XL.—*Certain Organic Phosphorus Compounds.*

By AUGUSTUS EDWARD DIXON, M.D.

SOME few years ago, the author called attention to the existence of a kind of tautomerism, in which the mobility of hydrogen, or other monadic radicle, plays no part. The phenomenon, which takes the form of an apparent variability in the mode of attachment of a whole group, is observable amongst the so-called "thiocyanates" of organic acids, many of these exhibiting the power to interact, according to the conditions under which they are placed, either as such or as thiocarbimides (Trans., 1901, **79**, 541). Following up the study of this peculiar behaviour, which seems to be confined exclusively to members of the class named,* the writer was led to inquire whether a like

---

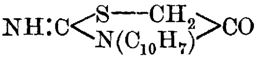
* The isomeric rearrangement of a thiocyanate into a thiocarbimide is well known, for instance, that of allyl thiocyanate into the corresponding thiocarbamide, a change which occurs spontaneously on keeping. Amongst paraffinoid derivatives, the tendency to change is slight; nevertheless, a case has been observed, for Hofmann has recorded (*Ber.*, 1885, **18**, 2197) the partial conversion of methyl thiocyanate into methylthiocarbimide by heating for several hours at a temperature of some 50° above the boiling point of the former. But these rearrangements are not

power would be manifested by the thiocyanates of mineral acid radicles, and some evidence was adduced (*loc. cit.*) to show that phosphorus and phosphoryl thiocyanates (which, however, were only obtained in solution) possess to a certain extent the characters of thiocarbimides. Since then, means have been found of isolating both these compounds with but little difficulty and the present paper includes a description of the methods employed, the properties of the products, and the results obtained by bringing them into contact with nitrogenous bases.

Before proceeding to the experimental data, it should, perhaps, be recalled that many new facts have lately come to our knowledge concerning the thiocyanates of organic radicles and their isomerides, the "mustard-oils," H. L. Wheeler having especially contributed in this direction. Amongst other things, it has now been established that double decomposition between metallic thiocyanates and halogen derivatives of substituted methanes does not necessarily lead to the formation of the corresponding thiocyanates, but that thiocarbimides are sometimes produced instead. Thus, potassium thiocyanate, when heated with phenyl-*p*-tolylmethyl bromide dissolved in benzene, yields the thiocarbimide, $C_6H_4Me{\cdot}CHPh{\cdot}NCS$, although benzyl-*p*-tolyl bromide is mainly converted into the corresponding thiocyanate (Wheeler and Jamieson, *J. Amer. Chem. Soc.*, 1902, **24**, 746).

Phenyl-α-naphthylmethyl bromide and di-α-naphthylmethyl bromide under like treatment yield the thiocarbimides $C_{10}H_7{\cdot}CHPh{\cdot}NCS$ and $(C_{10}H_7)_2CH{\cdot}NCS$ respectively. Diphenylmethyl bromide gives either $Ph_2CH{\cdot}SCN$, or $Ph_2CH{\cdot}NCS$, according to the conditions (Wheeler, *loc. cit.*, 1901, **26**, 353), but ethyl phenyl-α-chloroacetate yields the thiocyano-derivative, $CO_2Et{\cdot}CHPh{\cdot}SCN$; the latter, however, unites with aniline, giving rise to "diphenyl-ψ-thiohydantoin,"  $PhN{:}C{<}{}^{S\cdot CHPh}_{NH-CO}{>}$.

Further evidence of the tendency of thiocyanogen compounds to alter the character of their grouping is shown by the fact that chloroacetyl-α-naphthalide, $CH_2Cl{\cdot}CO{\cdot}NH{\cdot}C_{10}H_7$, gives, with potassium thiocyanate, a "labile α-naphthyl-ψ-thiohydantoin,"



$$NH{:}C{<}{}^{S-CH_2}_{N(C_{10}H_7)}{>}CO$$

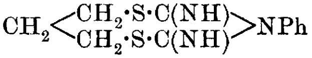
(m. p. 147°), which changes, on boiling in dilute alcoholic solution, into the stable form,  $C_{10}H_7N{:}C{<}{}^{S-CH_2}_{NH\cdot CO}{>}$ (m. p. 213—214°). Moreover,

---

tautomeric in this sense, inasmuch as when once effected they are permanent ; at least, conditions have not yet been discovered under which an alkyl thiocarbimide will behave as the thiocyanate of its own radicle. It may be noted incidentally that the ·NCS group, when once established, cannot be transferred by any known direct method from the radicle with which it is combined to another.

from chloroacetyl-*m*-xylidide, the thiocyano-derivative,

$$Me_2C_6H_3\cdot NH\cdot CO\cdot CH_2\cdot SCN,$$

can be isolated, which readily undergoes isomeric change into the stable form of thiohydantoin (Johnson, *loc. cit.*, 1903, **25**, 483). It may be added here that the formulæ given by Wheeler and others for the stable varieties confirm those previously advanced (Dixon, Trans., 1897, **71**, 629) for the ordinary so-called thiohydantoins. The present writer observed many years ago that chloroacetanilide, when heated in dilute alcohol with potassium thiocyanate, yields not only phenylthiohydantoic acid, but, in addition, a considerable proportion (62 per cent. of the theoretical) of phenylthiohydantoin, a substance which is also produced either from chloroacetanilide and thiocarbamide, or from phenylthiocarbamide and ethyl chloroacetate (Meyer, *Ber.*, 1877, **10**, 1965). However, the fact that this substance results indifferently from compounds containing thiocyano- or thiocarbimino-groups does not conclusively prove that the former radicle changes into the latter. Another interesting action, which shows the power of the $\cdot SCN$ radicle to combine occasionally with a base, is the union of 1 mol. of aniline with trimethylene thiocyanate, thereby forming phenyl-*ψ*-trimethylenedithiobiuret,  $CH_2\left\langle\begin{array}{l}CH_2\cdot S\cdot C(NH)\\CH_2\cdot S\cdot C(NH)\end{array}\right\rangle NPh$ (Wheeler and Merriam, *loc. cit.*, 1902, **24**, 446).

The case of acidic thiocyanates is somewhat complex. Since the electro-positive character of the unsaturated hydrocarbon groups is commonly less marked than that of the saturated, it might be anticipated that the thiocyanates of pronounced electro-negative radicles would tend still more readily to pass into the thiocarbimidic form, and to some extent this is true, for the derivatives of benzenoid acids exhibit mainly (although not exclusively) the properties of thiocarbimides; in fact, Miquel, the discoverer of benzoyl "thiocyanate" (*Ann. chim. phys.*, 1877, [v], **11**, 300), states that if pure it is hydrolysed by water into benzamide and carbon oxysulphide, but yields no thiocyanic acid, and hence ought to be regarded as a true thiocarbimide.

Now, the substance in question, when formed by heating benzoyl chloride dissolved in benzene with lead thiocyanate for a few minutes, may give, by combination with alcohols or nitrogenous bases, yields of the corresponding additive products amounting to fully 90 per cent. of the theoretical (compare Trans., 1896, **69**, 1603; 1899, **79**, 379), and hence if benzoyl thiocyanate is formed at all in the initial decomposition, which necessarily occurs at a very moderate temperature, its existence as such is short.

On the other hand, thiocyanates derived from certain fatty acids appear capable of exhibiting the kind of tautomerism previously mentioned, with respect to the CNS group : stearyl thiocyanate, for example, gave (*loc. cit.*, 1602) with benzylaniline more than 95 per cent. of the possible yield of the trisubstituted thiocarbamide, whilst with ammonia the products were substantially thiocyanic acid and stearamide.

Occasionally, a substance of this class can not only act separately in either form, but also simultaneously in both : acetyl thiocyanate, for instance, is decomposed by water (Miquel, *loc. cit.*), mainly into acetic and thiocyanic acids ; it can unite almost quantitatively with *p*-toluidine to form acetyl-*p*-tolylthiocarbamide ; whilst if brought into contact with aniline at the ordinary temperature, it yields acetylphenylthiocarbamide and acetanilide, together with aniline thiocyanate. In relation to aniline, Doran's observation has already been mentioned, that the power of acetyl thiocyanate to behave either as such, or as acetylthiocarbimide, is conditioned mainly by the temperature at which the interaction is brought about (Trans., 1901, **79**, 543 ; *Proc.*, 1904, **20**, 20).*

If any analogy may be looked for between the thiocyanates of electro-negative organic, and of electro-negative mineral radicles, it would presumably take the form of a similar capacity, on the part of members of the latter class, to manifest thiocarbimidic in addition to thiocyanic functions ; or possibly, under certain conditions, to act as thiocarbimides, pure and simple. No investigation from this point of view seems as yet to have been conducted, excepting a superficial one by the writer. The present study, indeed, notwithstanding that upwards of two years have been devoted to it, has scarcely passed the preliminary stage, but circumstances having arisen which will for some little time interfere with the prosecution of this research, an account of the principal results so far attained is now submitted.

Phosphorus "Trithiocyanate."

Phosphorus trichloride interacts spontaneously with dry ammonium thiocyanate ; the violence of the direct action may be suitably checked by mixing the finely-powdered thiocyanate with enough benzene to make a thin paste, and then adding the phosphorus halide diluted with three or four times its own volume of the same solvent. The mixture instantly becomes hot, and must be kept in rapid motion for a short

---

* The behaviour of these substances is sometimes very puzzling. For instance, propionylthiocarbimide and benzylaniline gave (Trans., 1896, **69**, 859) nearly 90 per cent. of the possible yield of propionylphenylbenzylthiocarbamide, but with piperidine it afforded piperidine thiocyanate. In another experiment, sodium ethoxide was added to the acetyl compound, dissolved in benzene, in the hope of realising the change, NaOEt + AcNCS = NaOAc + EtNCS ; vigorous action occurred, the products being sodium thiocyanate and ethyl acetate, but not a trace of ethylthiocarbimide could be detected.

time, otherwise a portion of the contents may be projected out of the flask. It is well to use about one and a half times the amount of thiocyanate calculated from the equation,

$$PCl_3 + 3NH_4{\cdot}SCN = 3NH_4Cl + P(SCN)_3;$$

if the process is successfully conducted, there is but little change of colour, and in a few minutes the benzene solution becomes practically free from chlorine. By using dilute solutions, all danger of violent action is precluded, but it may then be necessary either to allow the mixture to remain for about a day, or to boil in order to eliminate the chlorine, and in these circumstances a yellow or bright orange-coloured solid develops, which appears to consist mainly of pseudosulphocyanogen together with *iso*perthiocyanic acid. When cool, the residue of ammonium chloride and thiocyanate is filtered off at the pump, washed a few times with dry benzene, and the clear filtrate heated on the water-bath under reduced pressure until no more solvent can be extracted. On distilling the pale brown liquid thus obtained *in vacuo*, the thermometer rose quickly to about 168°, when a few drops of liquid passed over; the contents of the flask now became very dark and semi-solid, and from this product, by careful heating, a clear, pale yellow oil could be distilled, the whole distillate usually passing over within one or two degrees. In various preparations, the following boiling points and pressures were observed: 170°/20 mm.; 172°/21 mm.; 173° and 175°/27 mm.; 175°/28 mm., and 180°/30 mm. On rectification, two specimens were obtained boiling at 169°/20 mm. and at 161°/14 mm. respectively; the latter sample, when again rectified, boiled at 163°/15 mm.; in all cases, a considerable amount of dark, viscid residue was left. These figures are mentioned in detail, because, although they seem to indicate a perfectly definite compound, reasons will be assigned later on for doubting whether the product is really homogeneous.

The distillation is rather troublesome, being attended with much spirting and frothing of the viscid paste, and the slight irregularities noticeable in the boiling points are perhaps due to the projection of liquid drops against the bulb of the thermometer.

The best yield, from 14 grams of trichloride, was only 41 per cent. of the theoretical. The smaller yields obtained from larger batches were probably due to the decomposition of the substance caused by prolonged exposure at the somewhat high temperature.

Potassium thiocyanate interacts very imperfectly with phosphorus trichloride (compare Trans., 1901, **79**, 545), and although the corresponding lead salt acts well enough, the mixture sometimes requires prolonged boiling in order to complete the change.

When exposed to air, the distilled oil slowly evolves fumes of thiocyanic acid, but does not spontaneously inflame, even on warming. In the cold, it has a faint alliaceous odour, which becomes penetrating and exceedingly disagreeable on heating the oil with water; this mixture is not luminous in a darkened room; even when very slightly impure, the liquid soon darkens and becomes turbid. A specimen, when thrice distilled, was found to have a sp. gr. 1·487 at 15·5°; this figure differs considerably from that given by Miquel (*loc. cit.*), who found a sp. gr. 1·625 at 18° for a product distilled under the ordinary pressure. In relation to solvents, it corresponded with his description in all respects, except one, which will be mentioned later.

Analysis gave: $S = 46{\cdot}9$; $N = 20{\cdot}1$; $P = 15{\cdot}0$.
$C_3N_3S_3P$ requires $S = 46{\cdot}83$; $N = 20{\cdot}48$; $P = 15{\cdot}12$ per cent.

When thrown into water, the oil at once commences to dissolve, but does not entirely disappear, the solution containing thiocyanic and phosphorous acids. These, however, are not the only products, for if it is mixed with silver nitrate and the precipitated silver thiocyanate dissolved by ammonia, the liquid remains dark and turbid, owing to the presence of a little silver sulphide; moreover, if it is heated with alkaline solution of lead salts, very perceptible desulphurisation occurs. Consequently, although the oil behaves mainly as a thiocyanate in so far as the aqueous extract is concerned, the latter also gives to some extent the reactions of a thiocarbimide. On the other hand, if the oil is dropped into hot alkaline solutions of lead or silver salts, copious desulphurisation occurs instantly, the substance thus exhibiting in a marked degree the characters of a thiocarbimide.

On mixing the oil (1 mol.) and aniline (3 mols.) in warm benzene, much heat was developed and a tenacious oil separated; after prolonged exposure to air, this became partly crystallised, but when the oil was removed by means of acetone, the crystalline residue proved to be merely phenylthiocarbamide. With cooled solutions, a pasty, amorphous solid was obtained, which hardened when kept out of contact with moisture, but which, when powdered and washed successively with benzene and light petroleum, still retained a trace of viscid matter; it softened at about 67° and melted somewhat indefinitely two degrees higher. The yellow powder contained a little aniline thiocyanate, for if shaken with water, in which it was practically insoluble, the liquid was distinctly reddened by ferric chloride, and gave with bleaching powder the violet reaction for aniline. When heated with water, it dissolved readily, a little hydrogen sulphide being evolved; the solution reacted freely for thiocyanic and phosphorous acids and for aniline, and deposited phenylthiocarbamide on cooling. It was easily soluble in ether, alcohol, and some other solvents, but when recovered from solution, either by evaporation or by precipitation, it always separated either as a liquid or a paste. The indefinite melting point was suggestive of an impure compound, but as no satisfactory method of purification could be devised, the well-washed crude product was partially analysed, with the following results:

Found, S = 21·3; N = 16·5; P = 6·2.

These figures agree only indifferently with the composition $P(SCN)_3,3C_6H_5{\cdot}NH_2$ or $C_{21}H_{21}N_6S_3P$, which would require S = 19·83; N = 17·35; P = 6·4 per cent.

o-Toluidine, when employed in a similar manner, yielded a smeary brown oil, from which only *o*-tolylthiocarbamide could be extracted. The distilled oil was soluble in alcohol, with which it interacted at once, considerable heat being developed; thiocyanic acid escaped, and a viscid paste was left which did not crystallise or become solid even after two months.

It has already been mentioned that in one respect the phosphorus thiocyanate did not correspond with Miquel's description. According to this author, the substance is but very slowly acted on by water, which decomposes it into thiocyanic and phosphorous acids. This was not exactly the present writer's experience, for cold water attacked the oil rapidly, the solution obtained by shaking the two together for a few seconds containing a large amount of thiocyanic acid. Yet, on attempting to determine quantitatively the amount of this acid, it was found that, although the oil rapidly diminished in bulk when first placed in contact with warm water, it could not be made to dissolve completely, even by prolonged boiling, nor did the substitution of fresh water for that now charged with the decomposition products appear to diminish the amount of residual oil; moreover, the latter, after repeated extractions, ceased to afford any reaction for thiocyanic acid, even if kept for several hours in contact with water, but it was copiously desulphurised by alkaline lead or silver salts. In fact, the liquid was now apparently free from phosphorus thiocyanate, although it still displayed the characteristic properties of a true thiocarbimide.

In order to ascertain the nature of this residual oil, experiments were now conducted on a larger scale: 16·4 grams of freshly distilled oil were shaken with successive amounts of about 50 c.c. of hot water and then repeatedly boiled with this solvent; the aqueous portions at first contained large quantities of phosphorous and thiocyanic acids, but after some fifteen extractions, the cold aqueous extract no longer developed any red coloration with ferric chloride. Cold water was used in this experiment, because it was found that, no matter how often the treatment with boiling water was performed, a trace of ferric thiocyanate always appeared. After a few additional extractions, the residual oil was drawn off, its amount in this experiment being 54 per cent. of the weight initially taken. In another experiment with thrice-distilled oil, the yield was 65 per cent. When dried over calcium chloride, the oil was distilled under reduced pressure, the boiling points observed being 173—174° and 168° under 22 mm. and 17 mm. pressure respectively; distillation now occurred with much less bumping than before, the contents of the flask did not solidify or even thicken, and the amount of dark-coloured residue was very small. It will be noted that the former boiling point lies very close to that observed for an unwashed specimen, whilst the latter is not very far removed from the mean of 163° and 169° under 15 and 20 mm. pressure respectively, observed on rectifying the unwashed products.

The distillate was a clear, colourless, highly refractive oil; the sp. gr. of the two specimens were 1·483 and 1·488 at 16°, whilst that of the unwashed oil, as mentioned above, was 1·487 at 15·5°. Considering that only 2 to 5 c.c. of liquid were used in the determinations, these figures are practically identical; in other words, the removal, by washing, of from about one-half to one-third of the substance of the oil did not materially affect either its specific gravity or its boiling point. These facts are consistent with the view that the oil is a homogeneous compound; for, if only slowly soluble in water, a portion might be withdrawn, leaving a residue with properties unchanged, but this refers to the physical properties alone, and does not explain why hydrolysis no longer occurs after some extractions, or why water dissolves only a portion of the oil.

On examining the distillate, it was found to undergo copious desulphurisation when warmed with alkaline solutions of lead salts or when its alcoholic solution was mixed with ammoniacal silver nitrate. But when shaken with water, the aqueous portion gave not a trace of red coloration with ferric chloride, and hence, not only was the phosphorus trithiocyanate (assuming that to be the source of the thiocyanic acid produced by contact with water) completely removed by washing, but, moreover, the residual portion did not regain the power to behave as a thiocyanate after having been subjected to a moderately high temperature. Excepting that it was practically insoluble in water, the new substance had properties very similar to those of the unwashed material, and when analysed gave the following results:

Found, S = 47·2. N = 20·9; P = 15·2.
$C_3N_3S_3P$ requires S = 46·83. N = 20·49; P = 15·12 per cent.

Now if true phosphorus trithiocyanate is hydrolysed by contact with water, the liquid isolated by the foregoing method must be an isomeride, and hence, presumably, the hitherto unknown phosphorus trithiocarbimide. Obviously, the next step was to ascertain whether it possessed the characteristic property of uniting with a primary nitrogenous base so as to yield the corresponding thiocarbamide.

In order to test this point, a benzene solution of aniline was slowly added from a burette to a weighed quantity of the pure oil, freely diluted with this solvent, and kept near the freezing point of the mixture. A finely-divided white solid at once began to separate, and the addition of the aniline was continued until a portion of the filtered liquid, when treated with a few drops of the solution, just ceased to yield any further precipitate, this stage being reached when, for each mol. of the oil taken, one mol. of aniline had been used. Excess of base was avoided, because it readily combines with the solid product, turning it into a viscid paste. The white powder was filtered off and washed thoroughly with dry benzene; on allowing the filtrate to evaporate, there was scarcely any residue, thus showing that the aniline had almost completely removed the dissolved oil; the solid product, when dry, amounted to nearly 98 per cent. of the total weight of materials used.

When heated in a narrow tube, the substance melted sharply without effervescence at 116—117° (corr.), changing into a golden-yellow liquid.

Found, S = 32·1. N = 18·2; P = 10·25.

$C_9H_7N_4S_3P$ requires S = 32·21; N = 18·79; P = 10·40 per cent.

Accordingly, the product was a definite additive compound, $P(CNS)_3,C_6H_5{\cdot}NH_2$. Cold water had practically no effect on it excepting after prolonged contact, but if warmed on the water-bath the mixture gradually became clear, a little hydrogen sulphide being evolved; when this was boiled off, the solution contained a large amount of thiocyanic acid, and was freely desulphurised by heating with alkaline lead tartrate. The source of the desulphurisation was phenylthiocarbamide, which separated in large crystals as the liquid cooled; only a trace of aniline could be detected and the solution, when oxidised by nitric acid, gave the reactions of phosphoric acid with magnesia mixture and with ammonium molybdate.

It is curious to note that, whilst the parent oil is scarcely affected by water, even at the boiling point, yet after union with 1 mol. of aniline the resultant compound is easily hydrolysed, the uncombined CNS groups when thus separated making their appearance mainly as thiocyanic acid, although a little hydrogen sulphide is also formed. In order to follow more clearly the course of the hydrolysis, some quantitative experiments were carried out, a few of which may be mentioned.

To determine the amount of hydrogen sulphide liberated, a weighed quantity of the solid was digested on the water-bath for half an hour with excess of arsenious acid solution slightly acidified with hydrochloric acid; the arsenious sulphide was collected, washed, dissolved by boiling for some hours with water, and the arsenic estimated by standard iodine; the sulphur thus precipitated amounted to about 4 per cent. Then, by boiling a weighed quantity with water, allowing to cool, and collecting the phenylthiocarbamide formed, it was found that six-sevenths of one-third of the total sulphur, or 9·2 per cent., came out in this form, instead of 10·7. The solution of a weighed quantity, hydrolysed by water alone, was next treated with excess of silver nitrate, the mixed sulphide and thiocyanate separated by means of ammonia, and the latter salt, after precipitation with dilute nitric acid, collected, dried at 110°, and weighed; the mean of three fairly concordant determinations was 18 per cent. of sulphur in the form of thiocyanic acid, thus accounting for 97 per cent. of the total sulphur. The last result was checked in another way, by colorimetric estimation with a ferric salt, using *N*/400 potassium thiocyanate as standard; although this process is not very accurate, it was thus found that approximately two-thirds of the sulphur were hydrolysed to thiocyanic acid.

Neglecting the formation of the hydrogen sulphide, the hydrolysis takes the following course: one ·NCS radicle is eliminated with the aniline residue as phenylthiocarbamide, and the two remaining CNS groups appear as thiocyanic acid; these results may be summed up by the equation:

$$PhNH\cdot CS\cdot NH\cdot P(CNS)_2 + 3H_2O = CSN_2H_3Ph + 2HSCN + H_3PO_3.$$

Assuming, for the moment, that the parent compound is wholly thiocarbimidic as to the contained CNS, it may appear strange that of the three ·NCS groups one alone should exhibit pronounced activity in uniting with aniline, but so far as this is concerned the case is not without a parallel, the author having already observed a similar peculiarity with carbonyldithiocarbimide, $CO(NCS)_2$; this substance, when treated with aniline until the precipitation of solid matter was just complete, gave carbonylthiocarbimidophenylthiocarbamide, SCN·CO·NH·CS·NHPh (Trans., 1903, **83**, 89). In this case, it was found possible, by allowing the thiocarbimide to remain for a day or so in contact with excess of base, to obtain the dithiocarbamide, $CO(NH\cdot CS\cdot NHPh)_2$, but with benzylaniline only 1 mol. could thus be added. From these few data, it would be unsafe to generalise; nevertheless, so far as they go, they tend to indicate that, as ·NCS groups accumulate in the acid molecule, their characteristic power of uniting with primary and secondary nitrogenous bases to yield thiocarbamides becomes weakened. This may be equally true for certain combinations with inorganic radicles, and, if so, when a single phosphorus atom is united with three supposed thiocarbimidic radicles, the fact that one alone is capable of readily discharging the function peculiar to these groups, although no more intelligible than before, is nevertheless not quite abnormal.

Without making assumptions with regard to the nature of the contained CNS groups, it is convenient to call that portion of the phosphoretted oil which is removed and hydrolysed by water, "phosphorus thiocyanate," and that fraction which is not, "phosphorus thiocarbimide." The monophenylthiocarbamidic derivative of phosphorus thiocarbimide, when suspended in warm benzene and mixed with 2 mols. of aniline, united with the latter quantitatively, forming a viscid oil, which slowly hardened; after powdering and washing with benzene, the ill-defined product resembled that obtained by the direct action of 3 mols. of aniline on one of the unwashed distillate, and when treated with hot water, underwent hydrolysis, yielding much aniline thiocyanate, together with phenylthiocarbamide.

Found, S = 19·7; P = 5·9; $P(CNS)_3,3PhNH_2$ requires 19·83 and 6·4 per cent.

That the further quantity of aniline taken up by the monophenyl compound had not entered into true thiocarbamidic combination, was made evident by the result of hydrolysis, when only 30 per cent. of the total sulphur made its appearance in the form of phenylthiocarbamide.

It has been stated above that phosphorus trithiocarbimide is not attacked by water, and this is practically true. But if the oil, repeatedly washed with boiling water until the residue, when vigorously shaken with the cold or tepid solvent, does not cause the latter to give the slightest coloration with ferric chloride, is now left in contact with cold water, thiocyanic acid slowly passes into solution, so that after a few days the colour reaction may again be produced. A few washings with hot water suffice to remove all trace of the acid, but on leaving the residue with a fresh quantity of water for two or three days, thiocyanic acid can be found in solution, just as before: a sample of washed and distilled oil, thus treated nine times at intervals of five or six days, had in the end become perceptibly reduced in bulk, but the residual oil, when thoroughly washed with boiling water and then left in contact with the cold solvent, gave the reaction apparently as markedly as at the beginning. When left for six months, with occasional changes of water, the oil had not disappeared, and what was left did not seem changed, except in amount. The solution, if decidedly reddened by ferric chloride, always gave a slight, but distinct, desulphurisation when heated with alkaline lead or silver salts; it is therefore probable that the "phosphorus thiocarbimide" slowly dissolves in the water as such, but cannot accumulate to any appreciable extent, because the solution soon undergoes hydrolysis. If the aqueous mixture is kept for a month, it still gives only a slight desulphurisation when freed from the oil, whilst the thiocyanic reaction has now become strongly marked.

Sharply contrasted with this reversion, which is so slow and minimal that it might easily escape notice, is the copious and rapid production of thiocyanic acid, which occurs on dissolving the monophenyl compound in warm water; a possible explanation is that, when once the molecule is broken by the splitting off of the group $\cdot NH \cdot CS \cdot NHPh$ (representing it as symmetrical), the residue becomes unstable, and decomposes forthwith into thiocyanic and phosphorous acids.

It is not easy, from the facts at present available, to understand the precise nature of the distillate first obtained from phosphorus trichloride and ammonium thiocyanate before its thiocyanic characters (with respect to water) have been practically destroyed by washing. The view that phosphorus trithiocarbimide is first formed and then decomposes partially into trithiocyanate is contrary to experience with other thiocarbimides, and is further negatived by the fact that when the trithiocarbimide has once been freed from thiocyanate, it does not afford a trace of the latter on redistillation. On the other hand, the converse assumption is not without some basis, for whilst a specimen, only once distilled, but apparently pure, judging from the analytical results, lost only about half its weight on treatment with water, another, thrice distilled, lost only about one-third. However, the preparations were not always made under precisely identical conditions as regards temperature, time, dilution, &c., so that this argument should not be pressed too far; and the direct evidence cannot yet be obtained, namely, that pure "phosphorus thiocyanate" is able to change at all into the thiocarbimide, since no means is known whereby the former can be isolated.

It might seem obvious, at first sight, that "phosphorus thiocyanate," which is acted on readily by water, must be a substance chemically distinct from "phosphorus thiocarbimide," which is not; but as the presence of much thiocyanate has scarcely any perceptible effect on either the density or the boiling point of the latter, there can be but little dissimilarity between them in respect of these physical properties. So far as the present experiments have gone, the washed oil appears to have a slightly higher boiling point than the unwashed, but the difference, if it exists, cannot exceed some two or three degrees within the limits of pressure specified. Amongst hydrocarbon derivatives, the thiocyanate of a given radicle boils, on the average, some 11 or 12° above the thiocarbimide,* so that, unless the difference is very small in the case of acid derivatives, the only reason for supposing the original distilled oil to be a mixture of two distinct substances lies in the fact that the rate of attack by water undergoes great retardation as the process of washing is continued. As regards the power to unite with one or three mols. of base, it does not appear to matter whether the "thiocyanate" is removed or not; moreover, it will presently be shown that a phosphoryl derivative, not washed, gives additive products precisely similar to those obtained with the washed phosphorus "trithiocarbimide."

Phosphoryl "Thiocyanate."

When phosphoryl chloride, diluted with dry benzene or toluene, was allowed to remain in contact with about one and a half times the amount of carefully-dried potassium or ammonium thiocyanate required according to the equation:

$$POCl_3 + 3NH_4{\cdot}SCN = PO(SCN)_3 + 3NH_4Cl,$$

interaction took place spontaneously: the mixture was then separated by means of the pump into (1) a solid residue, and (2) a clear yellow filtrate, no longer smelling of oxychloride. When treated with cold water, this residue yielded chloride and unchanged thiocyanate, leaving a yellow, amorphous powder, mostly soluble in boiling water, and giving the reactions of *iso*perthiocyanic acid. The filtrate was heated on the steam-bath, under reduced pressure, until the solvent was eliminated, and the residue, a viscid, reddish-yellow syrup, was submitted to distillation in a vacuum. The clear, pale yellow, highly refractive oil thus obtained boiled at 175° (uncorr.) under 21 mm. pressure; it had a faintly pungent odour, and slowly evolved fumes of thiocyanic acid when exposed to ordinary moist air. If tolerably pure, it may be kept for weeks without material alteration, otherwise it quickly becomes turbid, depositing a red, pasty substance.

The yield of distilled product was not very satisfactory, the best attained being only 43 per cent. of the calculated quantity. As the crude oil bumps and froths considerably, a relatively large flask must be used, and the amount of material taken should not be large, for when the distillation is much retarded a good deal of black tar accumulates, which apparently is formed from the oil by prolonged heating at the boiling temperature.

A freshly distilled specimen was analysed, with the following results:

---

* The difference in specific gravity is usually inconsiderable for each pair of isomerides.

Found, N = 19·15; S = 43·7; P = 14·2.

$C_3N_3S_3OP$ requires N = 19·02; S = 43·45; P = 14·02 per cent.

The sp. gr. is 1·52 at 13·5°.

When mixed with excess of cold water, the oil dissolved, undergoing hydrolysis tolerably rapidly; the solution gave with ferric chloride a deep blood-red coloration, and with ammonium molybdate or magnesia mixture the reactions of phosphoric acid. The change under these conditions is mainly that represented by the equation: $PO(SCN)_3 + 3H_2O = 3HSCN + H_3PO_4$, for a dilute solution, when treated successively with excess of ammonia and silver nitrate, became only slightly darkened, and was not markedly desulphurised by boiling with alkaline lead tartrate. Moreover, about half a gram of the fresh oil, when decomposed by cold water, and treated with ammonia and magnesia mixture, yielded a quantitative amount of phosphoric acid, as calculated from the above equation.

So far, therefore, the substance displays mainly the properties of a thiocyanate, but when added directly to and shaken with an alkaline solution of lead tartrate, a white precipitate was formed, which slowly became yellow and orange, and finally black; this change, which is due to the production of lead sulphide, occurred instantly on gently warming, and the alcoholic solution, when mixed with silver nitrate and ammonia, was abundantly desulphurised, even in the cold; in these circumstances, the substance exhibited markedly the characters of a thiocarbimide.

In the case of the phosphoryl compound, it was not found possible to eliminate the thiocyanate, leaving a thiocarbimidic residue, for on shaking 5 grams of the oil with about 20 c.c. of cold water, heat was developed, and the whole of the oil, except a decigram or so, rapidly dissolved, and when left for some little time, a yellow solid appeared, which was found to consist principally of *iso*perthiocyanic acid; with 14 grams of oil, a similar result was obtained.

Since a thiocarbimide, as such, could not be isolated, an attempt was made to combine the oil with organic amines, so as to obtain substituted thiocarbamides, but the experimental difficulties are very great, for, although combination occurs readily enough, the products are very unsatisfactory. Even when formed from apparently pure materials, they are often far from pure, and although usually presenting the appearance of crystallisable compounds, they have, so far, resisted every attempt made in this direction. By contact with water or with solvents containing even traces of it, they are readily hydrolysed, so that, after many failures and in the absence of any better method, carefully purified materials were used for the preparations; the products were thoroughly washed successively with benzene and light petroleum, dried at the ordinary temperature as far as possible in the absence of moisture, and then analysed.

It will be seen from what follows that phosphoryl thiocyanate is capable of fixing primary amines, of which 1 mol. is held for each SCN group present, and this, without the formation of basic thiocyanate; nevertheless, the products are not true thiocarbamides (or, if so, differ from those at present recognised), since, when hydrolysed, they yield, not thiocarbamide alone, but a mixture of thiocarbamide with basic thiocyanate. The results obtained in the experiments were not invariably the same, although approximately so; each account given below is that of observations actually made, and not the average of a number of experiments.

Action of Aniline.—Eight grams of the oil were mixed with three molecular proportions of aniline, each reagent being diluted with about twice its volume of dry benzene; interaction occurred instantly, the temperature rising to the boiling point of the mixture, and a yellow, doughy paste separated, which quickly became hard, and, when broken up and dried, formed a mobile powder, the weight of which approximately equalled that of the materials taken. The substance had no definite melting point; it became translucent at 89° and frothed at 95—97°. When added to water, it was apparently quite insoluble, the mixture, even after thorough shaking, being neutral to litmus, and giving no reaction with ferric chloride or with calcium hypochlorite solution; consequently, the powder was free from aniline thiocyanate. When left for an hour or so with cold water, the mixture began to give the red thiocyanate coloration with ferric chloride, which slowly increased with the time. But if boiled with water, the solid quickly dissolved, evolving a little hydrogen sulphide and leaving a trace of viscid oil; the solution now obtained was intensely acid, contained large amounts of aniline, thiocyanate, and phosphoric acid, and on cooling deposited large crystals of phenylthiocarbamide. The production of the latter is not due to isomeric change of the aniline thiocyanate through heating, for the original solid, when dissolved in cold spirit, is desulphurised by ammoniacal silver nitrate; moreover, if it is dissolved in cold dilute aqueous caustic potash and treated with a lead salt, a white precipitate is formed, becoming successively yellow, orange, brown, and finally jet-black; the last change occurs at once on gently warming. It is unnecessary to describe in further detail the properties of this compound, for they agreed in every respect with those observed for the product obtained from the cumene solution, supposed to contain phosphoryl thiocyanate (Trans., 1901, 79, 549). Concerning the last-named product, it was mentioned (*loc. cit.*) that when hydrolysed with boiling water it yielded barely one-third of the phenylthiocarbamide which should be formed according to the equation:

$$PO(NH{\cdot}CS{\cdot}NHPh)_3 + 3H_2O = H_3PO_4 + 3CSN_2H_3Ph.$$

Whether the limited production of phenylthiocarbamide was normal or otherwise could not then be decided, since it was uncertain whether the cumene solution contained one substance only. This time, however, there could be little doubt as to the chemical individuality of the oil, seeing that, apart from the analytical figures, the whole 8 grams of product distilled within about 1°.

In repeating the experiment, 5 grams of the aniline compound were dissolved in 50 c.c. of boiling water, and the solution filtered from a trace of viscid oil; on cooling, pure phenylthiocarbamide was deposited, the weight being 1·4 grams, corresponding with 28 per cent. of the theoretical as reckoned above; in another experiment, 30 per cent. was obtained. A further small quantity remained in solution, but this could not safely be collected by evaporation to a small bulk, because the aniline thiocyanate present gradually changes, under the influence of heat, into phenylthiocarbamide. This result, seeing that the experiment was only a rough one, does not differ materially from that previously recorded. Although the substance used had been well washed with benzene, it was evidently not quite pure, as shown by the ill-defined melting point, and by its failure to dissolve perfectly in water; an estimation of sulphur gave 18·9 per cent. against 19·21 calculated for $C_{21}H_{21}N_6OS_3P$, and the nitrogen was also too low; the phosphorus, however, was found = 6·5, the calculated number being 6·45 per cent.

Until the methods and results now given can be improved, it may provisionally be concluded that phosphoryl thiocyanate is a definite chemical compound, which, when in contact with water, behaves as a true thiocyanate, but in presence of benzene alone can quantitatively fix three molecules of aniline, thus behaving as a typical (tri)thiocarbimide; the product, although free from aniline thiocyanate, can, nevertheless, readily yield it by hydrolysis, together with a little hydrogen sulphide, somewhat less than one-third of the contained sulphur being simultaneously liberated in the form of phenylthiocarbamide. Of the three CNS groups present in the molecule, it appears, therefore, that only one is capable of exerting the power peculiar to the thiocarbimidic residue, ·NCS, of uniting with an amine so as to yield an atomic complex devoid of thiocyanic characters; the two remaining groups, when once the former is saturated, appear to be thiocyanic in nature, although possessing a certain capacity to hold the base in combination.

It is possible to bring about union between the thiocarbimidic group alone and aniline, leaving the other two groups uncombined, as shown by the following experiment.

To a cooled solution containing 1 mol. of freshly distilled oil in about ten times its volume of benzene, 1 mol. of aniline was very slowly added with constant stirring; a minutely-divided, white, amorphous solid was precipitated, the liquor from which gave no further precipitate with aniline, and left scarcely any residue on evaporation; the solid, when thoroughly washed successively with benzene and light petroleum and dried by gently heating, was equal to 93 per cent. of the total weight of materials combined. Had the aniline combined equally with all the SCN groups, much thiocyanate must have been left, whilst the yield of solid could not have exceeded 53 per cent. of the total weight of the reagents.

The powder softened at 119° and melted at 120—121° (corr.); it was insoluble, or nearly so, in cold water, the mixture giving a feeble reaction for thiocyanic acid, but, on warming, it soon dissolved, the solution being highly acid, and containing free phosphoric and thiocyanic acids, together with phenylthiocarbamide. As usual, a trace of hydrogen sulphide was evolved, but the solution gave only a faint reaction for aniline.

Analyses gave: $S = 30{\cdot}3$; $P = 9{\cdot}95$.

$C_9H_7N_4OS_3P$ requires $S = 30{\cdot}6$; $P = 9{\cdot}87$ per cent.

The phenylthiocarbamide produced by hydrolysis was collected and dried at 100°; it amounted, as in the case of the phosphorous analogue, to six-sevenths of that which could be formed according to the equation: $PhNH{\cdot}CS{\cdot}NH{\cdot}PO(CNS)_2 + 3H_2O = CSN_2H_3Ph + H_3PO_4 + 2HSCN$.

When the above monophenyl compound (1 mol.) was suspended in benzene and warmed on the water-bath with aniline (2 mols.), combination occurred, a clear, brown oil being formed, which hardened to a brittle resin on cooling, the latter, when powdered, washed with benzene, and dried, amounting to 96 per cent. of the weight of materials taken; it resembled in all respects the product obtained by treating the trithiocyanate directly with 3 mols. of aniline, and gave, on analysis, $N = 17{\cdot}3$ and $S = 18{\cdot}8$ per cent., the calculated values being $N = 16{\cdot}84$ and $S = 19{\cdot}21$ for $PO(SCN)_3,3C_6H_5NH_2$.

A portion, hydrolysed by warming with water for three-quarters of an hour, yielded 41 per cent. of its sulphur in the form of phenylthiocarbamide; this unusually high percentage is probably due to the transformation of a portion of the aniline thiocyanate due to prolonged heating.

Action of p-*Toluidine* (3 mols.).—When brought into contact with one another in warm dilute benzene solution, the reagents united vigorously, the mixture boiling freely, and a trace of hydrogen sulphide being evolved; on cooling, an oil was deposited, which, when left for a few days in a vacuum, hardened to a pale yellow, amber-like resin, still smelling of benzene. The solvent evaporates very slowly, for, on analysis eight days later, the nitrogen and sulphur, although giving the ratio N_2 : S, were both found to be more than 1 per cent. below the calculated values; eventually, the solvent was removed by gently warming the powdered substance in a flask, through which a current of dry air was kept passing for some hours; it now gave the following results:

Found N = 15·15; S = 17·8; P = 5·8.

$C_{24}H_{27}ON_6S_3P$ requires N = 15·53; S = 17·73; P = 5·72 per cent.

The yield of dry solid was not far from quantitative (about 95 per cent.); no definite melting point could be observed, the substance gradually softening from 95° onwards, until at 100° it formed a liquid evolving a gas.

When shaken with cold water, the mixture gave a scarcely perceptible reaction for thiocyanic acid; if boiled, it dissolved almost entirely, evolving a little hydrogen sulphide; the solution, on cooling, deposited *p*-tolylthiocarbamide, and the mother liquor gave the reactions of thiocyanic acid, phosphoric acid and *p*-toluidine. A rough experiment, made as in the case of the corresponding phenyl homologue, gave, for 1 mol. of substance, five-sixths of a mol. of *p*-tolylthiocarbamide.

Action of a-Naphthylamine (3 mols.).—On mixing the reagents, precisely the same phenomena were observed as in the case of aniline, the product being a doughy mass, which quickly hardened; when broken up, washed, and dried, it formed a pale yellow powder, the weight of which amounted to 96 per cent. of that of the materials used.

Found, S = 14·85; P = 4·6.

$C_{33}H_{27}ON_6S_3P$ requires S = 14·77; P = 4·77 per cent.

Heated in a narrow tube, it frothed up at 119—120°; cold water had no effect on the finely-powdered substance; when heated, phosphoric and thiocyanic acids passed into solution, and a bulky, white solid was left, which was recrystallised from alcohol and identified as α-naphthylthiocarbamide.

Another experiment was made, using only one molecular proportion of α-naphthylamine; the semi-solid product, which amounted to 96 per cent. of the weight of materials taken, presently became hard and brittle. It had properties resembling those of the corresponding aniline derivative, but was dirty orange in colour, and gave very unsatisfactory numbers on analysis, every attempt to purify the substance having failed.

Action of Benzylaniline.—When equal mols. were brought together in benzene solution, the mixture became warm, but remained clear. On cooling, small, white crystals separated, which were thoroughly washed with benzene; they melted sharply at 137—138° (uncorr.) and amounted to exactly the sum of the weights of the materials employed.

Found, $N = 13{\cdot}9$; $S = 21{\cdot}2$; $P = 7{\cdot}1$;
$C_{16}H_{13}ON_4S_3P$ would require $N = 13{\cdot}89$; $S = 23{\cdot}78$; $P = 7{\cdot}67$ per cent.

The substance was insoluble in cold water, the mixture being neutral, and giving no red coloration with ferric chloride; on boiling, there was little sign of solution, but the iron salt now produced a distinct reddening. Warm dilute caustic potash attacked the compound, forming a basic oil, probably benzylaniline, and the solution contained much thiocyanic acid. But the mixture with caustic potash was not desulphurised by boiling with lead tartrate, and the alcoholic solution darkened only slightly when treated with ammoniacal silver nitrate, so that the product of hydrolysis did not contain any considerable proportion of *aa*-phenylbenzylthiocarbamide (Trans., 1893, **63**, 325). The analytical numbers for sulphur and phosphorus being unsatisfactory, an attempt was made to crystallise the substance from alcohol, but the product, an acid syrup, refused to crystallise, and the experiment was abandoned.

Summary and Conclusion.

It appears from the foregoing experimental work that phosphoryl thiocyanate is a definite chemical compound, behaving towards water exclusively as a thiocyanate. Distilled phosphorus thiocyanate, although apparently a definite substance, can be resolved, by treatment with water, into two fractions, one of which, like the whole of the phosphoryl compound, is hydrolysed with ease, whilst the other fails to undergo hydrolysis, except to a minimal extent, although its physical properties (specific gravity and boiling point) are practically the same as at first. Moreover, between that portion which no longer reacts with water and the original distillate, which may lose about half its substance by contact with this liquid, there is no material difference as regards power to combine with aniline, for either can unite with 3 mols. of this base, but holding only a portion (approximately one-third) of this amount in ordinary thiocarbamidic combination. So far, therefore, as total aniline-fixing power is concerned, it does not appear to matter whether the phosphorous derivative holds its ·CNS groups in a form capable of acting towards water as ·SCN or otherwise: in any case, one of the three will behave as ·NCS towards the base.

Consistently with this unexpected result, phosphoryl thiocyanate, notwithstanding that water eliminates the whole of its ·CNS as thiocyanic acid (the formation of *iso*perthiocyanic acid is easily explained by the interaction of the liberated phosphoric and thiocyanic acids), can also fix three mols. of aniline, of which only one appears as phenylthiocarbamide, when the product is hydrolysed. Again, if only one molecular proportion of aniline is presented to one of phosphoryl thiocyanate, it will not distribute itself uniformly over the contained ·SCN, but will unite entirely with a single group, which behaves as ·NCS in this sense, that practically the whole of the combined base may on hydrolysis be recovered as phenylthiocarbamide. In like manner, if the phosphorous analogue, deprived by washing of practically all its power of behaving towards water as thiocyanate, is treated with one mol. of aniline, the latter will be so fixed that it may be almost completely recovered in the form of phenylthiocarbamide; but if the additive product be combined with an additional 2 mols. of aniline, the compound thus obtained will still give only one mol. of phenylthiocarbamide when hydrolysed.

The hydrolytic experiments were usually completed within a few minutes, the temperature being in the neighbourhood of 80°, so that the process, as conducted, could not lead to any material isomeric rearrangement of whatever basic thiocyanate might be formed; in these circumstances, the amount of substituted thiocarbamide produced was taken as a measure of the thiocarbimidic power available in each substance.

Wheeler has proposed the treatment with thiolacetic acid as a means of distinguishing between thiocyanates and thiocarbimides (*J. Amer. Chem. Soc.*, 1901, **23**, 285; *Amer. Chem. J.*, 1901, **26**, 348), the substances which yield carbon disulphide (and substituted amide) being regarded as thiocarbimides, and those which do not as thiocyanates. Although this appears to be a useful method of discrimination where hydrocarbon derivatives are concerned, it cannot be regarded as absolutely final in the case of acidic compounds; or, at most, it can only be used to decide how the ·CNS group behaves towards that particular substance at the moment of interaction, and this information does not go far enough with acidic thiocyanates, which are all more or less prone to undergo tautomeric change. Applying this method, he decides that acetyl thiocyanate is a true thiocyanate, a conclusion arrived at by Miquel from another point of view, and which is doubtless perfectly correct under certain conditions. But the totally different behaviour which it can exhibit on changing the conditions of interaction (Miquel calls it "abnormal") is most easily explained by supposing the compound to have assumed, for the time being, the thiocarbimidic configuration. It is conceivable that in the formation of acetylphenylthiocarbamide by the action of aniline, a compound, AcS·C(NH)·NHPh, might be the first product; if, now, the acetyl group migrated to the imino-group and the sulphur atom became doubly linked to carbon, the "abnormal" production of the disubstituted thiocarbamide could be explained. Indeed, the migration of the acetyl group in compounds already thiocarbamidic in structure is not unknown, Wheeler having adduced evidence (*Amer. Chem. J.*, 1902, **27**, 274) that the change of Hugershoff's acetylphenylthiocarbamide (m. p. 139°) (*Ber.*, 1899, **32**, 3649) into the isomeride melting at 171° occurs as follows:

$$\mathrm{AcPhN{\cdot}CS{\cdot}NH_2} \longrightarrow \mathrm{AcNH{\cdot}CS{\cdot}NHPh}.$$

With the data hitherto secured, it is not possible to state with certainty what is the mechanism whereby such changes are produced; but the author at present holds the view that in so far as a CNS compound unites spontaneously with aniline to yield a phenylated thiocarbamide or its immediate normal derivative it should be regarded as a thiocarbimide; from this standpoint, it becomes necessary to postulate the existence of tautomerism amongst certain "thiocyanates."

Another method of distinction proposed by Wheeler (*Amer. Chem. J.*, 1901, **26**, 349) consists in reducing the alcoholic solution of the CNS compound with sodium, when thiocyanic acid is produced from a thiocyanate, but not from a thiocarbimide; this test, however, is too drastic for members of the acidic class. Thus, benzoyl thiocyanate unites directly with primary and secondary amines to form thiocarbamides; with alcohols, to form alkyl esters of thiocarbamic acid, and with phenylhydrazine to form a disubstituted thiosemicarbazide. Its behaviour towards water has already been mentioned. Even with ammonia, which often brings about double decomposition amongst the acidic thiocarbimides, it yields benzoylthiocarbamide, and consequently there can be no question as to the marked preponderance of thiocarbimidic character in this substance. Yet, as usual, a limit to the power of retaining the ·NCS configuration can be reached, for on treating the compound with sodium, thiocyanic acid passes into solution. Wheeler also records certain observations by T. B. Johnson, showing that when it was made to interact with ethyl sodiomalonate, sodium formanilide, sodium phenoxide or ethyl sodioacetoacetate, the ·NCS group was removed as sodium thiocyanate.

In the light of all the facts now available with respect to the acidic "thiocyanates" as a class, it seems tolerably safe to venture the general statement that there is no known member of this class, however pronounced its thiocarbimidic characters may be, which cannot be made to behave as a thiocyanate.

Returning now to the phosphorus compounds, it must be admitted that, since no satisfactory means of purification could be found for their derivatives, the composition of the latter has been based on the analysis of somewhat ill-defined substances; on the other hand, most of the foregoing experiments have been repeated much oftener than appears in the paper, so that the general results may be taken as being fairly trustworthy. Probably the selection of this particular class of substances as objects of study was not a happy one, seeing that even when a single CNS group is combined with an acid radicle, it may lose its definite configuration and oscillate between ·SCN and ·NCS. When two such groups are present, one may be highly active, as ·NCS, whilst the other is comparatively sluggish, and easily hydrolysed out of combination, as ·SCN, although capable ultimately of exerting its full thiocarbimidic power. Under suitable conditions, the behaviour of carbonyldithiocarbimide, referred to earlier (p. 359), may be cited as a case in point. With three such groups attached to a single mineral radicle, their limited capacity to act as ·NCS might perhaps almost have been anticipated. On the other hand, experiments conducted with the view of obtaining mono- and di-thiocyanates of purely inorganic acid radicles have hitherto proved unsuccessful.

In conclusion, the writer desires to express his indebtedness to Mr. R. E. Doran for assistance rendered in connection with the experimental work described above.

CHEMICAL DEPARTMENT,
QUEEN'S COLLEGE, CORK.