CCXV.—*Study of the Constitution and Properties of the Rhodanides of Inorganic Radicles. Part I.*

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It is well known that certain more or less electronegative atomic complexes, for example, CNS, CNO, CN, or NO₂, may yield with a given electropositive organic radicle in each case two isomeric compounds, the isomerism of which is conditioned by the mode of attachment of the particular atomic complex. Thus the chemical differences between the two forms of ethyl rhodanide, C₂H₅(CNS), are satisfactorily explained by the constitutional formulæ Et·S·C:N and Et·N:C:S respectively.

Our knowledge regarding the combinations of distinctly electronegative organic radicles with such electronegative atomic complexes is confined in effect to the series of compounds derived from carboxylic acids. Here no case of isomerism has yet been observed, the same being true with respect to the combinations of hydrogen and of the metals with the atomic complexes just mentioned; for instance, no isomeride is known of hydrocyanic acid or of potassium thiocyanate. Ammonium thiocyanate, it is true, has the same molecular composition as thiourea, NH:C(SH)·NH₂, but the production of the strict isomeride, namely, ammonium *is*thiocyanate, NH₄·N:C:S, still remains to be accomplished.

Rhodanides of the carboxylic acids may be prepared by the action of a suitable metallic thiocyanate on the corresponding acylogen, for instance :

(Miquel, *Ann. chim. phys.*, 1877, [v], 11, 295). Of such compounds, thirty or so have now been prepared.

Since by direct union with an alcohol these rhodanides yield the corresponding acyl-substituted thiocarbamates, and with primary or

secondary nitrogen bases the corresponding thiocarbamides or thioureas, they must presumably be classed as thiocarbimides, $R \cdot NCS$.

Not infrequently, however, the two forms of change, namely, thiocarbimidic union and thiocyanic decomposition :

occur concurrently, the relative extents being determined by various external conditions (Doran, *Trans.*, 1905, **87**, 331; Dixon and Hawthorne, *ibid.*, 1906, **89**, 468), from which it might be imagined that the rhodanide constitutes an equilibrium mixture of thiocyanate and thiocarbimide in ratios determined by these conditions.

This, however, is not the case, for the molecular refraction of acetyl rhodanide is sensibly constant between 13° and 75° , and the refraction value of its CNS-group is equal to that determined by experiment for various thiocarbimides, whilst differing widely from that found for aliphatic thiocyanates (Hawthorne, *Trans.*, 1906, **89**, 536).

Furthermore, it has been observed that when α -acetyl-*bb*-diphenyl-thiocarbamide, $CH_3 \cdot CO \cdot NH \cdot CS \cdot N(C_6H_5)_2$, is caused to dissociate into its constituents, namely, diphenylamine and acetylthiocarbimide, $CH_3 \cdot CO \cdot NCS$, the latter is identical with ordinary acetyl "thiocyanate," this chemical evidence going to confirm the conclusion already reached by Hawthorne on purely physical grounds. Careful examination of the properties, both physical and chemical, of several different acyl rhodanides has served to corroborate the view that, although these compounds may be caused to yield thiocyanic acid by hydrolysis, they are nevertheless thiocarbimidic in constitution (Dixon and Taylor, *Trans.*, 1908, **93**, 691).

Whether an acyl thiocyanate is formed, even temporarily, from a strongly acid chloride and a metallic thiocyanate seems doubtful; thus Miquel observed (*loc. cit.*) that when benzoyl chloride is added to alcoholic potassium thiocyanate, maintained at 0° , the organic product of the interaction unites with the alcohol to form a substituted thiourethane, and hence, presumably, consists of benzoylthiocarbimide :

Why acyl radicles should be so reluctant to enter into thiocyanic combination it cannot at present be stated with certainty. Disposing causes, however, may be suggested; for instance, the similarity in electrical character of the two constituent groups. Even amongst undoubted thiocarbimides of this class, the union between the acyl and the rhodanic complex may very readily be sundered; thus, so well marked a thiocarbimide as that of benzoyl gave with alkali more than 88 per cent. of its contained sulphur in the form of thiocyanic

acid, and, what is still more remarkable, when treated with alcoholic ammonia yielded more than 50 per cent. of its sulphur as ammonium thiocyanate (Dixon and Taylor, *loc. cit.*). Amongst purely hydrocarbon thiocarbimides, this elimination of the rhodanic group is not known to occur; in fact, it does not usually happen even with hydrocarbon thiocyanates, which tend to yield mercaptans and the like.

Again, transformation of the $\cdot\text{SCN}$ group into $\cdot\text{NCS}$ is by no means uncommon, even when the associated radicle is not definitely electro-negative, as in the case of allyl thiocyanate. If conjoined with a distinctly acid radicle, and hence but loosely held, the rhodanic group could still more readily alter its mode of attachment, and would presumably do so in whatever manner leads to the most stable kind of union between the two constituent groups. As to electrical character, it is not very easy to compare the two configurations of the rhodanic complex. But seeing that the thiocyanates of the alkali metals are neutral saline compounds, the residue $\cdot\text{SCN}$ must be strongly electro-negative, and in this respect comparable with the residues of the mineral acids. On the other hand, the known combinations of the group $\cdot\text{NCS}$ do not appear to be saline, nor does it unite with the metals of the alkalis or alkaline earths; on these grounds, at least, the group $\cdot\text{NCS}$ may be considered less electronegative than the group $\cdot\text{SCN}$. Consequently, if a strongly acid radicle is conjoined, even for the moment, with the group $\cdot\text{SCN}$, the latter might pass rapidly into the more electropositive configuration $\cdot\text{NCS}$. On similar principles, the rhodanic group if transferred to a distinctly electropositive radicle, such as K, Na, etc., may be compelled to assume the form, $\cdot\text{SCN}$. This would seem to be the case, for when acetylthiocarbimide is treated with sodium ethoxide in presence of benzene, the action takes place as follows:

(Dixon, *Trans.*, 1904, 85, 353). The rhodanic group of acetylthiocarbimide, which is desulphurisable by alkaline salts of lead or silver, is transferred, not to the ethyl, but to the sodium, and when there attached, has lost the property of becoming desulphurised; had it passed (as $\cdot\text{NCS}$) to the ethyl group, the new rhodanide would have been desulphurisable; presumably, therefore, the configuration of the group is changed.

Since alkalis and alkaline nitrogenous bases tend to hydrolyse the acyl thiocarbimides with production of thiocyanic acid, whilst non-alkaline bases, such as the primary arylamines, have much less effect in this way, it might be anticipated that still more feeble bases—

such, for instance, as diphenylamine—would show even less power to cause hydrolysis, and, concurrently, more to enter into thiocarbimide union. Adequate material on which to judge is still wanting, but so far as may be learned from the behaviour of acetylthiocarbimide, this appears to be the case (compare Doran, *Trans.*, 1905, **87**, 341; Dixon and Hawthorne, *loc. cit.*; Dixon and Taylor, *loc. cit.*). It seems, therefore, not improbable that what conditions the “thiocyanic” decomposition of acyl thiocarbimides is not any reluctance on the part of the $\cdot\text{NCS}$ groups to enter into ordinary thiocarbimide reactions, but rather the tendency of the electropositive material offered for combination to seize instead directly on the electronegative group of the thiocarbimide, and so to liberate its rhodanic radicle.

If it be true that strong electronegative character in an organic radicle may entail the attachment of the rhodanic group solely as $\cdot\text{NCS}$, it is reasonable to anticipate the existence of a similar mode of union amongst the rhodanides (at present known as “thiocyanates”) of well-marked non-metallic radicles.

Hitherto but few non-metallic rhodanides have been prepared, the only certainly known examples being the thiocyanates of phosphorus, silicon, and arsenic (Miquel, *loc. cit.*), together with phosphoryl “thiocyanate” (Dixon, *Trans.*, 1901, **79**, 541). The silicon derivative has been re-examined carefully by Emerson Reynolds, who concludes (*Trans.*, 1906, **89**, 204) that it is really a thiocyanate; on the other hand, the phosphorus and phosphoryl compounds have been studied to some extent from the chemical point of view by one of the present writers (Dixon, *loc. cit.*), with somewhat different results.

The latter study has now been resumed, in the hope of learning by physical methods something further as to the constitution of these two rhodanides. To this end, the molecular refractions have been measured, but, since the inferences drawn rest on the interpretation of the numerical results, it seems desirable to indicate by reference to other cases how the experimental figures have been applied towards the solution of the problem.

Using the molecular refraction M_D obtained from the formula:

$$M_D = \frac{p(\mu_D - 1)}{d_{4^\circ}^{t^\circ}},$$

where p = molecular weight, μ_D = index of refraction for the spectral line, D , and $d_{4^\circ}^{t^\circ}$ = density at t° referred to water at 4° , Hawthorne found (*loc. cit.*) for methyl and ethyl thiocyanates at the ordinary temperature the figures 32.1 and 40.2 respectively. These, less 9.0 and

16.7—the refraction values for CH_3 and C_2H_5^* —gave as the effect of SCN , 23.1 and 23.5, or a mean of 23.3 units.

Ethylthiocarbimide and allylthiocarbimide gave at 15° , after deduction of the calculated values for the hydrocarbon radicles, 28.0 and 27.63 for $\cdot\text{NCS}$, and benzylthiocarbimide, after deduction of the mean value observed for C_7H_7 (obtained from chlorotoluene and from benzyl chloride), gave 27.84, or a mean refraction effect for $\cdot\text{NCS}$ of 27.82. When this method was applied to acetyl rhodanide (M_D at $20^\circ = 46.1$), the value 17.8 for acetyl being deducted, the difference, 28.3, lay so near to the above figure for $\cdot\text{NCS}$ that he decided in favour of the constitution represented by the formula $\text{CH}_3\cdot\text{CO}\cdot\text{NCS}$.

The mean of all these values for $\cdot\text{NCS}$ is 27.92, which differs by roughly one-third of a unit from the highest and lowest obtained.

Cyclic thiocarbimides, for some reason not yet understood, give results far in excess of the calculated numbers. It is possible, nevertheless, by determining the effect of the cyclic group in conjunction with CNS in a known compound, and by allowing for the former, to ascertain the refraction value of the rhodanic group when conjoined with similar benzenoid radicles. Thus, if from the mean number for phenylthiocarbimide, namely, about 77.6 (Nasini and Scala, *Gazzetta*, 1886, **16**, 70; Berliner, *Diss.*, Breslau, 1886), there be deducted what the present writers consider the most probable value for $\cdot\text{NCS}$, namely, 28.1, the difference, 49.5, represents approximately the refraction value of the phenyl group in such combinations. For example, it was found (Dixon and Taylor, *Trans.*, 1908, **93**, 692) that for *o*-tolylthiocarbimide, $M_D = 85.8$; this, less 49.5 (Ph) and 7.7 (CH_3), gives 28.6, a number not far from 28.1, the above "most probable value" for NCS .

Benzoyl rhodanide gave (*loc cit.*) $M_D = 85.7$, which, less 49.5 and 8.5 (C_6H_5 and $\text{C}\cdot\text{O}$), leaves 27.7; from this it was concluded that the substance is a thiocarbimide. In like manner, carboxymethyl and carboxyethyl rhodanides, $\text{CO}_2\text{Me}\cdot(\text{CNS})$ and $\text{CO}_2\text{Et}\cdot(\text{CNS})$, when compared with acetylthiocarbimide on the lines indicated, gave for the $\cdot\text{NCS}$ group the figures 28.7 and 27.9 respectively; of the seven values given above for $\cdot\text{NCS}$, the mean is 28.1, a number differing approximately by one-half unit from the highest and the lowest. Considering the difficulty of obtaining and of preserving these substances in a pure condition, that in calculating the molecular refraction the specific refraction ($\mu_D - 1/d$), and hence the experimental error in its determination, may have to be multiplied by very large numbers (over 160 in the case of benzoylthiocarbimide), and lastly, that the end results are but differences depending ultimately on the precision

* The atomic refractions used were:

$\text{H} = 1.306$; $\text{C}' = 5.092$; $\text{C}:\text{C} = 12.25$; $\text{O}'' = 3.426$; $\text{Cl} = 9.864$.

with which the other factors are measured and on a constant value being obtained by these different combinations, the concordance of the various refraction values for the thiocarbimidic group seems reasonably close.

Whilst, then, the results are obviously no more than mere approximations to the exact figures (if, indeed, there be definite values at all), they serve, nevertheless, to show that the group $\cdot\text{NCS}$ exerts on light a tolerably constant effect, which is measurably different from that produced by the isomeric configuration $\cdot\text{SCN}$. To ascertain whether the refraction number, about 23.3, already obtained for the latter holds in the case of other than purely aliphatic hydrocarbon radicles, we have now examined benzyl thiocyanate, the molecular refraction in alcoholic solution being calculated from the formula :

$$100 \frac{(\mu - 1)}{d} = \frac{(\mu' = 1)}{d'} r + \frac{(\mu'' - 1)}{d''} (100 - r),$$

where μ , μ' , and μ'' = indices of mixture, substance, and solvent respectively for the D line, and d , d' , and d'' = densities corresponding, r being the weight of substance in 100 parts by weight of the mixture.

The mean of two determinations in solutions containing respectively about 11 and 13 per cent. of thiocyanate was 75.7. This, less 52.3 for the benzyl radicle (see above), leaves for the $\cdot\text{SCN}$, 23.4, a figure agreeing closely with the mean value obtained in other cases, namely, 23.3.

On the basis, therefore, that a refraction number for the rhodanic group of about 23.3 units on the above scale implies the configuration $\cdot\text{SCN}$, and that of about 28.1 units the configuration $\cdot\text{NCS}$, we have examined the supposed thiocyanates, $\text{P}(\text{SCN})_3$ and $\text{PO}(\text{SCN})_3$.

Phosphorus Trirhodanide, $\text{P}(\text{CNS})_3$.

The preparation of this compound having already been described (Dixon, *loc. cit.*), details of the procedure are unnecessary. Instead, however, of ammonium thiocyanate, the hygroscopic character of which entails some difficulties, the corresponding lead salt was employed. It may be noted, also, that the bumping and frothing during distillation, which are always more or less troublesome, are considerably lessened if the phosphorus trichloride is freshly distilled before use.

The boiling points previously recorded were confirmed, a specimen twice rectified distilling at 164—165° under a pressure of 16 mm.; the density, given before as 1.487 at 15°/4° (different specimens when washed with water and redistilled gave also 1.483 and 1.488), was now found at 15°/4° to be 1.483.

The refractive index of the oil approaching very nearly to the limit

of the highest prism in the Pulfrich refractometer employed, its value was determined by the method of mixture specified above. In this way, μ_D was found to be 1.71739 at 15°; whence $M_D = 99.17$.

The refractive index of phosphorus trichloride, as determined by Gladstone and Dale (*Phil. Trans.*, 1863, **153**, 341), when combined with the careful determinations of its density by Thorpe (*Trans.*, 1880, **37**, 334), gives for M_D at 28.5° and at 38°, 44.96 and 44.97 respectively. This we checked, finding for μ_D at 150° the figure 1.5152; whence $M_D = 44.7$. A determination by Nasini and Costa (*Pub. dell. Ist. chim. Roma*, 111, 1891) gives by interpolation for the *D*-line the value 45.2; the mean of these three is 44.95. The refraction of the three chlorine atoms being in round numbers 3×9.9 , or 29.7, the difference for the phosphorus is 15.25.

Deducting now from the molecular refraction of phosphorus tri-rhodanide the above value for phosphorus, we have for the joint total effect of the three rhodanic groups $99.17 - 15.25 = 83.92$, or, assuming them all to be equal, about 28 units for each.

So far, therefore, as this purely physical method of examination may be relied upon as affording evidence of chemical structure, the conclusion seems justified that phosphorus tri-rhodanide is *not a thiocyanate* (M_D for which would be about 85.1 units, instead of the 99.2 found), *but a thiocarbimide*.

Chemical evidence to the same effect, as might be anticipated, is more difficult to secure. For, as it has been mentioned already, the rhodanides of negative organic radicles invariably may be hydrolysed with formation of thiocyanic acid; and it is doubtless by reason of the ease with which in many cases this change takes place that such particular compounds as show the reaction have generally been accepted as thiocyanates. But, since the mere production of thiocyanic acid by hydrolysis is plainly insufficient to characterise a given organic acid rhodanide as a thiocyanate, the formation of this substance in the case of an electronegative inorganic rhodanide can equally afford no clue as to the constitution of the material which yields it. Indeed, considering the high affinity of phosphorus for oxygen, and its relatively slight tendency to form amino-compounds, one could scarcely anticipate the occurrence of the "thiocarbimide" hydrolysis:

Only by cautious treatment, therefore, avoiding the presence of water or strong bases, might one reasonably expect to make manifest the thiocarbimide power of a compound the molecule of which is obviously prone to total disruption (Miquel, *loc. cit.*). To present in the absence of water a feeble base seemed most hopeful, since the hydrolytic effect (or the tendency of the basic residue to withdraw

the phosphorus) would be minimised, thereby giving to the supposed $\cdot\text{NCS}$ groups a chance to enter into their characteristic thiocarbamidic combinations.

To secure these conditions, aniline and the still more feeble diphenylamine were employed; so far successfully, that definitive, additive thiocarbamidic combination has been accomplished, although not to the full extent betokened by the presence of three $\cdot\text{NCS}$ groups. But that additive change may to some extent be realised is shown by the following experiments.

Phosphorus Trithiocarbimide and Aniline.—To 4.93 grams of freshly-distilled oil, dissolved in cold benzene, 2.22 grams of pure aniline, also in benzene, were added (instead of 2.24, the calculated weight for equal molecules). The precipitated granular solid was filtered off, and to the filtrate were added two or three drops more of aniline, this causing a slight further precipitate; on concentrating somewhat and filtering again, the filtrate when treated with aniline now remained clear. The precipitates, after drying, weighed in all 7.15 grams; the amount calculated for an equimolecular compound being 7.176 grams, that obtained represents 99.6 per cent. of the theoretical.

In the main product, a cream-white powder, ready-formed aniline thiocyanate was absent, for when the solid was shaken up with water the aqueous portion gave with ferric chloride a barely perceptible colour change, and no detectable reaction for aniline. On standing with cold water, hydrolysis occurred slowly, the reaction with hydrochloric acid and ferric chloride becoming gradually more marked, and, after some four or five days, intense. On boiling, the thiocyanic reaction was obtained at once, a perceptible trace of hydrogen sulphide being evolved; aniline was now detectable, although in very small amount, and phenylthiourea crystallised out as the solution cooled.

That the phenylthiourea did not result through ordinary isomeric change of aniline thiocyanate, conceivably formed in the hydrolysis, was established by the following observations. Aniline thiocyanate, when heated to boiling in dilute aqueous solution together with a little alcohol, yielded in one minute no perceptible amount of phenylthiourea, as tested by the action of boiling alkaline lead or silver salts on the solution; after three or four minutes' boiling, a very slight desulphurisation began to show, which increased steadily as the time of boiling of the aqueous solution was prolonged; in the cold, no reaction was noticeable after many hours' standing. On the other hand, the solution of the phosphorus compound in alcohol gave with silver nitrate a white precipitate, which was blackened gradually on standing in the cold, or instantly on warming. The compound gave also with cold dilute alkali an opalescent solution; a portion of this,

when acidified, gave with ferric chloride an intense red coloration ; another portion, when treated with an alkaline lead salt, gave a primrose-yellow precipitate, which became black, gradually in the cold, or immediately on gentle warming. Phenylthiourea, dissolved in alkali hydroxide, behaved so far as the desulphurisation with lead solution is concerned in precisely the same way, save that the darkening was somewhat slower in the cold.

It has already been shown (Trans., 1904, **85**, 359) that of the total sulphur contained in this compound, about 4 per cent. escapes on rapid hydrolysis as hydrogen sulphide, and that of the remainder, about one-third crystallises out as phenylthiourea (in practice, nine-tenths of this fraction was collected), whilst about two-thirds appear as thiocyanic acid. Apart, therefore, from the slight change first mentioned, the main decomposition may be represented thus :

Very remarkable is this sharp union in the cold of a single molecule of aniline with but one of the three $\cdot\text{NCS}$ groups in the tri-thiocarbimide. Possibly, but not very probably, it may be due to steric hindrance that the remaining groups fail to combine ; in this case, however, one would rather have anticipated the ready union of two $\cdot\text{NCS}$ groups with aniline, the difficulty arising in connexion with the third. Cases, however, are not uncommon in which, if several like atoms or atomic complexes are charged upon a single other atom, the atoms or complexes so conjoined show inequality of power to interact. Thus, for example, of the two chlorine atoms in carbonyl dichloride, but one reacts very readily with alcohol, the resultant ethyl chlorocarbonate uniting only slowly with excess of alcohol. Carbonyldithiocarbimide, $\text{CO}(\text{NCS})_2$, too, when mixed with alcohol, takes up but one molecule to form $\text{SCN}\cdot\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{OEt}$ (Dixon, Trans., 1903, **83**, 87). With bases, it combines readily in equimolecular proportions ; two molecules of base are not taken up in any case so readily as one, and in certain instances (namely, with naphthylamine and with benzyaniline), even although excess of base is used, a single molecule alone enters into combination. Similar instances might be multiplied, but it would serve no other purpose than to show that our knowledge of the chemical power of a radicle, singly held, cannot always be extended by mere arithmetic to cases where there are two or more, especially if these be attached to one particular atom.

Phosphoryl Trirhodanide, PO(CNS)₃.

In preparing this substance, potassium and lead thiocyanates were tried, and, as solvents in each case, benzene or cumene, the best yield being obtained from the lead salt with cumene. Previous distillation of the phosphoryl chloride was found very advantageous in reducing the tendency of the solution to bump and froth during the fractionation; commercial cumene, which contains naphthalene, is unsuitable, for the latter, unless removed, is left ultimately mixed with the rhodanide, and causes difficulty.

The solvent was distilled off under diminished pressure by the aid of a water-bath; the residual oil was then collected separately and rectified. Its properties agreed with those already described (*loc. cit.*), the boiling points observed in various preparations being 159°/11 mm., 160°/12 mm., and 164°/14 mm., the previous figure being 175°/21 mm. Its density, the mean of three closely concordant determinations from different specimens, was 1·518 at 15°/4°. The refractive index at about 15° was found to be, as the mean of three concordant determinations for material once rectified in each case, $\mu_D = 1·6882$, and from three preparations, each doubly rectified, $\mu_D = 1·6918$. From these figures, $M_D = 100·02$ and $100·48$ respectively; the latter value is used below.

Since the phosphoryl group, as shown by Gladstone (Trans., 1870, 23, 112), has an abnormally low refraction effect, at least in meta- and ortho-phosphoric acids, it was necessary to ascertain directly what the value is in phosphoryl chloride, POCl₃. From Gladstone and Dales' determination (*loc. cit.*), namely, $\mu_D = 1·4882$ at 17°, and Thorpe's careful measurement of its density (*loc. cit.*), namely, 1·6805 at 17°/4°, M_D for POCl₃ = 44·6. This, less Cl₃ (3 × 9·9, or 29·7), leaves for the group :PO the value 14·9, something less than that of the phosphorus which it contains.

Consequently, the total effect of the rhodanic groups in phosphoryl rhodanide is about 100·5 – 14·9, or 85·6, one-third of which (assuming them to be alike), or 28·5, gives the value of each; this figure is obviously much nearer to that representing ·NCS (28·1) than the 23·3 which measures the effect of ·SCN. If phosphoryl rhodanide contained three of the latter groups at the value named, M_D would be 84·8, instead of about 100·5.

Judging from the above results, the conclusion appears to be justified that *phosphoryl rhodanide*, like the corresponding phosphorus compound, is *not a thiocyanate, but a thiocarbimide*,

Notwithstanding that phosphoryl trithiocarbimide is hydrolysed with ease into phosphoric and thiocyanic acids, there is no difficulty in obtaining also from it the reactions characteristic of a thiocarbimide. For example, the cold alcoholic solution, when treated with alkaline lead tartrate, gave a turbid mixture, which very quickly became black, owing to desulphurisation. Silver nitrate, followed by ammonia in the cold, gave a like result, and mercuric or cadmium salts in presence of alkali yielded at once, on gentle warming, the corresponding black or yellow sulphide. To ascertain to what extent the thiocyanic hydrolysis is accomplished in presence of alkali and water, a weighed quantity of the oil (about $1\frac{1}{4}$ grams) was dissolved in hot water containing 5 equivalents of *N*-sodium hydroxide; the faintly alkaline solution was neutralised exactly by very dilute nitric acid, made up to a known volume, and boiled to expel a trace of hydrogen sulphide; the contained thiocyanic acid was then determined by Barnes and Liddles' method, using *N*/10-copper sulphate. Of the total sulphur present in the oil, 90.75 per cent. was found as $\text{H}\cdot\text{SCN}$, a figure close to that obtained for benzoylthiocarbimide and for carboxyethylthiocarbimide, namely, about 89 and 93 per cent. respectively (Dixon and Taylor, *loc. cit.*).

Phosphoryl Trithiocarbimide and Aniline.—To a benzene solution of the freshly-distilled oil, one molecular proportion of aniline was slowly added, the latter also being dissolved in benzene; the weight of the yellow, granular precipitate which formed at once, together with that of another small quantity which separated from the mother liquor on standing, amounted to precisely the sum of the weights of materials employed. The melting point, 121.5° , with previous softening at 120 — 121° , was practically identical with that observed before (Dixon, *loc. cit.*), and a sulphur determination, made as a check, fell a fraction of a per cent. below the figure calculated for an equimolecular compound. Cold water, shaken up with the solid, extracted from it scarcely a trace of thiocyanic acid, and no detectable amount of aniline; on standing, however, hydrolysis began to occur, the process running a course exactly similar to that with the corresponding phosphorus derivative. The action is very slow at the ordinary temperature; thus, in an experiment where a quantity of the additive compound was mixed with about twenty times its weight of water, the mixture being shaken up frequently during a fortnight, thiocyanic acid and phosphoric acid passed into the solution in slowly increasing amount; but on washing the residual solid until the filtrate ceased to react for thiocyanic acid when tested with ferric chloride, and again leaving the solid residue in contact with water, these two acids continued as before to accumulate in the solution.

With dilute alkali, or with hot water, the hydrolysis takes place

rapidly. Thus, when a weighed quantity of the solid was digested on the water-bath for twenty minutes with a slight excess over four equivalents of $N/10$ -alkali, together with some water, and the solution just acidified and diluted to a known bulk, the latter mixture, by comparison with a standard solution of thiocyanate and ferric chloride, was found to contain sixteen-seventeenths of the thiocyanic acid, which could result from the change

The colorimetric method, according to our experience, working at a concentration of $N/1000$, gives results which are accurate to within about 5 per cent. of the total amount evaluated. Barnes and Liddles' process proved unavailable, the phenylthiourea formed in the hydrolysis combining with the copper solution to produce some double compound, the nature of which we did not investigate beyond verifying that it is also precipitated when copper sulphate is added to phenylthiourea in presence of alkali bisulphite; it is not formed from these two in the absence of the bisulphite.

These results are so far confirmatory of those previously obtained (*loc. cit*) as to establish with reasonable certainty the propositions: (i) that phosphoryl trirhodanide in the cold enters at once into definite chemical combination with a single molecule of aniline, one only of its three rhodanic groups thereby becoming engaged with the base added; (ii) that, apart from a trifling side-reaction leading to the production of hydrogen sulphide, the additive compound is hydrolysed very readily into phosphoric acid, two molecules of thiocyanic acid, and one molecule of phenylthiourea; (iii) that the original additive compound does not contain aniline thiocyanate, neither does the phenylthiourea produced by the hydrolysis result from the transformation of aniline thiocyanate, conceivably formed during the act of hydrolysis.

What occurs, then, in the combination of aniline in the circumstances named is this: of the three rhodanic groups attached to the phosphoryl residue, one alone absorbs the base, entering with it into definite thiocarbimide combination; the other two remain intact. On hydrolysis, the phenylthiocarbimido-complex is removed as phenylthiocarbimide (or phenylthiourea); the hydrolysis is completed by the elimination of the two remaining rhodanic groups, during which, as with other acylthiocarbimides, a small fraction of the sulphur escapes by thiocarbimide hydrolysis as carbonyl sulphide, the main part of it decomposing as (CNS) and yielding thiocyanic acid.

The next point to be decided was whether more than one molecule

of aniline can be united with a molecule of the trirhodanide. Since a single molecular proportion of aniline precipitates and removes completely from benzene solution the whole of the dissolved rhodanide, the experiment was now reversed, one molecular proportion of the phosphorus compound being added, drop by drop, in cold benzene to two molecular proportions of aniline, similarly dissolved, and kept cool. As before, a precipitate formed; when washed with benzene and dried in the steam-bath, its weight amounted to 99.8 per cent. of the total weight of material employed for combination. The benzene mother liquor contained a mere trace of thiocyanic acid, but no detectable amount of aniline.

The product, faint yellowish-white in colour, shrank at 113° and melted between 114.5 and 115.5°. On analysis:

0.407, fused with NaOH + KNO₃, gave 0.600 BaSO₄. S = 23.2.

C₁₅H₁₄ON₅SP requires S = 23.58 per cent.

The compound therefore is PO(NCS)₃ + 2C₆H₅·NH₂.

As in the case of the preceding compound, aniline thiocyanate was not present ready formed, for the solid when shaken up with water was practically insoluble, the aqueous portion giving with hydrochloric acid and ferric chloride a barely perceptible red coloration, but, on boiling, the reaction was given abundantly.

Strange to say, the second molecule of aniline is not held in the same thiocarbamidic combination as the first, or if it is, the decomposition occurs differently. For when the compound was hydrolysed as in the preceding case, and the liberated thiocyanic acid measured colorimetrically (Barnes and Liddles' method proving inapplicable), the amount of this acid formed, as nearly as can be judged by this process, was that corresponding with two-thirds of the total sulphur present. The hydrolysed mixture gave the reaction for aniline.

How to explain this curious behaviour, save conjecturally, we do not yet know, but on the ground that aniline thiocyanate is not present as such in the product (which, moreover, was at no stage of its formation pasty, as is generally observed if this substance is formed), the hydrolysis may provisionally be represented as follows:

When one molecular proportion of the rhodanide was added to three molecular proportions of aniline in the cold, a solid separated, but part of the base did not enter into combination, for the benzene liquor reacted freely for aniline. On warming the mixture on the water-bath to about 65°, the solid melted to a clear oil, and the benzene now no longer gave the reaction for aniline. Apparently, therefore, three molecules of the base had been absorbed, but on

pouring off the mother liquor, and allowing the oily residue to stand, it slowly changed into a yellow, pitchy resin, so unlike a definite chemical compound that no attempt was made to analyse it. With cold water the powdered resin behaved somewhat like the preceding compounds, save that the mixture when acidified and treated with ferric chloride gave a distinct, although not strong, red coloration.

Phosphoryl Trithiocarbimide and Diphenylamine.—From 10.574 grams of thiocarbimide and 7.14 of diphenylamine (equal molecules), both in benzene, there separated 17.5 grams of a faintly yellow product consisting of microscopic needles. When heated in a narrow tube, these shrank slightly at 138°, and melted between 140° and 141° (uncorr.). A sulphur determination showed the substance to be an equimolecular compound:

0.377, fused with NaOH + KNO₃, yielded 0.662 BaSO₄. S = 24.2.

C₂₇H₂₀ON₅S₃P requires S = 24.6 per cent.

Cold water had little effect on this diphenyl compound, the mixture at the end of four days, during which it was frequently shaken up, giving with ferric chloride no more than a faint red coloration; on boiling, a well-marked reaction was obtained.

Under the action of dilute alkali hydroxide, hydrolysis occurred readily; thus, when 5.85 grams of the solid were suspended in hot water, and *N*-sodium hydroxide added, drop by drop, until the solution became just alkaline to litmus, 48 c.c. were required. Since, for the above quantity of substance, each 15 c.c. of normal solution represents one equivalent, a little more than three equivalents had been absorbed. When cold, the mixture was separated by filtration from the white solid, which now no longer yielded thiocyanic acid when boiled with potassium hydroxide, and was free from phosphorus; it was recrystallised from alcohol, and identified as *αα*-diphenylthiocarbamide. Its weight, apart from what remained in the aqueous portion (for the substance is not quite insoluble in water), amounted to 3.08 grams, that is, nine-tenths of what could be formed according to the equation:

All the phosphorus had passed into the aqueous filtrate, which reacted intensely for thiocyanic acid, and gave the usual reactions for phosphoric acid; it contained, in addition, a trace of dissolved thiocarbamide.

Phosphoryl trithiocarbimide, when added to two molecular proportions of diphenylamine dissolved in cold benzene, yielded the above unimolecular additive compound in a somewhat impure condition; the mother liquor, when concentrated by evaporation, afforded a further small crop of a mixture melting between 150° and 165°, and, when

allowed to evaporate to dryness, left a residue containing much unchanged diphenylamine.

From these results it would appear that diphenylamine, in the circumstances given, is less disposed than aniline to form with phosphoryl trithiocarbimide a compound containing two molecules of the base. In this connexion, it may be recalled that, whilst the dithiocarbimide of carbonic acid, $\text{CO}(\text{NCS})_2$, can unite with either one or two molecules of aniline or of toluidine, it combines with but a single molecule of naphthylamine or of benzylaniline, even although the latter bases be present in excess (see p. 2156).

Earlier in this paper it has been suggested that the mode of union of a rhodanic group may depend on the character of the radicle to which it is attached. Since hydrogen, like the hydrocarbon residues, represents a kind of electrical mean between strongly electropositive radicles, such as K, Na, etc., and strongly electronegative, such as $\text{CH}_3\text{CO}\cdot$, $\text{O}\cdot\text{P}<$, and the like, it also might be expected to yield the two rhodanides, $\text{H}\cdot\text{SCN}$ and $\text{H}\cdot\text{NCS}$.

It seems probable, however, that the great mobility of hydrogen, coupled with its generally electropositive character, may suffice to preclude its permanent association with the rhodanic complex, save in the one form $\text{H}\cdot\text{SCN}$, and similarly with other radicles, such as CNO , CN , NO_2 , etc., which with hydrocarbon residues can give isomeric combinations, whereas with hydrogen they yield in each case but a single form. However this may be, the fact remains that when a thiocarbimide is hydrolysed, the products may contain carbonyl sulphide or thiocyanic acid, but not hydrogen thiocarbimide, $\text{H}\cdot\text{NCS}$.

It being tolerably clear, in a general way, that the less electropositive the base presented for interaction to an acidic thiocarbimide the less is the resulting thiocyanic decomposition (and concurrently, the greater is the percentage of thiocarbamidic union), the idea occurred of trying whether chemical action could be brought about with distinctly electronegative "bases." For, although the amides do not combine directly with thiocarbimides containing hydrocarbon radicles, yet diphenylamine, which is little disposed to unite with these, does so vigorously with many acylthiocarbimides, and hence it seemed worth while to experiment on the lines indicated.

The combinations attempted were: (i) benzoylthiocarbimide in benzene or acetone with oxamide, benzamide, acetanilide, and urethane, all in the cold; (ii) carboxymethylthiocarbimide with benzamide and with urethane, also in the cold; (iii) acetylthiocarbimide with urethane in boiling toluene. In no case could any sign of combination be detected.

It is plain, therefore, that a certain amount of "basicity" is requisite for the combination of "base" and thiocarbimide; more-

over, acetylthiocarbimide can furnish with aniline the compound *ab*-acetylphenylthiocarbimide, whilst phenylthiocarbimide, it appears, cannot unite with acetamide to yield the same compound. Yet the hydrogen of the NH_2 -group in acetamide is not especially difficult of removal, for it may be replaced directly either by bromine or by sodium. Ethylthiocarbimide, too, fails to combine with sodium acetanilide (Dixon, *Trans.*, 1899, **75**, 384), and phenylthiocarbimide with asparagine (*ibid.*, 410); neither does acetyl chloride react with phenylthiocarbimide dissolved in aqueous sodium hydroxide (Dixon and Hawthorne, *loc. cit.*), a liquid supposed to contain the sodium derivative of phenylthiourea. In the present state of our knowledge, to explain these facts is more than difficult.

Although the only organic acyl rhodanides so far isolated are those derived from carboxylic acids, there is some reason to hope that certain non-carboxylic acids may afford similar products. For when the chlorides of phenylsulphonic and ethylsulphuric acids respectively were heated in presence of hydrocarbon solvents with lead thiocyanate, the liquor in each case was desulphurised by lead and silver salts, and hence may have contained dissolved thiocarbimide (Dixon, *Trans.*, 1897, **71**, 640). Owing to the difficulty of securing complete interaction without decomposing the organic product, these experiments were abandoned until better methods should become available; it is now intended to resume the study, in the hope that more satisfactory conditions may be realised. It is proposed, also, to examine the molecular refraction of rhodanides containing inorganic radicles other than those of phosphorus and phosphoryl, with the view of learning whether, in such cases, the above physical method will serve as a means of distinguishing statically between the thiocyanic and the thiocarbimidic form of linking.

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