III.—*Acylogens and Thiocarbamides.*

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It has been shown in previous communications (Dixon and Taylor, *Trans.*, 1907, **91**, 912; see also Dixon and Hawthorne, *ibid.*, 122) that the reaction between certain well-defined acylogens and thiocarbamide, or its aryl monosubstitution derivatives,* leads to the production of halogen salts derived from iminothiocarbamic acid, thus:

As a rule, salts of class (i) are easily hydrolysed with regeneration of thiocarbamide, but undergo molecular change when heated, the acyl group becoming associated with one of the nitrogen atoms to form an acyl-substituted thiocarbamide:

Those of class (ii) are distinctly more stable, yielding, by cautious withdrawal of the combined halogen acid in the cold, a substance having the empirical formula of the corresponding base, namely,

This substance, however, is not the base, but an isomeride,

the acyl group, as soon as the halogen acid is neutralised, parting from the sulphur to become associated with that nitrogen atom which already holds in combination a hydrocarbon radicle.

Under the influence of heat, or of a dilute alkali (compare Hegers-

* Although in many reactions thiocarbamide behaves, not as $\text{CS}(\text{NH}_2)_2$, but as iminothiocarbamic acid, $\text{NH}:\text{C}(\text{SH}) \cdot \text{NH}_2$, and the like is true as regards a large number of its substitution derivatives, yet in the present paper (save where a definitely established structure forbids) they are all represented on the thiocarbamide type, and named accordingly. This usage is adopted, however, not to express any view as to their respective constitutions, but solely to avoid the clumsiness of attaching two or more names and formulæ to a single compound. For instance, the so-called phenylthiocarbamide, $\text{PhNH} \cdot \text{CS} \cdot \text{NH}_2$, may react as $\text{PhN}:\text{C}(\text{SH}) \cdot \text{NH}_2$, or as $\text{PhNH} \cdot \text{C}(\text{SH}) \cdot \text{NH}$; possibly, also, as a true thiocarbamide; or it may be a thiocarbamide in the static condition. The *ab*-disubstituted thiocarbamides, it would seem, are capable of reacting in three different forms, according to circumstances; if "the constitution of a compound" is to be inferred from its chemical behaviour, it is not easy to judge, in a case like this, how any save a conventional nomenclature is to be applied.

The present being principally a descriptive paper, the authors desire to confine themselves to the experimental results, and to the above statement of the convention respecting names and formulæ.

hoff, *Ber.*, 1899, **32**, 3649), the first intramolecular movement of the acyl group is followed by a second; this time to the remaining nitrogen atom, where, in the configuration :

the acyl radicle appears to have reached a position of maximum stability.

These statements outline in a merely approximate way the main results hitherto observed. Deviations of various sorts occur; for example, in certain cases, the benzoyl group, when liberated from the sulphur, moves so readily to the non-substituted nitrogen atom (to form an *ab*-disubstituted thiocarbamide) that, although the existence of an *aa*-form was recognisable (*loc. cit.*) through the characteristic reaction whereby thiocyanic acid is produced,

the movement could not be arrested at the substituted nitrogen atom long enough to permit of the isolation of the *aa*-compound.

On the other hand, in the case of the acyl groups, $\cdot\text{CO}_2\text{Me}$ and $\cdot\text{CO}_2\text{Et}$, the electronegative character of which is somewhat feeble, the first transfer from sulphur to nitrogen,

is brought about very readily, whilst the second, to produce

could not be accomplished; a failure the more remarkable, considering that by other means the synthesis of the *ab*-compound presents no difficulty.

It may be noted, too, regarding the behaviour of compounds such as $\text{PhNH}\cdot\text{C}(\text{NH})\cdot\text{S}\cdot\text{CO}_2\text{R}$, HCl , that it is not a matter of indifference whether the radicle, R, be fatty or benzenoid; for, in the latter case, on the withdrawal by alkali of the combined hydrogen chloride, no *aa*-thiocarbamide, $\text{PhN}(\text{CO}_2\text{Ar})\cdot\text{CS}\cdot\text{NH}_2$, is formed, but, instead, decomposition occurs with production of carbon dioxide, the phenol, ArOH , and phenylthiocarbimide.

Beyond the facts here roughly indicated, our knowledge of the behaviour of acylogens with thiocarbamides does not extend very far; interesting work has lately been carried out on the alkyl- ψ -thiocarbamides, derivatives of the type $\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{SAlk}$, but, for the present purpose, it is unnecessary to particularise the conclusions.

In this communication, the writers give the results of an inquiry directed mainly in order to learn (i) the effect of using an acylogen the acid radicle of which contains a second halogen element, and (ii) the behaviour of certain acylogens towards thiocarbamides containing non-aromatic substituting radicles.

EXPERIMENTAL.

α-Bromopropionyl Bromide and Phenylthiocarbamide.

If the reaction between these substances is analogous to that where ordinary alkylogens are concerned, it must proceed primarily as follows :

On the other hand, when halogenised radicles are presented for combination with the nitrogen of a thiocarbamide, ring-closing frequently occurs with elimination of halogen acid ; thus, for example, Hirsch has shown (*Ber.*, 1890, 23, 971) that methylthiocarbimide yields with β -bromopropylamine, not the expected methylbromopropylthiocarbamide, $\text{CH}_3 \cdot \text{NH} \cdot \text{CS} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CHBr} \cdot \text{CH}_3$, but, instead, the hydrobromide of an isomeric ring-compound,

This action may obviously be represented by supposing the thiocarbamide first to be produced, and then to be changed into the labile or tautomeric form, $\text{CH}_3 \cdot \text{NH} \cdot \text{C} \begin{array}{l} \nearrow \text{N} \cdot \text{CH}_2 \\ \searrow \text{SH} \end{array} \text{CHMeBr}$, whence, by loss of the elements of hydrogen bromide, the above ring-compound would result.

In like manner, if phenylthiocarbamide were first to yield with α -bromopropionyl bromide the product already formulated, this might easily transform itself into a ring-form, thus :

Experiment gave the results described below.

Vigorous action took place on mixing the constituents, dissolved in molecular proportions, in warm acetone, and, on cooling, small, white, glistening plates were deposited, giving with water a clear acid solution. When heated in a narrow tube, the solid darkened slightly at 215° , shrank at 230° , and melted with effervescence and charring at $238\text{--}239^\circ$ (uncorr.).

From the solution in water or alcohol, no picrate could be obtained, from which it seemed improbable that α -bromopropionyl- ψ -phenylthiourea hydrobromide, $\text{PhNH} \cdot \text{C}(\text{NH}) \cdot \text{S} \cdot \text{CO} \cdot \text{CHBr} \cdot \text{CH}_3, \text{HBr}$, had been formed ; neither did the solution in concentrated alkali yield any trace of red coloration when acidified and treated with ferric chloride ; hence there was no reason to suppose that migration of the acyl

group had occurred with production of *aa*-bromopropionylphenylthiocarbamide, $\text{CH}_3\cdot\text{CHBr}\cdot\text{CO}\cdot\text{NPh}\cdot\text{CS}\cdot\text{NH}_2$.

A bromine determination, however, gave figures concordant with the latter formula:

0.368 required 12.75 c.c. *N*/10 silver nitrate. $\text{Br} = 27.75$.

$\text{C}_{10}\text{H}_{11}\text{ON}_2\text{BrS}$ requires $\text{Br} = 27.87$ per cent.

But on further examination the compound proved to be a hydrobromide, and, since it was not desulphurised by boiling with an alkaline solution of lead, the sulphur must evidently be held in a closed-ring, which could have only the constitution figured above, namely,

$\cdot\text{C} \begin{smallmatrix} \text{N}\cdot\text{C} \\ \text{S}\cdot\text{CO} \end{smallmatrix}$, or, the alternative form, $\cdot\text{C} \begin{smallmatrix} \text{N}\cdot\text{CO} \\ \text{S}\cdot\text{C} \end{smallmatrix}$. That the latter of these is correct was shown by the fact that the substance, when boiled with baryta water, gave with hydrochloric acid, ferric chloride, and ammonia the purple reaction characteristic of the thioglycollic acids, and hence contains the typical linking: $\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}\cdot$.

No indication was observed of the presence of any other product than that described, which was obviously the hydrobromide of one of the various forms of so-called phenylmethylthiohydantoin, probably

$\text{PhN}:\text{C} \begin{smallmatrix} \text{S}-\text{CHMe} \\ \text{NH}\cdot\text{CO} \end{smallmatrix}$, otherwise, *N*-phenyl- α -methylthiourantoin (see

Dixon, *Trans.*, 1897, **71**, 629, 639).

Therefore, in the circumstances given, when two halogens (one being connected with the CO group of an acyl radicle, and the other a substituent in its hydrocarbon nucleus) are presented simultaneously to the SH group of $\text{PhN}:\text{C}(\text{NH}_2)\cdot\text{SH}$, the hydrogen of this combines preponderantly, if not exclusively, with the substituent halogen; hence the ring-formation which occurs also must depend mainly, if not altogether, on the union of the halogen of the $\cdot\text{COBr}$ with the hydrogen of an amino- or imino-group.

To ascertain whether temperature may influence either the direction of the primary combination (that is, which halogen unites with the SH-hydrogen) or the fact of ring-closing, the experiment was repeated in a freezing mixture at about -8° . No substantial difference of any sort was noticed, the sulphur of the product appearing, just as before to be linked solely as $\cdot\text{S}\cdot\text{CHMe}\cdot$.

Chloroacetyl Chloride and Phenylthiocarbamide.

Although, in view of the results described above, there could be little doubt as to how these substances would interact, the experiment was tried, the constituents being mixed in cooled acetone. The white product, a hydrochloride, decomposed at 230° with blackening and intumescence; from its aqueous solution, when

neutralised, a white solid crystallised out, having the melting point (177—178°) of "phenylthiohydantoin," and giving the reactions of this compound.

Acetyl Chloride and Allylthiocarbamide.

These substances combined vigorously in presence of acetone, the product, a white, apparently crystalline powder, melting at 103—104° with decomposition and effervescence. Analysis showed it to be a molecular additive compound:

0.389, dissolved in hot ammonia, gave 0.499 Ag_2S , and the filtrate contained 0.2822 AgCl . $\text{S} = 16.55$; $\text{Cl} = 17.95$.

$\text{C}_6\text{H}_{10}\text{ON}_2\text{S}_2\text{HCl}$ requires $\text{S} = 16.45$; $\text{Cl} = 18.25$ per cent.

The interaction may be represented as follows:

and then

or

Water dissolved the substance very freely, but with considerable decomposition, so that the corresponding *picrate*, an orange-yellow, crystalline solid, could be obtained only in poor yield.

Action of Caustic Alkali.—Twelve grams of the hydrochloride were dissolved in water, and to the solution, without delay, there was run in something less than one equivalent of $N/3$ alkali; the white precipitate was then collected by the aid of the pump. The filtrate, which was strongly acid, required for neutralisation about half an equivalent more of alkali, and now contained both chloride and acetate; consequently, about one-half of the hydrochloride had undergone hydrolysis with regeneration of allylthiocarbamide; no thiocyanate was present.

The crystalline precipitate, free from chlorine, melted at 95—96°, and, when recrystallised from dilute alcohol, formed brilliant needles, showing the same melting point as before. It was now practically insoluble in hydrochloric acid, and its solution in dilute alcohol yielded no picrate; hence the product did not consist of the base: $\text{C}_3\text{H}_5\cdot\text{NH}\cdot\text{C}(\text{NH})\cdot\text{S}\cdot\text{CO}\cdot\text{CH}_3$.

It was soluble, however, in dilute alkali, the solution being desulphurised by heating with a lead salt; on the other hand, when heated with strong (30 per cent.) potassium hydroxide, it gave at first a clear solution, which presently became turbid owing to the separation

of an oil; the mixture, whilst reacting intensely for thiocyanic acid, was but slightly darkened by boiling with a lead salt, and hence practically all the contained sulphur had been eliminated as thiocyanate, the oil being doubtless allylacetamide. From the above result, it appears that this form of decomposition, so characteristic of the *aa*-acylarylthiocarbamides (see Hugershoff, *Ber.*, 1899, **32**, 3649; compare also Dixon and Hawthorne, *Trans.*, 1907, **91**, 133; Dixon and Taylor, *ibid.*, 916), holds equally in the *aa*-acylalkyl class:

The above formula was checked by analysis:

0.316 required 40.2 c.c. *N*/10 barium chloride. $S = 20.4$.

$\text{C}_6\text{H}_{10}\text{ON}_2\text{S}$ requires $S = 20.25$ per cent.

It had now to be learned whether this second form of acetylallylthiocarbamide could be transformed, through migration of the acyl group, into the third, or symmetrical, variety; that such is the case is proved by the result of the following experiment.

Action of Heat.—A quantity of the *aa*-compound was maintained for some time at a temperature between 100° and 105° . After half an hour, the liquid, when treated with caustic alkali, still reacted very strongly for thiocyanic acid, but after some two hours' further heating responded but feebly to the test. On cooling, the brown melt solidified, and the solid, when twice recrystallised from boiling, dilute alcohol, formed long, silky needles melting at 73 – 74° . With hot water, the product yielded an almost neutral solution, giving no precipitate with excess of picric acid; it was soluble also in cold strong alkali, the solution being desulphurised by boiling with a lead salt, but giving with hydrochloric acid and ferric chloride no trace of red coloration. On analysis:

0.158 gave 0.230 BaSO_4 . $S = 20.0$.

$\text{C}_6\text{H}_{10}\text{ON}_2\text{S}$ requires $S = 20.25$ per cent.

This product, accordingly, was isomeric with the last described, and consisted of *ab*-acetylallylthiocarbamide. The series of changes, starting from the compound of allylthiocarbamide and acetyl chloride, may be summed up as follows:

When *ab*-acetylallylthiocarbamide was cautiously heated somewhat above its melting point, the pungent odour of acetylthiocarbimide became perceptible, and the fusion, when treated with water and ferric chloride, gave an intense blood-red coloration. This behaviour

of acylated thiocarbamides has already been pointed out and discussed (Dixon, *Trans.*, 1906, **89**, 905).

From the foregoing experiments, it may be concluded that when a fatty acylogen reacts with a monosubstituted thiocarbamide the general behaviour of the product, as regards intramolecular movement of the contained acid radicle, is independent of whether the substituting group of the thiocarbamide is cyclic or otherwise. It remained for experiment to show how acetyl chloride would behave with a disubstituted thiocarbamide containing the allyl group.

Acetyl Chloride and ab-Phenylallylthiocarbamide.

When acetyl chloride was added in slight excess to phenylallylthiocarbamide dissolved in warm benzene, a clear, yellow oil was precipitated, showing even after long keeping no tendency to become solid. The product, a hydrochloride (containing a trace of phenylthiocarbimide), was rather sparingly soluble in water, but easily so in alcohol, the latter solution yielding with alcoholic picric acid a *picrate*, crystallising in long, transparent needles, resembling monoclinic sulphur in colour and appearance, and melting at 154—155° (corr.).

With dilute caustic alkali, the aqueous solution of the hydrochloride gave an oil, soon changing to a crystalline solid; the latter, after two recrystallisations from boiling dilute alcohol, separated in needles melting at 117—118° (corr.). The product was slightly alkaline; when treated with hydrochloric acid, it yielded again the oily hydrochloride, and then in turn the *picrate*: hence it was plain that the acetyl group, if united originally to sulphur, had not undergone the usual movement to a nitrogen atom, since in that case the basic character would have been lost. Moreover, that the acetyl group had not remained attached to sulphur was evident from the facts, that on boiling the base with caustic alkali and a lead salt the mixture was not darkened, and that the alcoholic solution gave with silver nitrate a white precipitate, sparingly soluble in ammonia and showing no sign of desulphurisation when boiled with it.

Boiling with concentrated nitric acid failed to produce any detectable amount of sulphuric acid; nevertheless the compound contained sulphur, for on ignition with zinc filings, metallic sulphide was obtained, and by fusion with caustic alkali and nitre, alkali sulphate. The sulphur therefore must form part of a ring; from which it was inferred that the acetyl group had probably gone to saturate the allyl group, in which case, ring formation could easily occur in either of the following ways:

if now, as usual, the chlorine and the SH-hydrogen interact,

whence, as before,

Analysis, however, failed to substantiate this view, for :

0.20 gave 24.6 c.c. moist nitrogen at 15° and 748 mm. N = 14.7, whilst the compounds just formulated would require N = 11.97 per cent.

The percentage of nitrogen found agrees closely with that calculated for phenylallylthiocarbamide itself, namely, 14.58, and a comparison of the properties of the product with those of the isomeride of phenylallylthiocarbamide, "*N*-phenylpropylene-ψ-thiourea,"

obtained by Prager (*Ber.*, 1889, 22, 2992) from the first-named and concentrated hydrochloric acid at 100°, shows them to be the one compound. Prager gives for the melting points of base and picrate, 117° and 154° respectively; the authors' figures, as stated above, were 117—118° and 154—155°.

If the mechanism of this unexpected change operates as supposed, the chlorine of the acetyl chloride must have united primarily with the middle carbon atom of the allyl group as represented in case (ii) above; here, by the simple exchange of hydrogen for acetyl, however this be conditioned, the propylene configuration would result :

Considering that allylthiocarbamide reacts with hydrochloric acid at 100° in precisely the same way as does phenylallylthiocarbamide (that is, propylene-ψ-thiourea is formed, $\text{NH}_2 \cdot \text{C} \begin{array}{l} \text{N} \cdot \text{CH}_2 \\ \text{S} \text{---} \text{CH} \cdot \text{CH}_3 \end{array}$; see Gabriel, *Ber.*, 1889, 22, 2985), it seems curious that the two should behave so differently with acetyl chloride.

The question naturally arising whether an acylogen less electro-negative than acetyl chloride would behave similarly to the latter, the alkyl chlorocarbonates were selected for the purpose of experiment.

Methyl Chlorocarbonate and Phenylallylthiocarbamide.

Slight excess of methyl chlorocarbonate was added to a gently warmed solution of phenylallylthiocarbamide in acetone. No heat was evolved, nor did the mixture become turbid, but on evaporation at the ordinary temperature, beautiful, large, vitreous prisms were obtained; after being well washed with ether and dried, they melted with copious effervescence at about 87°.

The product dissolved in sulphuric acid with frothing and evolution of hydrogen chloride. On analysis:

0.3006 required 10.5 c.c. *N*/10 silver nitrate. Cl = 12.4.

$C_{13}H_{14}O_2N_2S, HCl$ requires Cl = 12.39 per cent.

About 88 per cent. of the theoretical yield was obtained. The gas expelled by heating the hydrochloride proved to be carbon dioxide; by maintaining the heat cautiously until the effervescence ceased, an oily residue was obtained, the solution of which in water gave with caustic alkali a white, oily precipitate having a strong odour of mercaptan and yielding with a lead salt the yellow lead mercaptide. The chlorocarbonate residue therefore had become attached to the sulphur atom (and not to the allyl group), the change by heat proceeding thus:

Action of Water on the Hydrochloride.—When added to water, the hydrochloride yielded a very acid solution, which, if treated at once with picric acid, gave the bright yellow picrate; with caustic alkali, it furnished a white precipitate, soluble in excess, the solution having a distinct odour of mercaptan, and undergoing desulphurisation when heated with a lead salt. On the other hand, the aqueous solution, when kept for a short time, became turbid (the same change occurred at once on warming), owing to the separation of an oil, soon changing to a crystalline solid; the liquor from this, when treated with picric acid, yielded no precipitate, neither did caustic alkali give any precipitate or produce the odour of mercaptan; when the alkaline mixture was treated with a lead salt, no mercaptide was formed, but desulphurisation occurred on warming:

The material precipitated by the action of water on the dissolved hydrochloride contained no chlorine and had lost all basic properties; it was now insoluble in dilute hydrochloric acid, and did not yield a picrate. When recrystallised from dilute alcohol, it formed long, colourless prisms, melting at 82—83° without effervescence. The solution in caustic alkali gave no mercaptan on heating, and when mixed with a lead salt was slowly desulphurised by boiling.

These phenomena are so nearly in accordance with those observed for the compounds of ethyl chlorocarbonate with phenylthiocarbamide and its congeners (Dixon and Taylor, *loc. cit.*) as to leave no doubt that all belong to the same class.

What occurs therefore in the attack by water may be explained as follows. Dissociation of the hydrochloride takes place, the hydrochloric acid passing into solution] with liberation of the free base, either carboxymethyl- ψ -*n*-phenyl- ν -allylthiourea,

or its tautomeride, carboxymethyl- ν -phenyl- ψ -*n*-allylthiourea,

which is unstable in presence of water, probably by reason of the feeble attraction between sulphur and the acidic group. In a case such as this, at least so far as we yet know, if neither of the nitrogen atoms of the thiourea be substituted, the acid group simply leaves the molecule by hydrolysis, whereupon the corresponding thiocarbamide is regenerated; but if one be substituted, the acyl group now moves to it, and there becomes attached, so as to produce an *aa*-disubstituted thiocarbamide. In this particular instance, where both nitrogen atoms are substituted by different radicles, the acyl group might become attached to either, or distributively to both; it was observed, however, that in the attack by caustic alkali, phenylthiocarbimide was always produced, a fact which gives some clue to the position of the phenyl group. For, when caustic alkali decomposes an *aa*-disubstituted acidic thiocarbamide, the interaction takes place almost quantitatively as follows:

That is, of the two hydrogen atoms available, one goes to form substituted amide, the other yielding $\text{H}\cdot\text{NCS}$, a compound which does not exist as such in contact with water, but passes rapidly into the form, $\text{H}\cdot\text{SCN}$. If the behaviour of a trisubstituted derivative is similar, then, when the one remaining hydrogen atom has passed over to the disubstituted nitrogen atom to form the corresponding amide, there remains only $\text{CSN}\cdot\text{R}$, a thiocarbimide, the radicle, R , being that originally associated with the hydrogenised nitrogen. Since, then, in the above decomposition, phenylthiocarbimide is produced (no thiocyanic acid could be detected), there is at least some ground for supposing the composition of the parent compound to be:

unless it be the isomeric (or tautomeric) thiourea, from which at present there is no means of distinguishing it.

To check the composition of the supposed trisubstituted derivative, it was analysed :

0.250 gave 0.239 BaSO₄. S = 13.1.

C₁₂H₁₄O₂N₂S requires S = 12.80 per cent.

Ethyl Chlorocarbonate and Phenylallylthiocarbamide.

By operating as described in the last case, precisely similar results were obtained, the end product being a crystalline, white hydrochloride, melting with effervescence (due to the escape of carbon dioxide) at 96° :

0.601 required 19.7 c.c. N/10 silver nitrate. Cl = 11.6.

C₁₃H₁₆O₂N₂S.HCl requires Cl = 11.81 per cent.

In all respects save one, the properties of this hydrochloride resembled those of the preceding, and hence need not be described in detail. The one point of difference was that the oily precipitate, which separated from the aqueous solution of the hydrochloride, did not solidify, even after remaining for some time at -8° and then for six months in a vacuum desiccator. Otherwise it resembled the methylic homologue, being gradually desulphurised, for example, by hot alkaline lead tartrate, without yielding any odour of mercaptan. Trisubstituted thiocarbamides, containing hydrocarbon groups, are not desulphurised readily, if at all, by this treatment ; it is probable therefore that the change mentioned, which is markedly slower than in the case of the parent phenylallylthiocarbamide, is due to the withdrawal of the contained acyl group by means of the alkali.

On analysis, the oil gave the following result :

0.2664 yielded 0.232 BaSO₄. S = 12.0.

C₁₃H₁₆O₂N₂S requires S = 12.12 per cent.

Hence it was a form of carboxyethylphenylallylthiocarbamide.

In addition to the above, a number of experiments were conducted with the view of learning whether union could be effected of (1) benzyl chloride with acetylthiocarbamide, and (2) acetyl chloride with benzyl-ψ-thiourea, thus :

and if so, whether the products would be identical or would differ from one another, owing to the occurrence of tautomeric forms.

Both these combinations, it was found, could easily be effected, the latter occurring vigorously when the constituents, dissolved in cold acetone, were mixed together ; in each case, a white, crystalline hydrochloride was isolated, and shown by analysis to be an additive compound. From each hydrochloride, too, a corresponding base was

liberated, the sulphur contents of which agreed closely with the figures calculated.

Nevertheless, such considerable variations of melting point were encountered amongst the hydrochlorides that no definite conclusion could be drawn as to their identity or otherwise, and the same was true regarding the bases. The melting points of the latter were generally wanting in sharpness, overlapping one another somewhere in the neighbourhood of 140° ; by recrystallisation (during which benzyl mercaptan was freely evolved), they could be made to coincide at $210\text{--}211^{\circ}$, the product, acetylcarbamide, resulting, no doubt, from the acetylcyanamide formed by loss of benzyl mercaptan:

The compounds being so unstable that there seemed little prospect of isolating them in a really pure condition, the experiments in this direction were not pursued; it may perhaps be added that continued work with benzyl mercaptan is very disagreeable.

With benzylthiocarbamide in acetone, acetyl chloride gave a white hydrochloride, which became pasty even when kept in a desiccator, and had an odour of acetyl chloride. Ferric chloride gave with the aqueous solution no trace of red coloration; but on treatment with strong alkali, thiocyanic acid was produced in abundance, showing that the acetyl group had migrated to the benzylated nitrogen atom. The amount of material being small, no attempt was made to isolate the *aa*-acetylbenzylthiocarbamide. The isomeric *ab*-compound, produced by Werner (Trans., 1891, 59, 562) from benzylthiocarbamide and acetic anhydride, gives no thiocyanic acid when treated with alkali.

Summary and Conclusion.

Briefly put, the main results of the present inquiry are as follows:

(1) When an ordinary acylogen, $\text{R}\cdot\text{CO}\cdot\text{X}$ (X =halogen), unites with phenylthiocarbamide, the product is a derivative of phenylthiourea, $\text{PhNH}\cdot\text{C}(\text{NH})\cdot\text{SH}$, having the form:

If, however, the acylogen contains a second halogen as substituent in the aliphatic nucleus, R, the interaction takes place differently, the sulphur atom now becoming engaged, not with the carbon of the CO group, but with the other carbon atom which originally was halogenised; concurrently, the halogen of the group $\cdot\text{CO}\cdot\text{X}$ withdraws hydrogen from the non-phenylated nitrogen, and ring-closing occurs with production of a substituted "thiohydantoin."

(2) Acetyl chloride behaves with allylthiocarbamide precisely as with monosubstituted arylthiocarbamides, yielding a hydrochloride,

30 CLARKE, LAPWORTH, AND WECHSLER: CONDENSATION OF

$C_3H_5 \cdot NH \cdot C(NH) \cdot SAc, HCl$, the acetyl group of which may be caused to migrate within the molecule so as to yield, first,

and then $C_3H_5 \cdot NH \cdot CS \cdot NHAc$; the latter compounds melt at 96° and 74° respectively.

(3) With *ab*-phenylallylthiocarbamide, acetyl chloride yields "*N*-phenylpropylene ψ -thiourea," $PhNH \cdot C \begin{smallmatrix} \swarrow N \cdot CH_2 \\ \searrow S \cdot CH \cdot CH_3 \end{smallmatrix}$, the acetyl group being eliminated.

(4) *ab*-Phenylallylthiocarbamide unites with methyl chlorocarbonate to form a hydrochloride, probably

by mere dissolution in water, this substance loses hydrogen chloride, the carboxymethyl group thereupon migrating to yield a trisubstituted thiocarbamide, probably $C_3H_5 \cdot N(CO_2Me) \cdot CS \cdot NHPh$. With ethyl chlorocarbonate, similar combinations are obtained.

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