  per cent.

Ferric chloride gives no coloration. When mixed with alcohol and treated with ammoniacal silver nitrate, little change occurs, probably on account of the insolubility of the compound, but, on heating, the mixture blackens at once. It is also easily desulphurised by warming with alkaline solution of lead.

*Symmetrical Succinyl-ab-dimethyldiphenyldithiurea,*  
 $C_2H_4[CO \cdot N : C(SH) \cdot N(CH_3)C_6H_5]_2$ .

This substance was obtained from the dithiocarbimide and methyl-aniline as a yellowish solid, which, after washing with benzene, became white. From its solution in boiling spirit, it was deposited in hard, colourless, seemingly rhombic, prisms melting at a much lower temperature than the isomeric tolyl derivative, namely, 138—139° (corr.).

0.20 gave 0.2253 BaSO<sub>4</sub>. S = 15.48.

$C_{20}H_{22}N_4S_2O_2$  requires S = 15.47 per cent.

It is insoluble in water, ether, and carbon bisulphide, sparingly and slowly soluble in alcohol, chloroform, acetone, and benzene. Like the other compounds mentioned above, it dissolves in sulphuric acid (the solution is precipitated by the addition of water), and in cold, dilute alkali. The latter solution is precipitated by hydrochloric acid, and is desulphurised only to a very trifling extent by even prolonged boiling with alkaline lead tartrate. Warm nitric acid vigorously attacks the substance, yielding a greenish liquid, which, when mixed with excess of alkali, becomes turbid and intense crimson in colour.

*Symmetrical Succinyl-ab-diphenyldibenzoyldithiurea,*  
 $C_2H_4[CO \cdot N : C(SH) \cdot N(C_6H_5) \cdot CH_2 \cdot C_6H_5]_2$ .

Obtained, with evolution of heat, from succinyldithiocarbimide and benzyaniline; when recrystallised from boiling alcohol, it formed rosettes of slender, white needles, melting, without effervescence, at 137—138° (corr.), to an orange liquid.

It is insoluble in water, sparingly soluble in ether and carbon bisulphide, moderately in boiling alcohol or benzene, much less so in the cold, freely in acetone, chloroform, and sulphuric acid.

0.214 gave 0.1831 BaSO<sub>4</sub>. S = 11.76.

$C_{32}H_{30}N_4S_2O_2$  requires S = 11.32 per cent.

This compound, like other tertiary thionreas (see Trans., 1893, 63, 318), is not desulphurised by boiling for a short time with alkaline lead tartrate.

*Action of Caustic Alkali.*—The substance dissolved readily in warm, dilute, caustic potash, but the solution soon began to become turbid, and a copious, finely divided precipitate then rapidly formed, the contents of the vessel setting so that it could be inverted without loss. The product was drained by means of the vacuum pump, and recrystallised from very dilute spirit, whereby it was obtained in brilliant, vitreous prisms, melting at 136—137°.

The recrystallised material is insoluble in water, practically insoluble in warm dilute potash, but easily soluble in hot alcohol. It is desulphurised at once by cold ammoniacal silver nitrate, or gradually by boiling with alkaline solution of lead. In respect of all the characters mentioned, it agrees with *aa*-phenylbenzylthiourea, melting at  $136\cdot5^{\circ}$  (Werner, Proc., 1892, 96); its identity with this was further established by a sulphur determination.

0.20 gave 0.1929 BaSO<sub>4</sub>. S = 13.26.

CSN<sub>2</sub>H<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>)(C<sub>7</sub>H<sub>7</sub>) requires S = 13.23 per cent.

*Succinyl-ab-diphenyldisemithiocarbazide*,  
C<sub>2</sub>H<sub>4</sub>(CO·NH·CS·NH·NH·C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>.

Theoretical proportions of dithiocarbimide and phenylhydrazine were mixed in benzene solution; the heavy oil, which at once separated, became almost solid after standing for several days. By warming with a little alcohol, most of the adherent red oil was extracted, the yellow, solid residue was then dissolved in boiling glacial acetic acid, and, to the clear hot solution, water was added to incipient precipitation. On cooling, the substance was deposited in cream-coloured crystals, which sintered at  $210^{\circ}$ , and melted, somewhat indistinctly, at about  $220^{\circ}$  (corr.).

0.2001 gave 0.2224 BaSO<sub>4</sub>. S = 15.28.

C<sub>18</sub>H<sub>20</sub>N<sub>6</sub>S<sub>2</sub>O<sub>2</sub> requires S = 15.39 per cent.

This compound is insoluble in water, sparingly soluble in boiling alcohol, moderately easily in warm, dilute, caustic potash. The latter solution\* is not affected by continued boiling with alkaline lead tartrate, neither is the hot alcoholic solution desulphurised by ammoniacal silver nitrate.

*Diethylic Succinyl-di-β-thiocarbamate*, C<sub>2</sub>H<sub>4</sub>(CO·NH·CS·OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>.

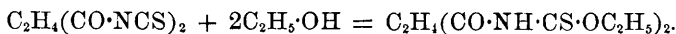
Four grams of the dithiocarbimide, in benzene solution, were mixed with excess of anhydrous ethylic alcohol. No perceptible rise of temperature occurred, but, after about 12 hours' standing, the deep red colour of the mixture began to change to greenish-brown, and granular masses of crystals, having a beautiful, delicate sea-green colour, were slowly deposited, the separation being complete after three days. By recrystallisation from boiling alcohol, the compound was obtained in tufts of thick, white prisms, melting at  $166$ – $167^{\circ}$  (corr.), with effervescence and separation of a white, crystalline substance.

\* Hydrochloric acid gave a precipitate with the potash solution, but this, on analysis, proved to be unchanged semithiocarbazide.

A sulphur determination gave figures agreeing with the formula of the di- $\beta$ -thiourethane.

0.2007 gave 0.317 BaSO<sub>4</sub>. S = 21.71.

C<sub>10</sub>H<sub>16</sub>N<sub>2</sub>S<sub>2</sub>O<sub>4</sub> requires S = 21.94 per cent.

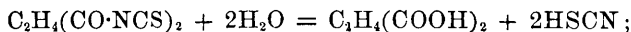


Succinyldithiodiurethane is insoluble in water or carbon bisulphide, and nearly so in ether. It dissolves sparingly in chloroform and benzene, moderately in boiling alcohol, much less so in cold. The solution in weak spirit gives no coloration with ferric chloride; with ammoniacal silver nitrate, a white precipitate falls, which blackens on heating; the sulphur is also removed by boiling with alkaline lead tartrate. When heated alone, the substance decomposes with effervescence and evolution of hydrogen sulphide and ethyl mercaptan.

Between alcohol and succinyldithiocarbimide the interaction goes very smoothly; the mixture, as already mentioned, does not become sensibly warm, neither are sticky bye-products formed; the substance deposited, save for a faint greenish coloration, is pure, and the yield is fair. With acetylthiocarbimide and alcohol, on the other hand, as previously recorded by one of us (*Trans.*, 1892, **61**, 529), the action is almost explosively violent and the decomposition profound; instead of acetylthiourethane, the products were ethylic acetate, thiocyanic acid, pseudosulphocyanogen, and free (fused) sulphur.

#### *Action of Water on Succinyldithiocarbimide.*

Two grams of the thiocarbimide in benzene were added to excess of cold water, the mixture frequently shaken, and the benzene allowed to evaporate gradually at the ordinary temperature. A small quantity of brownish, amorphous powder was removed by filtration, and the clear filtrate examined; it was strongly acid to test-paper, and gave, with ferric chloride, an intense thiocyanic reaction; when just neutralised, it gave, with the same reagent, a dull brownish-red, amorphous precipitate, and, with barium chloride, ammonia, and alcohol, a white precipitate. The main decomposition may accordingly be represented as follows.



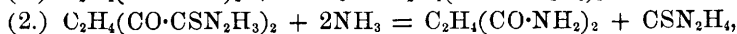
it does not, however, occur quantitatively, for not only is the brown, amorphous powder formed (the quantity of this was too small for investigation), but, in addition, the aqueous solution contains a substance—the amount of which diminishes gradually on keeping—which is desulphurised by boiling with alkaline lead tartrate.



*Action of Alcoholic Ammonia on Succinyldithiocarbimide.*

To the cooled thiocarbimide, a considerable excess of alcoholic ammonia was added; the mixture became warm, and an olive-coloured solid was deposited, accompanied by a clear, brownish oil. By recrystallisation, first from alcohol and next from alcohol and animal charcoal, the former was obtained in white needles, free from sulphur, soluble in hot, but only sparingly in cold, water, insoluble in absolute alcohol, melting at  $241-242^{\circ}$ , and consisting of succinamide (m. p. of succinamide,  $242-243^{\circ}$ ). Analysis showed the substance to contain 24.38 per cent. of nitrogen;  $C_2H_4(CO \cdot NH_2)_2$  contains 24.25.

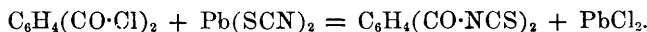
Owing to an accident, the oily product was lost; the reaction, however, probably runs in two stages as follows.



that is, succinyldithiourea is first formed, and decomposes then with the excess of ammonia, as in the case of the phenylated analogue.

Further experiments were now made with the view of obtaining a benzenoid analogue of succinyldithiocarbimide. A mixture of phthalyl chloride with dry lead thiocyanate in molecular proportions was gently warmed in presence of benzene; it soon began to turn reddish, and a vigorous action commenced, the solution boiling briskly of itself for some time; the process goes rapidly in this case, for, after further heating for a couple of minutes to the boiling point, the liquid was free from chlorine. A yellow, solid residue, consisting mainly of lead chloride, was removed by means of the filter-pump, and washed well with benzene; the filtrate, rich scarlet in colour, was further diluted, as in the case of the succinyl compound.

At the ordinary temperature, the benzene solution soon changed, even in a vacuum, and a little deep red, sticky semi-solid was deposited; on evaporating the benzene, dark reddish crystals separated, which, after washing with benzene, melted at  $112-113^{\circ}$  to a pasty, bromine-coloured liquid, but could not be obtained fit for analysis; they were probably the impure thiocarbimide, produced thus—



The benzene solution, when mixed with spirit, is easily desulphurised by silver and lead salts.

*Action of Water.*—The experiment was carried out as in the case of the succinyl analogue, the phenomena being similar to those already described. The solution became strongly acid, and thiocyanic acid was

found to be present, together with phthalic acid (m. p. observed,  $203^{\circ}$  corr.); in addition, a brownish semi-solid was formed, insoluble in water, and the aqueous solution contained a trifling quantity of a substance desulphurisable by boiling with alkaline lead tartrate.

*Action of Bases.*—Numerous experiments were made, using various bases, but with unsatisfactory results, the products usually separating as viscid pastes, hardening partially on keeping. By pouring off the benzene, digesting the residues with cold alcohol, and recrystallising, some of the compounds were obtained approximately pure, but always in very limited quantity.

Thus, from *aniline*, a substance was obtained which separated from hot acetic acid in fine needles, moderately soluble in hot alcohol, desulphurised by silver, but not by lead salts, softening at  $208^{\circ}$ , and melting at  $210$ – $211^{\circ}$  (corr.). The *orthotoluidine* product, after being well washed with spirit, formed a cream white powder, sintering at  $175^{\circ}$ , and melting at  $177$ – $178^{\circ}$  (corr.). It dissolved, like the succinyl analogues, in warm, dilute potash, and, on the addition of hydrochloric acid to the solution, it gave white needles melting at  $160$ – $161^{\circ}$  (m. p. of orthotolylthiourea,  $160$ – $161^{\circ}$ ; Trans., 1892, **61**, 525). *Benzylamine* gave rosettes of white needles, sparingly soluble in alcohol, softening at  $161^{\circ}$ , and melting at  $163^{\circ}$ . The *naphthylamine* and *benzylaniline* compounds were not obtained even approximately pure. With secondary *butylamine*, a clear, reddish oil was produced, insoluble in water, sparingly soluble in benzene, miscible with alcohol, and desulphurised by silver or lead solutions.

Sulphur found = 15.82; Cal. for  $C_6H_4(CO \cdot NH \cdot CS \cdot NHBu)_2$ , S = 16.25 per cent.

*Methylaniline* yielded a substance crystallising from alcohol in vitreous prisms, and melting at  $188$ – $189^{\circ}$  (corr.). It is not desulphurised by alkaline lead solution, but gives up its sulphur to ammoniacal silver nitrate, on warming. It is vigorously attacked by hot, fuming nitric acid, with production of a substance crystallising in pale yellow needles, melting at  $127^{\circ}$ , and possessing all the properties of trinitrophenylmethylnitramide,  $C_6H_2(NO_2)_3 \cdot NMe(NO_2)$ .

These compounds are still under investigation.

In the absence of any means of deciding, on the data so far obtained, whether the formulæ of (*e.g.*) the thiocarbimides should be written  $R'' < \begin{smallmatrix} C(NCS)_2 \\ \text{CO} \end{smallmatrix} > O$  or  $R'' < \begin{smallmatrix} CO \cdot NCS \\ CO \cdot NCS \end{smallmatrix}$ , the latter has been provisionally adopted. With respect, moreover, to some of the thiourea derivatives, there is the same uncertainty regarding the structure of the "thiocarbamidic" fraction of the molecule, which still attaches to compounds produced from mustard oil and secondary amine. Thus, for example, assuming the symmetrical constitution

for succinyldithiocarbimide, the product of its union with benzyl-aniline may be represented either as (1)  $C_2H_4(CO \cdot NH \cdot CS \cdot NPhBz)_2$ , or (2)  $C_2H_4[CO \cdot N : C(SH) \cdot NPhBz]_2$ . From experiments made by Billeter and Strohl (*Ber.*, 1888, **21**, 106), it seems probable that the normal\* trisubstituted thioureas are of the form  $XN : C(SH) \cdot NYZ$ ; a similar formula (2) has accordingly been used to represent the corresponding dithioureas.

Judging from the results described in this communication, and from other similar experiments (Miquel, *loc. cit.*), it appears that the interaction between lead thiocyanate and an acid chloride is as definite and generic as that between the alkylogens and potassium thiocyanate.

But whilst, in the latter case, an alkylic thiocyanate alone is produced, in the former, on the other hand, the product is a thiocarbimide, practically free from thiocyanate, saving what little may be formed owing to the presence of traces of moisture. Whether the lead salt itself functions as a thiocarbimide, or whether the acid radicle is specially concerned in the rearrangement of the SCN-group, is still under investigation.

It is curious that the earliest discovered acid thiocarbimide,  $CH_3 \cdot CO \cdot NCS$  (Miquel, *loc. cit.*), notwithstanding its activity, and the fact that, when treated with amines, it afforded well-marked thiocarbamide derivatives, was expressly regarded as a thiocyanate. Possibly its ready decomposition in contact with water is accountable for this— $CH_3 \cdot CO \cdot NCS + H_2O = CH_3 \cdot COOH + HSCN$ .

But the production of thiocyanic acid, does not necessarily involve the view that the parent compound is a thiocyanate; the formation of this acid is easily explained by supposing that hydrogen thiocarbimide,  $H \cdot NCS$ , is first liberated, and thereupon undergoes isomeric rearrangement into the more stable form. It seems also quite possible that the substance produced by the interaction of these thiocarbimides with water, which at first strongly desulphurises alkaline lead solution, but gradually, on keeping, almost entirely loses this power, may be  $H \cdot NCS$ , slowly reverting, in dilute solution, to  $H \cdot SCN$ .

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\* As distinguished from "pseudo"-thioureas, in which the sulphur is directly engaged with an alkyl group.