

XIII.—*On some Derivatives from the Olefines.*

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First Memoir.

THOSE hydrocarbons which consist of equal numbers of equivalents of hydrogen and carbon ($H = 1, C = 6$) of which ethylene is the historical prototype, have of late received a large share of the attention of chemists. During the first quarter of the present century, the separation of ethylene from ethylic alcohol by substances which have strong affinity for water, was accepted by many as evidence of this body being the true radical of alcohol. The possibility of the synthesis of alcohol from the same hydrocarbon,

which was early indicated, and which has of late received complete corroboration, naturally supports the same view.

The isolation of the so-called organic radicals, the hydrides of the olefines, and more especially the *manner* of their isolation, has so far substantiated their claim to being viewed as radicals in the earlier restricted sense of the word; but the idea conveyed by the term radical has, meanwhile, undergone a wide extension.

In order to define the sense in which I employ this term, it may be remarked that between a compound body and its ultimate elements there exist certain possible derivatives of an inferior "order," each of which, as well as the ultimate elements themselves has strictly an equal claim to be considered as a radical of the body. The number of such derivatives depends of course upon the complexity or, *ceteris paribus*, upon the equivalent of the original substance.

Thus from ethylic alcohol we may obtain aldehyde, hydride of ethyl, ethyl, ethylene, hydride of methyl, carbonic acid, water and others; each of which is a *proximate* radical, in distinction to carbon, hydrogen, and oxygen, which are *ultimate* radicals or elements.

In this sense a radical is nothing more than a proximate element or molecule: and the continual reappearance of one and the same such molecule is to be taken, less as proof of an innate combining effort of its parts, than as evidence of uniformity in the physical influences to which it is subjected. The arrangement of the constituents of a substance, and the expression thereof by a formula can only be considered absolute as long as such influences remain invariable. But when the latter are so changed as so affect a recombination of the elements in a different order, then the rational formula must recognize such rearrangement and vary in accordance with the forces which effect it. When, therefore, one body determines the splitting of a complex second body into certain molecules, such molecules are the radicals of the second body *relatively* to the first, and to the physical conditions accompanying the change.

Partly on account of the olefines being in this sense radicals of their alcohols, partly on account of their belonging to the class of so called diatomic bodies, whose discussion has thrown much light on organic chemistry, I have thought them deserving of special study.

Ethylene has the property of combining directly with two equivalents of chlorine, bromine and iodine, forming therewith the well known compounds $C_4H_4Cl_2$, $C_4H_4Br_2$, $C_4H_4I_2$, for our

knowledge of which we are indebted to Deimann and his associates, to Balard and to Faraday respectively. Löwig has moreover shown that the corresponding sulphur-compound $C_4H_4S_2$ may be obtained by the action of protosulphide of potassium upon the first of these bodies. Although many derivatives have been obtained from these substances, both by the substitution of the halogens for hydrogen, and by the elimination of the hydric acids by alkaline oxides, their history is still very incomplete: firstly, inasmuch as the analogy between the ethylene compounds and those of the higher olefines is very imperfect; and further, because few successful attempts have been made to determine the character of the diatomic haloid-molecule, in the sense of ascertaining if, and when, one or both of its atoms may be replaced by similar ones, or by molecules functioning as such.

A description of some experiments performed in this direction furnishes the matter of the present memoir.

In selecting suitable olefines, ethylene and amylene appeared to offer the greatest promise of interesting results: partly because they can both be obtained in a state of great purity, partly because, being somewhat widely separated upon the olefine series, analogous derivatives or reactions common to both would point to similar ones in the two intermediate terms, propylene and butylene; while the nature of their dissimilarities would also to some extent indicate the nature of the derivatives from the same two bodies and their behaviour under similar conditions.

My first object was to combine these two olefines with some of the combinations of the halogens which are known to exist, and some of which are exhibited in the following table:—

Cl_2					
$ClBr$	Br_2				
ClI	BrI	I_2			
ClO	BrO	IO	O_2		
$ClCy$	$BrCy$	ICy	OCy	Cy_2	
$\{ClS$	BrS	IS	OS	CyS	S_2
$\}ClS_2$					

Although some of these bodies have not yet been obtained, and the definite nature of the composition of others is still doubtful, yet there can be little question as to the possibility of the existence of all. As, however, the members of the first or chlorine column have been most fully studied, and as chlorine itself shows pre-

eminently the power of combining with the olefines, the behaviour of these chlorides towards ethylene and amylene was the first subject of investigation.

*Action of the Chlorides of Sulphur upon Ethylene and
Amylene.*

I shall call the body ClS_2 , the bisulphide of chlorine, and the body ClS or Cl_2S_2 the chloride of sulphur; it will be seen in the sequel that this nomenclature avoids the introduction of an ambiguity in speaking of the derivatives of the two compounds.

Action of bisulphide of chlorine upon amylene.—Into a flask containing 52 grms. of bisulphide of chlorine, pure and dry amylene was allowed to drop slowly, the flask being kept cold by agitation in water. Immediate combination, accompanied by the liberation of heat, ensued, no permanent gas being evolved. The amylene was added until no further evolution of heat occurred on the addition of fresh quantities. The flask containing the product so obtained was then heated for several hours in a water-bath at 100°C . A distillate was thereby obtained, which consisted entirely of the excess of amylene only contaminated by a slight trace of hydrochloric acid. The residue in the flask, which had deepened somewhat in colour, weighed 104 grms. The bisulphide of chlorine had therefore combined with exactly its own weight of amylene, that is, 52 grms. In another experiment 51 grms. of this bisulphide, combined with 52.1 grms. of amylene, giving 103.1 of product. If now one molecule of the bisulphide combined with one molecule of amylene, 52 grms. of the former would require 53.9 grms. of the latter, giving 105.9 grms. of product; and 51 grms. of the former would require 52.8 grms. of the latter, giving 103.8 grms. of product. The quantities actually found show that this had been in fact the proportion of combination, the numbers being as nearly in accordance as synthetical experiments of this kind allow. The substance so formed was not rendered in the least turbid on digestion with water, showing that the whole of the bisulphide was in combination. Before subjecting the compound to analysis, it was decolorized as far as possible, by being dissolved in about four times its own weight of ether, and digested with animal charcoal. After filtering, expelling the ether in a water-bath, and drying in vacuo over sulphuric acid, a product was obtained, the

analysis* of which confirmed the above synthetically derived composition.

I. 0.4721 grm. gave 0.4741 grm. of chloride of silver.

II. 0.4734 grm. gave 0.7530 grm. of sulphate of baryta.

III. 0.4239 grm. gave 0.6808 grm. of carbonic acid, and 0.2849 grm. of water.

	Calculated.		Found.	
		I.	II.	III.
C ₁₀	43.64	„	„	43.80
H ₁₀	7.27	„	„	7.47
S ₂	23.27	„	23.93	„
Cl	25.82	24.73	„	„
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	100.00			

This body may therefore be called the *Bisulphochloride of amylene*. Its formula is C₁₀H₁₀S₂Cl. Bisulphochloride of amylene is a transparent liquid of light yellow colour, and syrupy consistence; it is miscible in all proportions with ether, soluble in strong alcohol, especially on warming, but quite insoluble in water. Its taste, which is at first insipid, becomes very pungent and bitter; its smell is faint, and at first not unpleasant; it becomes, however, very fœtid when exposed to the air. Heated by itself, it blackens, leaving a carbonaceous residue, and giving off compounds containing sulphur as well as hydrosulphuric and hydrochloric acids. Hence neither its boiling point nor vapour-density could be determined. Its specific gravity is 1.149 at 12°C.

Action of Bisulphide of Chlorine on Ethylene.

Dry ethylene may be passed for hours through bisulphide of chlorine at temperatures varying from 0° to 100°C. without the occurrence of any appreciable chemical change, the resulting liquid being completely decomposed by water, and the products being identical with those due to the decomposition of pure bisulphide of chlorine by the same liquid.

Remembering however the readiness with which amylene combines with the same body, there can be little doubt but that on employing an arrangement by which the ethylene and bisulphide are brought together under increased pressure, the two would

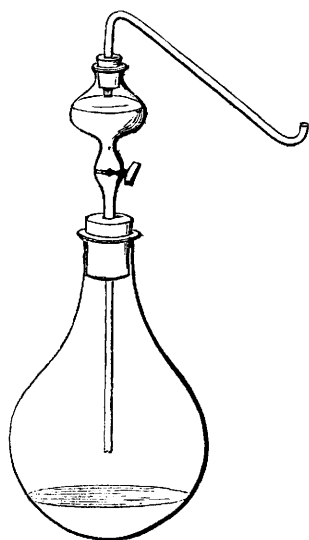
* In this and subsequent analyses, the chlorine was determined by heating with quick lime, the sulphur with carbonate of soda and chlorate of potash, the carbon and hydrogen with oxide of copper, using the ordinary precautions.

unite directly and give a product similar to the above described amylene compound.

Action of Chloride of Sulphur upon Amylene.

It has been called in question whether the instable body, chloride of sulphur, which contains chlorine and sulphur in equal numbers of atoms (SCl) is really a definite compound, or a solution of chlorine in S_2Cl , or a mixture of S_2Cl with the hypothetical analogue of sulphurous acid SCl_2 . The ready elimination of chlorine which it undergoes on distillation, and the consequent continual diminution of the amount of chlorine in the successive distillates, can, however, scarcely be accepted as evidence of the heterogeneous nature of the substance,—innumerable instances occurring in which bodies, whose composition is unquestionably definite, undergo a similar decomposition, even at low temperatures (such are the hydrate of chlorine, the bisulphide of hydrogen, etc.).*

The chloride of sulphur employed in my experiments, was obtained by saturating the bisulphide of chlorine with dry chlorine at 10°C . and collecting the distillate obtained from this product, which came over on rectification between 70° and 90°C .



The action of this body upon amylene is one of very great energy; the two liquids, when brought together, hissing as when anhydrous phosphoric acid is thrown upon water. Even when the liquids are kept quite cold, a slight evolution of permanent gas attends their combination. The following arrangement was found convenient in following this reaction and examining the gas evolved.

Into a flask immersed in ice-water, 19.6 grms. of chloride of sulphur were brought. The flask was provided with a funnel-tube bearing a stop-cock, bulb, and gas-delivery tube. The bulb of the funnel-tube was filled with dry amylene. On turning the stop-cock a very little way, a portion of the amylene entered the flask;

* Carius (Ann. Ch. Pharm. cvi. 294.) has satisfactorily shewn that the solid body said to be produced by the action of chlorine upon S_2Cl contains oxygen, introduced by moisture in the chlorine.

the heat thereupon evolved, and the consequent expansion of the vapour in the flask, checked the ingress of the amylene; and the excess of permanent gas being forced to bubble through the latter, was thereby deprived of all traces of mechanically diffused vapour of chloride of sulphur. In this manner, the action was made intermittent and self-regulating. The permanent gas evolved was, however, small in quantity, and resulted from the action of the excess of chlorine upon the amylene. We shall, in fact, subsequently see that, unless very great precautions are employed, chlorine does eliminate hydrogen from amylene.

As soon as an excess of amylene had been added, the funnel-tube was removed, and the flask heated for some hours in a water-bath. The product so obtained was digested in a water-bath with dilute caustic soda, then washed with water, dissolved in ether, shaken with animal charcoal, filtered, warmed in a water-bath to expel the ether, and dried in vacuo over sulphuric acid. The product weighed 31 grms. The weight of combined amylene was therefore 11·4 grms. (neglecting the small quantity of hydrochloric acid evolved). If two molecules of the chloride of sulphur unite with one of amylene, 19·6 grms. of chloride of sulphur would combine with 13·3 grms. of amylene, giving 32·9 grms. of product.

The analysis of the body, prepared as above described, showed that such direct combination had in fact been effected.

I. 0·3723 grm. gave 0·4831 grm. carbonic acid, and 0·1786 grm. water.

II. 0·4280 grm. gave 0·5260 grm. sulphate of baryta.

III. 0·1437 grm. gave 0·7113 grm. chloride of silver.

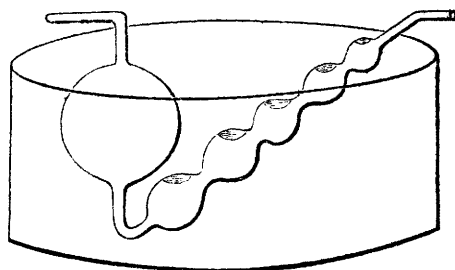
	Calculated.	Found.		
		I.	II.	III.
C ₁₀	31·88	35·39	„	„
H ₁₀	5·81	5·33	„	„
S ₂	18·61	„	16·86	„
Cl ₂	40·70	„	„	39·61
	<hr/> 100·00			

This body may be called the *Bichlorosulphide of amylene*. Its specific gravity is 1·138 at 14°C. Its colour is similar to that of the bisulphochloride, but deeper; its odour is more penetrating. It is miscible with ether, soluble in hot alcohol. Like the bisulphochloride, it is not volatile by itself without decomposition. Heated with alcoholic solution of caustic potash, it gives rise to

volatile products having the same physical properties, and being in all probability identical with those produced by the same reagent upon the bisulphochloride of amylene. We shall subsequently discuss the products produced in both cases; the fact, however, that the potash removes the whole of the chlorine from the bichlorosulphide, may be here noticed, because it proves that this body does not contain bichloride of amylene; for the latter body, when treated with the same reagent, gives up half its chlorine in combination with hydrogen, being converted into chloride of fusyl* ($C_{10}H_9Cl$)

Action of Chloride of Sulphur upon Ethylene.

Ethylene acts with so much less energy than amylene upon chloride of sulphur, that it is necessary for the chloride to present



as large a surface as possible to the ethylene, in order that combination may be effected. An ordinary bulb wash-tube (fig. 2) answers for this purpose. Into such a tube, chloride of sulphur was brought, and dry ethylene allowed to bub-

ble slowly through. The bulb-tube was at first immersed in cold water. However dry the ethylene may be, and however slowly it is delivered, complete absorption never occurs, a certain quantity of the excess of chlorine in the chloride decomposing a portion of the ethylene (as in the ordinary process of forming bichloride of ethylene when the combination balloon becomes too hot or too strongly illuminated) and giving rise to hydrochloric acid. The ethylene should be allowed to pass through at the rate of about a bubble in a second. As the saturation approaches completion (a process which, with two or three ounces of the chloride, occupies about twelve hours) the liquid in the bulb-tube loses colour, changing from the garnet-red of the chloride of sulphur to the straw-yellow of the bisulphide of chlorine; at the same time heat ceases to be evolved. In order to complete the

* Here, and subsequently, I call the bodies C_4H_3 and $C_{10}H_9$ *vinyl* and *fusyl* respectively, reserving the names acetyl and valeryl for the oxygenated radicals $C_4H_3O_2$ and $C_{10}H_9O_2$.

re-action as far as possible, and to remove any bichloride of ethylene formed, the bulb-tube must be heated in a water-bath to 100°C . and a more rapid current of ethylene passed through for an hour or two. It seems, however, impossible, without expending an unreasonable time, to combine all the chloride with ethylene, the gradually increasing dilution of the uncombined chloride of sulphur in the liquid product of the combination being unfavourable to the exercise of its affinity. To remove the uncombined chloride of sulphur, the liquid contents of the bulb-tube were dropped into water at 80°C ., repeatedly and vigorously shaken with fresh quantities of water at the same temperature, and allowed to stand for some days in contact with dilute caustic soda. The resulting product is a heavy liquid, sluggish and opaque from suspended sulphur. The latter is removed by shaking the liquid with about 100 times its volume of dry ether, filtering, driving off the ether by the heat of a water bath, redissolving in a minimum of ether, filtering, evaporating, and finally drying in *vacuo* over sulphuric acid.

I. 0.2705 grm. gave 0.2000 grm. carbonic acid, and 0.0671 grm. water.

II. 0.1844 grm. gave 0.3540 grm. sulphate of baryta.

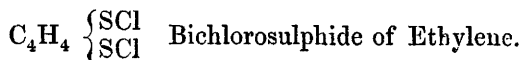
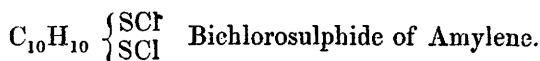
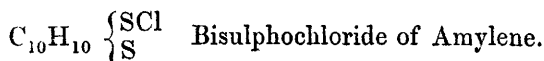
III. 0.2957 grm. gave 0.6110 grm. chloride of silver.

	Calculated.	Found.		
		I.	II.	III.
C_4	18.32	20.17	„	„
H_4	3.05	2.76	„	„
S_2	24.43	„	25.74	„
Cl_2	54.20	„	„	51.12
	<hr/> 100.00			

These results agree sufficiently with the formula $\text{C}_4\text{H}_4\text{S}_2\text{Cl}_2$. The body so found is therefore a result of the direct combination of chloride of sulphur with ethylene, being the *bichlorosulphide of ethylene*. In colour, bichlorosulphide of ethylene is almost identical with the bisulphide of chlorine. Its smell is pungent and not unpleasant, resembling that of oil of mustard; its taste is astringent and similar to that of horse-radish. The small quantities of vapour which it diffuses attack the thin parts of the skin, as between the fingers and around the eyes, destroying the epidermis. If allowed to remain in the liquid form on the skin, it raises a blister. It is soluble in about fifty times its own volume of boiling ether, slightly soluble in hot, almost insoluble in cold alcohol, and

quite insoluble in water. Heated by itself, bichlorosulphide of ethylene is decomposed, giving off hydrochloric and hydrosulphuric acids, besides bodies containing carbon and sulphur, and leaving a carbonaceous residue. Its specific gravity at 13°C is 1.408.

In looking back upon these bodies $C_{10}H_{10}S_2Cl$, $C_{10}H_{10}S_2Cl_2$ and $C_4H_4S_2Cl_2$, and admitting them to be analogues of bichloride of ethylene, we seem at first at liberty to choose between two views as to their rational composition. The inorganic molecule, for instance, of the body $C_{10}H_{10}S_2Cl$ may be regarded as consisting of chloride of sulphur and sulphur. So that, preserving the above indicated analogy, its formula would be written $C_{10}H_{10} \left\{ \begin{matrix} SCl \\ S \end{matrix} \right.$ or secondly, as chlorine and sulphur $C_{10}H_{10} \left\{ \begin{matrix} S_2 \\ Cl \end{matrix} \right.$ where the two atoms of sulphur are monomolecular. Nor can the existence of such bodies as $C_4H_4S_2$ be considered hostile to the latter view, for sulphur is pre-eminently polybasic. But we are not in the same manner at liberty to choose between the formulæ $C_{10}H_{10} \left\{ \begin{matrix} S_2Cl \\ Cl \end{matrix} \right.$ and $C_{10}H_{10} \left\{ \begin{matrix} SCl \\ SCl \end{matrix} \right.$ to represent the bichlorosulphide of amylene, because the existence of $C_{10}H_{10}S_2Cl$ proves that S_2Cl is bimolecular, and hence that the second of the above formulæ, namely, $C_{10}H_{10} \left\{ \begin{matrix} SCl \\ SCl \end{matrix} \right.$ is alone admissible. Admitting, then, the formula $C_{10}H_{10} \left\{ \begin{matrix} SCl \\ SCl \end{matrix} \right.$ we must allow SCl to be monomolecular: and hence returning to the bisulphochloride of amylene, its formula must be $C_{10}H_{10} \left\{ \begin{matrix} SCl \\ S \end{matrix} \right.$ and not $C_{10}H_{10} \left\{ \begin{matrix} S_2 \\ Cl \end{matrix} \right.$. The rational formula of the three bodies are hence, probably—

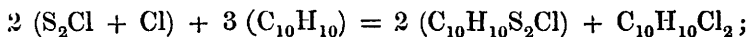


But although the formulæ $C_{10}H_{10} \left\{ \begin{matrix} SCl \\ S \end{matrix} \right.$ is the most rational *statical* formula for the bisulphochloride of amylene, we shall see

that towards certain substances, it behaves like the chloride of a sulphur-containing radical $C_{10}H_{10}S_2$.

The behaviour of ethylene towards chloride of sulphur is further of interest, as affording, I believe, proof that the latter body is a definite compound, or at all events that it does not consist of bisulphide of chlorine and dissolved chlorine. For were this its composition, the free chlorine would unquestionably combine with the ethylene; but as direct experiment described before has convinced me that ethylene is almost entirely without action on bisulphide of chlorine, under the circumstances by which bichlorosulphide of ethylene is actually produced, the latter body (bisulphide of chlorine) being deprived of the excess of chlorine would remain unchanged: whereas, in fact, it is almost completely combined with the ethylene.

Moreover, in the synthesis of the bichlorosulphide of amylene, if half the chlorine in the chloride of sulphur had acted independently of the other half, the reaction would have been as follows:—



according to which, 19.6 grms. of the chloride would have required 19.5 grms. of amylene instead of 11.4 as observed: a difference beyond the limits of observational error.

Action of ammonia upon bisulphochloride of amylene.—Aqueous ammonia may be digested with bisulphochloride of amylene for hours without any sensible change taking place.

On warming an alcoholic solution of the bisulphochloride of amylene with an alcoholic solution of ammonia, an immediate and abundant precipitation occurs. The following process was followed in tracing this reaction:—

About 50 grms. of the bisulphochloride in alcoholic solution were heated in a water-bath, in a retort connected with an inverted condenser. Ammonia evolved from an aqueous solution, and not dried, was passed through the tubulus and made to bubble through the alcoholic liquid. The gas having been passed through for several hours, the contents of the retort were allowed to stand for 24 hours. At the end of that time, they smelt strongly of ammonia. The liquid was then filtered, the insoluble portion being washed with ether. This insoluble residue was a white crystalline powder, which, after drying in *vacuo* over sulphuric acid, was not attacked by hydrochloric acid; it gave off hydro-

chloric acid without blackening, on treatment with sulphuric acid.

0.1396 grm. gave 0.3706 grm. of chloride of silver.

0.1623 grm. gave a platinum-salt containing 0.2098 grm. of platinum.

	Calculated.	Found.
NH ₄ . .	33.65	34.84
Cl . .	66.35	65.67

It was therefore pure chloride of ammonium.

The filtrate from the chloride of ammonium did not contain any sulphide of ammonium. On evaporating off the alcohol from a water-bath, and adding water, a heavy liquid was separated, which, after washing with water, still contained a small quantity of chlorine. To remove this, it was heated for five hours in a sealed tube in a water-bath at 100°C. with a fresh quantity of alcoholic ammonia. Thereupon a fresh crop of chloride of ammonia was produced. The mother-liquid was drained off, heated for some hours in a basin, in a water-bath, and precipitated with water (as long as alcohol is present, large quantities of the product are retained in solution: these may be completely precipitated by adding aqueous ammonia). The heavy liquid which separated out, after washing and mechanical drying, was dissolved in ether, digested with animal charcoal, filtered, the ether expelled by the heat of the water-bath, and the product finally dried in *vacuo* over sulphuric acid.

This substance showed on analysis the following percentage composition:—

I. 0.2134 grm. gave a platinum-salt containing 0.0123 grm. platinum.

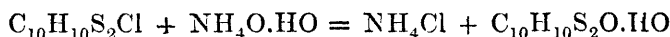
II. 0.2129 grm. gave 0.1752 grm. water, and 0.4011 grm. carbonic acid.

III. 0.2763 grm. gave 0.2271 grm. water, and 0.5224 grm. carbonic acid.

IV. 0.2405 grm. gave 0.4790 grm. sulphate of baryta.

	Calculated.	Found.			
		I.	II.	III.	IV.
(N) . .	0.00	0.82	„	„	„ „
C ₁₀ . .	50.42	„	51.38	51.19	„ „
H ₁₁ . .	9.25	„	9.14	9.13	„ „
S ₂ . .	26.89	„	„	„	27.15 „
O ₂ . .	15.44	„	„	„	„ 11.72

The ammonia is evidently present as an impurity only, probably either as chloride of ammonium, or as bisulphide of fusylamine, the latter supposition being the more probable, owing to the excess of carbon found; in either case, the amount of oxygen would be increased by its removal. The body formed is the *hydrated oxide of bisulphamylen* $C_{10}H_{10}S_2O.HO$, its formation taking place according to the equation—



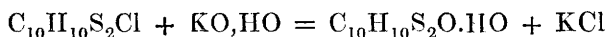
The alcohol employed serves only as a solvent medium, and remains chemically passive.

The formation of this body under the circumstances above-mentioned, namely, the assumption of water in its generation, is another and instructive example of hydration by means of ammonia, a phenomenon which is generally significant of the formation of an alcohol.

The hydrated oxide of bisulphamylen is not volatile without decomposition; when heated, it emits a most fœtid odour, blackens, and leaves a carbonaceous residue. Its specific gravity at 8°C. is 1.049. It is quite transparent, viscid and of an orange-yellow colour: its smell is faint and meaty. It is insoluble in water, but miscible with bisulphide of carbon, ether and absolute alcohol.

The action of alcoholic caustic potash upon bisulphochloride of amylen is similar to that of ammonia.

On heating the bisulphochloride for a few minutes in a water-bath with an excess of alcoholic caustic potash, the whole of the chlorine separates out as chloride of potassium, the hydrated potash giving up both oxygen and water, and converting the bisulphochloride into the hydrate of the oxide of bisulphamylen.



Five grammes were treated in this way with alcoholic potash. The excess of alcohol being expelled on a water-bath, the residue was washed with water and dried in *vacuo* over sulphuric acid.

0.3225 grm. gave 0.2759 grm. water and 0.6050 grm. carbonic acid.

	Calculated.	Found.
C ₁₀ . . .	50.42	51.16
H ₁₁ . . .	9.25	9.50
S ₂		
O ₂		

The water with which the liquid had been washed did not contain any sulphide of potassium.

The liquid obtained by caustic potash is, therefore, identical with that formed by ammonia. Aqueous caustic potash, like aqueous ammonia, does not exert any action upon bisulphochloride of amylene.

As bisulphochloride of amylene is converted into a hydrated oxide by the hydrated oxide of an alkaline metal, so is it converted into an anhydrous oxide by an anhydrous metallic oxide. This is the case, even when water is present, so long as the latter is not in chemical combination with the oxide employed; for example:—

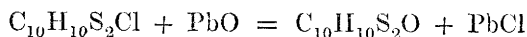
A large excess of oxide of lead (PbO) was digested over a water-bath for several hours with an alcoholic solution of bisulphochloride of amylene, the alcohol being continually renewed as it evaporated. As soon as a drop of the solution showed, on testing, that the whole of the chlorine had been removed, fresh alcohol was added, the product filtered, the filter washed with alcohol, and the filtrate evaporated and dried in *vacuo* over sulphuric acid. An almost colourless heavy liquid was obtained, which, after drying, gave the following percentage composition:

I. 0.2576 grm. gave 0.2094 grm. water and 0.5187 grm. carbonic acid.

II. 0.3222 grm. gave 0.6836 grm. sulphate of baryta.

	Calculated.	Found.	
		I.	II.
C ₁₀	. 54.51	54.92	„
H ₁₀	. 9.03	9.03	„
S ₂	. 29.03	„	29.21
O	. 7.23	„	„
	—————		
	100.00		

This agrees with the composition of *oxide of bisulphamylene*, C₁₀H₁₀S₂O:—the oxide of lead having simply substituted oxygen for chlorine.



The oxide of bisulphamylene is an almost colourless, yellowish, sluggish, transparent liquid of nauseous taste and smell: it is not volatile without decomposition. It is miscible with alcohol, ether

and bisulphide of carbon, immiscible with water; its specific gravity is 1.054 at 13°C.

It is noteworthy that in the preparation of the hydrated oxide of bisulphamylenes described before, if the solution of potash in alcohol contained a very large quantity of potash, a product was obtained containing an amount of carbon intermediate between that of the simple oxide and the hydrated oxide. This is undoubtedly due to the actual formation of some oxide by the hydrated potash.*

The difference in chemico-negativism of the chlorine and sulphur in the bisulphochloride of amylenes and the consequent introduction of oxygen in place of the former element, evinced in the above reactions, suggests at once the possibility of introducing an organic group in place of the chlorine from some compound in which such group is itself chemico-negative. The ethylates of the alkalis offer us examples of such bodies, and the discoverer of zinc-ethyl has placed a further instance of the same class in the hands of chemists.

Nevertheless, the first of the reactions indicated does not appear to take place under ordinary circumstances. If ethylate of soda and bisulphochloride of amylenes be warmed together, the two react with considerable energy. In an experiment of this kind, an excess of ethylate of soda was warmed in a flask with bisulphochloride of amylenes: chloride of sodium was formed. The resulting liquid was shaken with water, and the product formed was extracted by ether. After filtering, evaporating, washing and drying the ethereal solution, it was analysed. (It did not contain chlorine, and the wash-water was free from sulphur.)

I. 0.3424 grm. gave 0.6878 grm. carbonic acid and 0.2787 grm. water.

In a second portion from another quantity, in the preparation of which the utmost pains were taken to leave the ethylate of potash free from hydrate of potash:

II. 0.3759 grm. gave 0.7559 grm. carbonic acid and 0.2974 grm. water.

These results agree far better with the simple oxide of bisulphamylenes than with the ethylate of oxide of bisulphamylenes sought.

* This anhydrous oxydation harmonizes with the fact that hydrated potash dissolved in amylic alcohol, reacts upon iodide of ethyl, forming ethylate of amylic. (See *Phil. Mag.*, September, 1857.)

		Found.		
		I.	II.	$C_{10}H_{10}S_2O.C_4H_5O$
C .	$C_{10}H_{10}S_2O$. 54.54	54.78	54.85	57.15
H .	. 9.09	9.05	8.70	10.20

Hence the ethylate of potash does not act as the hydrate of potash, that is the oxide of ethyl does not combine with the oxide of bisulphamylene on the formation of the latter. In other words, there is no *double ether* formed. The ethylate of potash, in short, has the same action as oxide of potassium would undoubtedly have and as we have already seen the oxide of lead to possess.

In consequence of this negative result, I have not submitted the bisulphochloride to the action of other alkaline ethylates.

We have already discussed the action of hydrated potash upon bisulphochloride of amylene at temperatures below $100^{\circ}C$. If, however, after the two have reacted at this temperature, the product be submitted to distillation in presence of an excess of potash, further decompositions are effected. In tracing these, the following method was pursued. Caustic potash was dissolved in alcohol and evaporated so far that it solidified on cooling; it was then brought into a tubulated retort connected with a very well cooled condenser, and heated till it became quite fluid. Bisulphochloride of amylene was allowed to drop upon it through a funnel-tube passing through the tubulus and provided with a stop-cock. The temperature was at first moderated, the first action (the formation of the hydrated oxide of bisulphamylene) being determined at low temperatures. Increased heat was gradually applied until the lower part of the retort became red-hot, oily drops still continuing to pass over. When the distillation was complete, water was added, and the light liquid which thereupon separated out was washed with water and dried over chloride of calcium. The volume of product so obtained was about two-thirds that of the amylene compound employed. On rectification, it began to boil between 50° and $60^{\circ}C$. The boiling point remained for some time stationary between 110° and $115^{\circ}C$, after which it rose rapidly. There were consequently, at least, three liquids present; fortunately, however, their respective boiling-points were so far apart as to allow of their separation by rectification.

The more volatile portion was submitted to rectification by itself, the distillate being collected in an artificially cooled condenser. A considerable product was obtained, having the fixed boiling-point $39^{\circ}C$.

SOME DERIVATIVES FROM THE OLEFINES.

125

I. 0.1635 grm. gave 0.5093 grm. carbonic acid and 0.2132 grm. water.

II. 0.1751 grm. gave 0.0362 grm. sulphate of baryta.

III. 0.1743 grm. gave only a trace of chloride of silver.

Calculate ^d .	I.	Found.	III.
C ₁₀ . . .	81.95	„	„
H ₁₀ . . .	14.18	„	„
(S) . . .	„	2.83	„
(Cl) . . .	„	„	Trace

This body was therefore amylene; the presence of sulphur is due to the body next to be described, with which the amylene was contaminated, and which could not be completely separated by rectification.

The portion of the original distillate which came over between 110° and 115°C. was next submitted to rectification.

Its boiling-point, after four rectifications, became constant at 112°C.

0.2687 grm. gave 0.5746 grm. of sulphate of baryta.

0.2581 grm. gave 0.5615 grm. of carbonic acid and 0.2276 grm. of water.

	Calculated.	Found.	
		I.	II.
S ₂ . . .	31.68	29.29	„
C ₁₀ . . .	59.40	„	59.33
H ₉ . . .	8.91	„	9.84
	99.99		

This substance, the bisulphide of fusyl C₁₀H₉S₂ is perfectly colourless and transparent, miscible in all proportions with ether, soluble in alcohol, insoluble in water. Its smell is not disagreeable. Its specific gravity is 0.880 at 13°C.

The analysis given would not by itself be conclusive as to the composition of the above-described body. Both bisulphide of amyl and amyl-mercaptan as well as bisulphide of amylene would give analytical results according with the above within the limits of analytical error. My reasons for assigning to it the above compositions are: (1) its boiling-point, bisulphide of amyl boiling at 250°C.; (2) its indifference both alone and in alcoholic solution

towards both protoxide of mercury and acetate of lead, with which amyl-mercaptan combines with great energy; and (3) its being a volatile liquid soluble in ether and alcohol, bisulphide of ethylene being non-volatile and insoluble in these media.

Besides these two products, bisulphochloride of amylene gives rise in presence of caustic potash at high temperatures to other volatile products of boiling-points above 112°C . which I have not examined.

None of the bodies described above became solid at -18°C .

A description of some derivatives from the other two sulphur-chlorine compounds above described, $\text{C}_{10}\text{H}_{10}\text{S}_2\text{Cl}_2$ and $\text{C}_4\text{H}_4\text{S}_2\text{Cl}$, as well as of some direct derivatives from the two olefines, I reserve for a future communication.

Since writing the above, I have succeeded in combining ethylene with bisulphide of chlorine in such a manner as leaves no doubt that the product is $\text{C}_4\text{H}_4\text{S}_2\text{Cl}$. If this be the case, there can be little doubt but that such a body will give rise to a series of compounds similar to those considered above, belonging to the corresponding amylene-olefine.
