XXVIII.—*On some Derivatives from the Olefines.* By FREDERICK GUTHRIE,
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(Read 18th March 1861.)

Some years ago I commenced an examination of the behaviour of the so-called olefines towards certain compound halogens. I was induced to this by the conviction that the bodies resulting from the union of a group of unequally chemico-negative elements with an olefine, would place an instrument of great power into the hands of systematic chemists, especially of synthesists. My expectations have been more than realized. The few olefines which I have examined in their relation to compound chemico-negative groups have given rise to a series of new bodies remarkable alike for their great number and for the elegance and importance of the reactions attending their formation and recompositions.

It will probably be found that the Ketons and other oxygeniferous bodies may enjoy some of the properties of the olefines proper: but we must be content to define an olefine provisionally as a hydrocarbon capable of uniting directly with halogens. According to this definition, we find olefines falling naturally into two groups. Of the one group, Naphthaline is the sole representative. This olefine unites with two or four equivalents of halogen, to form, expressed generally,

and the numerous class of bodies idiotypic with these, of which the following are examples:

The other group of olefines has the general formula

For the chemical saturation of the members of this group, two equivalents of halogen are necessary and sufficient:

BERTHELOT has shown that an olefine of the latter form may indeed unite with a hydrohalogen and that the result is a body identical with the halide of the corresponding radicle.

The question, which has been already partly discussed,* and the continued discussion of which forms the subject of the present communication, is, whether olefines of the form

may not, like naphthaline, unite with groups consisting of dissimilar halogen elements: and amongst what class of organic salts such combinations are to be ranked.

Since with such olefines there appears to be only one stage of saturation, we are induced to examine the behaviour of the compound halogens already formed towards the olefines, rather than to effect the same purpose by the successive application of dissimilar ones.

The olefines whose behaviour in this direction I have as yet chiefly examined are Ethylen or Olefant gas, and Amylen. These olefines have been principally considered in their relation to the sulphides of chlorine.

The ethylen employed was formed by heating quickly a mixture of three parts by volume of oil of vitriol with one part of alcohol of 85% and sufficient sand to make a thick paste, passing the gas in succession through dilute caustic soda and strong sulphuric acid, and collecting over lime water. Ethylen so prepared, which, before used, is dried by passing through strong sulphuric acid, I have analyzed on several occasions, and found absolutely pure.

The amylen† employed had been prepared by the action of chloride of zinc on amylic alcohol. After a few rectifications it boiled constantly at 38° C. at 758 m.m. pressure. It has the specific gravity of 0.6727 at 12°C. On burning with oxide of copper it showed the following composition:—

I. 0.2346 grm. gave 85.77 per cent. carbon and 14.11 hydrogen.					
II. 0.2627 grm. gave 85.79 per cent. carbon and 14.22 hydrogen.					
	$C_{10} H_{19}$		Pound.		
	requires		I.	II.	Mean.
C	85.71 ...	85.77 ...	85.79 ...	85.78	
H	14.29 ...	14.11 ...	14.22 ...	14.16	
	<hr/>				<hr/>
	100.00				99.94

The results which I have already obtained in this direction are briefly as follows:‡—

* I. Chem. Soc. Quart. Jour., vol. xii. p. 109. Ann. der Ch. u Ph., cxiii. p. 266; Annales de Ch. et Phys., vol. lix. p. 461.

II. Chem. Soc. Quart. Jour., vol. xiii. p. 35. Ann. der Ch. u Ph., cxvi. p. 234.

III. Chem. Soc. Quart. Jour., vol. xiii. p. 129.

† From Messrs SIMPSON, MAULE, and NICHOLSON.

‡ M. WURTZ (Ann. de Ch. et Phys., vol. lix.), in referring to the bodies (1), (2), (3), (4), (9), (10), remarks,—

“ SCl_2 correspondant à SO_2 étant diatomique, il en résulte en effet que $SCl_2 - Cl$ c'est à dire SCl doit être monatomique. Vous ferons remarquer, néanmoins, que l'on peut envisager la constitution de ces composées d'une autre manière, en supposant qu'ils renferment le groupe diatomique,

“Sulphure d'éthylène ($C_4 H_4 S_2$)” et

The bodies Cl S_2 and S Cl unite directly with the olefines $\text{C}_4 \text{H}_4$ and $\text{C}_{10} \text{H}_{10}$ to form

- * (1) $\text{C}_4 \text{H}_4 \text{S}_2 \text{Cl}_2$ Bichlorosulphide of ethylen.
- * (2) $\text{C}_4 \text{H}_4 \text{Cl S}_2$ Bisulphochloride of ethylen.
- * (3) $\text{C}_{10} \text{H}_{10} \text{S}_2 \text{Cl}_2$ Bichlorosulphide of amylen.
- * (4) $\text{C}_{10} \text{H}_{10} \text{Cl S}_2$ Bisulphochloride of amylen.

At elevated temperatures, $\text{C}_4 \text{H}_4$ acts upon $\text{S}_2 \text{Cl}$ to produce

"Sulphure d'amyène ($\text{C}_{10} \text{H}_{10} \text{S}_2$)" correspondant aux oxydes. Ces groupes en se combinant à 2 atomes de chlore forment les deux chlorures suivants—

"Quant aux chlorure $\text{C}_{10} \text{H}_{10} \text{S}_2 \text{Cl}$ nous doublons son équivalent et nous représentons sa constitution par la formule

"On sait que 2 atomes d'oxyde d'éthylène peuvent se réunir pour se combiner à 1 atom d'eau. Il n'est pas donc extraordinaire que 2 atomes de sulphure d'amyène de réunissent pour se combiner à 2 atomes de chlore. Si cette manière de voir est exacte on doit représenter la constitution de l'oxyde de disulphamyène et celle de hydrate d'oxyde de disulphamyène par les formules

With regard to the first portion of M. WURTZ's remark relative to the bichlorosulphides, I have to observe that the body SCl_2 has not been shown to exist, and, therefore, how its atomicity would be affected by a withdrawal of chlorine is a premature speculation.

Further, if the diatomic olefines are combined with two atoms of sulphur ("corresponding to the oxides"), why do they combine with two more atoms of halogen? Not, I think, because they have two stages of saturation, as M. WURTZ's view would indicate, but because halogen groups may have the same index of saturation as simple halogens. In this manner

Concerning the bisulphochlorides, there is perhaps as much reason for doubling their formulæ as for doubling that of water; and so for the bisulphoxide.

M. WURTZ's proposed formula for the hydrated bisulphoxide of amylen, viz.,

I cannot interpret, unless it belong to the class of "mixed types."

On the other hand, we may regard it as

which, I insist, is more congenial to analogy.

But, in truth, if the function of a formula be to express potential recomposition, these bodies eminently show the insufficiency of a single formula.

When the latter body is submitted to the action of chlorine, there is formed

A body identical with that got by the action of chlorine upon the bisulphide of ethyl—

Further, chlorine acts upon the bisulphochloride of amylen to form

Moreover, oxide of lead converts the body (4) into

while hydrated ammonia and hydrated potash give rise to the hydrate of (9)

The manner of the formation of these bodies, and the definite and integral nature of the reactions which they show, is alone sufficient to prove that they are true single chemical compounds, and not mixtures. Since, however, they are none of them volatile without decomposition, their boiling points and vapour condensation, useful criteria of homogeneousness, are wanting. The same fact, however, may be equally well established by another method; that, namely, of "fractional solution." This method, which is of very wide application, has been already successfully employed in determining the homogeneous nature of gases. The principle may be enunciated as follows:—

"If a body be partly dissolved in a solvent, and if the dissolved part and the undissolved part, or the dissolved part and the whole, have the same composition, then the body is a simple one."

The converse of this law is not true, because solution may effect decomposition. Nor is the law itself any more or less true than that no two different bodies are soluble under the same circumstances to exactly the same extent in the same medium. This seems to be true in all cases but where the solubility is infinite, or indefinite miscibility possible.

This method was applied to the bisulphochlorides of amylen and ethylen, because, as we shall immediately see, they give rise to numerous derivatives, and because their definite nature should be therefore set at rest.

A few grammes of the bisulphochloride of ethylen were warmed with strong alcohol until about half dissolved. The alcoholic solution was poured off, evaporated to expel the alcohol, then washed with water, and dried over sulphuric acid in *vacuo*.

On analysis,

	Grms.
I.	0.4436 gave 25.27 per cent. carbon and 4.36 hydrogen.
II.	0.4280 gave 33.88 per cent. sulphur.
III.	0.2838 gave 36.00 per cent. chlorine.

Comparing this analysis with the one given of the entire substance, "Quarterly Journal of Chemical Society," we find—

$C_4 H_4 S_2 Cl$ requires	Entire subst.	Dissolved portion.
C=25.13	25.93	25.27
H= 4.19	4.32	4.36
S=33.51	33.47	33.88
Cl=37.17	36.29	36.00
<hr/> 100.00	<hr/> 100.01	<hr/> 99.51

Which proves that the substance is single. The bisulphochloride of amylen, on being treated in a similar manner, gave a substance which showed the following composition :—

- I. 0.3934 grms. gave 23.81 per cent. sulphur.
 II. 0.2677 grms. gave 25.66 per cent. chlorine.

Comparing this with analysis, "Quarterly Journal of Chemical Society," vol. xii. p. 113,

$C_{10} H_{10} S_2 Cl$ requires	Total subst.	Soluble portion.
C=43.64	43.80	...
H= 7.27	7.47	...
S=23.27	23.93	23.81
Cl=25.82	24.73	25.66
<hr/> 100.00	<hr/> 99.93	

I considered a determination of the carbon unnecessary.

Having thus established the right of these bodies to be considered pure and homogeneous, the next thing was to examine the action of chlorine upon the bisulphochloride of ethylen.

If dry chlorine be made to act upon bisulphochloride of ethylen in the dark, hydrochloric acid is evolved, together with chloride of sulphur: the temperature rises considerably. If the action be assisted by the heat of a water bath, and the excess of chlorine be expelled by a current of dry carbonic acid, a product is obtained which is identical with that got by the action of chlorine either upon the bisulphochloride of clorethylen $C_4 \frac{H_3}{Cl} Cl S_2$, or upon the bisulphide of ethyl.*

For on analysis,

- I. 0.3824 grms. gave 70.69 per cent. of chlorine.
 II. 0.4380 grms. gave 10.63 per cent. of sulphur.

$C_4 H_2 Cl_3 S$ requires	I.	II.
C=16.16	...	...
H= 1.35	...	...
S=10.76	...	10.63
Cl=71.73	70.69	...
<hr/> 100.00		

* Chem. Soc. Quart. Jour., vol xiii.

Showing that the product, as in the two other cases, is the chlorosulphide of bichlorethylen.

Hence we are led to the general conclusion that, *towards chlorine a body of the form* $C_n H_n S_2 Cl$ *behaves like one of the form* $C_n H_{n+1} S_2$. For the three bodies $C_4 H_4 S_2 Cl$, $C_4 H_5 S_2$, and $C_4 H_3 S_2 Cl_2$ all yield, when acted upon by chlorine, $C_4 H_2 S Cl_3$. Accordingly, the most rational formulæ for these three bodies *towards chlorine* will be—

Bisulphide of ethyl.

Bisulphochloride of ethylen.

Bisulphochloride of chlorethylen.

—the ultimate action of chlorine (at $100^\circ C$. in the dark and at ordinary pressures) being in all cases to form the body,

I shall not assert that the identity of the ultimate products is a decisive proof, even in this case, of the identity of original constitution; but if it be admitted as such, the union of the olefines with the bisulphide of chlorine must be placed side by side with the union of hydrobromic acid with ethylen; namely, we must look upon the resulting products in the first case as being the bisulphides of the monochlorinated radicals.

Further, if we indulge in the assumption that the bichlorosulphides of ethylen and amylen,

are constructed upon the same type, we are induced to the formulæ,

which would in truth compel the admission, that $S_2 Cl$ *may* saturate a single hydrogenoid. This proposal will startle us the less when we remember on the one hand the equality in saturating power between chlorine and cyanogen; and, on the other, the monosaturating power of sulphocyanogen.* We shall hereafter see that the olefines may unite with the elements of one equivalent of sulphocyanogen, and with compound groups of which such an equivalent forms a part,

* I may not here discuss the composition of the sulphocyanides. Whether they be isotypic with the cyanates or the cyanides, or whether such a distinction be at all a substantial one, is here a matter of secondary importance.

showing that either the olefines have more than one index of saturation, or that the diverse grouping of the halogen equivalents must compensate for the absolute number of their equivalents concerned.

The general direction of argument then, hitherto, tends to show that *towards chlorine, the bisulphochlorides of ethylen and of amylen behave like the sulphides of chlorine-containing radicals.*

Other reactions show these bodies in a different perspective.

The Hydrated Bisulphoxide of Ethylen.

If an alcoholic solution of hydrated potash be added to an alcoholic solution of the bisulphochloride of ethylen, an immediate precipitation of the chloride of potassium ensues—a precipitation which removes the whole of the chlorine, provided the first solution be in excess. The alcoholic filtrate from the precipitated chloride of potassium is then freed from the excess of alcohol by the gentle heat of a water bath, and the heavy oily drops which appear are washed with water, to remove the still adhering alcohol and chloride of potassium, and then dried *in vacuo* over sulphuric acid.

On analysis—

- I. 0.4333 grms. gave 31.33 per cent. carbon, and 6.67 hydrogen.
 II. 0.2984 grms. gave 42.26 per cent. sulphur.

Requires	I.	II.
C=31.17	31.33	...
H= 6.49	6.67	...
S=41.56	...	42.26
O=20.78	...	...
<hr/> 100.00		

Hence, the body formed is the hydrate of the bisulphoxide of ethylen, its formation having taken place according to the equation,

a reaction precisely similar to that which directs the formation of the hydrate of the bisulphoxide of amylen. Of course both of these reactions may be viewed as consisting in the replacement of the chlorine by peroxide of hydrogen.

I must leave the further description of this body, and of the bisulphoxide of ethylen $\text{C}_4 \text{H}_4 \text{S}_2 \text{O}$, and of some other derivatives from the bisulphochloride of ethylen, for another opportunity—merely insisting here upon the curious fact, that *towards oxides and hydrated oxides, the bisulphochlorides of amylen and ethylen behave like the chlorides of radicals of the form $\text{C}_n \text{H}_{n+1}$*

Viewed from this aspect, the bisulphochlorides of ethylen and amylen are the chlorides of sulphur-bearing radicals,—

which may indeed be isotypic with the chlorides of ethyl and amyl; but if they are so, they indicate that 32 of sulphur may replace 1 of hydrogen. Certainly the sulphur is combined with great energy, as we have seen formerly in the preparation of sulphide of fusyl,

and the numerous other reactions. Further instances of this are furnished by Bithiocyanide of amylen, $\text{C}_{10} \text{H}_{10} \frac{\text{S}_2}{\text{Cy}}$, and Bithiosulphocyanide of amylen, $\text{C}_{10} \text{H}_{10} \frac{\text{S}_2}{\text{S}_2 \text{Cy}}$.

The formation of these substances is so akin to the already described formation of the oxide and hydrated oxide of bisulphide of amylen, that a detailed description is superfluous. In both cases, an alcoholic solution of the bisulphochloride of amylen is heated on a water bath with an alcoholic solution of the cyanide or sulphocyanide of potassium. The precipitated chloride of potassium is separated by filtration, the excess of alcohol expelled on a water bath, and the resulting product washed with water and dried *in vacuo*.

The bithiocyanide of amylen showed the following percentage composition on analysis:—

- I. 0.2432 grms. gave 55.65 per cent. carbon and 7.60 hydrogen.
 II. 0.3881 grms. gave 24.66 per cent. sulphur.

$\text{C}_{10} \text{H}_{10} \frac{\text{S}_2}{\text{Cy}}$	Pound.	
requires	I.	II.
C=56.25	55.65	...
H= 7.81	7.60	...
S=25.00	...	24.66
N=10.94	...	...
<hr/>		
100.00		

The bithiocyanide of amylen has the specific gravity 1.07 at 13° C. It appears as a yellow liquid of nauseous smell.

The bithiosulphocyanide of amylen gave, on analysis,

- I. 0.2336 grms. gave 44.46 per cent. carbon, and 6.54 hydrogen.
 II. 0.3768 grms. gave 39.32 per cent. sulphur.

$C_{10} H_{10} S_2 Cy$	Found—	
requires,	I.	II.
C=45.00	44.46	...
H= 6.25	6.54	...
S=40.00	...	39.32
N= 8.75	...	...
<hr/> 100.00		

The specific gravity of the bithiosulphocyanide of amylen is 1.16. Like the preceding compound, it is also a liquid.

These bodies are perhaps chiefly interesting as showing how many halogens may be introduced to an olefine, provided they be offered in a systematic manner.

Looking at these manifold substitutions of chlorine in the bisulphochloride of amylen there seems to be no reason why oxygen acids should not be also introduced in place of the chlorine; that is, why such bodies as

should not be formed, which would be the analogue of acetic ether.

The alcoholic nature of the hydrated bisulphoxide of amylen appears to be further evinced by its forming a copulated acid when dropped into a large excess of sulphuric acid, which is kept quite cold.

The Bisulphide of Amylen, $C_{10} H_{10} S_2$.

The behaviour of the bisulphide of chlorine towards the olefines of the form

and the varied transformations which we have seen presented by the compound resulting from the union of bisulphide of chlorine with amylen, lend additional interest to the formation and properties of the bisulphide and bichloride of amylen,

As neither of these bodies has been described, a short account of their preparation will not be out of place here.

If an alcoholic solution of the bisulphochloride of amylen be treated with zinc and sulphuric acid, the whole of the chlorine is removed, as chloride of zinc and hydrochloric acid, after a few hours' digestion on a water bath. The reduction, however, does not stop at this point; sulphuretted hydrogen is evolved. The organic compound, however, under all the conditions I have employed, refuses to part with the whole of its sulphur, the result being a product which, after purification from the alcohol by evaporation and washing with water, is indeed rich

in sulphur and wholly volatile, with but trifling decomposition. But both analysis and the fact of the evolution of sulphide of hydrogen show that it contains less sulphur than belongs to the compound

Its boiling point rises from *circa* 60° C. to 260° C.

Nascent hydrogen proves, therefore, too powerful a dehalogenizer for the end in view.

Metallic zinc enjoys the curious power of removing the whole of the chlorine and leaving the sulphur intact, according to the equation,

The necessity for only one equivalent of zinc in the above equation attaches the reaction rather to the reduction of kakodyl from its chloride by means of zinc

or the reduction of ethyl from its iodide by sodium

than to the reaction obtaining between the iodide of ethyl and zinc.

To prepare the bisulphide of amylen, an alcoholic solution of the bisulpho-chloride is treated with water, nearly sufficient to produce precipitation. Granulated zinc is added, and the retort containing the reagents is attached to an inverted condenser, and gently boiled in a water bath for some hours.

To test whether the reaction is accomplished, a few drops of the solution are evaporated in a crucible until the alcohol is expelled. The residual liquid is then washed with water, redissolved in alcohol, and treated with a fragment of sodium. The whole is then gradually heated to redness, and the chlorine tested for in the ordinary way. The slightest trace of chlorine may be thus detected in all bodies soluble in alcohol.

The whole of the chlorine being eliminated, the product is treated with water, and the oil which rises to the surface is removed. After repeated washings with water, it is dried over chloride of calcium and rectified. The portion which boils between 200° and 208° is collected apart. From this a large product is obtained, which boils constantly at 200° C.

On analysis,

I. 0.8012 grms. gave 30.60 per cent. of sulphur.				
II. 0.2833 grms. gave 58.32 per cent. carbon and 10.36 hydrogen.				
III. 0.3270 grms. gave 58.26 per cent. carbon and 10.24 hydrogen.				
$\text{C}_{10} \text{H}_{10} \text{S}_2$	Found—			
requires,	I.	II.	III.	Mean.
C=58.82	...	58.32	58.26	58.29
H=9.80	...	10.26	10.24	10.25
S=31.37	30.60	...	...	30.60
<hr/>				<hr/>
99.99				99.14

From this analysis it would appear that the repeated distillation which the body had undergone had not materially affected its constitution.

The bisulphide of amylen is a light yellow, limpid liquid, of offensive smell. Its specific gravity at 13° C. is 0.907. Its boiling point *circa* 200° C. It shows no tendency to combine with the oxides of lead or mercury, like a mercaptan; nor does it, under ordinary conditions, combine with oxygen acids or sulphide of hydrogen, showing, in this respect, an essential difference from its oxygen isotype the binoxide of ethylen, which unites directly and readily with oxygen acids and chloride of hydrogen.

The Bichloride of Amylen, C₁₀ H₁₀ Cl₂.

All my efforts to combine chlorine directly with amylen have failed. Both dry and wet chlorine are absorbed with the greatest avidity by amylen. But the reaction is not a simple union. Even when freshly-made ice-cold chlorine water is shaken with amylen in the dark, conditions perhaps the most favourable for direct union, abundance of hydrochloric acid is eliminated, and the product, which, after the expulsion of the amylen, is heavier than water, shows no constant boiling point, and contains chlorine-substitution products, either of amylen or of its chloride.

But, indirectly, the bichloride of amylen may be prepared with facility; and as the method is both elegant and remarkable, I may describe it here. It is based upon the power which amylen enjoys of reducing the pentachloride of phosphorus to the state of terchloride, a reaction which at once reminds us of the analogous one which is frequently used to prepare the bichloride of ethylen; namely, the elimination by that olefine of two equivalents of chlorine from the pentachloride of antimony.

If pentachloride of phosphorus be finely powdered and treated with perfectly dry amylen, a rise in temperature of a few degrees Centigrade takes place. No hydrochloric acid is evolved. The amylen disappears after a time, and the solid becomes more bulky. Successive quantities of amylen are added as long as these changes occur, and the mixture is allowed to stand for some days. The pasty mass is then transferred to a basin, which is set to float upon a bowl of water, the whole being loosely covered. The moist atmosphere causes the whole to become liquid in about twelve hours, and the uncombined amylen escapes. The residual liquid has now to be washed, at first with water, and finally with dilute caustic potash, till all acid reaction disappears. It should be then gently warmed on a water bath to expel all traces of amylen, then dried over chloride of calcium, and rectified.

The product, which, after some rectifications, boils constantly between 141° C. and 147° C., is pure bichloride of amylen, C₁₀ H₁₀ Cl₂.

On analysis,

- I. 0.2866 grms. gave 42.22 per cent. carbon and 7.40 hydrogen.
 II. 0.4279 grms. gave 50.88 per cent. chlorine.

$C_{10} H_{10} Cl_2$ requires,	Found—	
	I.	II.
C = 42.55	42.22	...
H = 7.09	7.40	...
Cl = 50.35	...	50.88
<hr/>	<hr/>	<hr/>
99.99		100.50

The bichloride of amylen is a colourless liquid, of aromatic smell, and sweet and camphorous taste. It burns with a smoky flame. Its boiling point is between $141^{\circ}C.$ and $147^{\circ}C.$ Its specific gravity at $9^{\circ}C.$ is 1.058. It is insoluble in water, but miscible with ether. In alcohol, it dissolves freely on boiling; but on cooling an alcoholic solution saturated with the bichloride of amylen, the greater quantity separates out.

It is evident that, if the recomposition which takes place were a simple transference of two equivalents of chlorine from the pentachloride of phosphorus to the amylen, the entire product should be a liquid. This is never the case, even when a great excess of amylen is employed.

On the other hand, in the preparation of the bichloride of amylen, if the mixed product got by the action of the damp air upon the solid mass be exposed for only some hours, and then treated with water, a large quantity of amylen is still found in it.

From these two considerations, it seems probable that the terchloride of phosphorus, which is the supplementary product to the first equivalent of bichloride of amylen formed, unites with a second equivalent of amylen to form a solid easily decomposable by water, and analogous to the pentachloride of phosphorus,

Whether this be the case or not, the bichloride of amylen requires long-protracted washing before it ceases to yield acid to the water.

Binitroxide of Amylen.

Although the distinction between halogen salts, of which chloride of sodium is the prototype, and oxygen salts, of which sulphate of soda may be taken as the representative, is a convenient one, the line which separates the two classes has always been vague, and is becoming gradually obliterated. The isolation of the constituent groups in oxygen salts, supplementary to the metallic base, has contributed largely to this obliteration. Anhydrous sulphuric acid, peroxide of hydrogen and sulphocyanogen stand in the same relation respectively, to sulphite of potash, hydrate of potash, and sulphocyanide of potassium, as chlorine does to chloride of sodium,

This analogy between the simple and compound halogens is perhaps conserved most completely in the case of the nitrates,

Not only is NO_4 known in the free state; but, like chlorine, it possesses in a high degree the power of replacing hydrogen in organic compounds, equivalent for equivalent, giving rise to the endless catalogue of nitro-compounds. In all instances is the introduction of NO_4 analogous to that of chlorine,

In all cases of nitro-substitution hitherto observed there, is formed some body supplementary to the nitro-compound, namely, water or nitrous acid, corresponding to the hydrochloric acid of the chlorous substitution products.

This analogy may be carried one step further: just as chlorine may combine with an olefine directly, without the liberation of hydrochloric acid, so free NO_4 may combine with an olefine directly, such union being perfectly analogous to that effected by chlorine.

For these reasons we may call NO_4 "Nitroxine." Hence the following bodies are analogues:—

Chlorine. Cl or Cl Cl	Nitroxine. NO_4 or $\text{NO}_4 \text{NO}_4$
Chlorhydric Acid. HCl	Nitroxhydric Acid, Nitrite of Hydrogen. HNO_4
Hypochlorous Acid. OCl	Anhydrous Nitric Acid. ONO_4
Bichloride of Olefine. $\text{C}_n \text{H}_n \text{Cl}_2$	Binitroxide of Olefine. $\text{C}_n \text{H}_n 2\text{NO}_4$

The Binitroxide of Amylen, $\text{C}_{10} \text{H}_{10} 2\text{NO}_4$.

This remarkable body may be formed in two ways, either by the action of nitric acid upon amylen, or by the direct union of nitroxine with amylen.

At ordinary temperatures, nitric acid is without action upon amylen. At the temperature at which nitric acid boils, the action between the two is energetic. The difference between the boiling points of nitric acid and amylen involves too great a loss of the olefine, if the two be heated together until the nitric acid boils.

If air be saturated with amylen vapour, by being forced through a series of bulbs containing that hydrocarbon, and be then led into boiling nitric acid in such a manner that the products of the action may be collected, crystals are found in the receiver, which after washing with cold alcohol and recrystallizing from dry ether, are pure binitroxide of amylen.

* I only find one example of this last recomposition, namely, the formation of nitronapthaline by the action of NO_4 upon napthaline described by LAURENT.

- I. 0.3680 grms. gave 37.20 per cent. carbon, and 6.24 hydrogen.
 II. 0.1336 grms. gave 18.04 per cent. nitrogen.

$C_{10} H_{10} 2NO_4$	
requires,	Found—
C = 37.09	37.20
H = 6.18	6.24
N = 17.28	18.04

The formation of binitroxide of amylen under these circumstances may be explained in two ways,—either there is an initial oxidation of the amylen, the nitric acid being thereby reduced to nitric oxide, which joins with the oxygen of the air present to form nitroxine. This last thereupon unites with a fresh portion of amylen; or the nitric acid, on being boiled, splits up into NO_4 and O, whereof the former unites directly with one portion, while the oxygen goes to oxidize another portion of the amylen. Probably both actions are simultaneous, the result being the formation of $C_{10} H_{10} 2NO_4$, along with another product, containing apparently oxide of amyl and nitric acid.

If the gas obtained by the ignition of well-dried nitrate of lead be passed into amylen which is kept quite cold, a rapid absorption results, and crystals of binitroxide of amylen are obtained in great abundance. After washing and recrystallizing as before,

- 0.2682 grms. gave 37.26 per cent. carbon, and 6.51 per cent. hydrogen.
 0.2290 grms. gave 17.66 per cent. nitrogen.

$C_{10} H_{10} 2NO_4$	
requires,	Found—
C = 37.09	37.26
H = 6.18	6.51
N = 17.28	17.66

The product, as in the other method of preparation, is mixed with a liquid soluble in alcohol, resulting probably in this case from the presence of anhydrous nitric acid along with the nitroxine.

Binitroxide of amylen crystallizes in square and rectangular colourless, transparent tables, without taste or smell. It decomposes at $95^\circ C$. when heated alone, giving rise to a gas HNO_4 , and an oily liquid heavier than water. It is insoluble in water, in cold alcohol, and in amylen. It dissolves in hot ether and alcohol; also readily in warm glacial acetic acid. Its most convenient solvent, however, is chloroform. Thrown upon oil of vitriol it is instantly and violently decomposed, a conjugate acid being formed, which forms a soluble salt with baryta.

The binitroxide of amylen is decomposed in alcoholic solution by caustic potash and by sulphide of potassium; in the former case the binoxide of amylen, in the latter the bisulphide of amylen, being formed. Of these, the first will probably be soon described by those who are occupying themselves with the biatomic alcohols and ethers; the latter has been already described.

One of the most noteworthy transformations which this remarkable body undergoes, is its conversion into

The Bicyanide of Amylen, C₁₀ H₁₀ Cy₂, 5HO.

The bicyanide of an olefine is a compound which almost every chemist has sought to obtain, on account of the probability of such a body giving rise to an acid derivative, analogous to oxalic acid, on treatment with a hydrated alkali, in the same manner as cyanide of ethyl, under these circumstances, gives rise to propionic acid,*

The bicyanide of amylen is formed in the following manner:—Binitroxide of amylen in alcoholic solution is treated with an excess of alcoholic solution of cyanide of potassium; an abundant precipitate is formed, which, after washing and drying, is found to be pure nitrate of potash KNO₃, or nitroxide of potassium. The filtrate from this salt is then evaporated on a water bath, until it becomes syrupy. It is then washed repeatedly with small quantities of water, and dried *in vacuo* over sulphuric acid.

So prepared, the bicyanide of amylen appears as a syrupy liquid, of pleasant smell and bitter taste.

Submitted to analysis,

- I. 0.2760 grms. gave 9.16 per cent. hydrogen.
- II. 0.3500 grms. gave 9.16 per cent. hydrogen, and 51.26 per cent. carbon.
- III. 0.3079 grms. gave 16.00 per cent. of nitrogen.

C ₁₀ H ₁₀ Cy ₂ + 5HO requires,	(1.)	Found— (2.)	(3.)
C = 50.30	...	51.26	...
H = 8.98	9.16	9.16	...
N = 16.77	...	...	16.00

The presence of five equivalents of water with the bicyanide of amylen, indicated by the above analysis, might appear an accident. Analyses (1.) and (2.) were of the same preparation, but exposed *in vacuo* for different lengths of time. Analysis (3.) was of a fresh preparation.

The five equivalents of water may be fairly compared to water of crystallization of solid salts—(1.) Because, as will be afterwards shown, an anhydrous bicyanide of amylen exists; (2.) because the penthydrate of the cyanide is decomposed on heating, giving off water; (3.) because *four* equivalents of water are

* Dr M. SIMPSON has already announced the formation of bicyanide of ethylen, and the derivation therefrom of succinic acid.

essential to the recomposition pointed out above ; where, besides the two equivalents of water of the hydrate of potash, four others are necessary.

The penthydrated bicianide of amylen is soluble to a considerable extent in water ; it mixes with alcohol and ether. Under certain conditions, it enjoys basic properties.

As before indicated, one would expect that, on boiling with an aqueous solution of caustic potash, ammonia would be formed, and pinelate of potash generated,—

The discussion of the actual recomposition which takes place must be reserved for a subsequent communication.

The Bichloride of Amylen.

The relation between amylen, amyl, and hydride of amyl, and nitroxide of amyl,

induced me to try the action of nitroxine upon the second and fourth, in the expectation of some such body as the binitroxide of amylen resulting. In both cases the result was negative.

Connected with the binitroxide of amylen, are the bodies produced by the action of nitric acid on the bisulphochloride of amylen. Such action is twofold. The first stage seems to be a nitroxine replacement ; the second, a more precise oxidizing action. The result of the first is the formation of a neutral insoluble body containing NO_4 ; that of the second, the production of a peculiar acid, containing sulphur, carbon, and hydrogen, but neither chlorine nor nitrogen. This has not been further examined. The latter of these two stages is naturally accompanied by the separation of hydrochloric acid ; sulphuric acid is also formed, together with the ultimate product of the oxidation of the carbon, namely, oxalic acid. In tracing so complicated a reaction, it was necessary to employ a somewhat large quantity.

Twenty grammes of the bisulphochloride were treated, in a retort having a well-cooled condenser, with a large excess of nitric acid. On applying a gentle heat, copious fumes were evolved of nitric oxide, and these collected in the condenser, along with an acid distillate, a large quantity of a heavy liquid unmixable with it. This, after washing and drying, showed the following composition :—

- I. 0.2579 grms. gave 34.82 per cent. carbon, and 4.82 hydrogen.
 II. 0.2620 grms. gave 34.26 per cent. carbon, and 5.25 hydrogen.
 III. 0.1838 grms. gave 9.39 sulphur.

$C_{10} H_9 2 (NO_4) S$ requires,	I.	Found— II.	III.
C = 33.89	34.82	34.26	...
H = 5.08	4.82	5.25	...
S = 9.04	...	...	9.39

The body contained no chlorine, but abundance of nitrogen.

Writing, as before, the bisulphochloride of amylen

we may suppose that the nitric acid replaces one equivalent of hydrogen and one of Cl S by nitroxine, giving rise to the body

In fact, a similar phenomenon is here presented as was observed in studying the action of the same body upon chlorine,—that is, the group S Cl is, under both circumstances, more easily replaced than the remaining equivalent of sulphur.

The body formed by the action of nitric acid upon the bisulphochloride of amylen is therefore, according to the previously adopted nomenclature, the nitrosulphide of nitramylen, or, according to analogies already pointed out, the sulphide of binitramyl. It is a green, viscous liquid. It mixes with ether and strong alcohol, but is insoluble in water. Its taste is remarkably bitter and alliaceous, producing nausea.

They who have had occasion to prepare the organothionic acids, got by the action of nitric acid upon the various organic sulphides or sulphocyanides will have noticed that, before complete reaction,—that is, before the conversion of the whole of the substance acted upon by the nitric acid into the organothionic acid soluble in water,—it is generally possible, by arresting the action with water, to procure a liquid insoluble in and heavier than water, although the original organic body itself be lighter than that liquid. Such bodies do not appear to have been further examined, owing, probably, to the uncertainty as to whether an integral reaction has occurred, and the probability of the product being a mixture, the separation of whose constituents would present great difficulties. Bearing, however, in mind the analogies already pointed out between the chlorine substitution products of bisulphide of ethyl, bisulphochloride of chlorethylen, and bisulphochloride of ethylen, it seems highly probable that the bodies in question are analogous with the nitrosulphide of nitramylen.

The Synthesis of Cœnanthyl.

The construction of isotypic series in organic chemistry, which has proved of such great worth in classifying known bodies, and in indicating the possible

existence of yet undiscovered ones, confers an unique importance on the study of the olefines; for the latter bodies stand in much the same relation to many such series as does the "common difference" to an arithmetical one.

A common difference, whose successive chemical additions to any one term of such a series would yield, theoretically, every higher successive term, is methylen $C_2 H_2$.

According to some chemists, methylen has been obtained; according to others, its existence is possible, although never obtained; while, in the eyes of a third class, its existence is an impossibility. Up to the present time it is perhaps safe to assume that this hydrocarbon has not been prepared in the pure state.

Although, if we had only one term of such a series from which to start, the existence of methylen would be necessary and sufficient for the theoretical solution of the problem of the successive syntheses of the following terms in the manner above indicated, any multiple of methylen would furnish the means of forming successive terms, situated from one another at intervals of the magnitude of the hydrocarbon employed.

In general terms,—If $C_m H_n Q$ be the formula of the starting term, where Q denotes the whole of whatever constituents are present besides $C_m H_n$, then, by means of methylen, we may get, in succession,

But if the difference be ethylen, we can only form every alternate term—

With propylen, every third term; and so on.

Further, it is clear that, supposing we have ethylen as the common difference, we can fill up the entire series provided we have two starting points which differ by methylen—

in which the two series, derived from the two initial terms, are supplementary of one another.

Again, if we had only propylen at our disposal as a difference, we could still complete the series provided we had *three* consecutive starting terms. And so, *mutatis mutandis*, for the other limitations.

It will be shown that, with regard to certain alcohols of the formula $C_m H_{m+2} O_2$, and their derivatives, the above scheme is not merely a representation of an arithmetical possibility, but is the general expression of the result of a series of chemical phenomena, and that we are in possession of the means of deriving many of the higher alcohols from the lower ones by the introduction of olefines of the form $C_n H_n$.

I confine myself at present to the solution of the following problem:—To obtain a compound of ænanthyl from vinic alcohol and amylen.

The key to the solution of this problem is furnished by the facility with which the bisulphochloride of amylen parts with its chlorine, and the firmness with which it retains its sulphur. We have, in fact, seen numerous examples of the exchange of the chlorine in this body for other simple or compound halogens, as oxygen, peroxide of hydrogen, cyanogen, sulphocyanogen, &c., by the action of the corresponding compounds of the metals upon the bisulphochloride of amylen.

In zinc-ethyl, the ethyl is certainly the halogen; hence we may anticipate the reaction which in fact takes place between zinc-ethyl and the bisulphochloride of amylen—namely, the replacement of the chlorine in the latter body by the ethyl of the former.

Bisulphochloride of amylen and an ethereal solution of zinc-ethyl mix with one another in all proportions, giving a clear, light yellow product. Such a mixture, however, unless one or other of the constituents is present in very great excess, becomes hot after standing a few minutes; and unless ether be present to cool the liquid by its evaporation, a dangerous projection of zinc-ethyl may result. It is difficult to regulate the action by cooling from without. I have found the following the most convenient process:—

Three ounces of bisulphochloride of amylen are placed in a flask, having a doubly bored cork. Through one hole passes the zinc-ethyl delivery tube from the copper digester; the other holds a tube, which is bent down into a large narrow-mouthed bottle, containing a few drops of ether. The charge of iodide of ethyl for the above quantity of bisulphochloride of amylen should be about five ounces. This is mixed, as usual, with its own volume of dry ether. If these proportions are observed, the zinc-ethyl formed will be in excess. The charge of zinc-ethyl is distilled off in about six hours, and the recipient containing the bisulphochloride is not artificially cooled.

The product is found to consist of two layers,—the lower, a dark-brown slug-gish mass, almost solid when cold, contains the chloride of zinc; the upper, which is of a light-yellow colour, contains the bisulphide of ethyl-amylen (or bisulphide of ænanthyl), along with ether, and the excess of zinc-ethyl.

The upper layer is poured into water, whereon the zinc-ethyl is decomposed, and the alcohol formed is dissolved, while the precipitated oxide of zinc carries with it most of the bisulphide of œnanthyl, either in a purely mechanical manner, or in a state of the feeblest union. The pale-yellow mass so obtained is drained on a wet filter, then boiled and exhausted with strong alcohol. This gives an alcoholic solution (*a*) of bisulphide of œnanthyl, and an insoluble residue, consisting of pure oxide of zinc.

The lower layer* is also treated with water, whereupon chloride of zinc is dissolved out, and a liquid separates. The latter is dissolved in alcohol, and added to the solution *a*.

The mixed alcoholic solution is then heated in a water-bath, until most of the alcohol is expelled. Finally, it is washed with water, and dried over chloride of calcium and a few fragments of caustic potash.

On distillation, a few drops pass over about 140° C.; this is probably a little bisulphide of ethyl.

The great bulk passes over at 240° to 250° C. On rectification, its boiling point is nearly constant at 243° C.† A slight residue is formed on each distillation.

On analysis,—

(1.) 0.2730 grms. gave 65.31 per cent. of C., and 11.22 of H.			
(2.) 0.4122 grms. gave 65.42 per cent. of C., and 11.26 of H.			
(3.) 0.4186 grms. gave 23.72 per cent. of S.			
C ₁₄ H ₁₅ S ₂	Found—		
requires,	I.	II.	III.
C = 64.12	65.31	65.42	{ 65.36 11.24 } Mean.
H = 11.46	11.22	11.26	
S = 24.42	...	...	
			23.72
			100.32
	100.00		

The rather large excess in the carbon, and the defect in the sulphur, are perhaps owing to the presence of some monosulphide of œnanthyl. The bisulphide of œnanthyl is a light-yellow liquid, of perfect limpidity. Its smell is exceedingly offensive. It is quite insoluble in water, but readily soluble in ether and alcohol. Towards the oxides of lead and mercury it shows perfect indifference.

The so perfect reactional analogy between the bisulphochlorides of ethylen and of amylen, which I have had the honour of pointing out, and the perhaps equally well-established resemblance between the compounds of methyl, ethyl, and amyl

* The physical properties of this body, and the large quantity of liquid which water separates from it, seem to point to its being a compound of chloride of zinc, with bisulphide of œnanthyl.

† Bisulphide of ethyl boils *circa* 150° C. If Kopp's law hold good, a successive increment of 19° C. for every C₂ H₂ would point to 245° C. as the boiling point of bisulphide of œnanthyl. But in the cases of other bisulphides, a common increment of 33 would more nearly represent experimental results. Hence it is possible that this substance may only be an isomer of bisulphide of œnanthyl.

with zinc, place beyond doubt the possibility of the construction of various other compounds of the higher alcohol radicals from compounds of the lower ones. From the bisulphochloride of ethylen on the one hand, and zinc-methyl and zinc-ethyl on the other, we may confidently expect to obtain the bisulphides of all the radicals of the form $C_m H_{m+1}$ above the bisulphide of propyl, inclusive: while the formation of the corresponding alcohols from the bisulphides of the radicals may be a matter of labour, but cannot be one of uncertainty.

So far my examination of the behaviour of the olefines to compound chemico-negative groups has led to the formation of the following bodies:—

From Ethylen, $C_2 H_4$.

- $C_2 H_4 S_2 Cl$ Bisulphochloride of ethylen.
- $C_2 H_4 S_2 Cl_2$ Bichlorosulphide of ethylen.
- (a.) $C_2 H_2 S Cl_3$ Chlorosulphide of bichlorethylen.
- (b.) $C_2 H_2 S Cl_3$ Sulphide of terchlorethyl.
- $C_2 H_4 S_2 OHO$, Hydrated bisulphoxide of ethylen.

From Amylen $C_{10} H_{10}$.

- $C_{10} H_{10} S_2 Cl$ Bisulphochloride of amylen.
- $C_{10} H_{10} S_2 Cl_2$ Bichlorosulphide of amylen.
- $C_{10} H_7 S Cl_4$ Chlorosulphide of terchloramylen.
- $C_{10} H_{10} S_2 O$ Bisulphoxide of amylen.
- $C_{10} H_{10} S_2 OHO$ Hydrated bisulphoxide of amylen.
- $C_{10} H_9 S_2$ Bisulphide of fusyl.
- $C_{10} H_{10} S_2$ Bisulphide of amylen.
- $C_{10} H_{10} Cl_2$ Bichloride of amylen.
- $C_{10} H_{10} Cy_2 5HO$ Penthydrated bicyanide of amylen.
- $C_{10} H_{10} S_2 Cy$ Bithiocyanide of amylen.
- $C_{10} H_{10} S_2 Cy S_2$ Bithiasulphocyanide of amylen.
- $C_{10} H_{10} 2(NO_4)$ Binitroxide of amylen.
- $C_{10} H_{10} S_2 C_4 H_5$ Bisulphide of œnanthyl.

In the foregoing pages, I have been induced to employ some expressions which may need a word of explanation.

The term *recomposition* has been often used in place of decomposition. When the reaction which ensues between bodies is unaccompanied by the destruction of their form or type, the change may be more fitly called a recomposition than a decomposition. The latter word is suggestive of a degeneration, which the former word avoids, and the idea of which is in such cases out of place. Recomposition corresponds more nearly to the happier German term “*Umsetzung*,” as distinguished from “*Zersetzung*.”

Isotype, idio-type, isotypic, idiotypic. A body is an isotype of another, or isotypic with it, when the two are built on similar types. Thus, the fatty acids are isotypes. Idiotypic are bodies which are built on the same type. Thus all elementary replacement derivatives of a body are its idiotypes, or are idiotypic with it.

Consequently, the isotypes and idiotypes of one and the same body are related to one another as an atom complex is to an atom simple.

Certain of the bodies were procured in too small a quantity for their specific gravities to be taken in the ordinary method. When this was the case, and the substances were insoluble in water, a solution of nitrate of ammonia, or of chloride of calcium was so graduated by water, that a drop of the liquid under examination remained in indifferent equilibrium in the saline solution. The specific gravity of the saline solution is then taken in the ordinary manner, and is of course identical with that of the liquid examined.

I allow myself, in conclusion, to express a regret, that circumstances have prevented me from offering my results to the Society in a more elaborated form. I shall take the earliest opportunity of prosecuting this direction of research. Meanwhile, let me offer my thanks to Professor ROSCOE of Manchester, and Dr PLAYFAIR of Edinburgh, for having allowed me to carry on my experiments in their laboratories. To Professor KOLBE in Marburg I am also indebted, for having on all occasions, placed the resources of his laboratory at my disposal.

EDINBURGH UNIVERSITY LABORATORY,
March 1861.