XXXVIII.—*Action of Metallic Thiocyanates on Certain Substituted Carbamic and Oxamic Chlorides; and a New Method for the Production of Thiobiurets.*

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CONCERNING the action of lead and other metallic thiocyanates on halogenised organic compounds, a number of communications have recently been made from this laboratory (Trans., 1895, 67, 565,

1040; 1896, 69, 855, 1593; 1897, 71, 617); the present paper includes an account of results obtained with the chlorides of certain nitrogenous acids.

So far as data are yet available, the nature of the interaction between inorganic thiocyanates and halogenised organic compounds appears to depend mainly on the way in which the halogen is attached, although its occurrence and extent are further influenced by the presence or absence of solvent, the nature of the solvent, the temperature, the particular inorganic radicle employed, and the time occupied in withdrawing the halogen.

As regards the first point, every compound hitherto examined containing the group $\text{-CO}\cdot\text{Cl}$ united with an organic radicle, under suitable conditions exchanges its halogen for the thiocyanic residue, the product in each case functioning towards primary and secondary amines, alcohols, phenylhydrazine, and lead or silver solutions, not as a true thiocyanate, but as a thiocarbimide. Dicarboxylic acid chlorides yield analogous derivatives, for instance, $\text{C}_2\text{H}_4(\text{CO}\cdot\text{NCS})_2$, and carbonyl chloride itself, if heated with lead thiocyanate in presence of toluene, affords much thiocarbimide product, whether $\text{CO}(\text{NCS})_2$ or not is still uncertain.

From ordinary thiocarbimides, these acidic compounds differ in being more or less easily decomposable by water, with formation of thiocyanic acid or carbonyl sulphide; moreover, some of them, although uniting readily with amines, are broken up on contact with ammonia into a corresponding amide and thiocyanic acid; it may be that the unstable forms are tautomeric.

The chlorine united with certain negative groups other than carbonyl is similarly exchangeable; thus thionyl chloride, sulphuryl chloride, chlorosulphonic acid, ethylsulphuric and phenylsulphonic chlorides all interact with metallic thiocyanates, affording thiocarbimide products; but so far as they have yet been examined, these actions run less smoothly, and the complete withdrawal of the halogen appears to be a matter of difficulty. Phosphorus trichloride easily yields a substance having the general properties of an unstable acidic isothiocyanate, which is desulphurised by lead and silver salts, and combines spontaneously with aniline, to form a solid decomposable by water, with production of phenylthiourea. The study of this interesting action is still incomplete, but it seems as though the first product were phosphorus isothiocyanate, $\text{P}(\text{NCS})_3$, and the second, phosphorus triphenyltrithiourea, $\text{P}(\text{NH}\cdot\text{CS}\cdot\text{NHPh})_3$, the latter undergoing hydrolysis into phenylthiourea and an acid of phosphorus. Similar results have been obtained using phosphorus oxychloride.

It is well known that halogen in non-acidic combination can also be exchanged, but the products have no longer a thiocarbimide

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character; thus with ethylic bromide, benzylic chloride, ethylic monochloracetate, and so on, the process may be carried out in alcoholic solution, since true thiocyanates are formed, whilst if an acid chloride be employed under like conditions, the end-product (unless the chloride be itself destroyed by the alcohol) is a substituted thiourethane. It may be noted that substitution of NCS for the halogen in such 'negative' attachment is much more rapidly effected than when SCN replaces it in a purely hydrocarbon radicle; thus it is possible, from chloracetyl chloride, $\text{CH}_2\text{Cl}\cdot\text{COCl}$, to directly obtain the derivative $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NCS}$ (Trans., 1897, 71, 620).

It is not clear, from the above results, whether the introduction of $-\text{NCS}$ or $-\text{SCN}$ groups in place of a halogen is in some way dependent on whether or not the original compound is *generally* acidic in character. If so, one might expect chloracetylthiocarbimide to pass on, more or less readily, into glycolyldithiocarbimide, $\begin{array}{c} \text{CH}_2\cdot\text{NCS} \\ | \\ \text{CO}-\text{NCS} \end{array}$, but, on the other hand, it is conceivable that the $-\text{NCS}$ first introduced might 'protect' the remaining chlorine atom from attack; to test this speculation, some experiments were made with acidic monohalogen compounds. Monochloroacetic acid and picryl chloride were employed, under varying conditions as regards temperature, time, solvent, and nature of the metallic thiocyanate; the results may be summarised by stating that the latter gave no detectable thiocarbimide under any circumstances—in fact, it did not appear to interact at all; the former did not altogether escape attack, but the quantity of thiocarbimide product, even under the most favourable conditions, although sufficient to be easily detected, was but an insignificant fraction of the amount of acid used. Consequently, it would seem that the only halogenised compounds which undergo any material conversion into isothiocyanate, in this way, are those in which the halogen is in direct combination with a negative group.

The object of the present investigation was to ascertain whether the chlorides derived from certain nitrogenised carboxylic acids would undergo change into the corresponding isothiocyanates. Derivatives of carbamic acid were first tried, with a view to obtain a class of substances bearing towards the thiobiurets and ethereal salts of thioallophanic acid a relation somewhat analogous to that subsisting between ordinary thiocarbimides, on the one hand, and the corresponding thio-carbamides and thiocarbamic ethers on the other, and thus to lead up to a general synthetical method for the preparation of such compounds. As yet, the carbamic chlorides derived from benzenoid acids appear to be known only in the form of disubstitution derivatives;* the inter-

* Unless 'phenylisocyanate hydrochloride' be really $\text{NHPh}\cdot\text{COCl}$. Whether mono- or non-substituted carbamyl isothiocyanates can exist in the free state remains

action between these alone and metallic thiocyanates is dealt with in the present communication.

Assuming that the various classes of biurets, &c., above referred to are similar in constitution, their relations may be shown by the typical formulæ.

(where R and R' are supposed to be monad hydrocarbon radicles); and, as will be seen in the experimental part, representatives of all three latter classes have now been obtained. The isothiocyanates themselves, IV, could not be isolated, but their existence in solution was established by the production of members of classes V and VI, as well as of certain other derivatives, for instance, thiosemicarbazides, $\text{R}_2\text{N} \cdot \text{CO} \cdot \text{NH} \cdot \text{CS} \cdot \text{NH} \cdot \text{NHPh}$. Not many syntheses have been effected under class VI, benzylic alcohol alone of those employed uniting with the isothiocyanates in question, but the derivatives which have been obtained are interesting as representatives of a class of thioallophanates hitherto unknown.

From phenyloxamic acid, a corresponding isothiocyanate has also been prepared, $\text{NHPh} \cdot \text{CO} \cdot \text{CO} \cdot \text{NCS}$, and from this, in turn, a compound, $\text{NHPh} \cdot \text{CO} \cdot \text{CO} \cdot \text{NH} \cdot \text{CS} \cdot \text{NHPh}$; in type, it is related to biuret in somewhat the same way as oxamide is to urea.

Amongst substituted thiobiurets, isomerism of position may obviously occur with respect both to radicles and to the sulphur. The typical forms are generally represented as similar to thiocarbamide, $\text{NH}_2 \cdot \text{CS} \cdot \text{NH}_2$, but since the existence is now well established, amongst derivatives of the latter, of substances constituted or acting also on the 'thiourea' type, $\text{HS} \cdot \text{C}(\text{NH}) \cdot \text{NH}_2$, the occurrence of such labile forms amongst thiobiurets might be anticipated; moreover, in the case of certain substituted dithiobiurets, a variety of it has recently been observed (Billeter, *Ber.*, 1893, **26**, 1688). From these two causes alone, and without including the forms obtained by Billeter, the number of isomerides possible for a given compound is very high. Thus, a monosubstitution derivative, containing the simplest hydrocarbon radicle, may conceivably exist in ten different varieties three derived from $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CS} \cdot \text{NH}_2$, and seven more from

to be discovered; in such a combination as $\text{NHPh} \cdot \text{CO} \cdot \text{NCS}$, the NCS might possibly tend to unite with the NHPh group to form $\text{CO} \begin{smallmatrix} \text{NPh} \\ \text{NH} \end{smallmatrix} \text{CS}$ (carbonylphenylthiocarbamide), or else $\text{NPh} : \text{C} \begin{smallmatrix} \text{NH} \\ \text{O} \end{smallmatrix} \text{CS}$. However, the compound $\text{NHPh} \cdot \text{CO} \cdot \text{CO} \cdot \text{NCS}$ appears to be able to exist as such. See p. 409.

$\text{NH}_2 \cdot \text{CO} \cdot \text{N} : \text{C} \begin{smallmatrix} \text{SH} \\ \text{NH}_2 \end{smallmatrix}$, or $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C} \begin{smallmatrix} \text{SH}^* \\ \text{NH} \end{smallmatrix}$, whilst if the CONH_2 -group be also supposed capable of labile change, the number of isomerides reaches twenty-six. Unfortunately, no adequate nomenclature exists for expressing the constitution of even the known forms in this class of substances.

In this paper, the convention adopted, in order to define the position of substituting groups, is to mark the three nitrogen attachments, α , β , and ψ respectively, starting from the end atom, next the sulphur.

For convenience in naming such thioallophanic salts as are represented on the ordinary type, the term thioallophanic acid might be restricted to carboxythiocarbamide, the two nitrogen attachments being indicated, as in other thiocarbamides, by α and β respectively; if oxygen be otherwise replaced by sulphur, the position adjoining β might be marked β , whilst the ψ -symbol would serve, as usual, to indicate mercaptoid forms.

Derivatives of the typical compounds (1) $\text{NH}_2 \cdot \text{CS} \cdot \text{NH} \cdot \text{CO} \cdot \text{OH}$, (2) $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CS} \cdot \text{OH}$, and (3) $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{SH}$, would thus be named thioallophanates, β -thioallophanates, and ψ -thioallophanates respectively; the derivatives of dithioallophanic acid might be similarly distinguished. Of the above three typical forms of monothioallophanates, derivatives of (1) and (3) only have yet been recorded, for example, $\text{NHPh} \cdot \text{CS} \cdot \text{NPh} \cdot \text{CO} \cdot \text{OEt}$ (Seidel, *J. pr. Chem.*, 1885, [ii], 32, 263); $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{S} \cdot \text{C}_2\text{H}_5$ (Peitzsch and Salomon, *ibid.*, 7, 477); as stated earlier, representatives of (2) are now forthcoming—it may be, however, in a labile form.

Several years ago (Trans., 1893, 63, 318), the author drew attention to a peculiarity of the disubstituted fatty and allylic thiocarbamides namely, that they are not desulphurised by boiling with alkaline solution of lead tartrate, whereas if either (or both) of the groups be benzenoid in character, desulphurisation occurs. Acetyl, benzoyl, and anisoyl groups appear to function, in this respect, similarly to aromatic hydrocarbon radicles, but the group $\text{R}_2\text{N} \cdot \text{CO}$, contained in

* From its analogy to thiourea, it seems not improbable that monothioureter itself should be represented by one of the two latter formulæ; perhaps also the di- and tetra-substituted thiobiurets, described below. But, in the absence of any definite evidence regarding their structure, they are here provisionally represented on the ordinary biuret type.

the thiobiurets described below, seems to play the same part in relation to such desulphurisation as though it were an aliphatic residue ; thus, for instance, *c*-diphenyl- α -methyl (similarly, α -ethyl and α -benzyl) thiobiuret withholds its sulphur, whilst the corresponding *c*-diphenyl- α - (ortho- and para-)tolyl compounds give it up.

Alcoholic silver nitrate, as a rule, desulphurises the thiobiurets on warming ; this action serves as the basis of a rapid, but not very satisfactory, method for obtaining the corresponding biurets, a few of which, as well as a guanidine-like compound of the biuret class, have thus been prepared.

Some attempts were made to produce biurets through the direct action of carbamic chlorides upon substituted thioureas, for instance, to realise the interaction

Alcoholic solutions were first tried, and subsequently fusion of the mixed constituents, but without success. Thiocarbamilide was employed, with results which are detailed below ; benzylethylphenylthiourea gave no better results than the monophenyl compound.

I. *Derivatives of DiphenylcarbamyI Isothiocyanate.*

When lead or copper thiocyanate was heated with diphenylcarbamyI chloride, $(\text{C}_6\text{H}_5)_2\text{N} \cdot \text{COCl}$, in presence of alcohol, benzene, or toluene, little or no thiocarbimide product was obtained, and the addition of zinc dust appeared to exert no influence. Using cumene, a certain amount of action soon took place, although a solution perfectly free from chlorine was not obtained, even after prolonged boiling. With potassium thiocyanate, the phenomena were similar, but on substituting a mercurial salt, the difficulty was overcome. The chloride, dissolved in dry cumene, is mixed with about double the theoretical amount of sifted mercuric thiocyanate, and the mixture (which should contain enough cumene to be freely mobile) rapidly heated, with constant shaking. At or near the boiling point, action sets in ; the thiocyanate darkens, swells up, and becomes pasty ; on cooling, it hardens to a brittle mass, which is ground up in a mortar and the whole filtered and washed ; a pale yellow solution is thus obtained, generally free from chlorine—if the latter is still present, it must be removed by boiling up with a fresh charge of thiocyanate and filtering again. The flask should not be too small to allow of vigorous shaking—600 c.c. is a convenient size, preferably of Jena glass, and the conical form is best adapted to the (often troublesome) operation of breaking up and getting out the solid residue. A glass tube serves as condenser and to prevent the vapour from taking fire at the mouth of

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the flask ; the latter can be comfortably held with a thick asbestos glove. On the whole, it appears best to work with small charges (10 to 15 grams of chloride at a time) in order to get the action completed and the solution cooled without delay.

The liquid thus obtained is devoid of pungent odour, but contains a thiocarbimide in solution ; it is desulphurised by boiling with alkaline lead tartrate, and with ammoniacal nitrate of silver yields a precipitate of silver sulphide, even in the cold, but more readily on warming. When brought in contact with nitrogenous bases, action takes place spontaneously, with development of heat and formation of additive compounds ; with benzylic alcohol, combination occurs less readily. The formation of the thiocarbimide may be represented by the equation

but the yield, under the above conditions, falls considerably short of the theoretical ; some desulphurisation occurs, and the solution usually contains traces (and sometimes more than traces) of some yellowish, amorphous, metallic compound.

acc-Triphenylthiobiuret.—On adding aniline (1 mol.), dissolved in benzene, to the cumene solution, the mixture at once became warm, and solid matter presently began to separate. After it had stood for a little, the whitish product was collected and washed, first with benzene and then with light petroleum. When dry, its weight amounted to 62 per cent. of that obtainable according to the equation

and reckoned on the quantity of diphenylcarbamic chloride used.

On recrystallisation from boiling acetone, brilliant, pure white needles were obtained, melting at 163—163·5° (corr.) ; they were dried over sulphuric acid and analysed.

0·2 gave 0·1386 BaSO₄. S = 9·52.

0·2053 gave 0·1398 BaSO₄. S = 9·36.

0·2134 gave 22·1 c.c. moist nitrogen at 17° and 768 mm. N = 12·14.

C₂₀H₁₇N₃SO requires S = 9·23 ; N = 12·13 per cent.

The compound is therefore, as was expected, a triphenylthiobiuret.

It is insoluble in water, very sparingly soluble in ether, sparingly in carbon bisulphide, rather more easily in boiling alcohol and acetone, and moderately so in hot benzene and chloroform. Its alcoholic solution is slowly and imperfectly desulphurised by boiling with alkaline lead tartrate, whilst with silver nitrate a white precipitate is formed, which blackens quickly on the addition of ammonia. Strong nitric acid attacks the substance vigorously on gentle warm-

ing, evolving carbonic anhydride and yielding an orange solution; from this, water precipitates a bright yellow, amorphous solid, apparently a nitro-compound, and the aqueous solution contains sulphuric acid. The above solid is insoluble in cold water, but dissolves easily in warm spirit, forming a lemon-yellow solution, which, on the addition of excess of potash or ammonia, becomes rich scarlet, almost identical in colour with Nencki's beautiful 'rhodanic red.' It was found later that diphenylcarbamic chloride itself behaves similarly.

The compound dissolves in boiling acetic anhydride, with formation of phenylthiocarbimide, which, on adding water, separates in oily droplets, and the residual solution, on cooling, deposits white needles, probably acetyldiphenylcarbamide, $\text{NHAc} \cdot \text{CO} \cdot \text{NPh}_2$, but the action was not examined in detail.

An attempt was made, by dissolving the substance in (1 mol.) hot potash, and adding silver nitrate, to obtain the corresponding biuret; the product, however, formed brown, sticky granules, which presently changed into a black tar.

a-Orthotolyl-c-diphenylthiobiuret.—On adding the ortho-base, dissolved in benzene, to a freshly prepared solution of the diphenyl compound, the phenomena were similar to those observed in the preceding case, but the yield amounted to only 50 per cent. of the theoretical. By recrystallisation from boiling alcohol, fine, white needles were obtained, melting at $163.5\text{--}164^\circ$ (corr.). A sulphur determination yielded figures agreeing with those required for the thiobiuret, $(\text{C}_6\text{H}_5)_2\text{N} \cdot \text{CO} \cdot \text{NH} \cdot \text{CS} \cdot \text{NH} \cdot \text{C}_7\text{H}_7$.

0.2102 gave 0.1342 BaSO_4 . $\text{S} = 8.77$.

$\text{C}_{21}\text{H}_{19}\text{N}_3\text{SO}$ requires $\text{S} = 8.87$.

The substance is insoluble in water, moderately soluble in boiling alcohol or acetone, rather sparingly in cold. Its alcoholic solution is gradually desulphurised by boiling with alkaline lead tartrate; it is only darkened, in the cold, by ammoniacal nitrate of silver, but blackens at once on heating. Nitric acid vigorously oxidises the solid, yielding sulphuric acid, together with a bright yellow nitro-compound apparently identical with that obtained in like manner from the phenylic homologue.

Desulphurisation.—Alcoholic silver nitrate (2 mols.) was added to the thiobiuret (1 mol.) dissolved in a boiling mixture of chloroform and alcohol, the silver sulphide was removed by filtration, using the pump, and the greenish-brown, clear liquid thus obtained deposited microscopic prisms on cooling. After recrystallisation from spirit, they became slightly moist at 130° , melted at $132\text{--}133^\circ$ (corr.), and gave the following results on analysis.

0.2002 gave 20.9 c.c. nitrogen at 14° and 755 mm. $N = 12.19$.

$(C_6H_5)_2N \cdot CO \cdot NH \cdot CO \cdot NH \cdot C_7H_7$ requires $N = 12.20$ per cent.

The yield was 63 per cent. of the theoretical.

a-Diphenyl-*c*-orthotolylbiuret is insoluble in water, moderately soluble in hot alcohol, sparingly in cold alcohol, ether, and light petroleum, freely in benzene and chloroform. It is scarcely soluble in boiling caustic soda, and, as might be expected,* does not give the copper biuret reaction. It is insoluble in hydrochloric, but soluble in sulphuric acid, the solution being precipitated on dilution with water. Nitric acid attacks it vigorously, affording a nitro-compound, in the same way as the parent substance.

a-Paratolyl-*c*-diphenylthiobiuret.—Using paratoluidine, a nearly white solid was deposited, which, after being extracted by, and recrystallised from, boiling alcohol, in which it is rather sparingly soluble, was obtained in microscopic needles; it behaves towards solvents in much the same way as the phenylic homologue, and melts at $172\text{--}172.5^{\circ}$ (corr.).

0.2144 gave 0.1369 $BaSO_4$. $S = 8.77$.

$(C_6H_5)_2N \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_7H_7$ requires $S = 8.87$ per cent.

It is desulphurised by alkaline lead salts, or by ammoniacal silver salts, in the same manner as the preceding thio-compounds, and behaves similarly on treatment with nitric acid.

a-Methyl-*c*-diphenylthiobiuret.—Thirty-three per cent. aqueous methylamine was used, diluted with plenty of absolute alcohol; by recrystallisation from boiling spirit, in which it is only moderately soluble, the product was obtained in soft, white needles, insoluble in water, sintering at 166° and melting at $170\text{--}171^{\circ}$ (corr.). Alkaline lead solution does not withdraw the sulphur on boiling, but the alcoholic solution is immediately blackened, even in the cold, by ammoniacal nitrate of silver.

0.2132 gave 0.174 $BaSO_4$. $S = 11.22$.

$(C_6H_5)_2N \cdot CO \cdot NH \cdot CS \cdot NH \cdot CH_3$ requires $S = 11.24$ per cent.

a-Ethyl-*c*-diphenylthiobiuret.—Prepared, like the preceding, from ethylamine; ice-like plates were deposited which, after a couple of recrystallisations from spirit, formed brilliant, silky, flattened prisms, becoming somewhat electrical on friction, and melting at $137\text{--}138^{\circ}$ (corr.). The substance is insoluble in water, moderately easily soluble in boiling alcohol, sparingly in cold; it dissolves in warm, dilute, caustic alkali, the solution being precipitated on the addition

* If one hydrogen in each of the two NH-groups in biuret be substituted, the product no longer gives the biuret reaction (H. Schiff, *Annalen*, 1897, **299**, 260).

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of excess of hydrochloric acid. With lead and silver salts, it behaves like the methylic homologue.

0.2044 gave 0.1634 BaSO_4 . $S = 10.99$.

$\text{C}_{16}\text{H}_{17}\text{N}_3\text{SO}$ requires $S = 10.71$ per cent.

a-Benzyl-c-diphenylthiobiuret.—Combination occurred with evolution of heat, the yield of solid product amounting to something over 63 per cent. of the theoretical for the weight of chloride used. After two recrystallisations from alcohol (the second of which did not alter the melting point), the substance was deposited in beautiful tufts of white, feathery needles, sintering a little at 166° , and melting at $167\text{--}168^\circ$ (corr.).

0.2195 gave 0.1412 BaSO_4 . $S = 8.84$.

$(\text{C}_6\text{H}_5)_2\text{N}\cdot\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5$ requires $S = 8.87$ per cent.

The compound is insoluble in water, slowly and sparingly soluble in hot alcohol, very sparingly in cold. With ammoniacal nitrate of silver in the cold, or more readily on warming, its alcoholic solution yields a precipitate of silver sulphide, but it is not desulphurised by boiling with alkaline lead tartrate. Nitric acid acts on this compound in the way previously described; nitrobenzene was also formed.

c-Diphenylthiobiuret.—Alcoholic ammonia, in very slight excess, was added to the solution of the isothiocyanate, and in a few seconds the deposition of solid matter commenced; after recrystallisation, long, thin prisms were obtained, having a faint yellow tinge, and melting at 183° (corr.) to an amber-coloured liquid. Yield, nearly 70 per cent. of the theoretical.

0.2168 gave 0.1904 BaSO_4 . $S = 12.07$.

$(\text{C}_6\text{H}_5)_2\text{N}\cdot\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}_2$ requires $S = 11.82$ per cent.

c-Diphenylthiobiuret is insoluble in water, moderately soluble in boiling alcohol, sparingly in cold, easily in dilute caustic alkalis. It is desulphurised, although not readily, by lead tartrate, but gives up its sulphur easily to hot ammoniacal nitrate of silver. With nitric acid, it behaves like its higher substituted allies.

The isomeric *ac*-diphenylthiobiuret is still unknown; an attempt was made to obtain it by expelling with aniline the ethoxy-group in *a*-carboxyethyl-*b*-phenylthiocarbamide (Doran, *Trans.*, 1896, 69, 326), the desired interaction being

Molecular proportions were mixed and carefully heated, whereupon gas was evolved, smelling strongly of mercaptan, and burning with a

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bluish flame; the residue presently solidified, and on recrystallisation from alcohol gave a main crop of short prisms, followed by a lesser one consisting of leaflets; when again recrystallised, the latter melted at 130° , and proved to be the unaltered carboxy-derivative. The main product, on the other hand, was practically free from sulphur; it softened at 220° , melted at about $235\text{--}236^{\circ}$, and consisted, apparently, of carbanilide.

c-Diphenylthiobiuret and Chloracetic Acid.—Diphenylthiobiuret may obviously be regarded as diphenylcarbamythiocarbamide (or -thiourea); an experiment was therefore made, in order to learn whether it would behave as a thiourea with chloracetic acid, yielding a thiohydantoin-like derivative.

The former, dissolved in alcohol, was evaporated down on the water-bath with ethylic monochloracetate but this method not proving satisfactory, another portion was carefully fused over an argand burner, with a slight excess of the free acid, until effervescence commenced; the yellow melt was then allowed to solidify, dissolved in warm, dilute alcohol, and the solution exactly neutralised with caustic alkali. On cooling, a solid was deposited which, after recrystallisation from boiling alcohol, was obtained in beautiful tufts of thin, flexible needles, melting at $184\text{--}185^{\circ}$ (corr.) to a liquid of the colour of bromine. The compound is insoluble in water, moderately soluble in hot alcohol, easily in cold alkali, and when boiled with the latter, gives Andreasch's iron reaction for thioglycollic acid. It is not affected by boiling with alkaline lead solution; with ammoniacal silver nitrate, a white precipitate is soon formed, but it does not blacken, even on boiling.

0.2047 gave 0.1529 BaSO_4 . $S = 10.26$.

$\text{C}_{16}\text{H}_{13}\text{N}_3\text{SO}_2$ requires $S = 10.30$ per cent.

This compound is accordingly the expected *n*-diphenylcarbamythiourantoin (nomenclature, *Trans.*, 1897, 71, 638); its formation may be explained (representing the thiobiuret molecule in a labile form) as follows.

a-Benzylphenyl-c-diphenylthiobiuret.—Only a few experiments were made with secondary amines; this is the only case in which any definite compound could be isolated, and the yield was very poor. Benzylaniline was used, the first attempt being a failure; the second time, after concentrating on the water-bath, a clear brown solution was obtained, but it gave no sign of solid matter, even after being kept for many days. It was steam distilled in order to remove solvents, the

residual oil (which now sank in water) mixed with spirit, boiled up with animal charcoal, and heated on the water-bath to drive off the spirit; the treatment with spirit was repeated, and the dark-coloured, thick oil thus obtained, after being kept for some time over sulphuric acid, partially solidified. The solid, when separated from adherent oil, washed, and recrystallised from alcohol, occurred in tufts of white needles, becoming somewhat electrical on friction, and melting at $137-138^{\circ}$ (corr.).

0.2099 gave 0.1140 BaSO_4 . $S = 7.46$
 $(\text{C}_6\text{H}_5)_2\text{N} \cdot \text{CO} \cdot \text{NH} \cdot \text{CS} \cdot \text{N}(\text{C}_6\text{H}_5) \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_5$ requires $S = 7.33$ per cent.

This tetra-substituted thiobiuret is insoluble in water, freely soluble in hot alcohol, sparingly in cold, almost insoluble in weak potash. Its alcoholic solution is slowly desulphurised by boiling with alkaline lead tartrate, with formation of a speculum; ammoniacal nitrate of silver blackens it instantly in the cold.

With *piperidine*, the product was an oil which could not be made to solidify; it contained about 2 per cent. less sulphur than would be required for $\text{NPh}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CS} \cdot \text{N} \cdot \text{C}_5\text{H}_{10}$.

In the hope of effecting substitution at the remaining nitrogen attachment, *benzylethylphenylthiourea* and the chloride were heated together in chloroform, in the proportions required for the action

but combination failed to occur under these conditions, and the experiment was not pursued.

a-Diphenylcarbonyl-β-phenylthiosemicarbazide.*—With phenylhydrazine, in benzene, solid matter separated at once; after recrystallisation from boiling spirit, fine, almost pure white needles were obtained, melting at $152.5-153^{\circ}$ (corr.).

0.201 gave 0.1294 BaSO_4 . $S = 8.85$.

$\text{C}_{20}\text{H}_{18}\text{N}_4\text{SO}$ requires $S = 8.84$ per cent.

The interaction may be represented as follows.

The yield was fairly satisfactory, amounting to 76 per cent. of that required by the above equation, and reckoned, as usual, on the amount of chloride taken.

The thiosemicarbazide is insoluble in water, and only sparingly soluble in boiling alcohol; it dissolves in concentrated sulphuric acid, giving a fine, emerald-green solution, which is oxidised by ferric

* For nomenclature see *Trans.*, 1896, **69**, 861.

chloride, with formation of a buff-coloured precipitate. Its alcoholic solution, when treated with bleaching powder, acquires a reddish-brown coloration ; with Fehling's solution, it becomes deep blue (this colour-reaction is very intense), but no reduction occurs, even on boiling. Desulphurisation is not effected by lead or silver salts at the boiling point of the mixtures ; but the solid is attacked by strong nitric acid, with formation of sulphuric acid, and of the yellow nitro-derivative.

An attempt was made to combine ethylphenylthiosemicarbazide, in hot alcohol, with diphenylcarbonyl chloride, in the hope of obtaining a more completely substituted compound than the above, but without success.

Benzyl α-Diphenyl-β-thioallophanate.—When excess of benzylic alcohol was mixed with the isothiocyanate, no change appeared to occur in the cold, but on concentrating the mixture on the water-bath, a small quantity of an amorphous, yellowish powder separated, which blackened on heating with caustic alkali, owing to the formation of mercuric sulphide. After a time, the solution deposited thick, yellowish crystals ; these were dissolved in boiling spirit, and the solution filtered ; the crop of crystals thus obtained consisted of small, vitreous, apparently rhombic, prisms ; they softened a little at 140°, and melted at 141—142° (corr.). A sulphur determination gave the figures required for an additive compound.

0.2084 gave 0.1320 BaSO₄. S = 8.70.

C₂₁H₁₈N₂SO₂ requires S = 8.85 per cent.

The compound is insoluble in water, very sparingly soluble in light petroleum, easily in benzene and alcohol ; the latter solution is not desulphurised by boiling with alkaline lead tartrate. Ammoniacal nitrate of silver yields a pale, greenish-yellow precipitate, which, on heating, whitens and partially dissolves. Nitric acid vigorously oxidises the solid, producing sulphuric acid, together with the yellow nitro-derivative.

Attempts made to combine other alcohols with diphenylcarbonylthiocarbimide did not give satisfactory results. Methylic and ethylic alcohols were boiled with the cumene solution ; in another experiment, ethylic alcohol was heated with it at 100°, under pressure, for nearly an hour ; in another, cinnamic alcohol was employed, and the mixture steam distilled ; but in no case could any definite compound

be isolated. Sodium ethoxide, in absolute alcohol, was tried, but the mixture decomposed, yielding metallic sulphide together with mercaptan.

An attempt to isolate the thiocarbimide by steam distillation met with no better success; thiocyanic acid was found in the aqueous distillate, together with traces of some compound desulphurisable by lead and silver salts; the blackish residue gave up to alcohol a substance containing neither sulphur nor chlorine, it melted at 183–184° (corr.), and consisted, apparently, of tetraphenylurea, $\text{CO}[\text{N}(\text{C}_6\text{H}_5)_2]_2$. The action is doubtless similar to that occurring with many other acidic thiocarbimides, namely,

the former product then decomposing,

II. *Derivatives of Methylphenylcarbaryl Isothiocyanate.*

In the earlier experiments, methylaniline, dissolved in cumene, was mixed with the theoretical amount of carbonyl chloride in toluene solution, the methylaniline hydrochloride filtered off, and the filtrate then treated, as usual, with mercuric thiocyanate; the yields obtained on treatment with bases were, however, very poor, much oily or tarry product being formed. Subsequently, when the pure carbamic chloride was employed, the solution had little odour; it was pale yellow; if shaken up with cold water and mixed with ferric chloride, a barely perceptible thiocyanic reaction was produced, but if previously boiled with water, a distinct, although not very strongly marked, red coloration appeared. It was desulphurised in the cold by ammoniacal silver nitrate, and by lead salts on heating.

a-Phenyl-c-methylphenylthiobiuret.—In preparing this compound, as in all other cases, except where it is otherwise stated, the base was added dissolved in benzene; on concentrating on the water-bath, some mercuric sulphide was deposited (this happens, to a greater or less extent, in nearly all these preparations), and an oil left which was dissolved in spirit, treated with animal charcoal, and filtered. A sticky product was obtained, which eventually yielded woolly masses of needles, insoluble in water, freely soluble in hot alcohol, moderately in cold, and melting at 158–159° (corr.). The formula, $\text{CH}_3 \cdot (\text{C}_6\text{H}_5)\text{N} \cdot \text{CO} \cdot \text{NH} \cdot \text{CS} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$, was checked by a sulphur determination.

0.212 gave 0.1777 BaSO_4 . $\text{S} = 11.52$.

$\text{C}_{15}\text{H}_{15}\text{N}_3\text{SO}$ requires $\text{S} = 11.24$ per cent.

The alcoholic solution is desulphurised instantly by cold ammoniacal nitrate of silver, and moderately readily by heating with alkaline lead tartrate; the latter property serves to distinguish it from the isomeric α -methyl-*c*-diphenyl compound, which, in addition, melts 12° higher. Warm nitric acid vigorously attacks the solid, with evolution of carbonic anhydride and formation of sulphuric acid; water added to the solution precipitates a pale yellow, amorphous nitro-derivative, which dissolves in warm alcohol; if this solution is mixed with excess of alkali, a clear, rich, orange-red coloration appears.

a-Orthotolyl-*c*-methylphenylthiobiuret.—Orthotoluidine gave a solid which, on recrystallisation from alcohol containing a little benzene, formed shining needles (or, by slow evaporation, thick, vitreous prisms) insoluble in water, easily soluble in hot spirit, and melting at 108° (corr.).

0.2218 gave 0.1743 BaSO_4 . $S = 10.8$.

$\text{C}_{16}\text{H}_{17}\text{N}_3\text{SO}$ requires $S = 10.71$ per cent.

With lead and silver salts, it behaves like the phenylic homologue.

a-Paratolyl-*c*-methylphenylthiobiuret.—Paratoluidine, dissolved in absolute alcohol, was used; the solid product, when twice recrystallised from a mixture of benzene and alcohol, occurred in white, glistening plates, melting at 156 — 157° (corr.).

0.2048 gave 0.1634 BaSO_4 . $S = 10.97$.

Calculated $S = 10.71$ per cent.

The compound is insoluble in water, rather sparingly soluble in hot alcohol, much more easily in benzene. Like the preceding, it is desulphurised by lead and silver salts, and if left in contact with nitric acid, a violent action soon sets in, with formation of a nitro-compound.

a-Methyl-*c*-methylphenylthiobiuret.—Prepared like the corresponding α -methyl-*c*-diphenyl compound, the mixture solidifying after a week; by treatment with animal charcoal, colourless, leafy crystals were obtained having a pearly lustre, and melting at 90 — 91° (corr.).

0.2018 gave 0.2121 BaSO_4 . $S = 14.45$.

$\text{CH}_3 \cdot \text{N}(\text{C}_6\text{H}_5) \cdot \text{CO} \cdot \text{NH} \cdot \text{CS} \cdot \text{NH} \cdot \text{CH}_3$ requires $S = 14.36$ per cent.

The substance is insoluble in water, very freely soluble in hot alcohol, and easily so in cold; its solution gives no precipitate when treated with silver nitrate, but the mixture is blackened on boiling. With the ammoniacal nitrate, silver sulphide is precipitated in the cold, but the solution is not desulphurised by alkaline lead tartrate, even on boiling.

c-Methylphenylthiobiuret.—A trifle less than the calculated quantity of

alcoholic ammonia was used; the yellowish, crystalline product amounted to about 61 per cent. of the theoretical. From hot alcohol, it was deposited in very brilliant, colourless, apparently clinorhombic prisms melting at 166—167° (corr.).

0.2044 gave 0.2348 BaSO₄. S = 15.79.

0.4 gave, by wet combustion, 0.7563 CO₂. C = 51.56.

CH₃·N(C₆H₅)·CO·NH·CS·NH₂ requires S = 15.32; C = 51.62 per cent.

The compound is insoluble in water, easily soluble in hot alcohol, moderately in cold; its solution is neutral to litmus. It is desulphurised in the cold by ammoniacal silver nitrate, and, on heating, by the neutral nitrate or alkaline tartrate of lead.

Action of Chloracetic Acid.—Methylphenylthiobiuret and chloracetic acid were carefully fused together until hydrogen chloride ceased to escape, when the mass solidified. The yellow product was dissolved in hot spirit, potash added until exactly neutral, and the crystals which separated on cooling, after further recrystallisation from a mixture of chloroform and alcohol, were obtained as a yellowish, sandy powder, softening a little at 187°, and melting at 199—200° (corr.), with effervescence, to a liquid the colour of bromine.

0.2032 gave 0.1892 BaSO₄. S = 12.96.

CH₃·N(C₆H₅)·CO·N:C<S—CH₂
NH·CO requires S = 12.87 per cent.

n-Methylphenylcarbamylothiourantoin is insoluble in water, rather sparingly soluble in alcohol, more freely in chloroform. It dissolves easily in concentrated hydrochloric acid or in dilute caustic alkali; the latter solution is not desulphurised by boiling with a lead salt, but if boiled alone for a few minutes, gives the iron reaction for thio-glycollic acid. Ammoniacal silver nitrate gives no precipitate with the alcoholic solution, neither is the mixture blackened on heating.

In the hope of obtaining methylphenylcarbamyldioxythiazole, NMePh·CO·N:C<S·CH₂
O·CO, the above compound was boiled in hydrochloric acid solution; decomposition, however, seemed to occur, and the product, when mixed with caustic alkali, yielded ammonia, together with a dark-coloured oil smelling of methylaniline.

α-Methylphenylcarbamyyl-β-phenylthiosemicarbazide.—Heat was evolved on adding the hydrazine (in alcohol), and after some days tufts of needles began to appear; these were collected, washed thoroughly with spirit, and the melting point taken; it proved to be 119—120°, and the fused material, on being heated to 140°, showed no sign of change. The whole crop was dissolved in alcohol, a trace of hydrochloric acid added, and the mixture boiled for a short time; on cooling,

long, brilliant, vitreous prisms melting at 120—121° (corr.) separated, and the mother liquor deposited another crop, melting only 1° lower. It would seem, therefore, that stereoisomeric forms are not produced in this interaction, at least under the above conditions.

0.2034 gave 0.176 BaSO₄. S = 10.72.

CH₃·N(C₆H₅)·CO·NH·CS·NH·NH·C₆H₅ requires S = 10.68 per cent.

It is insoluble in water, moderately soluble in hot alcohol, rather sparingly in cold; its alcoholic solution, when boiled with alkaline lead tartrate, is not desulphurised, but develops a pale yellow coloration; alcoholic silver nitrate affords a yellowish precipitate, changing gradually, through orange and brown, to black. Copper sulphate yields an intense, bottle-green coloration; potassium ferricyanide produces no definite effect, but the solution becomes clear, bright orange if treated with bleaching powder, chlorine water, or ferric chloride.

Benzyl α-Methylphenyl-β-thioallophanate.—The constituents, after heating on the water-bath, gave an oily product, which, at the end of three weeks, began to solidify. After frequent recrystallisations from spirit, using animal charcoal, vitreous prisms were obtained, apparently rhombohedral, and melting at 90—91° (corr.).

0.216 gave 0.1704 BaSO₄. S = 10.84.

CH₃·N(C₆H₅)·CO·NH·CS·O·CH₂·C₆H₅ requires S = 10.68 per cent.

The substance is insoluble in water, easily soluble in alcohol; its solution is not affected by heating with alkaline lead tartrate, and with ammoniacal nitrate of silver yields a white precipitate which dissolves on warming.

Attempt to isolate the Thiocarbimide.—About 20 grams of chloride were converted into thiocarbimide, and the solution distilled under a pressure of 12 mm.; nearly all the cumene came over at 56—61°, and between 65° and 68° two very trifling fractions were taken, consisting mainly of cumene also; at this point, distillation practically ceased, the residue now beginning to decompose, with evolution of so much gas that the vacuum, at 95°, could not be kept below 45 mm. The temperature was pushed to 120°, but only 1 or 2 drops of an oily liquid distilled over, and brown fumes now began to appear, whereupon the process was stopped; only a few grams of a reddish-black tar remained, and this eventually hardened; it was found to be practically free from sulphur. The thiocarbimide was not completely destroyed, since all the fractions gave a reaction, more or less, with lead and silver salts; but it is evident that if it can be isolated at all in this way, it must be done at a much lower pressure than 12 mm. In preparing these compounds, it has frequently been noticed that the best yield is obtained when the chlorine is removed in the shortest time; if, for

example, a second heating with mercuric thiocyanate be required, the yield falls below the average; hence it seems probable that, when prepared in the above way, the temperatures of formation and decomposition (even in presence of much solvent) overlap to some extent.

Methylphenylcarbamic Chloride and Thiocarbanilide.—It was hoped that these substances would interact so as to afford a methyltriphenylthiobiuret,

On gently heating the substances together, in molecular proportion, the mixture first liquefied, then effervesced, and soon became almost solid; the escaping gas rendered lime-water turbid, and blackened alkaline lead paper, whilst the pasty residue smelt of phenylthiocarbimide. By distilling the residue with steam, it was ascertained that, for every 2 mols. of thiocarbanilide employed, 1 mol. of phenylthiocarbimide was produced. The solid left in the distilling flask was almost entirely soluble in boiling water, and when twice recrystallised from this solvent, formed white prisms, darkening and melting at about 238° (uncorr.). On further examination, it proved to be the hydrochloride of a *base*, melting at 144 — 144.5° , giving a *picrate* melting at 177 — 178° , and having the properties of *sym*-triphenylguanidine.

0.2022 gave 25 c.c. moist nitrogen at 14° and 773 mm. $N = 14.79$.

$(\text{NH}\cdot\text{C}_6\text{H}_5)_2\text{C}\cdot\text{N}\cdot\text{C}_6\text{H}_5$ requires $N = 14.67$ per cent.

III. *Derivatives of Ethylphenylcarbamyl Isothiocyanate.*

This compound was prepared as before, using ethylphenylcarbamic chloride, and the product, a clear, pale brown solution, resembled its congeners.

a-Phenyl-c-ethylphenylthiobiuret.—When the solvents evaporated, a viscid, dark brown oil was left, from which crystals very slowly separated. When purified, they formed white prisms, melting at 106 — 107° (corr.). The yield was poor.

0.2034 gave 0.1578 BaSO_4 . $S = 10.66$.

$\text{C}_6\text{H}_5\cdot\text{N}(\text{C}_6\text{H}_5)\cdot\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$ requires $S = 10.71$ per cent.

The compound is insoluble in water, easily soluble in hot, moderately in cold, alcohol. In its behaviour with silver salts, it resembles the isomeric *c*-diphenyl-*a*-ethyl derivative, but differs from this by melting more than 30° lower, and by giving up its sulphur to alkaline lead tartrate.

a-Orthotolyl-c-ethylphenylthiobiuret.—This was precipitated by light

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petroleum as a solid which crystallised from alcohol in pure white needles, resembling the preceding compound in regard to solvents, and melting at 124—125° (corr.). In this case, also, the yield was small. It is desulphurised by lead and silver salts, and is attacked by strong nitric acid in the same way as the *c*-diphenyl analogue.

0·2018 gave 0·1543 BaSO₄. S = 10·51.

C₁₇H₁₀N₃SO requires S = 10·23 per cent.

a-Paratolyl-*c*-ethylphenylthiobiuret.—When recrystallised from a mixture of chloroform and alcohol, it formed slender, white needles, becoming extraordinarily electrical on friction, and melting at 174° (corr.).

0·226 gave 0·1688 BaSO₄. S = 10·26. Calculated, S = 10·23 per cent.

It is insoluble in water, very slightly soluble in alcohol, benzene, or acetic acid, easily in chloroform.

c-Ethylphenylthiobiuret.—Exactly 1 mol. prop. of alcoholic ammonia was used, and a mass of thick crystals obtained, the yield being over 69 per cent. of the theoretical; when purified by several recrystallisations from spirit, large, flat pointed prisms were obtained, having a greasy lustre, and melting at 147—148° (corr.).

0·211 gave 0·2222 BaSO₄. S = 14·47.

C₂H₅·N(C₆H₅)·CO·NH·CS·NH₂ requires S = 14·36 per cent.

It is insoluble in water, easily soluble in hot alcohol, but only slightly in cold.

n-Ethylphenylcarbonyl-thiourantoin.—Obtained by fusing the above compound with monochloroacetic acid, and operating as previously described. After treatment with animal charcoal and two recrystallisations from a mixture of chloroform and alcohol, the product formed a sandy powder, still slightly yellow; it sintered at 182° and melted at 184—185° (corr.) to a deep red liquid.

0·2009 gave 0·1865 BaSO₄. S = 12·76.

C₂H₅·N(C₆H₅)·CO·N·C $\begin{matrix} \text{S} - \text{CH}_2 \\ \text{NH} \cdot \text{CO} \end{matrix}$ requires S = 12·17 per cent.

The solution in caustic alkali, when boiled for a few minutes, gives the iron reaction for thioglycollic acid; with respect to solvents, and to lead and silver salts, this compound resembles the *n*-methylphenyl homologue.

Benzyllic a-Ethylphenyl-β-thioallophanate.—Obtained at the temperature of the water-bath; when purified, it formed small, vitreous prisms, free from colour and melting at 119·5—120·5° (corr.).

Found, S = 10·13 ; C = 64·87 per cent.

$C_2H_5 \cdot N(C_6H_5) \cdot CO \cdot NH \cdot CS \cdot O(CH_2 \cdot C_6H_5)$ requires S = 10·20 ;
C = 64·92 per cent.

It is insoluble in water, moderately soluble in hot alcohol ; the solution in benzene is precipitated by adding light petroleum ; it is not desulphurised by alkaline lead salts ; nitrate of silver yields a white precipitate which dissolves in ammonia on warming.

IV. *Derivatives of Benzylphenylcarbamyyl Isothiocyanate.*

The parent compound formed a yellow solution having no distinctive odour ; with ferric chloride, it gave a slight thiocyanic reaction, and otherwise resembled its congeners.

a-Phenyl-c-benzylphenylthiobiuret.—Colourless prisms, insoluble in water, easily soluble in hot alcohol, and melting at 102·5—103·5°(corr.).

Found, S = 8·75. $C_7H_7 \cdot N(C_6H_5) \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_6H_5$, requires S = 8·87 per cent.

It is isomeric with the *a*-benzyl-*c*-diphenyl compound melting at 168°, from which it also differs by giving up its sulphur to alkaline lead tartrate.

a-Orthotolyl-c-benzylphenylthiobiuret.—The crude product, the yield of which amounted to over 72 per cent. of the theoretical, after recrystallisation from a mixture of alcohol and chloroform and then from spirit alone, formed brilliant, vitreous lozenges, only moderately soluble in boiling alcohol, easily in chloroform, and melting at 131—132° (corr.). It is desulphurised in the cold by neutral or ammoniacal silver nitrate, and by alkaline lead salts on boiling. With nitric acid, it gives a canary-yellow solid, whose alcoholic solution acquires a fine ruby colour when mixed with excess of alkali.

Found, S = 8·60. $C_{22}H_{21}N_3SO$ requires S = 8·54 per cent.

Desulphurisation.—By desulphurising certain of the thiobiurets described in this paper, a number of corresponding biurets have been obtained, a complete account of which is deferred for the present ; the compound mentioned below was got by chance in one of these preparations, owing to the incautious use of ammonia, and is here introduced in order to show that the substituted carbamyl group may also take part in the formation of a guanidine derivative.

The orthotolyl compound, dissolved in boiling alcohol with the assistance of a little caustic potash, was mixed with alcoholic ammonia and treated with the calculated quantity of ammoniacal silver nitrate ; the metallic sulphide was filtered off, and the filtrate precipitated by water. The solid product, when recrystallised a few times from

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alcohol, occurred in well-formed, hard, vitreous prisms insoluble in water, easily soluble in hot alcohol, melting at $136-136.5^\circ$ (corr.) yielding 15.39 per cent. of nitrogen, and hence not consisting of the expected biuret, $C_7H_7 \cdot NPh \cdot CO \cdot NH \cdot CO \cdot NH_2To$, which would require $N = 11.73$ per cent.

A complete combustion gave the following data.

0.2042 gave 0.55 CO_2 and 0.1216 H_2O . $C = 73.45$; $H = 6.6$.

0.2011 „ 26.8 c.c. moist nitrogen at 15° and 767 mm. $N = 15.81$.

These figures lead to the formula $C_{22}H_{22}N_4O$.

	C.	H.	N.	O (by diff.).
Experiment.....	73.45	6.6	15.81	15.39
Theory.....	73.69	6.15	15.68	4.48

Consequently, the ammonia, which was added merely to hinder the precipitation of silver oxide, itself takes part in the change, the product being a benzylphenylcarbamylothotolylguanidine,

a-Methyl-c-benzylphenylthiobiuret.—White prisms, melting at $99-100^\circ$ (corr.); insoluble in water, moderately soluble in hot alcohol; desulphurised by ammoniacal silver nitrate in the cold. Alkaline lead tartrate gives a white precipitate, easily soluble in excess of warm, dilute alkali; this solution is not perceptibly affected by boiling.

S found, 10.97. $C_{16}H_{17}N_3SO$ requires $S = 10.71$ per cent.

a-Ethyl-c-benzylphenylthiobiuret.—The product was dark coloured and sticky; after standing for about 6 weeks, it began to solidify, and eventually yielded white, pointed prisms, moderately soluble in cold alcohol, easily in benzene, and melting at $67-68^\circ$.

Found, $S = 10.35$. $C_{17}H_{19}N_3SO$ requires $S = 10.26$ per cent.

Its properties are similar to those of the preceding compound.

c-Benzylphenylthiobiuret.—Was deposited from a mixture of chloroform and alcohol in beautiful, vitreous, apparently rectangular, prisms, becoming slightly moist at 178° and melting at $179-180^\circ$ (corr.) with effervescence.

Found, $S = 11.47$. $C_6H_5 \cdot N(C_7H_7) \cdot CO \cdot NH \cdot CS \cdot NH_2$ requires $S = 11.24$ per cent.

Properties: rather sparingly soluble in hot alcohol, more readily in chloroform; it dissolves easily in warm, dilute alkali, and the solution is desulphurised by boiling with lead tartrate. Neutral silver nitrate gives no precipitate; the ammoniacal nitrate yields a

white, curdy derivative, which is stable in the cold, but dissolves partially on warming, the solution soon becoming black. Nitric acid gives a yellow nitro-compound.

n-Benzylphenylcarbamylthiourantoin.—Prepared like its analogues; when twice recrystallised, it was a yellowish, sandy powder softening at 193° and melting between 194° and 195° (corr.) to a deep red liquid. It gives the iron reaction for thioglycollic acid when boiled with potash, and generally resembles the corresponding *n*-methylphenyl compound.

Found, S = 9.75. $C_6H_5 \cdot CH_2 \cdot N(C_6H_5) \cdot CO \cdot N : C \begin{smallmatrix} S-CH_2 \\ NH \cdot CO \end{smallmatrix}$ requires
S = 9.85 per cent.

Benzyllic α-Benzylphenyl-β-thioallophanate.—Sixty-five per cent. of the theoretical yield was obtained; on recrystallisation from a mixture of alcohol and chloroform, and finally from alcohol alone, the product was obtained in brilliant, vitreous prisms, melting at 133–134° (corr.) to a dark liquid.

Found, S = 8.58. $C_{22}H_{20}N_2SO_2$ requires S = 8.52 per cent.

In regard to solvents, &c., it resembles its congeners already described.

V. Phenylloxamyl (Oxanilyl) Isothiocyanate.

A solution of this compound was obtained by heating phenyloxamic chloride, dissolved in anhydrous toluene, with excess of lead thiocyanate; * the temperature must not be allowed to rise too high, otherwise decomposition sets in, with brisk evolution of gas. The solution, when cooled thoroughly and filtered, was clear reddish-brown in colour, free from halogen, possessed no characteristic odour, and gave, with lead and silver salts, the usual thiocarbimide reactions. When shaken up with cold water, the mixture gave a slight red coloration with ferric chloride, and on heating with water, the thiocyanic reaction, although not intense, was appreciably increased.

The interaction which it was desired to realise between lead thiocyanate and oxanilic chloride runs as follows.

It was quite possible, of course, that the NCS-group, if formed, might unite with the hydrogenised residue, NHPh, so as to produce some ring compound, such as phenylthioparabanic acid, $CS \begin{smallmatrix} NPh \cdot CO \\ NH \cdot CO \end{smallmatrix}$.

* The mercury salt gave less satisfactory results, owing to its tendency to produce some soluble, amorphous, metallic compound.

On the other hand, the power of NCS to combine with an amidic residue is paralysed, or at least greatly weakened, if the latter be in direct union with an acidic group; * it therefore appeared probable that $\text{NHPh}\cdot\text{CO}\cdot\text{CO}\cdot\text{NCS}$ would be able to exist as such, and in effect this proved to be the case, for the compound exhibits the 'unsaturated' thiocarbimide character, uniting directly with aniline to form a thiocarbamide.

Action of Aniline.—When the pure base (1 mol.) was dissolved in absolute alcohol and mixed with aniline, the mixture soon became hot, and a finely-divided, crystalline solid was deposited, which, on recrystallisation from a mixture of benzene and alcohol, formed microscopic needles having a lemon-yellow colour, which was not removed by treatment with animal charcoal; it melted at $172\text{--}173^\circ$ (corr.).

0.2200 gave 0.1732 BaSO_4 . $\text{S} = 10.82$.

0.2072 „ 25 c.c. moist nitrogen at 20° and 765 mm. $\text{N} = 14.00$.

$\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$ requires $\text{S} = 10.71$;

$\text{N} = 14.08$ per cent.

The product, *a-phenyloxamyl-b-phenylthiocarbamide*, or diphenylthio-oxaluramide, is insoluble in water or hydrochloric acid, moderately soluble in hot alcohol or acetone, more easily in benzene, very freely in chloroform. The alcoholic solution is desulphurised in the cold by ammoniacal silver nitrate, and by warming with alkaline lead tartrate; with ferric chloride, it gives no coloration, either directly or after previous heating with alkali. The solid dissolves gradually in hot caustic potash, and if the solution is now mixed with a slight excess of hydrochloric acid, phenylthiourea is precipitated.

Action of Ammonia.—On passing excess of the gas into the toluene solution, a solid was precipitated which, after recrystallisation from spirit, was obtained in pearly, flattened crystals practically devoid of sulphur and melting at about 223° ; the mother liquor, from which the solid had been deposited, contained thiocyanic acid. The crystals, which were not analysed, consisted, probably, of phenyloxamide, the melting point of which is 224° .

In conclusion, the author desires to acknowledge his indebtedness to the Research Fund Committee for a grant in aid of the purchase of materials used in the above investigation; and to Mr. R. E. Doran, for assistance rendered in connection with it.

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* Phenylthiocarbimide does not interact, under ordinary circumstances, with acetamide or acetanilide; it does not even seem able to combine with asparagine.