XLIV.—*α-Hydrindone and its Derivatives.* Part I.

By F. STANLEY KIPPING, Ph.D., D.Sc.

DURING the investigation of the hydrocarbon, truxene, an account of which has been recently published (this vol., 269), it became desirable to prepare a considerable quantity of *α*-hydrindone (*α*-ketohydrindene) to study its condensation products. At that time, however, the only recorded methods by which this ketone had been obtained were, (1) the hydrolysis of ethylic orthocyanobenzylacetate (Gabriel and Hausmann, *Ber.*, **22**, 2019),

and (2) the distillation of orthocarboxyhydrocinnamic acid or of its calcium salt (*König. Inaug. Diss.*, Leipzig, 1889).

Although of importance from a theoretical standpoint, these reactions were, nevertheless, unsatisfactory when regarded as methods of preparation, as in both cases the necessary materials could only be procured after considerable expenditure of time and trouble; this consideration, and the desirability of facilitating the study of hydrindone derivatives in general, led the author to attempt the preparation of the ketone in some simpler manner, with the results which are now to be described.

A survey of the recent rapid development of our knowledge of the derivatives of hydrindene and of indene, lengthy as it would necessarily be, does not lie within the scope of this paper, so that in dealing with the literature, reference will be made only to those papers which immediately concern the present work. In this category must be classed that of v. Miller and Rohde (*Ber.*, **23**, 1887), who have shown that many of the substitution derivatives of phenylpropionic acid, $\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$, such as the meta- and para-halogen derivatives, and of *α*-methylphenylpropionic acid, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{COOH}$, may be converted into the corresponding derivatives of hydrindone with the aid of concentrated sulphuric acid, just as certain substitution products of cinnamic acid may be converted into the corresponding derivatives of indone (*α*-ketoindene), as first shown by Roser (*Ber.*, **20**, 1273; *Annalen*, **247**, 129).

On attempting to apply this reaction to the preparation of *α*-hydrindone, v. Miller and Rohde were unsuccessful; on heating phenylpro-

pionic acid with sulphuric acid at 140° they got a small quantity of a substance melting at about 134° , the nature of which was not determined, but they were unable to obtain hydrindone. This result is, at first sight, rather remarkable, as there is no apparent reason why the presence of some substituting atom or group should have such a marked influence on ring formation. Although it recalls the failure of Fittig and Erdmann to convert cinnamic acid into indone (*Annalen*, **216**, 179), and also the wide difference in behaviour between this acid and some of its substitution derivatives as regards their condensation to indone derivatives, the two cases can hardly be quoted as analogous, because, in the latter, stereochemical isomerism may play an important part, as already suggested by Roser and others. It is not impossible, however, that hydrindone is actually produced under the conditions observed by v. Miller and Rohde; if it were formed, it would, doubtless, rapidly undergo condensation, and the substance melting at about 134° , may be identical with the condensation product described later, in which case the formation of the ketone would be proved.

As, from v. Miller and Rohde's experience, and from the results of observations made by the author on the behaviour of phenylpropionic acid with phosphoric anhydride, there were grounds for doubting the possibility of devising any method of preparing hydrindone by the action of dehydrating agents on the acid in question, experiments were commenced in other directions, and the interaction of phenylpropionic chloride and aluminium chloride was investigated in the hope of obtaining the ketone in accordance with the equation

This work had not been carried very far, and had not led to any very definite results, when the author's attention was directed to a note by Hughes (*Proc.*, **96**, 70), who, at Marsh's suggestion, had attempted to prepare hydrindone in the above-mentioned manner, but without success; having communicated with Marsh, and learnt that he did not intend to continue the work, further experiments were made, and ultimately it was found that, under suitable conditions, the quantity of hydrindone produced by the action in question is so large (namely, about 55—60 per cent. of the theoretical) that the method is eminently suitable for preparing the ketone, and is, in fact, the best which is at present known. The reason that Hughes' experiments failed is not far to seek; in this, as in very many other cases in which aluminium chloride is used, all depends on the conditions, and a slight alteration in the temperature, in the solvent, or in the relative quantities of the several substances may reduce the yield of the desired product to the vanishing point.

Having now at command a considerable quantity of hydrindone, and having established its identity with the ketone described by Gabriel and Hausmann, and by König, its condensation products and a number of its derivatives were investigated. As regards the readiness with which it undergoes condensation, α -hydrindone seems to resemble $\alpha\alpha$ -diketohydrindene (W. Wislicenus, *Annalen*, **246**, 347; W. Wislicenus and Kötze, *ibid.*, **252**, 72, and W. Wislicenus and Reitzenstein, *ibid.*, **277**, 362) far more closely than its isomeride, β -hydrindone, $\text{C}_6\text{H}_4\langle\text{CH}_2\text{CH}_2\rangle\text{CO}$ (Benedikt, *Annalen*, **275**, 351; Schad, *Ber.*, **26**, 222), of which no condensation products have yet been described. This is clearly shown by the ease with which α -hydrindone is converted into "anhydrobishydrindone" (p. 495) on treatment with boiling, moderately dilute, sulphuric acid, just as the $\alpha\alpha$ -diketo-compound is converted into "anhydrobisdiketohydrindene" by boiling water; as, moreover, the similarity doubtless extends to the constitutions of the two products, "anhydrobishydrindone" may be represented by the formula (I), which corresponds with that (II) assigned by Wislicenus and his co-workers to the substance obtained from diketohydrindene.

It is also noteworthy that both these dimolecular condensation products are capable of undergoing further condensation, "anhydrobishydrindone" yielding the hydrocarbon, truxene, as already shown, whereas "anhydrobisdiketohydrindene" gives two products, one of which is red, the other yellow (Wislicenus and Reitzenstein, *loc. cit.*); the former has the composition $(\text{C}_9\text{H}_4\text{O})_n$, but no views as to its constitution are put forward; the yellow compound, which is formed in small quantity only, was not analysed, and its properties are not described, so that it would seem rash to suggest its identity with "tribenzoylenebenzene" (Trans., *loc. cit.*), although such a surmise seems to have some foundation in the great similarity of the dimolecular condensation products.

There is, however, a marked difference in the behaviour of "anhydrobishydrindone" and "anhydrobisdiketohydrindene" with respect to their capability of forming metallic derivatives; whereas the latter dissolves in alkalis affording a red liquid, and forms stable compounds, the former is insoluble, gives no coloration, and is apparently incapable of forming metallic derivatives; this difference, nevertheless, is in accordance with the above constitutional formulæ, to which, in consequence, it affords some support.

The less important hydrindone derivatives which have been pre-

pared require no special mention here, but one other point of interest may be referred to, and that is the conversion of hydrindone oxime into hydrocarbostyryl (p. 489). The formation of a substituted amide from an oxime, in accordance with the equation $\text{R} \cdot \text{C}(\text{NOH}) \cdot \text{R}' = \text{R} \cdot \text{CO} \cdot \text{NH} \cdot \text{R}'$ or $\text{R} \cdot \text{NH} \cdot \text{CO} \cdot \text{R}'$, has been shown to occur in so many instances, and in the case of compounds so widely different in constitution, that the action may now be regarded as general; hitherto, however, it has been applied almost exclusively in the case of oximes of open-chain ketones, and the study of the behaviour of cycloid compounds, under similar conditions, has, to a great extent, been neglected. The oxime of camphor, one of the few closed-chain compounds which has been investigated in this direction, does not undergo intramolecular change on treatment with acetic chloride, sulphuric acid, phosphorus pentachloride, &c., but yields the well-known substance, campholenonitrile; menthonoxime (Beckmann, *Annalen*, **250**, 322; Wallach, *Annalen*, **277**, 154), carvoxime (Golschmidt and Kisser, *Ber.*, **20**, 2078), thujonoxime (Wallach, *loc. cit.*), and other compounds of this class yield isomerides of unknown constitution, whereas isonitroso-camphor appears to undergo the normal intramolecular change as shown by its conversion into camphorimide (Angelo, *Ber.*, **26**, 59, and Manasse, *ibid.*, 241). The only case, in fact, in which the oxime of a cycloid ketone of known constitution has been transformed into a substituted amide appears to be that of phenanthraquinonemonoxime, which, as Wegerhoff has shown (*Ber.*, **21**, 2355, *Annalen*, **252**, 1), is converted into diphenimide, the closed chain of 6 carbon atoms becoming one of 7 atoms by the introduction of an imido-group.

It was, therefore, a matter of considerable interest to study the behaviour of hydrindone oxime, as it appeared probable that it might be made to undergo intramolecular change into hydrocarbostyryl or ketotetrahydroisoquinoline.

The desired result was accomplished with the aid of phosphorus pentachloride, the oxime being transformed into a substance which had the properties of hydrocarbostyryl, and which was proved to be that compound by an examination of its crystallographic character. It is possible, therefore, to introduce an imido-group into a closed

chain of five carbon atoms, and thus to form one containing six atoms, a process which recalls the conversion of pyrroline into pyridine derivatives, but which is more closely analogous to the production of hydroquinoline derivatives from those of indole (E. Fischer and Steche, *Ber.*, **20**, 818, 2199; *Annalen*, **242**, 348).

Methyl lindole.

Dimethyltetrahydroquinoline.

Phenylpropionic Chloride, $\text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COCl}$.

A description of the preparation of phenylpropionic acid (hydrocinnamic acid) by the reduction of cinnamic acid with sodium amalgam is unnecessary, as the operation is simple and the yield almost quantitative; in preparing the acid chloride, however, attention to certain details is imperative in order to obtain a good yield, so that the following account may not be without value:—The theoretical quantity (69 grams) of phosphorus pentachloride is gradually added to dry phenylpropionic acid (50 grams), contained in a large flask, care being taken not to add it too quickly, as the rapid evolution of hydrogen chloride causes a brisk effervescence; as a rule, the whole of the pentachloride is acted on after a very short time, but if this be not the case, the mixture, which is already warm, is gently heated on a water bath until a homogeneous yellow liquid is obtained. A large proportion of the phosphorus oxychloride may now be distilled off under ordinary atmospheric pressure, but as the liquid darkens considerably during this operation, it is better to carry out the whole of the distillation under reduced pressure; as soon as most of the oxychloride has passed over, the remaining oil is fractionated under a pressure of not more than about 35 mm. Under these conditions the phenylpropionic chloride passes over colourless, leaving only a trace of brown residue; the yield is about 95 per cent. of the theoretical. On the other hand, if the pressure be too high, a large quantity of a thick black tar will remain in the distilling flask, and the yield consequently diminished. Phenylpropionic chloride is a colourless, mobile, disagreeably smelling liquid, and has all the ordinary properties of an acid chloride; it boils at 125–136° under a pressure of about 33 mm., and at 154–155° under a pressure of about 75 mm.; the pure substance does not appreciably decompose even when distilled under a pressure exceeding 75 mm.

Preparation of Hydrindone from Phenylpropionic Chloride.

A great many experiments have been made in order to determine the conditions under which the action expressed by the equation

may be best brought about without the occurrence of secondary changes; the following is the method finally adopted. Phenylpropionic chloride (25 grams), prepared and purified in the manner described, is dissolved in petroleum (40 grams) boiling at 60–70°, and anhydrous aluminium chloride (25 grams) added to the solution; the flask is then connected with a reflux condenser and gently heated on a water bath, shaking from time to time, until the liquid begins to boil and a rapid effervescence sets in owing to the evolution of hydrogen chloride. The flask is now taken off the water bath (but without disconnecting it from the condenser) and placed on a cloth until the evolution of gas shows signs of abating; it is then replaced on the water bath and heated until a vigorous action again sets in. These two operations are repeated alternately, the flask being vigorously shaken; two experiments may conveniently be made simultaneously, the one flask being heated and shaken while the other is on the cloth, so that the whole of the operator's attention is occupied. After the action has proceeded for a short time, the solution turns brown, the aluminium chloride disappears, and the previously homogeneous liquid separates into two layers, the lower of which becomes very thick and dark brown, whilst the petroleum is but slightly coloured; at the expiration of 20 to 30 minutes the evolution of hydrogen chloride suddenly slackens, although it does not cease completely, and the operation is then at an end.

When quite cold, the contents of the flask are carefully treated with water in the usual way, whereupon the brown, tarry liquid below the petroleum gradually changes into a pale, yellow, semi-solid, or pasty mass; this substance is probably some additive compound of hydrindone and aluminium chloride, and seems to be fairly stable in presence of water; when, however, the mixture is heated on a water bath the yellowish substance undergoes decomposition, and is converted into a brown oil, which dissolves in the petroleum. This preliminary heating is by no means necessary, and the product may be at once submitted to distillation in a current of steam; the petroleum, which passes over during the first few minutes, and which contains very little hydrindone, may be collected separately, and the ketone which afterwards collects in the receiver as an oil, but which solidifies readily on cooling and adding a crystal of the pure compound, may then be separated by filtration; as, however, the compact crystals of the ketone are not easily dried, it is better not to change the receiver, but to continue the distillation as long as oil passes over, and then to separate the petroleum solution of the hydrindone. This solution is washed with dilute sodium carbonate to extract small quantities of phenylpropionic acid (which is thus recovered), dried with calcium chloride, and the petroleum distilled off on a water bath; the oily

residue is slightly yellow, but consists of practically pure hydrindone, and on cooling solidifies to a mass of almost colourless crystals, which are freed from petroleum by exposure to the air.

The quantity of hydrindone obtained from 25 grams of phenylpropionic chloride is usually about 11 grams, or 55—60 per cent. of the theoretical, no account being taken of the small quantity (0.5—3 grams) of the acid which is recovered; in some experiments the yield was as much as 75 per cent. of the theoretical, but such a result can only be attained after some practice, as a slight change in the conditions influences the course of the action to a very great extent. If, for example, the heating be too long continued, only traces of the ketone may be obtained, the principal product being a thick, brown oil, which is not volatile with steam; the nature of the solvent has also considerable influence, depending doubtless on its boiling point, for if carbon bisulphide be employed instead of light petroleum, a yellowish, granular powder will be formed, and but little, if any, hydrindone. A few experiments were made, using anhydrous ferric chloride in the place of the aluminum compound, but they were not successful, the chief product being a dark brown oil which did not distil in steam.

Phenylchloropropylenehydrindone, $C_6H_5O \cdot CCl \cdot CH \cdot CH_2 \cdot C_6H_5$.

After separating the hydrindone by steam distillation, there remains in the flask a dark brown, very thick oil, which consists partly of phenylpropionic acid, partly of some aluminium compound. If this oil is separated by filtration, washed with water, and dissolved in cold alcohol, the filtered solution, on evaporation at ordinary temperatures, yields brown, rosette-like crystals, which, however, do not melt sharply even after several recrystallisations, and which are decomposed by caustic soda, yielding a ketone. alumina passing into solution. As the investigation of this aluminium compound was of little interest, the crude oil was dissolved in ether, the solution shaken with soda to extract the phenylpropionic acid and decompose the aluminium compound, and the dried ethereal solution evaporated; the brown, oily residue was then repeatedly extracted with boiling petroleum, and the solutions allowed to evaporate at the ordinary temperature, the yellowish crystals which were deposited being subsequently recrystallised from the same solvent, but with the addition of a little ethylic acetate.

The substance obtained in this way crystallised in lustrous, colourless plates, and melted at 81—82°; it dissolved freely in all ordinary solvents with the exception of light petroleum, in which it was only sparingly soluble; its solution in acetic acid decolorised potassium permanganate at ordinary temperatures.

It contained chlorine, and, on analysis, gave results pointing to the formula $C_{18}H_{15}ClO$.

0.1540 gave 0.4324 CO_2 and 0.0763 H_2O ; $C = 76.57$; $H = 5.50$.

0.2111 „ 0.1036 $AgCl$; $Cl = 12.14$.

$C_{18}H_{15}ClO$ requires $C = 76.48$; $H = 5.31$; $Cl = 12.56$ per cent.

Taking into consideration its origin and its composition, and the fact that it is a ketone (as shown by the production of the oxime described later), it appeared probable that the formation of this product was due, in the first place, to the interaction of phenylpropionic chloride and hydrindone in presence of aluminium chloride; assuming that this action took a normal course, it would give a substance of the composition, $C_9H_7O \cdot CO \cdot CH_2 \cdot CH_2 \cdot C_6H_5$, which, after undergoing tautomeric change into $C_9H_7O \cdot C(OH) : CH \cdot CH_2 \cdot C_6H_5$, might be converted into a chloroketone of the constitution

by the action of the hydrogen chloride which is generated during the formation of hydrindone.

In order to test the accuracy of this view, and to obtain some clue to the constitution of the bye-product, a small quantity of the pure compound was boiled with dilute nitric acid until the whole of the oil was oxidised and ruddy fumes ceased to be evolved; after evaporating to dryness and repeatedly taking up with water to get rid of the nitric acid, a yellowish, solid oxidation product remained, which, when heated gently between watch-glasses, sublimed readily in slender, colourless needles. These crystals melted at 128° , had the characteristic appearance of phthalic anhydride, and, after being dissolved in warm caustic soda and reprecipitated with hydrochloric acid, yielded a substance which had the properties of phthalic acid.

This result shows that the compound in question has not been produced by the substitution of a phenylpropionyl group,

for hydrogen in the benzene nucleus of hydrindone, that is to say, it is not derived from a compound of the constitution

because, if it had been, the oxidation products would have been benzoic acid and a tricarboxy-derivative of benzene; it is probable, therefore, that the chloroketone has the constitution

although the evidence is insufficient to allow of any definite conclusion being drawn.

The *oxime* of the chloroketone may be prepared in the usual way, the strongly alkaline solution of the several substances in dilute alcohol being kept for some time at ordinary temperatures; on adding water, the product is precipitated in needles which, although apparently free from impurity, do not melt at all sharply, and possibly consist of a mixture of stereoisomeric oximes. After repeated crystallisation, first from alcohol and then from a mixture of petroleum and ethylic acetate, a homogeneous substance is obtained, and analysis showed it to be the oxime of the ketone described above.

0.1376 gave 0.3658 CO_2 and 0.0679 H_2O ; $\text{C} = 72.5$; $\text{H} = 5.5$.

$\text{C}_{15}\text{H}_{15}\text{Cl}\cdot\text{NOH}$ requires $\text{C} = 72.6$; $\text{H} = 5.3$ per cent.

This oxime crystallises in long, colourless needles, or prisms melting, and apparently undergoing slight decomposition, at $163\text{--}164^\circ$; it is readily soluble in ether, ethylic acetate, and alcohol, but only moderately so in boiling, light petroleum, and insoluble, or nearly so, in cold, concentrated hydrochloric acid.

α -Hydrindone or α -Ketohydrindene, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CH}_2 \\ \text{CO} \end{smallmatrix}\rangle\text{CH}_2$.

The hydrindone prepared from phenylpropionic chloride is identical with the compound obtained by Gabriel and Hausmann from ethylic orthocyanobenzylacetate (*loc. cit.*), and by König from orthocarboxyhydrocinnamic acid (*loc. cit.*), as is proved not only by a comparison of the ordinary properties of the several preparations, but also by the fact that they yield identical derivatives with hydroxylamine and phenylhydrazine; as, therefore, it is unnecessary to mention those properties which have already been described, a brief statement of a few facts which have not yet been recorded will suffice.

In spite of its low melting point, which the author found to be $40\text{--}41^\circ$ (Gabriel and Hausmann give 40° , König gives $40\text{--}41^\circ$), hydrindone may be easily crystallised from light petroleum, from which it separates in irregular, transparent plates; it may also be recrystallised from water, but as it is only sparingly soluble in it, petroleum is to be preferred; it is less soluble in water containing sodium carbonate and other salts than in pure water. The manner in which hydrindone solidifies is highly characteristic, large, well-defined four-sided plates are formed at the surface of the liquid, and then gradually become merged in a mass of smaller irregular crystals.

Perhaps the most characteristic property of hydrindone is the readiness with which it undergoes condensation, either alone or with aldehydes and ketones, such as benzaldehyde and acetone; if boiled

with moderately dilute sulphuric acid, it yields the condensation product, "anhydrobishydrindone," described later, whereas, when heated with phosphoric anhydride or with concentrated hydrochloric acid, and also when treated in many other ways, it is converted into the hydrocarbon, truxene (*loc. cit.*).

Dr. Perkin very kindly measured the magnetic rotation of hydrindone for the author, as it seemed of interest to compare the results with those obtained in the case of hydrindene (W. H. Perkin, jun., this vol., 228). The following is an account of his observations.

" α -Hydrindone.

"Density.

$d_{45^\circ/45^\circ}$ 1.1011.	$d_{50^\circ/50^\circ}$ 1.0993.	$d_{55^\circ/55^\circ}$ 1.0977.
$d_{60^\circ/60^\circ}$ 1.0962.	$d_{65^\circ/65^\circ}$ 1.0947.	$d_{70^\circ/70^\circ}$ 1.0934.
$d_{75^\circ/75^\circ}$ 1.0921.	$d_{80^\circ/80^\circ}$ 1.0908.	

"Magnetic Rotation of Fused Substance.

<i>t.</i>	Sp. rotation.	Mol. rotation.
50.1°	2.0473	13.657

"Up to the present no compound absolutely analogous to hydrindone has been examined. The nearest to it is hydrindene, from which it differs in containing CO in place of CH₂ in the $\langle \text{CH}_2 \rangle \text{CH}_2$ group. In the following series—to which this group is closely allied—this would cause a difference of rotation of about -0.247 (Trans., 1882, 41, 573), and on comparing the rotation of these two compounds they are found to vary by this amount.

	Mol. rotation.	Diff.
"Hydrindene.....	13.904	} 0.247.
Hydrindone.....	13.657	

"The rotation of hydrindone being made at 50.1° gives a result which would be a little lower at the temperature at which the hydrindene was examined, namely, 19.25°, and this, if allowed for, would make the above difference not quite so large, but would not be enough to affect it greatly. These results, therefore, go to confirm the relationship of these two compounds."

Hydrindone Oxime, and its Conversion into Hydrocarbostyryl.

The preparation of hydrindone oxime was undertaken partly to ascertain if the ketone was identical with the α -hydrindone of Hausmann and König, but more particularly in order to investigate its behaviour with acetic chloride, sulphuric acid, &c. The compound in question is easily obtained by warming an aqueous alcoholic solution

of the ketone with hydroxylamine hydrochloride and excess of potash, for about 15 minutes; water is then added in considerable quantity, and, after cooling, the crystalline product is separated by filtration and recrystallised from hot, dilute alcohol; it then melts at about 140° , but after having been crystallised two or three times from a mixture of chloroform and light petroleum, its melting point rises to and becomes constant at $143\text{--}144^{\circ}$ (König gives $144\text{--}144.5^{\circ}$ and Hausmann 146°).

0.1694 gave 0.4562 CO_2 and 0.0954 H_2O ; $\text{C} = 73.4$; $\text{H} = 6.2$.

0.2079 gave 18.2 c.c. moist nitrogen at 23° and 760; $\text{N} = 9.9$.

$\text{C}_9\text{H}_9\text{NO}$ requires $\text{C} = 73.5$; $\text{H} = 6.1$; $\text{N} = 9.5$ per cent.

The ordinary properties of the oxime having already been placed on record by Hausmann and König, the method of converting it into hydrocarbostyryl may now be described. In the first place, experiments were made with sulphuric acid, but without success; on heating a solution of the oxime in the concentrated acid for some time at 100° , no change took place, and the compound obtained on subsequently adding water and dilute sodium carbonate, melted at $143\text{--}144^{\circ}$, and had all the properties of the original oxime. Acetic chloride was then tried, the dry oxime being treated with a considerable excess of this liquid at the ordinary temperature; slight development of heat occurred and the crystals became opaque, owing to the formation of the hydrochloride, but very little further action took place. On warming gently, however, the crystals slowly dissolved, and hydrogen chloride was evolved, owing to the formation of an *acetyl*-derivative; the latter was isolated by evaporating the solution almost to dryness and then adding a little light petroleum, when it was precipitated in colourless needles, which after recrystallisation from light petroleum melted at $84.5\text{--}85.5^{\circ}$; it was readily soluble in all the ordinary solvents, and, when boiled with alcoholic potash for a short time, it was converted into the oxime, melting at $143\text{--}144^{\circ}$, and not into the desired isomeride.

These experiments having failed, it became necessary to try phosphorus pentachloride; as, however, an almost explosive action occurred when the two solid substances were brought together, the oxime was dissolved in dry ether and a molecular proportion of the pentachloride added in small portions at a time. A fairly vigorous action, which necessitated cooling, set in, and a colourless powder separated from the solution in large quantities; this substance, however, contained chlorine and was doubtless the hydrochloride of the oxime, as it gave an immediate precipitate with silver nitrate, and was converted into the oxime on treatment with sodium carbonate. The mixture was, therefore, heated on a water bath for about 6 hours,

during which time traces of hydrogen chloride seemed to pass off, but otherwise no visible change occurred; a quantity of pentachloride equal to that already taken was then added, and the mixture again heated on the water bath for about two hours, when the greater part of the solid had dissolved, and the solution had become pink. After cooling, water was added, the ethereal solution separated with the aid of a funnel, and the residue, A, extracted two or three times with ether. This ethereal solution, which had the colour of dilute potassium permanganate, was washed with water, dried, and the ether evaporated, when a dark brownish-pink oil was left; this, on being submitted to distillation in a current of steam, was resolved into a pale-yellow, volatile oil, and a crystalline, non-volatile substance, which was deposited in pink crystals on filtering the hot, aqueous solution which remained in the distilling flask.

This crystalline product was purified by recrystallisation from alcohol and ether, dried at 100° , and analysed.

0.1536 gave 0.4126 CO_2 and 0.0874 H_2O ; $\text{C} = 73.3$, $\text{H} = 6.3$.

$\text{C}_9\text{H}_9\text{NO}$ requires $\text{C} = 73.5$; $\text{H} = 6.1$ per cent.

This result, taken in conjunction with the fact that the compound melted at 163° , which is the melting point of hydrocarbostyryl, indicated its identity with the last-named substance, and this view was confirmed by an examination of its properties; it was readily soluble in alcohol, ether, and hot concentrated hydrochloric acid, and crystallised from these solvents in well-defined prisms. Notwithstanding this agreement in properties, the question of identity could hardly be considered as satisfactorily established, since it was quite possible that the compound melting at 163° might be a stereochemical isomeride of hydrindone oxime, which, were it known, would probably crystallise unchanged from hydrochloric acid, and be soluble in the above mentioned liquids; for this reason, the following crystallographic examination, for which I am indebted to Mr. W. J. Pope, was necessary to settle the matter beyond doubt.

"Hydrocarbostyryl has been examined crystallographically by Bäckström (Groth's *Zeit. f. Krys.*, **17**, 427); the crystals are orthorhombic, with the axial ratio $a : b : c = 0.5980 : 1 : 0.6043$, and exhibit the forms $\{110\}$, $\{011\}$, sometimes also the pinakoid $\{001\}$. This description holds for the hydrocarbostyryl obtained by Dr. Kipping; on crystallising the substance from alcohol on a microscope slide, crystals were obtained in which the form $c\{001\}$ is the predominant one; the angle between the traces of the planes (110) and $(1\bar{1}0)$ on (001) was measured under the microscope and the axial ratio $a : b = \cotan. \frac{110 : 1\bar{1}0}{2}$ was found to be 0.5961, a number agreeing well with that

given by Backstrom, considering the large error to which microscopic measurements of angles are unavoidably liable.

"The angles $110:1\bar{1}0$ and $011:0\bar{1}1$ were also measured on large crystals, deposited from a solution in dilute methyl alcohol, and agreed well with the measurements given by Backstrom. The crystals obtained by the latter possessed a very good cleavage parallel to the basal pinakoid $\{001\}$; this observation, however, was not confirmed, the crystals obtained by Dr. Kipping showing only a poor conchoidal cleavage parallel to $\{001\}$. The optic axial plane is (100) , and (001) is normal to the acute bisectrix; the optic axes were seen emerging through this latter face. Although the optic axial angle could not be measured through a cleavage plate, the close agreement of these crystals with those examined by Backstrom, both in geometrical and optical properties, leaves no doubt that the substance in question is hydrocarbostyryl."

The quantity of hydrocarbostyryl obtained in the manner described above was very small (less than 10 per cent. of the theoretical), because the greater portion of this product remained in the strongly acid aqueous solution, A, which had been extracted with ether; when this solution was rendered strongly alkaline with soda, a considerable quantity of a dark-green oil, B, having a basic odour, was precipitated, but on acidifying again with dilute sulphuric acid the oil was partly redissolved. The portion insoluble in weak acid was extracted with ether and chloroform, the dried extract filtered from traces of some phosphorus compound, and evaporated; ether was then added to the oily residue, the solution filtered from a dark-green, semi-solid precipitate and allowed to evaporate. In this way, a second and rather larger crop of hydrocarbostyryl was obtained, but it did not crystallise very readily owing to the presence of oily impurity.

The various bye-products formed in the above reactions were not further investigated, except in so far that the substance to which the odour of the green oil, B, was due, was proved to be a primary amine by means of the carbylamine reaction.

Isonitrosohydrindone may be prepared by slowly adding a concentrated aqueous solution of sodium nitrite to a cold solution of the ketone in glacial acetic acid, any hydrindone which is precipitated being redissolved by adding acetic acid; on afterwards allowing the solution to evaporate at ordinary temperatures, the isonitroso-derivative is deposited in yellowish crystals.

0.1532 gave 11.1 c.c. moist nitrogen at 21° and 757 mm. $N = 8.2$.

$\text{C}_6\text{H}_7\text{NO}_2$ requires $N = 8.7$ per cent.

Isonitrosohydrindone crystallises from boiling benzene in flat needles or prisms, which have a yellowish colour; it turns black at about 200° , when heated moderately slowly, but when the capillary tube is placed in acid at about 210° it melts and decomposes at $218-220^{\circ}$; it is rather sparingly soluble in boiling chloroform, and also in cold alcohol. It dissolves in warm soda, and also in concentrated ammonia, giving yellow solutions, but on acidifying they become colourless; its solution in aqueous alcohol gives only a pale, yellowish-brown coloration with ferric chloride, but, on warming, the colour becomes much more intense, fading away again on cooling; this alternation may be brought about many times.

This compound was first obtained during some experiments on the action of phosphoric anhydride on phenylpropionic acid (this vol., p. 269); the brown mass produced on heating these two substances together at about 180° , having been submitted to distillation in a current of steam, the clear distillate was heated to boiling and a small quantity of phenylhydrazine acetate added, whereupon a yellowish turbidity, which gradually changed on cooling to a crystalline precipitate, was produced. This product was separated by filtration, purified by recrystallisation from hot dilute alcohol, and dried over sulphuric acid; analyses and an examination of its properties proved it to be the hydrazone of α -hydrindone.

0.1720 gave 0.5079 CO_2 and 0.0981 H_2O ; $\text{C} = 80.5$; $\text{H} = 6.3$.

0.1579 „ 0.4669 „ „ 0.0906 „ ; $\text{C} = 80.6$; $\text{H} = 6.4$.

0.2085 „ 23.6 c.c. moist nitrogen at 15° and 755 mm.; $\text{N} = 13.2$.

$\text{C}_{13}\text{H}_{14}\text{N}_2$ requires $\text{C} = 81.1$; $\text{H} = 6.3$; $\text{N} = 12.6$ per cent.

It crystallises from boiling light petroleum, in which it is only sparingly soluble, in very pale yellow plates or prisms, and is readily soluble in most of the ordinary solvents; like many other hydrazones, it slowly undergoes complete decomposition, becoming pink in the first place, on exposure to the air, a fact previously noticed by Hausmann. Various preparations, which had been repeatedly crystallised, sintered together at about 124° , and melted and decomposed at $127-128^{\circ}$, whereas the melting point given by König is $130-131^{\circ}$, and Hausmann simply states that the hydrazone turns brown at 120° and sinters to a brown oil a few degrees above this temperature; it is probable that as the substance is very unstable these differences depend to a great extent on the rate of heating.

The formation of hydrindonehydrazone under the above conditions proves that the ketone may be produced by the direct withdrawal of

water from phenylpropionic acid, so that its non-formation under the conditions employed by v. Miller and Rohde (*loc. cit.*) would seem rather improbable; the yield, however, is very small, and even when the theoretical quantity (1 mol.) of phosphoric anhydride is employed (instead of 2 mols., as in preparing truxene), it is less than 5 per cent. of the acid taken.

On endeavouring to regenerate hydrindone from its hydrazone, by heating the latter for some time with moderately concentrated hydrochloric acid in alcoholic or glacial acetic acid solution, a crystalline substance was deposited on adding water and then cooling; this product, however, was not the desired ketone but a compound of the composition $C_{15}H_{11}N$, as shown by the following analysis.

0.1513 gave 0.4867 CO_2 and 0.0757 H_2O ; C = 87.7; H = 5.56.

0.1965 „ 11.9 c.c. moist nitrogen at 19° and 758 mm.; N = 7.0.

$C_{15}H_{11}N$ requires C = 87.8; H = 5.4; N = 6.8 per cent.

Its formation may, therefore, be expressed by the equation

and it is doubtless identical with the "orthobenzyleneindene" obtained by Hausmann (*loc. cit.*) under similar conditions, as most of its properties were found to be in accordance with his statements; the melting point he gives (235°) is, however, too low as, even when heated moderately slowly, the substance does not melt until the temperature rises to about 245°, although it darkens from about 235° upwards. Here, again, the discrepancy is obviously due to decomposition taking place, the compound having, in fact, no definite melting point; when contained in a capillary tube and plunged into sulphuric acid at 250° it does not immediately liquefy, but rapidly undergoes decomposition into a black oil, part subliming unchanged in colourless, lustrous plates.

No experiments were made to ascertain whether the constitution of this substance is represented by the formula suggested by Hausmann, but molecular weight determinations by the ebullition method in phenol solution gave results which agreed well with those required by a compound of the molecular formula given above (this vol., *loc. cit.*).

The high melting point and the comparatively slight solubility of "orthobenzyleneindene" render it serviceable in the detection of small quantities of hydrindone, the test being carried out as follows: The oil, or the solution, is boiled for a few minutes with a few drops of pure phenylhydrazine and a little glacial acetic acid, and the hydrazone, which is very readily formed, is then precipitated by adding water; if this product be sufficiently pure it will solidify, and may be recrystallised from alcohol and identified in the usual manner, but

if not, it is boiled with concentrated hydrochloric acid until all the oily impurities have volatilised with the steam, and the hydrazone has been converted into orthobenzyleneindene; the last-named compound separates from the acid in crystals, and is easily obtained in a state of purity.

Nitrohydrindone, $C_9H_7O \cdot NO_2$.

The preparation of nitrohydrindone, except in small quantities, is by no means easy, and is not always successful, owing to the fact that if very concentrated acid is employed the reaction sometimes gets beyond control, whereas, when dilute acid is used nitration does not take place very readily. The following description, however, may be given as an approximate statement of suitable conditions. The pure ketone is added in small portions at a time to nitric acid of sp. gr. 1.5, care being taken that the temperature does not rise above about 15°; after keeping for a few minutes, the solution is poured into water, and the mixture left until the nitro-compound, which is precipitated as an oil, has completely solidified. The product is then separated by filtration, well washed with water, and dried in the air, after which it is repeatedly recrystallised from a mixture of chloroform and light petroleum; this operation is attended with considerable difficulty, as, owing to the presence of some impurity, the substance is generally deposited as a brown oil; finally, however, it is obtained in colourless crystals, which consist of the mononitro-derivative, as shown by the following analysis.

0.1591 gave 0.3546 CO_2 and 0.0573 H_2O . C = 60.8; H = 4.0.

$C_9H_7O \cdot NO_2$ requires C = 61.0; H = 3.9 per cent.

Nitrohydrindone crystallises from boiling light petroleum—in which it is only very sparingly soluble—in long, slender needles; it dissolves freely in most other solvents, even in the cold, and, on evaporating the solutions at ordinary temperatures, it is deposited in compact prisms; its melting point is 77–78°.

CONDENSATION PRODUCTS OF α -HYDRINDONE.

The study of the condensation of products of hydrindone was undertaken with the object more especially of determining the constitution of truxene (*loc. cit.*), and it has already been shown that this hydrocarbon may be obtained from the ketone in a great many ways; under certain conditions, however, hydrindone yields what, compared

with truxene, may be regarded as a primary condensation product, the properties of which have not yet been described.

This compound is formed in small quantities when hydrindone is dissolved in ether and treated with phosphorus pentachloride, but the chief product is a colourless oil, which is volatile with steam, and which is probably identical with the dichlorindene described by Hausmann. It is also produced when hydrindone is gently heated with concentrated sulphuric acid for a few minutes and the solution then poured into water; the precipitate consists of a mixture of truxene and the primary condensation product, but the yield is poor.

The best method of preparing the substance in question is by boiling hydrindone for some time with moderately dilute sulphuric acid, and the operation is so simple that a detailed account is unnecessary. It may be noted, however, that when a mixture of equal volumes of the commercial acid and water is employed, the process occupies about 10 minutes, and the product consists of about equal parts of hydrocarbon and primary condensation product; when, on the other hand, more dilute acid is used (say, one volume to two of water), the proportionate quantity of hydrocarbon is considerably smaller, but the operation takes much longer; it is therefore advisable to separate the condensation products from the unchanged hydrindone from time to time with the aid of very dilute alcohol, as in this way the formation of truxene is reduced to a minimum.

The solid mixture finally obtained is boiled with alcohol, the solution filtered from hydrocarbon, and the crystalline substance which is deposited on cooling purified by recrystallisation from alcohol or ethylic acetate.

This condensation product has the molecular formula $C_{18}H_{14}O$, as proved by the analyses and by the results of molecular weight determinations in boiling aniline solution, both of which have been already recorded (this vol., *loc. cit.*); as, therefore, it is formed from 2 mols. of hydrindone with elimination of 1 mol. of water, just as "anhydrobisdiketohydrindene" is produced from diketohydrindene (*loc. cit.*), it may be named "anhydrobishydrindone," and its constitution may be represented by the formula given above or by the tautomeric expression.

"Anhydrobishydrindone" crystallises from alcohol and ethylic acetate in pale yellow needles or prisms, melts at $142-143^{\circ}$, and is readily soluble in most of the ordinary solvents at their boiling points; it is, however, insoluble in, and apparently unchanged by, warm concentrated soda and ammonia, in which respect it differs very markedly from "anhydrobisdiketohydrindene." Its solution in glacial acetic acid decolorises potassium permanganate at ordinary temperatures, but the oxidation product was not examined. Although

according to the above view of its constitution, this condensation product is a ketone, it does not interact readily with hydroxylamine in alkaline alcoholic solution, and, even after heating on the water bath for some time, it is not converted into an oxime; moreover, its behaviour with phenylhydrazine also appears to be abnormal. In both respects further investigation is necessary.

The conversion of "anhydrobishydrindone" into truxene on treatment with moderately dilute sulphuric acid or with phosphoric anhydride has already been described, but hitherto all attempts to resolve it into 2 molecules of hydrindone have been unsuccessful; in one experiment, the compound was boiled with sulphuric acid, diluted with an equal volume of water, and steam passed through the mixture at the same time, but not a trace of hydrindone could be detected in the distillate, although a considerable quantity of truxene was formed. This result affords evidence in support of the dimolecular formula for the hydrocarbon, because, if it had the trimolecular formula, it must be assumed that the "anhydrobishydrindone" is first resolved into 2 molecules of hydrindone, which then undergo condensation in a different manner.

Bromo-derivative of "Anhydrobishydrindone."—"Anhydrobishydrindone" seems to combine directly with bromine, yielding an additive compound, which is unstable at ordinary temperatures, undergoing decomposition into hydrogen bromide and a substance of the composition $C_{15}H_{13}BrO$; the latter is therefore obtained on adding the halogen in molecular proportion to a chloroform solution of "anhydrobishydrindone" and warming the solution, from which a yellowish-brown powder is deposited, until the evolution of gas is at an end; the product is then separated by filtration, washed with hot ethylic acetate, and recrystallised from boiling glacial acetic acid.

0.2612 gave 0.1498 AgBr. $Br = 24.4$.

$C_{15}H_{13}BrO$ requires $Br = 24.6$ per cent.

"Bromanhydrobishydrindone" crystallises in light yellow needles or prisms, which gradually become yellowish-brown on exposure to the air; it is soluble in boiling ether, alcohol, light petroleum, &c., but by no means readily, although it dissolves freely in boiling acetic acid. It has no very definite melting point, but begins to decompose even below 180° ; when the capillary tube containing the substance is placed in sulphuric acid at about 190° , and the temperature quickly raised, the melting or decomposition point is about 194 – 195° .

The constitution of this substance is probably represented by the formula

and of the two, for reasons given below, the former is perhaps the more likely; in either case, it would appear to have little analogy to the bromo-derivative of "anhydrobisdiketohydrindene," which, according to the views of Wislicenus and Reitzenstein (*loc. cit.*), is a product of direct substitution.

The principal object in studying the action of bromine on "anhydrobishydrindone" was to obtain, if possible, a monobromo-derivative, which, like the parent substance, might be caused to lose the elements of water, yielding a brominated hydrocarbon of the constitution $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C}=\text{C}-\text{CHBr} \\ | \quad | \\ \text{CH}_2-\text{C}=\text{C}-\text{C}_6\text{H}_4 \end{array}$; if, then, this product were found to be a monobromo-derivative of truxene, the molecular formula of the hydrocarbon might have been deduced with tolerable certainty. For this reason, and in spite of the fact that there were grounds for doubting that the bromo-compound had been formed by direct substitution, many attempts were made to bring about its intramolecular condensation, and to obtain a substance of the composition $\text{C}_{18}\text{H}_{11}\text{Br}$. It was boiled with moderately dilute sulphuric acid, heated with phosphoric anhydride under various conditions, and treated in many other ways, but in no case could the formation of the desired product be detected, either dark coloured, readily soluble, amorphous substances were produced, or the bromo-derivative remained unchanged. The experiments were therefore abandoned, and the more readily because it was noticed that, when change did occur, it was usually accompanied by evolution of hydrogen bromide, so that, even if condensation had taken place, the composition of the product would have thrown no light on the point at issue.

It cannot, however, be inferred from the failure of these experiments that a compound represented by the second of the above two formulæ is incapable of undergoing condensation; it might, in fact, be concluded, with perhaps even greater reason, that the non-formation of a condensation product is evidence in favour of the other one, or that the constitution of the bromo-derivative is really represented by one of several other admissible formulæ.

α -Hydrindone, like $\alpha\alpha$ -diketohydrindene (Wislicenus and Kötze, *loc. cit.*), readily undergoes condensation with benzaldehyde; when the former is dissolved in the latter, and a little alcoholic potash added, heat is generated, and, after a very short time, crystals are deposited, the mixture gradually solidifying almost completely, especially on warming gently. The product is separated by filtration, washed with water, and recrystallised from hot alcohol, by which

means it is separated from traces of some other substance of higher melting point.

0.1607 gave 0.5122 CO_2 and 0.0832 H_2O ; $\text{C} = 86.8$; $\text{H} = 5.7$.

$\text{C}_{16}\text{H}_{12}\text{O}$ requires $\text{C} = 87.3$; $\text{H} = 5.4$ per cent.

The analysis shows that this compound is produced in accordance with the equation

so that, for many reasons, its constitution is probably that given above.

Benzylidenehydrindone crystallises from boiling light petroleum (b. p. $80-90^\circ$) in well-defined, very pale yellow plates and prisms, and is readily soluble in ether, benzene, and chloroform at ordinary temperatures; it seems to be insoluble in, and unacted on by, boiling soda, whereas benzylidenediketohydrindone is decomposed with formation of benzaldehyde. The crystals obtained from a solution of benzylidenehydrindone in a mixture of chloroform and light petroleum melt sharply at $109-110^\circ$; if, however, after the substance has solidified, it is re-heated, it melts at about 90° , but not always completely, the remainder melting at $109-110^\circ$. In some cases, the portions which have been melted once, begin to liquefy at 90° , and then, although the temperature is rising, gradually become completely solid, melting for the second time at $109-110^\circ$; it is also a curious fact that the presence of the liquid formed by the crystals melting at 90° does not lower the melting point of the modification which liquefies at $109-110^\circ$; on keeping the crystals of lower melting point at ordinary temperatures, they are transformed into the more stable modification.

On adding bromine to a solution of benzylidenehydrindone in chloroform, combination takes place, but not very readily at the ordinary temperature, and only traces of hydrogen bromide are evolved; after a short time, the solution deposits an almost colourless compound, which is separated by filtration and crystallised from boiling light petroleum. This product is *benzylidenehydrindone dibromide*, and has the composition $\text{C}_{16}\text{H}_{12}\text{Br}_2\text{O}$.

0.1602 gave 0.2963 CO_2 and 0.0478 H_2O ; $\text{C} = 50.4$; $\text{H} = 3.3$.

$\text{C}_{16}\text{H}_{12}\text{Br}_2\text{O}$ requires $\text{C} = 50.5$; $\text{H} = 3.2$ per cent.

It crystallises from petroleum, alcohol, &c., in colourless needles, melts at $144-145^\circ$ with slight decomposition, and is readily soluble in benzene, but only moderately so in hot alcohol and petroleum, and almost insoluble in the cold; when boiled with alcoholic soda for a short time, it gives a deep violet solution, and is reconverted into benzylidenehydrindone, a similar change taking place, but without the

production of colour, when it is heated with sodium acetate or potassium iodide in alcoholic solution.

Acetone and hydrindone do not interact as readily as hydrindone and benzaldehyde, but, on warming the two substances together in presence of a little alcoholic potash, condensation takes place slowly, the solution turns blue, then black, and a dark coloured solid is precipitated on subsequently adding water; this product does not crystallise very readily, and is best obtained in a state of purity by allowing its solution in methyl alcohol to evaporate at the ordinary temperature; analysis showed it to have the composition $C_{12}H_{12}O$, so that it is doubtless analogous to benzyldenehydrindone in constitution.

0.1614 gave 0.4940 CO_2 and 0.1008 H_2O ; $C = 83.5$; $H = 6.9$.

$C_{12}H_{12}O$ requires $C = 83.72$; $H = 6.98$ per cent.

It crystallises from warm dilute alcohol in almost colourless plates, but when its solutions are allowed to evaporate slowly it is deposited in well-defined, four-sided prisms, which have a decided yellow colour, owing probably to the presence of some impurity. It melts at $102-103^\circ$, and is readily soluble in petroleum, chloroform, ether, &c., but only very sparingly in boiling water.

Derivatives of Hydrindone containing Halogen.

Various halogen derivatives of hydrindone are already known; tetrachlorhydrindone, $C_6H_4\langle\begin{smallmatrix} CCl_2 \\ CO- \end{smallmatrix}\rangle CCl_2$, was first obtained indirectly by Zincke from dichloroketoindene (*Ber.*, **20**, 2053), and was afterwards prepared by König from hydrindone (*loc. cit.*); the corresponding tetrabromo-derivative has also been described by Roser (*Annalen*, **247**, 138), whilst the dichloro- and dibromo-compounds have been prepared by König and Hausmann respectively.

Monobromhydrindone, one of the substitution products which has not hitherto been obtained, is described below, and a short account is also given of some properties of the dibromo- and dichloro-derivatives already mentioned; these compounds were prepared partly in order to study their behaviour with dehydrating agents, and partly with the object of converting them into derivatives of indone by eliminating 1 molecule of halogen acid, but in neither case have the experiments afforded very definite results up to the present.

Monobromhydrindone was prepared by acting on the ketone with a molecular proportion of bromine in acetic acid solution, the mixture being kept for some time at the ordinary temperature in order that the somewhat sluggish action might be completed. On submitting the product to distillation in a current of steam, a bromo-derivative

was obtained as a colourless oil, which soon solidified, and which, after having been dried in the air, separated from light petroleum in colourless, fern-like crystals; a halogen determination showed it to be a mono-substitution product of the composition C_9H_7BrO .

0.1658 gave 0.1456 AgBr; Br = 37.4; theory 37.9 per cent.

A small quantity of the dibromo-derivative, which was also formed, remained in the flask from which this compound had been volatilised.

Monobromhydrindone melts at $38-39^\circ$ and turns pale yellow on exposure to light; it dissolves freely in hot light petroleum and is very readily soluble in most organic liquids. When heated under the ordinary pressure, it distils with considerable decomposition, giving off vapours which have an intensely irritating effect on the eyes; in crystallising the crude, steamed product from light petroleum, intensely irritating vapours are also evolved, their action being as energetic as those of xylene dibromide and of the halogen derivatives of acetone, if not more so.

Monobromhydrindone seems not to undergo condensation on treatment with dilute sulphuric acid, as described in the case of hydrindone; this difference in behaviour, however, was only what might be expected, as the bromine atom has probably displaced hydrogen from the $-CH_2CO-$ group, on which so many of the properties of the ketone depend. When the bromo-derivative is dissolved in cold alcoholic potash, a deep violet or dark blue solution is obtained, but the product (possibly indone) has not yet been examined.

Dibromhydrindone, $C_9H_6Br_2O$, was prepared by direct bromination, employing chloroform as solvent, and the crystals, which were deposited in large quantities, were then recrystallised from boiling alcohol.

Dibromhydrindone melts at 132° (Hausmann gives $133-134^\circ$) and dissolves freely in most organic solvents; when freshly prepared, it is colourless, but on exposure to light it gradually assumes a yellowish-brown tinge. The crystals obtained from alcoholic solution were examined by Mr. Marshall, a student at this College, and the following is an account of his observations.

"The crystals examined consisted of lustrous, pale yellow, transparent tablets belonging to the orthorhombic system and showing an imperfect cleavage parallel to the pinakoid $a\{100\}$. The predominant forms present were the basal pinakoid $c\{001\}$ and the dome $d\{021\}$; the faces of both these forms were usually badly developed and gave multiple images. The form $e\{110\}$ gave good measurements and was well developed; this form, together with $c\{001\}$ and $d\{021\}$, were always observed. The dome $g\{101\}$ seemed only to be developed when the crystal lies on one of the $d(021)$ faces in the solution; the

faces of $g\{101\}$ were always small, but gave good images during the measurement. A darkly coloured, impure solution of the substance in ethylic acetate deposited crystals showing the form $d'\{011\}$; the latter, and indeed all the other forms on these crystals, are not well suited for goniometrical measurement owing to the dulness of the faces.

"Crystalline System. Orthorhombic.

$$a : b : c = 0.8884 : 1 : 0.8428.$$

"Forms present:—

c	$\{001\}$	$0P$
e	$\{110\}$	∞P
g	$\{101\}$	P_{∞}
d	$\{021\}$	$2P_{\infty}$
d'	$\{011\}$	P_{∞}

Angle.	No. of measure- ments.	Limits.	Mean.	Calculated.
$cg = 001 : 101$	24	$43^{\circ} 26' - 43^{\circ} 34'$	$43^{\circ} 29\frac{1}{2}'$	—
$gg = 101 : 10\bar{1}$	12	$92 56 - 93 7$	$93 1$	$93^{\circ} 1'$
$eg = 110 : 101$	20	$58 56 - 59 15$	$59 2$	—
$eg = 1\bar{1}0 : 101$	18	$120 49 - 121 9$	$120 59$	$120 58$
$ee = 110 : 1\bar{1}0$	16	$83 0 - 83 34$	$83 14$	$83 14$
$ee = 110 : \bar{1}10$	16	$96 26 - 96 56$	$96 44$	$96 46$
$ce = 001 : 110$	10	$89 58 - 90 2$	$89 59$	$90 0$
$ce = 00\bar{1} : 110$	10	$89 42 - 90 10$	$90 0$	$90 0$
$dc = 021 : 001$	30	$59 7 - 59 37$	$59 15\frac{1}{2}$	$59 19$
$dd = 021 : 02\bar{1}$	15	$61 8 - 61 39$	$61 28$	$61 22$
$de = 021 : 110$	30	$54 51 - 55 19$	$55 5\frac{1}{2}$	$55 10$
$de = 021 : \bar{1}10$	29	$125 10 - 124 41$	$124 54\frac{1}{2}$	$124 50$
$dg = 021 : 101$	8	$67 51 - 68 23$	$68 9$	$68 16$
$dg = 021 : \bar{1}01$	6	$111 32 - 112 5$	$111 39$	$111 44$
$cd' = 001 : 011$	2	$40 11 - 40 37$	$40 24$	$40 7$

"The optical characters of the crystals were determined with the assistance of Mr. H. A. Miers, of the British Museum. The face $b(010)$ is the optic axial plane, the brachy-axis (b) being the acute bisectrix; the double refraction is strong and negative. The apparent optic axial angle was measured in air through a plate cut perpendicularly to the a -axis; the dispersion is very strong, as will be seen from the following figures.

	Number of measurements.	2E.	
Red Li light.....	2	28°	9'
Yellow Na light	4	36	29
Green Tl ,, 	2	44	29 "

The halogen atoms in dibromhydrindone are readily eliminated, either partly or completely, on heating the substance with alcoholic potash, but under these conditions a complex action seems to take place, and the products, with one exception, are not easily isolated; the exception referred to is a substance which is deposited in long, very slender, yellow needles, and which, on account of its insolubility, is easily obtained in a pure condition. An examination of its properties showed it to be identical with "tribenzoylenebenzene," a substance the constitution of which has been recently discussed (Trans., *loc. cit.*); its formation, therefore, may be represented by the equation

and affords another example of the extraordinary readiness with which this peculiar condensation process takes place.

When dibromhydrindone is agitated with aqueous alcoholic potash in the cold, a deep, bluish-violet solution is obtained, and the crystals rapidly change their character, but apparently without passing into solution completely; the substance to which the coloration is due has salt-forming properties, and is precipitated as a yellowish-brown, flocculent mass on the addition of hydrochloric acid to the filtered solution; the residue, a grey powder, consists principally of dibromhydrindone, but also contains other substances, the nature of which is being investigated.

Dichlorhydrindone, $\text{C}_9\text{H}_6\text{Cl}_2\text{O}$, was prepared by passing chlorine into a glacial acetic acid solution of the ketone until the gas was no longer rapidly absorbed; after precipitating with water, the product was recrystallised from hot alcohol.

0.1590 gave 0.2266 AgCl: Cl = 35.5; theory, 35.6 per cent.

This analysis shows that the substance is a dichloro-derivative, and its properties prove it to be identical with the compound already described by König; its investigation on the lines already mentioned is being continued, and the properties of other hydrindone derivatives are being studied.

Mr. O. F. Russell, having assisted in the preparation and analysis of several of the compounds described in this paper, the author desires to express his thanks for these services.

*Chemical Department,
Central Technical College,
City and Guilds of London Institute.*