

April 7, 1845.—The President in the Chair.

Lieut.-Col. Yorke presented specimens of the Brown Iron Ores, which had formed the subject of his paper, to the Society's Museum; as also of Crystallized Oxide of Lead formed on Metallic Lead by the conjoined action of air and water.

Mr. Charles Button presented 8 volumes of old and scarce chemical works to the Library.

Henry Smith, Esq., and Alexander R. Arrott, Esq., were elected Members; and Mr. William Johnson an Associate of the Society.

The following papers were read:—

CXXXVIII. *On Styrole, and some of the products of its decomposition.* By Dr. JOHN BLYTH and Dr. AUG. WILHELM HOFMANN.

THE class of bodies comprehended under the general name of Balsams has not been forgotten in that active investigation of organic bodies to which chemists have with predilection devoted themselves, since the discovery of easier and securer methods of investigation have removed the chief difficulties. An examination of these substances was indeed highly desirable, as the knowledge of them derived from older works no longer corresponded to the present state of the science. The earlier investigations of these substances were purely qualitative; everything crystalline and which united with bases was benzoic acid; those, on the other hand, which did not enter into combination were described as camphor. If, on distillation, a volatile fluid body was obtained, it was considered sufficient to state that the substance contained also a volatile oil.

Since the discovery of the potash apparatus has introduced an entirely new mode of investigation, our knowledge on these points has considerably augmented. The labours of Fremy, Plantamour, Simon and Deville, are rich in interesting results.

Along with the proper balsams of Peru, Tolu, &c., there is also known in commerce a material whose extraction is uncertain, called liquid storax (*Styrax liquidus*), which, from its properties, is closely allied to this class of substances. Fluid storax has already been the subject of several investigations. The earliest known to us is that of Bouillon-Lagrange*. It contains no results at all deserving of notice. He considered the crystalline acid present in storax as benzoic acid. More lately, Bonastre† communicated observations on fluid storax. He investigated a crystalline deposit which had been formed in an alcoholic solution of the balsam long kept. These crystals, which Bonastre took at first for benzoic acid, were insoluble in cold and hot water, but soluble in alcohol; the solution had no acid reaction. To this indifferent crystallizable body he gave the name styracine. He found the same substance, along with many others, again in an investigation of the American Copal‡, a balsam which in many points resembles styrax.

The most complete investigation of fluid storax we owe more lately to Edward Simon§. This chemist first showed that the acid found in the balsam, and which had been hitherto taken for benzoic acid, possessed all the properties of cinnamic acid. An analysis of the silver salt made by Marchand|| put this beyond a doubt. Simon gave also some fuller details on the substance named styracine by Bonastre, and finally he examined the oil obtained from fluid storax by distillation with water, and which in its properties was quite different from that prepared by Bonastre from the Copal balsam. To this oil from storax he gave the name styrole.

The investigation of this chemist is rich in interesting observations; on the other hand it contains in proportion but few analytical determinations. From the analyses of Marchand, Simon gives the composition per cent. of styrole and styracine, without however at all attempting to give rational formulæ. The determination of such formulæ was however

* *Ann. de Ch. et de Phys.*, 1st ser., t. xxvi.

† *Journ. de Pharm.*, t. xiii. p. 149. 1827.

‡ *Journ. de Pharm.*, t. xvii. p. 338. 1831; and *Mag. für Pharm.*, Von Gieger und Liebig, Bd. xxxvi. S. 90.

§ *Liebig's Annal.*, B. xxxi. S. 265.

|| *Journ. für Prakt. Chem.*, B. xvi. S. 60.

of much interest, as only by these could the relations of the compounds to other groups be shown. To fill up this blank, we undertook, at the request of Prof. Liebig, to make some inquiries in this direction. These were performed in the laboratory of Giessen, and, we need scarcely add, that during their course we were assisted by his advice.

We commence with the description of the oil of storax.

Styrole.

1. *Preparation.*—The material which we employed for the preparation of styrole was the common commercial “liquid storax.” It possesses a dark gray colour, and at the temperature of summer is of a soft consistency, which allows it to be drawn into threads. At a low temperature (0° C.) it is hard and brittle. It has a highly aromatic odour, and is so rich in oil, that it can be pressed out with the fingers. Fluid storax oil can be obtained by distilling the balsam with water; but, as the latter contains also free cinnamic acid, it is more advantageous to add an alkali. For this purpose we followed Simon in employing carbonate of soda, in his proportions of 14 lbs. of crystallized soda to 20 of storax. We found that the half was quite sufficient.

The distillation was conducted in a copper retort with a gentle heat; the watery vapour loaded with oil was directed through a serpentine tube. In this way a milky-coloured water distilled over, on the surface of which the oil collected in a transparent, slightly yellow layer. We have submitted to distillation in the above method about 70 lbs. of storax. The material we employed was not all received at the same time, and gave very different amounts of oil. In the first operation we obtained 12 oz. of styrole out of 41 lbs. of storax. A later preparation, in which 27 lbs. of the balsam were employed, gave scarcely more than 3 oz. This difference arises, as Simon has already remarked, from the age of the balsam, as the styrole experiences in time a peculiar change. To this point we shall return later.

The volatile storax oil, as it is obtained by distillation, contains a small quantity of water, from which it can be easily freed by remaining over fused chloride of calcium. The fluid deprived in this way of water can be regarded as pure styrole, although it still possesses a shade of yellow. To obtain it quite colourless, it must again be submitted to distillation.

In this operation a peculiar phenomenon is observed, which was first indicated by Simon. When styrole is heated in a tubulated retort in which a thermometer is placed, a

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quantity of vapour is evolved at 100° to 120° C. At $145\frac{3}{4}^{\circ}$ the fluid begins to boil, and there distils over a clear, oily and beautifully iridescent fluid. For some time the thermometer remains stationary at the above temperature, then begins suddenly to rise so fast, that it must quickly be removed from the retort. The portion left behind has now completely changed its character to a thick, tenacious substance, through which the bubbles formed at the bottom of the vessel force their way with much difficulty to the surface. From this period scarcely any more oil distils over, and, on allowing the retort to cool, its contents become a solid transparent glass. The quantity of this solid residue is variable: it amounts sometimes to a third of the oil employed. We shall return to this point afterwards. The product of the distillation is perfectly pure styrole.

2. *Properties of Styrole.*—This body is in the form of a colourless, transparent fluid, of a burning taste and peculiar aromatic odour, resembling a mixture of benzole and naphthaline, which adheres tenaciously to linen. At a temperature of 20° C. it neither solidifies nor loses any of its extreme mobility. Exposed however to a mixture of solid carbonic acid and æther, it solidifies instantaneously into a beautiful white crystalline mass. It is in the highest degree volatile, and evaporates at all temperatures; the oily spots made by it on paper disappear after a few seconds. The boiling-point lies, as already stated, about $145\frac{3}{4}^{\circ}$ C. This same temperature was found in several trials. A wick dipped in styrole burns with a brilliant, smoky flame. Its vapour can be passed without decomposition through a red-hot tube.

Styrole is lighter than water: its specific gravity at the ordinary temperature of summer is 0.924. It disperses and refracts the rays of light in the highest degree. Its coefficient of refraction is for the red rays 1.532.

It mixes in all proportions with æther and absolute alcohol. Spirit of wine dissolves less according to the proportion of water it contains. It is soluble in pyroxylic spirit, acetone, bisulphuret of carbon, fat and æthereal oils. Water dissolves only a small proportion, but still sufficient to give it the burning taste and odour of the oil. The amount of water which can become mixed with the oil is equally small.

Styrole shows no reaction on vegetable colours. Like the æthereal oils, it dissolves by the aid of heat a large proportion of sulphur, which, on cooling, is deposited in the form of large prisms. Phosphorus is likewise soluble in hot styrole, from which it also crystallizes. Caoutchouc swells up by the aid

of heat in this substance; only a small portion however is dissolved.

3. *Composition of Styrole.*—We have already stated that on the occasion of Simon's investigation, Marchand analysed styrole. From his experiment it appears that this body consists of carbon and hydrogen, in the proportion of two of the former to one of the latter*. We have also analysed styrole, and our results confirm those of Marchand.

On combustion with oxide of copper, styrole prepared at two different periods gave the following numbers:—

I. 0·2722 grm. of styrole gave 0·9168 grm. of carbonic acid and 0·1935 grm. of water.

II. 0·4640 grm. of styrole gave 1·5745 grm. of carbonic acid and 0·3290 grm. of water.

Corresponding in the 100 parts to—

	I.	II.
Carbon . . .	91·86	92·54
Hydrogen . .	7·89	7·87

Theory requires—

		Mean of experiments.	
2 equivalents Carbon† =	150·0	92·30	92·20
1 ... Hydrogen =	12·5	7·70	7·88
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The above experiments leave no doubt as to the relative amount of the carbon and hydrogen, but give no idea of the absolute number of equivalents of the elements in the equivalent of styrole; or, in other words, lead to no conclusion as to the formula of the compound. This point it was however very desirable to ascertain, as we already possess two bodies, benzole and cinnamole, which have the same composition in the hundred parts.

The determination of a chemical formula for styrole was attended with some difficulty. Like benzole and cinnamole, this body formed no direct compounds, if we do not consider here the products obtained by the action of chlorine and bromine; in the case of the former substances, however, their formulæ were in a certain measure given by their origin

* The volatile oil which Bonastre (*Journ. de Pharm.*, t. xviii. p. 344) obtained from the Copal balsam is certainly a totally different carbo-hydrogen from styrole. Henry and J. Plisson (same Journal, p. 451) found its composition to be—

Carbon =	89·25
Hydrogen =	10·46
Oxygen =	00·29
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This oil is also distinguished from styrole by becoming solid at 0° C.

† Carbon = 75. Hydrogen = 12·5.

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from benzoic and cinnamic acids, and could be controlled by a determination of the specific gravity of their vapours. The origin of styrole, on the other hand, is quite obscure, and the determination of the specific gravity of its vapour was no longer to be thought of after we had observed the peculiar metamorphosis produced by the action of heat.

There remained therefore no other way to arrive at a proper formula than by studying the products of its decomposition. As we had already some information from Simon on this point, it appeared desirable to follow the same way. In the course of this memoir it will be seen that we were led to adopt $C_{16}H_8$ as the formula of styrole.

4. *Products of the Decomposition of Styrole. Action of Nitric Acid.*—In its physical properties styrole is closely allied to benzole and to benzoëne (toluine of Berzelius), lately discovered by Deville* as a product of the dry distillation of Tolu balsam. The interesting results obtained by Mitscherlich, and later by Deville, by the action of nitric acid on the above-named bodies, and particularly the remarkable transformation of nitrobenzide into aniline, observed a short time ago by Zinin†, indicated to us a method which promised to lead to a proper formula of styrole. Were a compound analogous to nitrobenzide to be obtained, or a base to be formed whose atomic weight could be easily determined, such data would at once lead to a knowledge of the proper constitution of styrole.

In the memoir already referred to, Simon has communicated some experiments on the action of nitric acid on styrole. He obtained a peculiar neutral body, which he named *nitrostyrole*, without however ascertaining its composition. Along with this body he observed the formation of benzoic and hydrocyanic acids.

Nitrostyrole.

The preparation of this substance is attended with difficulty. Notwithstanding a great number of experiments, we have not been able to find out a method to procure at will a considerable quantity of this body. According to Simon, storax oil must be distilled with nitric acid (but of what concentration is not stated) till it has become brown, and is completely converted into a resinous mass. After freeing it from nitric acid by washing, this resin is to be distilled with water, when the nitrostyrole volatilizes with the watery vapour.

By following the directions given by Simon, and employing

* *Ann. de Ch. et de Ph.*, 3rd ser., t. iii. p. 151; and *Ann. der Chem. und Pharm.*, Bd. xlv. S. 304.

† *Ann. der Chem. und Pharm.*, Bd. xlv. S. 286.

in the distillation ordinary nitric acid, we obtained indeed the peculiar substance named by him nitrostyrole, but in quantity bearing no proportion to the amount of oil employed. The oil is very slowly attacked by common nitric acid. On heating the mixture to boiling the styrole becomes of a yellow colour, but at the same time a large quantity of undecomposed yellowish oil distils over. Only after being five or six times poured back into the retort does it begin to change its character, by becoming heavier, more tenacious, and finally sinking to the bottom of the vessel. At this period the oil-drops which pass over with the water smell no longer of styrole, but possess a peculiar sharp odour of cinnamon, and violently attack the eyes. If the styrole has become quite brown and sunk to the bottom, it solidifies on the cooling of the retort into a resinous mass. The watery fluid above the resin, on the other hand, deposits a quantity of crystalline plates. On removing the crystals from the retort, washing the resin with water to free it from the nitric acid, and again heating to boiling the resin with water, the greater portion becomes dissolved, and there distils over a volatile matter possessing in the highest degree the odour of cinnamon. After a short time these oil-drops solidify in the retort. On allowing the retort to cool when no more of this substance passes over, the whole fluid becomes a crystalline mass. By long-continued distillation, a portion of this crystalline matter, which is, however, much less volatile than the nitrostyrole, also passes over into the receiver.

As already stated, the quantity of the volatile oil obtained was exceedingly small. Only after repeated operations, and at the sacrifice of several ounces of styrole, was a quantity prepared sufficient for analysis. It was separated by filtration from the fluid which distilled over with it, and after washing with water, which dissolves but a small proportion, again distilled with the vapour of water, and finally dissolved in boiling alcohol. On cooling, large beautiful prisms* crystallized from the solution, possessing the characteristic odour of cinnamon, and a sweet but highly burning taste.

The following results were obtained on combustion with oxide of copper, after the substance had been dried over sulphuric acid for several days:—

I. 0.2662 grm. of the crystals gave 0.6250 grm. of carbonic acid and 0.1190 grm. of water.

II. 0.1630 grm. of crystals gave 0.3885 grm. of carbonic acid and 0.0790 grm. of water.

* In the memoir of Simon exact measurements of these crystals are given from G. Rose.

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III. 0·2787 grm. of crystals gave 0·1255 grm. of water.

IV. The nitrogen was determined by the method of Dumas, by burning the substance in an atmosphere of carbonic acid. 0·5088 grm. of crystals gave 48· cub. cent. of moist nitrogen at 19° C. and 327^{mm} barom.

These numbers correspond to—

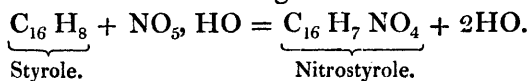
	I.	II.	III.	IV.
Carbon . .	64·04	64·50		
Hydrogen .	4·96	5·38	5·00	
Nitrogen	10·30

When we consider that the method of Dumas always gives an excess of nitrogen, we can from the above numbers deduce the following formula, $C_{16}H_7NO_4$, giving per cent.,—

		Mean of experiments.		
16 equiv. Carbon . .	1200·00	64·36		64·27
7 ... Hydrogen .	87·50	4·69		5·11
1 ... Nitrogen .	177·04	9·50		10·30
4 ... Oxygen . .	400·00	21·45		21·32
		<u>1864·54</u>	<u>100·00</u>	<u>101·00</u>

According to this formula, which will be further confirmed by the analysis of the bromine and chlorine compounds, the body investigated is analogous to nitrobenzide, which it resembles in many respects, and fully deserves the name of *nitrostyrole*, proposed by Simon.

If from this formula we deduce the composition of styrole, it must be expressed by $C_{16}H_8$, and the formation of nitrostyrole is shown in the following manner:—



As to the properties of nitrostyrole, we have but little to add to the statements of Simon. This body is particularly characterized by its odour, which strongly irritates the eyes to tears, and by the manner in which it affects the skin, long contact with which produces a painful burning, and finally blisters.

On distilling a mixture of nitrostyrole and an alcoholic solution of potash, after most of the spirits have passed over, there are obtained red oil-drops, which are not nitrostyrole. From want of materials we have not investigated this body: it is probably a compound analogous to the *azobenzide* of Mitscherlich. An exact study of this reaction will certainly lead to interesting results, but there will be some difficulty in obtaining a quantity of substance necessary for such a purpose.

We further endeavoured to transform nitrostyrole into a base by the action of sulphuret of ammonium. This body

would have had the composition $C_{16}H_9N$, and by treatment with oxidizing means would probably give compounds of the indigo series, perhaps *isatine*. We have hitherto, however, not succeeded in preparing it.

We have already stated, that by the treatment of styrole with nitric acid, there passes over, towards the end of the distillation, an oil which possesses in the highest degree the odour of nitrostyrole. This oil is nothing but a solution of nitrostyrole in several other fluid bodies, probably undecomposed styrole and some oil of bitter almonds. On exposing this mixture to a very low temperature ($-20^{\circ}C.$), it solidifies nearly completely into a crystalline mass, which can be separated from the adhering fluid oil by pressing in filtering paper: it is pure nitrostyrole.

Benzoic Acid.

The crystals which separate on the cooling of the watery fluid during the preparation of the resin for the formation of nitrostyrole, consist, according to the length of the distillation or the concentration of the nitric acid employed, either of benzoic or nitrobenzoic acid. In general we obtained a mixture of both.

To be quite certain on this point, we treated, in the repeated distillations which we undertook for the preparation of nitrostyrole, storax oil sometimes with quite dilute nitric acid.

By continuing the distillation for a considerable time, there passed over with the watery vapour a substance which condensed in the neck of the retort and in the receiver into a crystalline mass. This was dissolved in weak potash ley and boiled till all odour of nitrostyrole had disappeared. Acids produced in this alkaline solution a white crystalline precipitate, which was separated by filtration, washed, and dissolved in boiling water. From this solution large crystalline plates separate, which are identical with those deposited from the liquid above the resin (in the preparation of nitrostyrole), and which in every respect resembled benzoic acid. To remove every doubt, we formed benzole from it, and submitted the acid itself to analysis.

The following results were obtained by combustion with oxide of copper:—

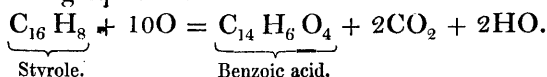
0.3260 grm. gave 0.8230 grm. of carbonic acid and 0.1545 grm. of water.

The amount per cent. calculated from these numbers corresponds exactly to the formula $C_{14}H_6O_4$, as is shown by the following statement:—

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	Theory.		Experiment.
14 equiv. Carbon . .	1050·00	68·85	68·85
6 ... Hydrogen . .	75·00	4·92	5·25
4 ... Oxygen . .	400·00	26·23	25·90
1 ... Benzoic acid =	1525·00	100·00	100·00

The transformation of styrole into benzoic acid is shown by the following equation:—



This equation merely represents the ultimate products of decomposition. It is, however, probable that an intermediate product precedes the formation of the benzoic acid. We have already mentioned a heavy oily liquid, which during the action of nitric acid on styrole condenses in the receiver. It contains, as stated, a large quantity of nitrostyrole; and also another fluid body, which we are inclined to consider as oil of bitter almonds. At least, at certain periods of distillation, the products acquired the strongest odour of that oil.

As the small quantity of the mixture we possessed excluded the possibility of a separation by distillation, we thought it might be possible to prove the presence of oil of bitter almonds by the formation of benzoine. For this purpose the mixture was treated, according to Zinin's method, with an alcoholic solution of potash and some cyanide of potassium*. We have, however, not been able to observe any crystals of benzoine, consequently the settlement of this point must be reserved for further investigation. The formation of oil of bitter almonds under the circumstances already mentioned would beside not have been very extraordinary. The investigations of Dumas and Peligot†, which were confirmed by Plantamour‡ and Simon§, have shown that cinnamic acid, treated by oxidizing means, produces hydruret of benzoyl before passing into benzoic acid. According to very recent observations of Cahours||, oil of anise, before being finally changed into anisic acid, is first converted into hydruret of anisyl, which stands in the same relation to the last acid as hydruret of benzoyl to benzoic acid.

Nitrobenzoic Acid.

If strong nitric acid, such as the commercial, has been employed in distillation with styrole, there are obtained, by the

* *Ann. der Chem. und Pharm.* Bd. xxxiv. S. 186.

† *Ibid.* Bd. xiv S. 59.

‡ *Ibid.* Bd. xxx. S. 349.

§ *Ibid.* Bd. xxxi. S. 271.

|| *Compt. Rend.* t. xix. 795.

solution of the residue, crystals which possess all the properties of nitrobenzoic acid discovered by Mulder*. We have made several analyses of this acid and its silver salt, which, however, we consider we may pass over, as, after proving the formation of benzoic acid, the appearance of nitrobenzoic acid was easily explained.

Simon states that hydrocyanic acid is one of the products of the action of nitric acid on styrole: we have not observed the formation of this acid.

It has been already stated that the amount of nitrostyrole obtained was exceedingly small. We have modified the process for forming it in several ways, in order to obtain, if possible, this interesting body in larger quantities.

The analogy which exists between nitrostyrole and nitrobenzide, both in their mode of formation and properties, appeared to indicate the way to a more advantageous method of preparation. For this purpose we dropped styrole into fuming nitric acid, which formed with it a deep red solution, with great evolution of heat. Here also, even by the employment of artificial cold, the formation of red vapours could not be avoided. From the nitric acid solution water precipitated a yellow resinous substance of soft consistency, which possessed in the highest degree the characteristic smell of nitrostyrole. After washing with water till the greater part of the nitric acid was removed, the yellow mass was submitted to distillation with water. A quantity of nitrostyrole volatilized with the watery vapour, greater than was obtained in the former method, but still out of all proportion to the amount of oil employed. We were equally unfortunate in the treatment with fuming nitric acid, which had been previously saturated with deutoxide of nitrogen.

If a current of nitrous acid (NO_2) be passed through styrole when warm, a violent reaction takes place with the evolution of vapours, which possess the irritating odour of nitrostyrole; at the same time there is formed a peculiar odourless crystalline substance, insoluble in water, alcohol and æther. This compound we have not studied.

In this reaction, which is certainly very complicated, nitrostyrole is likewise formed in only very small quantities.

Action of Chromic Acid on Styrole.

On submitting to distillation a mixture of styrole, bichromate of potash, sulphuric acid and water, the greater portion of the styrole passes with the watery vapour undecomposed into the receiver. A reaction takes place only after the contents of

* *Ann. der Chem. und Pharm.* Bd. xxxiv. S. 297.

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the retort have commenced to become solid; by continuing the distillation large crystals of benzoic acid collect in the receiver.

Action of fuming Sulphuric Acid on Styrole.

On mixing fuming Nordhausen sulphuric acid with styrole, a violent reaction takes place with the evolution of heat; the oil becomes tenacious, and assumes a dark colour. The addition of water produces the separation of a brown resinous mass. The fluid filtered from this substance gave, when treated with an excess of carbonate of baryta, a soluble baryta salt, which, however, could not be obtained in a crystalline form. The physical properties of these products, probably analogous to Mitscherlich's sulphobenzide and hyposulphobenzidic acid, are far from inviting to a nearer investigation.

Action of Bromine on Styrole.

Bromostyrole.—By the addition of bromine to the volatile oil of storax it becomes heated to boiling, and the evolution of hydrobromic acid always takes place. The oil is by this reaction completely transformed into a crystalline mass of a peculiar odour.

The formation of hydrobromic acid can be completely avoided by placing the flask in water and adding the bromine by drops. By waiting each time till the heat evolved has been removed, the product obtained is uniform.

The crystalline mass is insoluble in water, but communicates to it a highly peculiar penetrating odour and taste, which resemble a mixture of oil of citron and juniper. It is, on the other hand, very soluble in alcohol and æther. We have in vain endeavoured, by gentle evaporation of the æthereal solution, to obtain well-formed crystals. The boiling saturated alcoholic solution on cooling deposits the compound in the form of an oil, which covers the bottom of the vessel, and not unfrequently remains long fluid under the temperature at which it solidifies, until shaken, when it becomes solid. It fuses under boiling water. It is decomposed by an alcoholic solution of potash, bromide of potassium, and another compound containing bromine being formed.

The products submitted to analysis were of different preparations. Nos. I. and II. were formed directly by the treatment of styrole with an excess of bromine. The somewhat yellow substance was washed with spirits of wine till it appeared white, and after solution in the same menstruum was again precipitated by the addition of water, and washed with the same fluid till all trace of hydrobromic acid, which forms

in considerable quantity during the preparation, was removed. The substances employed in Nos. III. and IV. were made with great care; merely traces of hydrobromic acid were formed, which were also removed in the same manner.

The combustions, which were all made with chromate of lead, gave the following results:—

I. 0·3950 grm. of substance gave 0·5150 grm. of carbonic acid and 0·1155 of water.

II. 0·3095 grm. of substance gave 0·4085 grm. of carbonic acid and 0·0920 grm. of water.

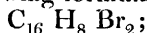
III. 0·3650 grm. of substance gave 0·4085 grm. of carbonic acid and 0·1047 grm. of water.

IV. To determine the bromine, the substance was carefully mixed with caustic lime and heated to redness in a combustion-tube. The heated mass was then dissolved in nitric acid, filtered, and precipitated by nitrate of silver. Treated in this way there was obtained from 0·2668 grm. of substance 0·3805 grm. of bromide of silver.

These numbers correspond per cent. to—

	I.	II.	III.	IV.
Carbon	35·85	35·99	36·23	
Hydrogen	3·23	3·27	3·18	
Bromine	59·83

From which the following formula is deduced,



giving per cent. the following numbers:—

16 equivts. Carbon	= 1200·00	36·85
8 ... Hydrogen	= 100·00	3·07
2 ... Bromine	= 1956·61	60·06
	<hr/>	
	3256·61	100·00*

Action of Chlorine on Styrole.

Chlorostyrole.—By the treatment with chlorine there is formed a compound analogous to the bromostyrole. The chlorine compound is fluid. It is extremely difficult to prepare the chlorine compound pure. A stream of the gas passed through styrole is rapidly absorbed, without any evolution of hydrochloric acid, if the current be not too rapid, and the temperature kept low, at the same time that the influence of the direct rays of the sun be avoided. By long treatment the oil changes into a thick fluid, which is chlorostyrole. As soon as the evolution of hydrochloric acid indicates that no more styrole exists free, the action must be interrupted. The evolution

* The loss of carbon in Nos. I. and II. arose evidently from a mixture of another product richer in bromine. The evolution of hydrobromic acid in the preparation can only take place from such a cause.

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of hydrochloric acid indicates that the decomposition is proceeding further, by the formation of products of substitution which contain fewer hydrogen equivalents than exist in styrole; whereas chlorostyrole is a simple compound of chlorine and styrole, or at least may be considered as such.

We have frequently prepared and analysed the first product of the action of chlorine on styrole. The analyses proved however to us that only on one occasion were we fortunate enough to have hit the proper moment when the action of chlorine must be interrupted. All the other combustions, which we pass over, gave a constantly varying, but always too small a proportion of carbon.

Burned with chromate of lead the following results were obtained:—

0.3553 grm. of chlorostyrole gave 0.7200 grm. of carbonic acid and 0.1505 of water.

From which the following formula and theoretical numbers are deduced, $C_{16}H_8Cl_2$.

	Theory.		Experiment.
16 equivts. Carbon . .	1200	54.91	55.26
8 ... Hydrogen . .	100	4.57	4.70
2 ... Chlorine . .	885.3	40.52	
1 ... Chlorostyrole	2185.3	100.	

By heating chlorostyrole it is decomposed into a new oily product with evolution of hydrochloric acid. This product, which is probably $C_{16} \left\{ \begin{matrix} H_7 \\ Cl \end{matrix} \right\}$, is obtained in more considerable quantities when chlorostyrole is distilled with caustic lime. We have not examined it more closely. The formula of styrole derived from nitrostyrole is thus completely supported by the analysis of the bromine and chlorine compounds.

By the continued action of chlorine for several days on styrole in direct sunlight, that oil is changed into a thick viscid fluid, with the evolution of a very large quantity of hydrochloric acid. This substance is not even the last product of the action, as by further continuance hydrochloric acid is still given off.

The same fact is observed on submitting styrole to the action of chlorate of potash and hydrochloric acid.

Action of Heat on Styrole.

Metastyrole.—The remarkable change experienced by styrole under the influence of heat has been already mentioned in the preceding pages. We stated that in rectifying the oil a considerable portion of pure unchanged styrole passed over

at first, but at a certain point the contents of the retort became thick, and on cooling solidified into a firm transparent vitreous mass.

On first observing this phenomenon we thought it arose from the conversion into resin by the action of the air of a portion of the raw oil which had been standing in a bottle only half-filled, and that this substance being held in solution by the remaining fluid oil, was separated on distilling the latter from it. A similar idea seems also to have occurred to Simon, from his bestowing the name of oxide of styrole on the residue found in the retort on submitting styrole to distillation.

We soon convinced ourselves that this idea was erroneous by distilling a second time a portion of newly-rectified oil. A very considerable residue of solid matter, though not quite so great as in the first distillation, was observed to remain in the retort. The same amount was further found in a third, fourth and every succeeding distillation. The rapidity with which styrole changes into the solid substance, indicated sufficiently that it could not be from combination with oxygen. This fact was besides established by direct experiment. Indeed so little attraction has styrole for oxygen, that it can be left exposed to air for weeks together without any change in its colour. A portion of oil was confined for several months over mercury in a tube filled with oxygen gas without the least diminution in the volume of the latter. We soon recognised that this metamorphosis of styrole takes place without loss of or addition to any one of its elements, and solely through a change in the molecular structure of this body produced by the action of heat. Analysis as well as synthesis has equally proved that styrole and the vitreous mass (for which we propose the name of metastyrole) possess the same constitution per cent.

Metastyrole, when prepared from colourless oil, is equally transparent, and possesses the same powers of refraction as the latter body*. On the other hand, it completely loses the characteristic odour and taste which distinguish styrole. Metastyrole is totally inodorous and tasteless. At the ordinary temperature this body is hard and can be cut with a knife. By heat it becomes soft, and can be drawn out into threads, which strikingly resemble spun glass. It is insoluble in water and alcohol, as well in the cold as when heated. In boiling æther a small portion is dissolved, which, on leaving the solution to spontaneous evaporation, becomes attached to the sides

* There is scarcely an organic body which refracts the rays of light so strongly as metastyrole. It is not improbable that it might be applied to several optical purposes.

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of the vessel in a thin almost transparent layer, that can be separated from the glass, and presents a most deceptive likeness to the thin membrane lining the shell of an egg. The portion which has not been dissolved in the æther swells to six or seven times its original volume. This mass contains, when dried at the ordinary temperature, a large quantity of æther, which is driven off only by heat. Turpentine oil also dissolves traces of metastyrole; sulphuric acid is in the cold without action, but on the application of heat carbonizes the metastyrole, with evolution of sulphurous acid. The action of nitric acid will be presently mentioned.

To obtain metastyrole completely pure, and in a condition fit for analysis, advantage was taken of its relations to æther. The vitreous mass was boiled in æther till it was completely converted into the swollen gelatinous matter from which the excess of æther was decanted; this contains the unchanged styrole that had remained in the resinous mass; and after heating the residue in a water-bath, to expel the æther, a completely inodorous and tasteless white spongy mass was left behind, which could be easily reduced to powder. This powder was again boiled in alcohol, dried, and burned with chromate of lead.

0.2955 grm. gave 0.9970 grm. of carbonic acid and 0.2130 grm. of water. Corresponding per cent. to—

Carbon	92.05
Hydrogen	8.00

Styrole contains—

Carbon	92.30
Hydrogen	7.70

This combustion is sufficiently decisive, but to remove all doubt the following experiment was made.

A portion of styrole was confined in a strong glass tube, hermetically sealed by the blowpipe lamp, and placed in an oil-bath, whose temperature was not allowed to rise above 200° C. At the end of half an hour *the styrole had completely changed into metastyrole*. The same result was obtained by sealing a portion of it in small glass bulbs, in which scarcely a trace of air was left, and submitting them to the temperature of boiling water. On the second day the styrole had become thick, and on the third solid.

A bulb of the same size was exposed to the heat of the sun in the hot summer months. The same transformation likewise took place; but at this temperature it required three weeks to produce the same effect as takes place almost imme-

diately at that of 200° C. Intensity and duration * of action are seen here, as everywhere else in nature, to be equivalent.

Light appears, however, to play a part in the transformation of styrole; at least a small portion sent to Professor Liebig five years ago by E. Simon, and which had been kept in a dark press, is still as fluid as if newly distilled.

This metamorphosis of styrole by heat is so much the more extraordinary, as this agent generally acts in a contrary direction, either to liquify or volatilize. The white of egg alone, in certain points, offers some analogy; and these two bodies, at a higher temperature, exhibit likewise, though in a distant degree, the same behaviour.

L. Gmelin † has shown that the coagulated white of egg, heated in a Papin's digester with water to 200° C., becomes again fluid, and forms with the water a yellow liquid. This observation has been lately confirmed by Wöhler and Vogel ‡.

If metastyrole is heated in a small retort over a spirit-lamp, it becomes again fluid, and a colourless oil distils over, which is pure styrole. By a carefully conducted distillation there remains scarcely any residue in the retort.

It was possible that the oil obtained by distilling metastyrole might be another body of the same composition as styrole and metastyrole, but possessing different properties. The regenerated oil forms instantaneously with bromine the characteristic smelling bromine compound. Besides this reaction, which, as will be seen immediately, is not decisive, the action of heat on the regenerated oil is quite conclusive. Heated to 200° C., in a tube hermetically sealed, it is converted into metastyrole, which by a higher temperature is again in its turn reconverted into styrole.

After having ascertained that styrole and metastyrole had the same composition per cent., and that the difference in their physical properties could only arise from a dissimilar arrangement of their molecules, it was of some interest to obtain an explanation of this arrangement. As the specific weight of the vapours of both bodies could not be compared with each other, there remained no other resource but to study more closely the products of decomposition of metastyrole. As bromine and chlorine act only very slowly on metastyrole, sulphuric acid carbonizes it, and by fusing with potash a sim-

* The varying amount of styrole obtained from the different sorts of storax is probably owing to the same metamorphosis produced in the course of time.

† *Handbuch*, 3te Ausgabe, Bd. ii. S. 1053.

‡ *Ann. der Chem. und Pharm.*, Bd. xli. S. 238.

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ple conversion into styrole follows; nitric acid was selected as the decomposing agent.

Action of Nitric Acid on Metastyrole.

Nitrometastyrole.—Common nitric acid, either warm or cold, attacks metastyrole but little. Even strong fuming nitric acid acts but feebly in the cold, but on the application of heat dissolves it quickly with the evolution of red fumes. If a sufficient quantity of nitric acid has not been employed, the new product is precipitated on cooling in the form of a slimy substance. On the other hand, if the acid has been in excess, the fluid remains quite clear, from which, on the addition of water, a white curdy mass, which sometimes has a shade of yellow, is precipitated. This is washed with water to remove all trace of nitric acid, and afterwards boiled in alcohol to get rid of any trace of benzoic acid which may have been formed from styrole still remaining in the pores of the metastyrole.

The body thus obtained, and for which we propose the name of nitrometastyrole, is when dry in the form of a white or yellowish, completely amorphous powder, insoluble in æther, alcohol and water, but soluble in fuming nitric and in sulphuric acid. By the application of a gentle heat it burns with a slight deflagration, like many bodies which possess the elements of hyponitric acid, and with a strong odour of oil of bitter almonds. As the physical properties of this body do not indicate any certainty of its purity, it was burnt to ascertain this point as nearly as possible. After some analyses it was recognised that the new product of decomposition retained traces of undecomposed metastyrole, from the nitric acid solution becoming very turbid on cooling. This fact was proved by dissolving the substance in concentrated sulphuric acid, when the undecomposed metastyrole remains undissolved. On the other hand, by boiling the solution of metastyrole too long in the nitric acid, a mixture was obtained, on precipitating with water, consisting for the most part of nitrometastyrole, and of a second product containing less carbon and more nitrogen.

Nitrometastyrole is obtained pure by dissolving metastyrole in a quantity of acid sufficient to hold it in solution on cooling. Nitric acid must be added to the hot solution as long as it is observed to become turbid on pouring a few drops out into a watch-glass.

The analysis of the substance prepared in this way gave the following results:—

I. 0.3235 grm. of nitrometastyrole gave 0.7230 grm. of carbonic acid and 0.1325 grm. of water.

II. 0.2830 grm. of substance gave 0.6535 grm. of carbonic acid and 0.1330 grm. of water.

III. 0.2865 grm. of substance gave 0.1170 grm. of water.

IV. 0.3142 grm. of substance gave 0.1278 grm. of water.

V. The nitrogen was determined by the method of Dumas, by burning the substance in an atmosphere of carbonic acid, and calculated from its volume.

0.6125 grm. of nitrometastyrole gave 53 cubic centimetres of nitrogen at 329" barometer and 9° C. thermometer. In per cent.

	I.	II.	III.	IV.	V.
Carbon . . .	60.95	61.69			
Hydrogen . . .	4.55	5.26	4.53	4.51	
Nitrogen . . .					10.06

These numbers correspond to the formula $C_{14}H_6NO_4$, as is shown by the comparison of the numbers found and calculated.

	Theory.	Mean of experiments.
14 equiv. Carbon . . .	$\overbrace{= 1050.00}$	61.69
6 ... Hydrogen . . .	$= 75.00$	4.40
1 ... Nitrogen . . .	$= 177.04$	10.40
4 ... Oxygen . . .	$= 400.00$	<u>23.51</u>
1 ... Nitrometastyrole	$= 1702.04$	100.00

Taking the most probable supposition, that nitrometastyrole stands in the same relation to metastyrole as nitrostyrole to styrole, or nitrobenzide to benzole, that is, that one equivalent of hydrogen in the carbo-hydrogen is replaced by one equivalent of hyponitric acid, the formula for metastyrole will then be $C_{14}H_7$, from which it is seen, that by the metamorphosis of the body, $C_{16}H_8$, the number of equivalents of carbon and hydrogen in the new compound has diminished by one-eighth.

The formula of nitrometastyrole differs from that of anthranilic acid and protonitrobenzoene by containing one equivalent less of hydrogen. The formula of the two latter bodies is $C_{14}H_7NO_4$. Late investigations* have shown that protonitrobenzoene, as well as anthranilic acid, when distilled with lime, is decomposed into carbonic acid and aniline. As nitrometastyrole is a body completely analogous to nitrobenzoene, we expected to form under similar circumstances a base with the formula $C_{12}H_6N$. The experiment did not however turn out to our expectation. On distilling a mixture of lime and nitrometastyrole, a very complicated reaction follows, a large quantity of carbon is deposited, ammonia is evolved, and at

* New Modes of Formation of Aniline, by Dr. J. S. Muspratt and Dr. A. W. Hofmann.—Chemical Memoirs, vol. ii.

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the same time a proportionately small quantity of a brown coloured oil passes over. Hydrochloric acid dissolves a large portion of this oil, from which it is again separated by the addition of alkalies. This oil is nothing but *aniline*, which is at once recognised by the dark violet colour it gives with a solution of chloride of lime, and the yellow colour its solution in acids communicates to pine-wood. The formation from nitrometastyrole of this base, which contains more hydrogen than the original substance, is certainly the result of a very complicated reaction, which cannot be exhibited in any equation.

The following is the series of bodies investigated in this memoir :—

Styrole	$C_{16} H_8$
Bromostyrole	$C_{16} H_8 Br_2$
Chlorostyrole	$C_{16} H_8 Cl_2$
Nitrostyrole	$C_{16} \left\{ \begin{array}{l} H_7 \\ NO_4 \end{array} \right\}$
Hydruret of benzoyl (?)	$C_{14} H_5 O_2, H$
Benzoic acid	$C_{14} H_5 O_3, HO$
Nitrobenzoic acid	$C_{14} \left\{ \begin{array}{l} H_4 \\ NO_4 \end{array} \right\} O_3, HO$
Metastyrole	$C_{14} H_7$
Nitrometastyrole	$C_{14} \left\{ \begin{array}{l} H_6 \\ NO_4 \end{array} \right\}$.

The experiments detailed in the preceding pages have proved that the formula of the carbo-hydrogen derived from the storax must be expressed by $C_{16} H_8$. This is, however, likewise the formula of the carbo-hydrogen analogous to benzole, and which is derived from hydrated cinnamic acid by the separation of two equivalents of carbonic acid.

Are Styrole and Cinnamole identical?

This question must necessarily present itself when we consider that storax contains large quantities of cinnamic acid, and that this balsam, according to the views of later celebrated pharmacologists (as Th. W. Martius*), is obtained not by incision but by a kind of distillation.

How easily in this operation a portion of the cinnamic acid might be converted in cinnamole and carbonic acid, we know from the fact of benzoic acid, when passed in vapour through a red-hot tube, being decomposed with ease into carbonic acid and benzole.

The details given us by different chemists on cinnamole

* *Grundriss der Pharmakognosie des Pflanzenreichs*, S. 346.

differ exceedingly from each other. Simon and Marchand prepared this substance by distilling cinnamic acid and caustic lime. Herzog* followed the same course; he obtained a yellowish fluid, which on rectifying gave a light colourless oil, whilst a yellowish-brown, heavy liquid remained in the retort. Cinnamole (named by Marchand and Simon cinnamomine) which has been prepared in this way boils at 89° C. and has a specific gravity of 0·88.

According to Mitscherlich† no product can be obtained in this way possessing a constant boiling-point. He considers the liquid which distils over on rectification as a mixture of different carbo-hydrogens of similar composition, and suspects that it contains benzole.

Finally, Gerhardt and Cahours‡ have stated that a mixture of 1 part cinnamic acid and 4 parts baryta, when distilled, gave a product having a constant boiling-point.

The formula $C_{16}H_8$ was controlled by a determination of the specific gravity of the vapour, and by the analysis of a bromine compound.

The properties described by the last two chemists as belonging to cinnamole (cinnamene), correspond completely with those of styrole. Cinnamole boils, according to Gerhardt and Cahours, at 140° C. It forms with chlorine a fluid, and with bromine a crystalline compound, the latter having the formula $C_{16}H_8Br_2$. With nitric acid it gives rise to a product which appears to be benzoic acid. In one point, however, they differ. Cinnamole does not possess the property of forming by heat an isomeric solid compound. Gerhardt and Cahours do not mention in their memoir anything of this phenomenon, which, if it existed, could not have escaped their observation in the determination of the specific gravity of the vapour. This determination could not in reality have been made at the temperature mentioned. Styrole was exposed for three or four hours in an oil-bath to a temperature of 182° C. (the same temperature by which Gerhardt and Cahours made the determination of the specific gravity of the vapour), without, however, being altogether volatilized. There remained constantly a considerable portion of metastyrole behind.

To obtain accurate results on this point, we prepared cinnamole by means of lime and baryta. With respect to the action of the lime, we obtained the same results as Mitscherlich. The distilled product is a mixture of different bodies.

* *Arch. der Pharm.*, 2 Reihe, Bd. xx. S. 167.

† *Monatsbericht der Ber. Acad. u. Lerb.* 4 Auf. Bd. i. S. 179.

‡ *Ann. de Chim. et de Phys.*, 3rd ser. t. i. p. 60, and *Ann. der Chem. u. Pharm.* Bd. xxxviii. S. 96.

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His suspicion of the presence of benzole we found to be also correct. The body described by Herzog under the name of cinnamole was evidently benzole mixed with traces of other materials. The boiling-point and specific gravity given by him are in themselves sufficient evidence. By distilling a considerable portion of cinnamic acid with lime we easily obtained proof of this identity in the following manner:—The rectified product was submitted again to an interrupted distillation. The oil which passes over under 100° C. was collected by itself, and after treatment with fuming nitric acid, was then exposed to the action of a reducing agent. Aniline was thus obtained, which is easily recognised by its characteristic properties.

It was probable that the portion of fluid which boils at a higher temperature contained cinnamole. We endeavoured by interrupted distillations to separate it, but could not obtain any liquid having a constant boiling-point. The thermometer rose at last above 200° . The portion distilled at 140° formed with bromine a white crystalline mass, which in appearance and smell possessed the most striking similarity to bromostyrole. This crystalline compound was probably *bromocinnamole*, as no styrole could be supposed to exist in it, no trace of residue being left in repeated distillations.

Cinnamole obtained, according to Gerhardt and Cahours' plan, by distilling cinnamic acid with baryta, proved, after rectification, a colourless fluid, which in point of smell was very similar to styrole, though the former was rather more agreeable than the latter. With bromine it forms a crystalline compound having very much the appearance of bromostyrole. Unfortunately a sufficient quantity was not obtained to determine the boiling-point.

As a further point of comparison, a portion of the product (prepared from lime and cinnamic acid), distilled at 140° , was sealed up in a strong tube. Another tube was filled with the oil made according to the plan of Gerhardt and Cahours, and several others with styrole. All these tubes were placed in an oil-bath heated to 200° C. After half an hour the bath was allowed to cool and the tubes removed, when the styrole was found to have become solid, whilst the substances prepared from cinnamic acid by lime and baryta had lost nothing of their fluidity.

This experiment appears at first sight to negative the idea of the identity of the two substances. When, however, it is considered that the product obtained on distilling cinnamic acid and lime contains other bodies besides cinnamole, and that the substance prepared from baryta and the same acid

was in too small a quantity to be more closely investigated, it is evident that the solution of this question must be reserved for future investigations.

Should these prove in an unequivocal way the difference of the two bodies, it would be of great interest to ascertain from what material styrole has its origin. For this purpose it would be in the first place particularly important to gain some information about the source from which *Styrax liquidus* is obtained. The only authentic information we possess on this point is given by Martius*, namely, that it is introduced through Suez and Trieste, is named by the East Indians *Cotter Mija*, and is produced from a tree called *Rosa Mallas*. From this tree two products are, according to Martius, obtained, the one, the common *Styrax liquidus*, through a sort of distillation; the other a balsam, which is very rarely to be met with in commerce. An investigation of the latter would be of great interest.

Postscript.

The preceding memoir was finished in its principal points when the investigation of the products of distillation of dragon's blood by Glenard and Boudault† appeared.

A short notice of this subject had been earlier laid before the French Academy‡. What was then stated, however, did not lead us to suspect in the slightest degree that the products obtained by distillation from dragon's blood could stand in any relation to our investigation of fluid storax. Their late memoir, which contains many essential corrections of the former communication, showed us at first sight the connection between it and our investigation. Messrs. Glenard and Boudault having communicated some striking results, not easily to be understood, it appears to us not to be without interest to conclude this memoir with a few remarks on the investigation of the French chemists, as our experiments furnish a key to their difficulties.

Glenard and Boudault, by distilling dragon's blood, obtained, in addition to water and some acetone and benzoic acid, a reddish-brown oily fluid, which is a mixture of different bodies. From this they isolated two carbo-hydrogens, which they named dracyl and draconyl.

For their preparation the raw oil was submitted anew to distillation, and the product, distilled at 180° C., was collected by itself; it contains dracyl and draconyl. To separate them,

* *Briefliche Mittheilung.*

† *Journ. de Pharm. et de Chem.* 3me ser. t. vi. p. 250.

‡ *Ibid.* t. i p. 274, and *Ann. der Chem. u. Pharm.* Bd. xlvi. S. 343.

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the mixture must be several times distilled at a low temperature, never reaching the boiling-point. What passes over is a colourless fluid, and consists of dracyl, with a small quantity of draconyl; the solid residue in the retort is entirely draconyl.

To free the dracyl from the draconyl, "*which passes over dissolved in the vapour of the former,*" it must, according to Glenard and Boudault, be several times distilled over hydrate of potash. The potash appears here to form no combination with the draconyl, "*but only to modify it in such a way that it is no longer soluble in dracyl.*" The draconyl remaining in the retort is to be washed with alcohol to remove the dracyl and then heated to 150° C., by which the last traces of dracyl are driven off.

Pure draconyl is, according to these chemists, a colourless mass of a shining appearance; insoluble in water, alcohol, æther and potash-ley, but soluble by heat in fat and æthereal oils.

Draconyl is not volatile, but by aid of another carbo-hydrogen it can be distilled. (Il n'est point volatile; toutefois, il peut distiller à la faveur d'un autre hydrogène carboné.)

From the analysis of Glenard and Boudault, draconyl contains two equivalents of carbon to one of hydrogen. The formula found for the substance obtained by the action of nitric acid on draconyl, and for which they proposed the name nitrodraconyl, was $C_{14}H_6NO_4$. This gives for draconyl $C_{14}H_7$. That substance sealed up in a tube and heated to a high temperature is converted into a yellow fluid, which boils at 140° C., and has the same composition as draconyl itself. Thus far are the details given by Glenard and Boudault. On comparing the results of these chemists with ours, it is at once seen that *metastyrole and draconyl are identical*. A satisfactory explanation is immediately found for some things in their memoir otherwise incomprehensible. We cannot, for instance, understand how a body with the properties given it, and totally devoid of volatility, can distil by the aid of another carbo-hydrogen. In boracic acid, indeed, we possess a body in itself completely fixed, but which volatilizes in not inconsiderable quantities with the vapour of boiling water; still this quantity is but a trace in comparison with the amount of the watery vapour. Our experiments however explain quite easily this difficulty. *Draconyl (metastyrole) exists in the corresponding product of the distillation of dragon's blood, not as such, but in the form of styrole.* After the distillation only is this styrole changed into metastyrole (draconyl). It is not easily understood why the mixture must be repeatedly distilled to obtain draconyl,

and why the distilled dracyl obstinately retains a small portion of draconyl (that is, in this case styrole), which can only be removed by continued heating with hydrate of potash. The hydrate of potash is here really unessential, the separation being produced by the action of the heat alone. The most certain and complete mode of separation would be to seal up the mixture in a strong tube of glass, and heat it for an hour at 200° C. in an oil-bath. On opening the tube, the dracyl could be directly distilled from the metastyrole (draconyl).

Although, on making a comparison of the two bodies, there can be no doubt of their identity, it appeared desirable to substantiate the assertion by direct experiment. The point would be settled could there be obtained from dragon's blood styrole or any of its compounds. We are indebted to Dr. J. S. Muspratt for a quantity of the oil collected at 180° C. in the rectification of the raw product. On submitting this to a new distillation, dracyl alone at first passes over; then a mixture of dracyl and styrole, and finally almost pure styrole shortly before the metastyrole (draconyl) is formed in the retort. With bromine it forms a crystalline body, possessing all the properties of bromostyrole. Much weight however was not to be attached to this reaction, as it was found that dracyl also formed with bromine a compound which crystallized in beautiful needles. To decide the point, a quantity of the fluid was sealed in a strong tube and heated in an oil-bath to 200° C. On withdrawing it at the end of an hour, the contents were not quite solid, but the original light, moveable fluid was converted into a jelly of tenacious consistency, which, on allowing the tube to cool, could scarcely be moved. The styrole had evidently contained a small quantity of dracyl.

The appearance of styrole in the products of distillation of storax and dragon's blood brings these two substances into close relation with each other; probably they both contain the same, or a similar principle, which by distillation is decomposed in a similar manner. Its isolation would be of great interest. For this purpose however the analysis of the resins must be conducted in a different manner than has hitherto been the case. Cinnamic acid has not as yet been observed in dragon's blood.
