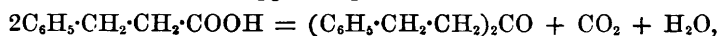


XXIX. *The Formation of the Hydrocarbon "Truxene" from Phenylpropionic acid, and from Hydrindone.*

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

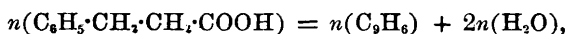
HAVING found that the higher acids of the $C_nH_{2n}O_2$ series may be readily converted into ketones with the aid of phosphoric anhydride (Trans., 1890, **57**, 532, 980; 1893, **63**, 452), it became of interest to study the behaviour of aromatic acids under similar conditions.

Phenylpropionic acid, a compound easily obtainable in large quantities, was therefore heated with phosphoric anhydride in the manner described later; it was soon evident, however, that dibenzylacetone, the formation of which appeared probable,



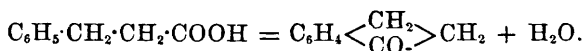
had not been produced, because carbonic anhydride was not evolved in any appreciable quantity.

One of the principal products of the action, and one which was isolated only after considerable difficulty owing to its unexpected properties, proved to be a hydrocarbon of the empirical formula C_8H_8 ; this substance was characterised by very slight solubility in the usual solvents, and its properties were generally indicative of high molecular weight. On considering its origin, it seemed not unlikely that 1 molecule of the hydrocarbon had been produced from 2 or more molecules of the acid,



in which case the probability suggested itself that the formation of the hydrocarbon had taken place in two stages; that in the first the phenylpropionic acid was converted into hydrindone,

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and that in the second, 2, or possibly 3 molecules of this intermediate product underwent condensation. Evidence in support of this view was soon forthcoming, as it was found that the complex product from which the hydrocarbon had been separated contained amongst other substances a ketone; although this ketone was present in such small quantities that only its hydrazone could be isolated, the latter was proved to have the composition $\text{C}_{15}\text{H}_{14}\text{N}_2$, and to be identical with the hydrindone hydrazone described by Hausmann (*Ber.*, **22**, 1919).

This fact doubtless gave some clue to the nature of the interaction of phosphoric anhydride and phenylpropionic acid, but, as it did not afford much aid in establishing the constitution of the hydrocarbon, the latter was carefully studied.

Notwithstanding that its formation from phenylpropionic acid involved the loss of the elements of water, the hydrocarbon did not combine directly with bromine, but yielded a substitution product of the composition $(\text{C}_6\text{H}_5\text{Br})_n$ which was even more sparingly soluble than the hydrocarbon itself. In other respects, the hydrocarbon was characterised by extraordinary stability; fusion with potash, even at high temperatures, seemed to be without action, and, on treatment with nitric acid of sp. gr. 1.38, it was only very slowly attacked. On oxidation with chromic acid, the hydrocarbon was converted into a yellow, very stable substance of the composition $(\text{C}_6\text{H}_4\text{O})_n$, which was practically insoluble in all ordinary solvents, but soluble in nitrobenzene, phenol, and aniline. The hydrocarbon readily dissolved in strong nitric acid of sp. gr. 1.5, and, on prolonged boiling with this acid, it yielded a mixture of at least three substances, one of which proved to be nitrophthalic acid,

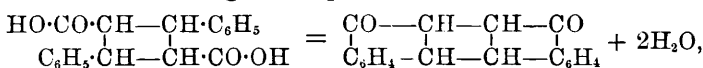


One of the most interesting observations regarding the hydrocarbon was that, in spite of its stability under most conditions, it was completely decomposed and converted into brown, or black, tarry products, when its solution in nitrobenzene was boiled during several hours.

These experiments, however, failed to establish the constitution of the hydrocarbon; the production of nitrophthalic acid showed that it contained the group $\text{C}_6\text{H}_4\left\langle\begin{array}{c} \text{C} \\ \text{C} \end{array}\right\rangle$, and thereby confirmed, to some extent, the original assumption of its formation from hydrindone; but otherwise the facts admitted of no precise interpretation. Nevertheless, they were not without value, as they showed that the compound differed very considerably from other hydrocarbons of high molecular weight, such as chrysene, naphthanthracene, and pyrene. The only

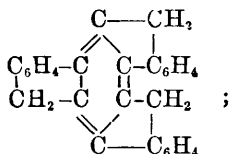
substances, in fact, to which it showed any close resemblance were the hydrocarbon, truxene, prepared by Liebermann and Bergami (*Ber.*, **22**, 782), and a hydrocarbon mentioned, but barely investigated, by Hausmann (*loc. cit.*).

Truxene was obtained by Liebermann and Bergami by reducing truxone with hydriodic acid, truxone having been prepared by treating α -truxillic acid with anhydrosulphuric acid; the facts at disposal being insufficient to establish the constitution of either of these compounds, Liebermann and Bergami merely suggested that the formation of truxone might be represented as follows,

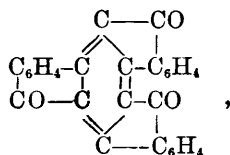


and that in its conversion into truxene (C_9H_6) $_n$, truxone ($\text{C}_9\text{H}_6\text{O}$) $_n$ had undergone condensation by which the value of n had become greater.

In a second paper (*Ber.*, **23**, 317), the constitutions of these compounds were more fully discussed in the light of an observation made in the meantime by Hausmann. The latter had found that a hydrocarbon of the composition (C_9H_6) $_n$ was formed on heating hydrindone with concentrated hydrochloric acid, and as the physical properties of the substance indicated high molecular weight, he came to the conclusion that it was probably "tribenzylenebenzene," $\text{C}_{27}\text{H}_{18}$, a compound of the constitution



he argued that it had been formed by the condensation of 3 molecules of hydrindone, just as mesitylene is produced from 3 molecules of acetone, and as Gabriel and Michael's "tribenzoylenebenzene" (*Ber.*, **10**, 1557),



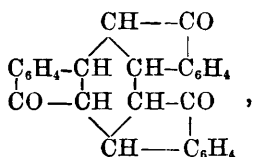
was assumed to be formed from 3 molecules of phthalylacetic acid. Hausmann, however, did not establish the nature of his hydrocarbon; although he submitted it to oxidation and obtained a substance which seemed to be identical with "tribenzoylenebenzene," he did not obtain sufficient pure material for an analysis.

These observations led Liebermann and Bergami to the conclusion,

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already suggested by Hausmann, that truxene is identical with the hydrocarbon the latter had obtained from hydrindone; they therefore oxidised truxene, and proved by direct comparison that its oxidation product is identical with Gabriel and Michael's "tribenzoylenebenzene;" having established this fact, they concluded that truxene is a "tribenzylenebenzene" of the constitution given above.

It now became necessary to alter their original view of the constitution of truxone in order to account for its conversion into truxene; they were thus driven to assume that truxone has the molecular formula $(C_9H_8O)_3$, and that it is a hexahydro-derivative of "tribenzoylenebenzene,"



in spite of the fact that this view did not accord with the ascertained behaviour of the compound, and could not well be reconciled with its formation from α -truxillic acid, which had been proved to have the molecular formula $C_{18}H_{16}O_4$ (*Ber.*, **22**, 2240).

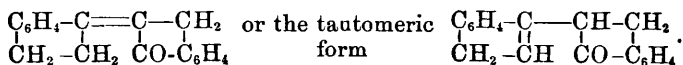
It will be evident from the foregoing that, even if the suspected identity of truxene and the hydrocarbon produced from phenylpropionic acid had been proved, the molecular formula and constitution of the compound would still have remained matters of speculation, since those of "tribenzoylenebenzene" could not be regarded as satisfactorily established.

This being the case, it appeared desirable to study the formation of the hydrocarbon from other stand-points, and to ascertain, in the first place, whether it was really produced by the condensation of hydrindone. The preparation of a considerable quantity of this ketone being necessary for this purpose, and the methods then known appearing very troublesome, attempts were made to devise some new mode of preparation; this having been accomplished, the investigation of the behaviour of hydrindone with dehydrating agents became possible, and led to the following results.

When hydrindone is heated with phosphoric anhydride it is converted into a hydrocarbon identical with that obtained from phenylpropionic acid, $nC_9H_8O = (C_9H_6)_n + nH_2O$. On treatment with moderately dilute sulphuric acid, hydrindone yields two products, namely, the hydrocarbon in question, and a compound of the composition $C_{18}H_{14}O = 2C_9H_8O - H_2O$; the latter on further treatment with sulphuric acid, or when heated with phosphoric anhydride, is converted into the hydrocarbon $(C_9H_6)_n$.

Returning now to Hausmann's "tribenzylenebenzene," it can hardly be doubted, in the face of these results, that this compound is identical with the hydrocarbon from phenylpropionic acid; both may be obtained from hydrindone, and, as far as can be judged from Hausmann's rather meagre statements, they are identical in properties. Truxene, which, according to Liebermann and Bergami, is identical with Hausmann's hydrocarbon, should therefore be identical with that from phenylpropionic acid. This also is the case, for although their identity could not be proved by direct comparison,* it was ascertained that the oxidation product of the hydrocarbon from phenylpropionic acid, like that of truxene, is identical with Gabriel and Michael's "tribenzoylenebenzene."

The most important questions, however, namely, those concerning the molecular formula and constitution of the hydrocarbon prepared by these different methods, have still to be discussed, and, in the first place, the evidence based on chemical considerations may be taken. That obtainable from the direct formation of the hydrocarbon from hydrindone and from phenylpropionic acid may at once be dismissed as affording no solution to the question, there being no means of deciding the value of n in the equations $n(\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}) = (\text{C}_9\text{H}_6)_n + 2n\text{H}_2\text{O}$ and $n\text{C}_9\text{H}_6\text{O} = (\text{C}_9\text{H}_6)_n + n\text{H}_2\text{O}$. The formation of the hydrocarbon from the compound of the composition $\text{C}_{18}\text{H}_{14}\text{O}$, on the other hand, is a fact of far greater significance, since the molecular formula of this intermediate product is established, not only by the results of analyses, but also by molecular weight determinations in boiling aniline solution (compare p. 284). Now, the constitution of this substance may be expressed by one of several theoretically possible formulæ; when, however, it is borne in mind that hydrindone contains the group $-\text{CH}_2-\text{CO}-$, that it is probably this group which takes part in the condensation, and that the substance in question is evidently analogous to the condensation product of diketohydrindone (Wislicenus and Kötze, *Annalen*, 252, 76), only one of these formulæ is readily admissible, namely,

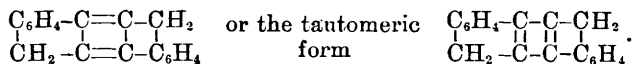


Since, therefore, the hydrocarbon is produced from this compound by elimination of the elements of water under conditions which seem to exclude the possibility of hydrolysis, the necessary conclusion is

* Having recently (Oct. 13, 1893) received a communication from Professor Liebermann, commencing "Erst heute kommt mir Ihre Abhandlung (*Proc. Chem. Soc.*, 1892, 107) zur Gesicht," and calling attention to the probable identity of the hydrocarbons from the two sources (a probability with which the author had been acquainted for nearly two years) an application for a sample of truxene was made; unfortunately Liebermann was unable to comply, having no material at disposal.

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that the hydrocarbon has the molecular formula $C_{18}H_{12}$, in which case its constitution might be expressed by the formula

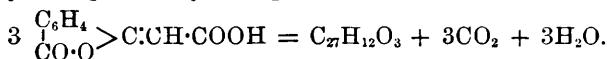


Omitting any discussion of the inherent probability or otherwise of these formulæ, the next point of interest is the formation of the hydrocarbon from truxone. Truxone, $(C_9H_6O)_n$, is produced by treating truxillic acid with anhydrosulphuric acid, and the molecular formula of truxillic acid has been shown to be $C_{18}H_{16}O_4$ (Liebermann and Bergami, *loc. cit.*); probably, therefore, truxone has the molecular formula $C_{18}H_{12}O_2$ rather than $C_{27}H_{18}O_3$, and since it is converted into truxene by treatment with hydriodic acid at 180° , the evidence is again in favour of the view that truxene is $C_{18}H_{12}$.

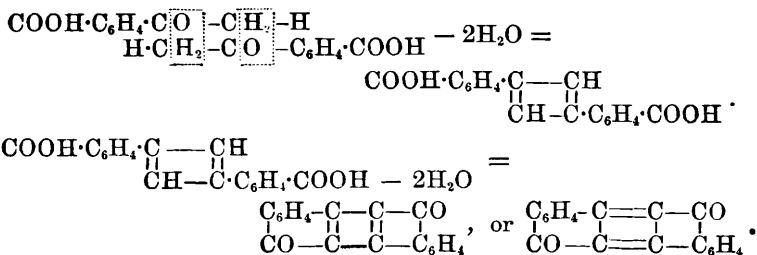
Considering now any chemical evidence which might be advanced as pointing to a different conclusion, there is only one fact of any importance, and that is the oxidation of the hydrocarbon to "tribenzoylenebenzene." The last-named compound has hitherto been assumed to have the molecular formula $C_{27}H_{12}O_3$, partly on account of its physical properties and methods of formation, but more particularly because triphenylbenzene is formed when the product obtained by fusing it with potash at a high temperature is distilled over lime.

It is evident, however, that any conclusions drawn from the conversion of "tribenzoylenebenzene" into triphenylbenzene have little or no weight, as the energetic treatment required to effect this may, and in many cases is known to, bring about very complex changes which are of no value and are often misleading in settling questions of constitution; it might, in fact, be assumed with just as much confidence that truxone is a derivative of anthraquinone because it is converted into "dihydrodiphenyleneoxyanthraquinone" on fusion with potash (Liebermann and Bergami, *Ber.*, **23**, 321).

According to Gabriel and Michael, the formation of "tribenzoylenebenzene" on heating phthalylacetic acid with concentrated sulphuric acid may be expressed by the equation



When, however, it is borne in mind that phthalylacetic acid is readily converted into carboxybenzoylacetic acid, $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_2\cdot\text{COOH}$, and that the latter is easily decomposed into carbonic anhydride and orthoacetylbenzoic acid, $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_3$, an equally rational explanation of the formation of "tribenzoylenebenzene" leads to the molecular formula $C_{18}H_8O_2$ in the following manner.



The formation of "tribenzoylenebenzene," on heating phthalic anhydride with sodium acetate and ethylic malonate, may also be accounted for by assuming that "tribenzoylenebenzene" has the molecular formula $\text{C}_{18}\text{H}_8\text{O}_2$. It may be supposed that methylenephthalide is first produced, in support of which view, the fact that this substance is obtained as a bye-product, may be quoted; the methylenephthalide might then be converted into orthoacetylbenzoic acid, a change which it is known to undergo on treatment with alkalis, and from this acid "tribenzoylenebenzene" could be formed in the manner shown above.

There was, therefore, no valid evidence whatever that "tribenzoylenebenzene" had the molecular formula $\text{C}_{27}\text{H}_{12}\text{O}_3$, and consequently its formation from the hydrocarbon could not be taken as a proof that the latter had the molecular formula $\text{C}_{27}\text{H}_{18}$ when evidence so much less open to objection pointed to the formula $\text{C}_{18}\text{H}_{12}$.

At this stage of the investigation, Beckmann's apparatus for determining molecular weight with the aid of solvents of high boiling point (*Zeit. Phys. Chem.*, 8, 223) was procured, and a large number of experiments were made, both with truxene and "tribenzoylenebenzene." Employing aniline as solvent, the molecular weight of the hydrocarbon was found to be 377, the determinations in phenol solution giving 341; in other words, the results point decidedly to the molecular formula $\text{C}_{27}\text{H}_{18}$ (= 342). The experiments with tribenzoylene gave 474 in phenol, and 464.5 in aniline solution, the calculated molecular weight for $\text{C}_{27}\text{H}_{12}\text{O}_3$ being 384.

It will be seen that these results, especially in the latter case, are decidedly abnormal, and the question arises, what weight is to be attached to them? Are they sufficiently conclusive to upset the chemical evidence already brought forward in favour of the bimolecular formulæ? If so, it must be assumed that phosphoric anhydride hydrolyses the compound of the composition $\text{C}_{18}\text{H}_{14}\text{O}$, and converts it into hydrindone, 3 molecules of which then undergo condensation; also that hydriodic acid decomposes truxone into 2 molecules of some simpler substance which then undergoes condensation, or, that truxone is a hexahydro-derivative of benzene, an assump-

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tion which is negatived by the experiments of Liebermann and Bergami.

If the results of the molecular weight determinations had agreed closely in both cases with those required by the trimolecular formulæ, the matter might have been regarded as settled in spite of these difficulties; the abnormal values obtained with "tribenzoylenebenzene," however, cannot be satisfactorily accounted for. Although the substance contains oxygen, it cannot be classed in the same category as acetic acid, benzoic acid, and other substances which give abnormal values, because, according to present views, it does not contain labile hydrogen; moreover, the solutions employed are necessarily so dilute that the high values obtained can hardly be attributed to concentration, although, as will be shown later, there are indications that this may be the case. If, then, "tribenzoylenebenzene" gives results which are on the average 22 per cent. too high for the trimolecular formula, it might be argued that those obtained with the hydrocarbon are equally, or even more, abnormal, and that in both cases the molecules are in reality aggregates, which are only partially resolved into simple molecules under the given conditions.

Notwithstanding arguments of this nature, and considering the results as a whole, it must be conceded that they point to the trimolecular formulæ; this conclusion, being directly contrary to that arrived at from a consideration of chemical facts of considerable weight, cannot be accepted as final, although it certainly casts doubt on the evidence in favour of the bimolecular formulæ, and again raises the whole question.* The further investigation of these remarkable compounds is therefore desirable, and the determination of the molecular weight of truxone would be of particular interest; many attempts have been made during the last few months to prepare some mono-derivative of the hydrocarbon, and thus settle the question beyond doubt; unfortunately they have not met with success.

Truxene.

Preparation from Phenylpropionic acid.—Phenylpropionic acid (20—30 grams), contained in a beaker placed in a metal bath, is heated at about 80—100°, and 2 mols. of phosphoric anhydride are quickly added in three approximately equal portions, stirring well after each addition; a considerable rise in temperature occurs, and the anhydride apparently dissolves, but without effervescence, traces of some irritating vapour (hydrindone?), which partially condenses

* The author's note in the Proceedings (No. 128, 1893, 67) was published before the molecular weight determinations had been made, and the views there expressed must be modified accordingly.

on the sides of the beaker, being evolved. Heat is now applied if necessary, but usually the temperature rises sufficiently high, namely, to about 180° , or even higher, in consequence of the fairly vigorous action; during this time the mixture turns yellow, and then brown, gradually changing from a moderately mobile liquid to a thick pasty or solid mass, at the edges of which pale yellow crystals of the hydrocarbon may sometimes be seen; after keeping the mixture at about 200° for a few minutes the operation is at an end.

When cold, the product is stirred up with water, and, if now the whole be submitted to distillation with steam, traces of hydrindone pass over, but usually in quantities so small that the distillate is clear; the presence of the ketone in solution is, however, indicated by the smell, and may be proved by heating the distillate with phenylhydrazine acetate, when a turbidity, due to the formation of hydrindonephenylhydrazone, is produced. The separation of this small quantity of hydrindone being of no advantage, the brown pasty product is simply extracted with boiling water to free it from phosphoric acid. The brownish extracts show a beautiful, greenish-blue fluorescence, and contain small quantities of an organic phosphorus compound (see below), whilst the residue consists of a brown, somewhat brittle substance, the weight of which, when dried, is usually about two-thirds that of the phenylpropionic acid employed. This residue is ground to a fine powder, and repeatedly extracted with boiling glacial acetic acid, which dissolves a brown, amorphous substance, the nature of which was not determined, and leaves a dirty grey or yellowish powder, consisting of the crude hydrocarbon; the yield of the latter, on the average, is about 40 per cent. of the theoretical, and the loss on subsequent purification is only very small.

The crude product may be purified by recrystallisation from boiling xylene, cumene, nitrobenzene, aniline, or similar solvents, but, owing to the rapidity with which crystals are deposited, such solutions are difficult to filter; the most convenient method is to place the crude product in a bag of filter paper, and suspend the latter in a flask containing xylene, and connected with a reflux condenser; on boiling, the hydrocarbon is gradually dissolved out of the bag, and is deposited in the flask in yellow crystals.

0.1515 of a sample obtained in this way gave 0.5250 CO_2 and 0.0710 H_2O . $\text{C} = 94.51$; $\text{H} = 5.21$.

C_3H_2 requires $\text{C} = 94.74$; $\text{H} = 5.26$ per cent.

The yellow solution, obtained on extracting the crude product of the action of phosphoric anhydride on phenylpropionic acid with water, if left for several weeks, deposits a small quantity of a reddish-

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brown substance in rosette-like, crystalline masses; this is insoluble, or nearly so, in chloroform and benzene, but may be recrystallised from a mixture of alcohol and glacial acetic acid; when boiled with aniline it is decomposed, yielding crystals of aniline phosphate and an oily or resinous substance which was not investigated.

Preparation from Hydrindone.—Pure hydrindone is dissolved in a mixture of about equal parts of water and ordinary concentrated sulphuric acid, and the brown solution heated on a sand bath; after a very short time the colour darkens slightly, and an oil begins to collect at the surface, but, even before ebullition sets in, the oil gradually solidifies and changes to a yellow, or brown, granular mass; after boiling for about three hours the product is separated by filtration, and extracted with boiling alcohol to free it from a small quantity of brown impurity. The yellowish, insoluble residue consists of practically pure hydrocarbon, and the yield is very good. For analysis it was purified by recrystallisation from xylene.

0.1528 gave 0.5286 CO_2 and 0.0722 H_2O . C = 94.35; H = 5.25.

C_3H_2 requires C = 94.74; H = 5.26 per cent.

Preparation from $\text{C}_{18}\text{H}_{14}\text{O}$.—If, in preparing the hydrocarbon from hydrindone, the boiling with sulphuric acid be interrupted as soon as the formation of a solid product seems to be at an end, which is usually the case after about 10 minutes, a compound of the composition $\text{C}_{18}\text{H}_{14}\text{O}$ is formed, together with a considerable quantity of hydrocarbon; the two substances are easily separated, as the former dissolves freely in hot alcohol, and crystallises from the filtered solution on cooling.

The properties of this condensation product will be described in a subsequent paper; its composition is proved by the following analyses.

0.1415 gave 0.4541 CO_2 and 0.0758 H_2O . C = 87.52; H = 5.96.

0.1638 gave 0.5287 CO_2 and 0.0842 H_2O . C = 88.03; H = 5.71.

$\text{C}_{18}\text{H}_{14}\text{O}$ requires C = 87.80; H = 5.69 per cent.

That this substance was, in fact, an intermediate product in the conversion of the ketone, hydrindone, into the hydrocarbon, seemed to be proved by its conversion into the latter. This change may be brought about by heating the compound, $\text{C}_{18}\text{H}_{14}\text{O}$, with a mixture of equal volumes of sulphuric acid and water for an hour or so, when it is almost quantitatively converted into the hydrocarbon; on extracting the solid product with hot alcohol, only traces of coloured impurity are dissolved, and the residue consists of practically pure hydrocarbon.

As the strongest argument in favour of the molecular formula $\text{C}_{18}\text{H}_{12}$ for the hydrocarbon is afforded by its formation from this

condensation product, some other method of preparation had to be effected, under conditions which seemed to render a resolution of the latter into hydrindone out of the question; this was accomplished with the aid of phosphoric anhydride.

The pure substance was heated to about 150° in a small beaker, and phosphoric anhydride was dusted in until the whole solidified; the mixture was then kept at about 150° for some minutes. When cold, the product was extracted with boiling dilute alcohol, the insoluble portion being reduced to a fine powder, and again extracted as before; the residue consisted of the crude hydrocarbon.

The hydrocarbon, prepared by any of these methods, crystallises from boiling xylene in flat needles or plates which sometimes exhibit a beautiful iridescence. It does not show any sign of change at 360°, although it sublimes slowly at about this temperature; when heated more strongly, it melts to a yellowish liquid, and then quickly sublimes in yellow needles, apparently with slight decomposition. It is characterised by unusual resistance to solvents of moderately low boiling point, as, for example, ether, alcohol, ethylic acetate, glacial acetic acid, &c., in all of which it is insoluble, or nearly so; it is, however, slightly soluble in chloroform, rather more readily in boiling xylene, and moderately easily in boiling nitrobenzene, aniline, and phenol.

In most respects the hydrocarbon is also characterised by great stability; even when fused with potash for some time it undergoes only very slight decomposition, practically the whole being recovered unchanged. It is only slowly acted on by boiling nitric acid of sp. gr. 1.38, by which it is converted into a deep canary-yellow substance, in spite of the fact that it does not pass into solution;* this product seems to be a mixture, as samples purified by recrystallisation from nitrobenzene differed widely in composition.

The action of oxidising agents, of bromine, and of nitric acid (sp. gr. 1.5) on the hydrocarbon, as well as its curious behaviour with nitrobenzene, are described subsequently.

When a few crystals of the hydrocarbon are shaken with ordinary concentrated sulphuric acid, the mixture slowly turns violet, and then deep blue, although apparently the crystals do not dissolve to any

* This behaviour with nitric acid for some time led the author to doubt the identity of the hydrocarbon with truxene, since the latter, according to Liebermann and Bergami (*Ber.*, 22, 786), is unchanged by nitric acid of sp. gr. 1.38. This statement, however, is doubtless incorrect, although easily accounted for, because, if the truxene with which the observation was made were not sufficiently pure, the slight change in colour, which indicates that action is taking place, would not be readily detected; nevertheless, it could not be overlooked, as, with the exception of its conversion into "tribenzoylenebenzene," Liebermann and Bergami describe no specific property of truxene by which it could be readily identified.

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appreciable extent, that is to say, the crystals alone are coloured, the acid remaining almost colourless; on warming, the colour changes to reddish-violet and then to brown, finally becoming pale yellowish-brown on adding water. This behaviour affords a ready means of identifying the hydrocarbon, and seems not to be due to the presence of impurity in the latter, as it is shown by samples which have been repeatedly crystallised, and also by portions of the hydrocarbon which have been fused with potash. The blue coloration, however, does not appear in presence of a drop of nitric acid, nor when pure sulphuric acid is used, except extremely faintly, and after keeping for many hours; the impurity in the ordinary concentrated acid to which the coloration is due seems not to be nitrous acid, as a trace of the latter immediately destroys the colour; solutions thus decolorised rapidly turn blue on shaking in the air, the coloration becoming more intense than at first; this destruction and reproduction of the colour may be repeated many times.

When heated at 100° with concentrated sulphuric acid, the hydrocarbon turns a variety of colours, and gradually passes into solution, doubtless forming a sulphonic acid; if the heating has been at all prolonged, no precipitation occurs on adding water, but on cooling the solution sets to a yellow jelly.

The identity of the several samples of hydrocarbon obtained in the manner already described is shown by the analyses and by the following facts:—Samples from the various sources melted practically simultaneously when heated on the bright surface of a metal bath; they all gave the same sequence of colours on treatment with concentrated sulphuric acid; they all showed the same highly characteristic behaviour with boiling nitrobenzene (see p. 286).

Samples from the four sources were separately recrystallised from boiling nitrobenzene and examined by Mr. W. J. Pope, who reports as follows:—"The four specimens consist of small, flattened, rectangular needles, which, on microscopic examination in polarised light, show straight extinction through the large face; this face is normal to a bisectrix, and the optic axial plane is parallel to the larger side of the plate. The axes emerge just outside the microscope field, and the crystals show interference colours of high orders in convergent polarised light. Exactly the same phenomena are observed with all the crystals, so that the four samples are apparently crystallographically identical and belong to the orthorhombic system."

The question of the existence of coloured hydrocarbons having been recently studied by Græbe (*Ber.*, **25**, 3146; **26**, 2354), and discussed by Armstrong (*Proc.*, 1892, 192), the hydrocarbon from hydrindone was carefully examined in this respect. Liebermann and

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Bergami describe truxene as "yellowish;" Hausmann's hydrocarbon, even when prepared under like conditions, varied in colour from golden-yellow to the palest light yellow, a fact which he attributed to the presence of small quantities of some impurity. The colour of the crude hydrocarbon prepared by the methods described above is very different, varying from a dirty, rather dark yellow, as exhibited by that from phenylpropionic acid, to very pale yellow, as in the case of that obtained from hydrindone. On recrystallisation from nitrobenzene, the colour becomes darker, doubtless owing to decomposition, but from boiling xylene lighter coloured crystals are usually deposited; if, after several recrystallisations from xylene, the hydrocarbon be now purified with the aid of chloroform it is obtained in microscopic crystals, which, if not colourless, are so slightly tinged with yellow that the colour is barely appreciable.

For the determination of the molecular weight of truxene and of "tribenzoylenebenzene" by the ebullition method, the most suitable solvents appeared to be aniline and phenol. As, however, the latent heat of vaporisation of these two liquids seems not to have been determined, except indirectly by Beckmann (*loc. cit.*), it was necessary, in the first place, to make a series of experiments with substances of known molecular weight in order to obtain the molecular rise in boiling point of the solvents.

For this purpose, the following experiments were made.

| Weight of solvent. | Weight of substance. | Grams substance in 100 grams solvent. | Rise in boiling point. | M. W. |
|--------------------|----------------------|---------------------------------------|------------------------|-------|
|--------------------|----------------------|---------------------------------------|------------------------|-------|

I. Solvent aniline.

Chrysene. M. W. = 228.

| | | | | |
|-------|--------|--------|--------|-----|
| 13·18 | 0·1719 | 1·304 | 0·190° | 226 |
| " | 0·4911 | 3·726 | 0·575 | 213 |
| " | 0·7364 | 5·587 | 0·865 | 212 |
| " | 1·1400 | 8·650 | 1·315 | 216 |
| 14·36 | 0·0977 | 0·6804 | 0·107 | 209 |
| " | 0·2477 | 1·725 | 0·270 | 210 |
| " | 0·3137 | 2·184 | 0·345 | 208 |

Condensation Product, C₁₈H₁₄O. M. W. = 246.

| | | | | |
|-------|--------|-------|--------|-----|
| 12·82 | 0·2150 | 1·677 | 0·245° | 225 |
| " | 0·3244 | 2·530 | 0·365 | 228 |
| 11·15 | 0·1945 | 1·744 | 0·240 | 239 |
| " | 0·3296 | 2·956 | 0·413 | 235 |

Acetanilide. M. W. = 135.

| | | | | |
|-------|--------|--------|--------|-----|
| 12·31 | 0·0802 | 0·6515 | 0·150° | 143 |
| " | 0·1716 | 1·394 | 0·328 | 140 |
| " | 0·2772 | 2·252 | 0·528 | 140 |

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| Weight of solvent. | Weight of substance. | Grams substance in 100 grams solvent. | Rise in boiling point. | M. W. |
|---|----------------------|---------------------------------------|------------------------|-------|
| II. Solvent phenol. | | | | |
| <i>Chrysene.</i> M. W. = 228. | | | | |
| 11·34 | 0·2153 | 1·898 | 0·264° | 218 |
| " | 0·4371 | 3·854 | 0·524 | 223 |
| " | 0·6672 | 5·884 | 0·837 | 214 |
| 13·88 | 0·6385 | 4·600 | 0·626 | 223 |
| " | 0·9842 | 7·091 | 0·953 | 226 |
| " | 1·1520 | 8·300 | 1·103 | 228 |
| <i>"Benzylideneindol."</i> M. W. = 205. | | | | |
| 12·97 | 0·3355 | 2·587 | 0·380° | 207 |
| " | 0·7174 | 5·531 | 0·840 | 200 |
| " | 1·0772 | 8·305 | 1·247 | 202 |

The average (uncorrected) value for the molecular rise in boiling point of 100 grams of aniline, calculated from the experiments with the three substances named above, is 33·7, a number which differs considerably from that (32·2) found by Beckmann in experiments with triphenylmethane, diphenylamine, and benzanilide; the discrepancy, however, is probably due to the difference in the substances employed, and not to a difference in thermometric or other corrections, because, in the case of phenol, the constant was found to be practically identical with that obtained by Beckmann. For this reason, the average of the two values, namely 32·9, was taken in calculating the molecular weight, both in the above experiments and in those with the hydrocarbon and "tribenzoylenebenzene."

In the case of the phenol solutions, the molecular rise in boiling point was taken as 30·4, as determined by Beckmann, the value calculated from the above experiments only being 30·9.

Although, in the case of the above-named substances, the concordance of the numbers obtained by this method leaves little to be desired, the experiments with the hydrocarbon and "tribenzoylenebenzene" gave values which differed from one another very considerably; this is due to the unavoidable increase in the experimental errors. The two substances are so sparingly soluble that very small quantities only must be employed, and even then solution takes place so slowly that the experiment occupies a considerable time; as, moreover, the rise in boiling point is comparatively very small, if changes in the barometer or variations in the gas pressure occur during the experiment, the results may be influenced to a very great extent. Even the apparently simple process of introducing the substance into the boiling tube is a source of error in determinations with substances such

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as those in question; pastilles, which are so convenient in ordinary cases, cannot be employed as they dissolve so very slowly; coarse powder and loose crystals are still more objectionable, as in both cases the substance sticks on the sides of the boiling tube, and is not thoroughly washed down for perhaps 10—15 minutes. Under these circumstances thin, square, loosely packed masses are to be recommended; after crystallising from boiling aniline or phenol and washing the crystals on a filter-pump, the felt-like cake is folded once or twice while still damp, then cut into blocks of the desired size and dried; such blocks can be introduced into the boiling tube and pushed down into the liquid with a platinum wire without leaving any of the substance adhering to the sides. Even then, however, there is still a source of error; small cakes of the substance may get carried to the bottom of the tube, where they remain for a long time (although the solution is not nearly saturated) and where they cannot be seen except on examination after the experiment is concluded.* For these reasons it was necessary to make a large number of experiments and take the average of the results; the determinations were all made in the morning, when the gas pressure is almost constant, the device suggested by Sakurai (Trans., 1892, 61, 986) being also employed to obviate as much as possible any local variations.

| Weight of solvent. | Weight of substance. | Grams substance in 100 grams solvent. | Rise in boiling point. | M. W. |
|--|----------------------|---------------------------------------|------------------------|-------|
| <i>Truxene</i> (C ₉ H ₈) _n = 228 or 342. | | | | |
| I. Solvent aniline. | | | | |
| 12·25 | 0·1820 | 1·486 | 0·135° | 362 |
| 14·03 | 0·0763 | 0·5438 | 0·053 | 337 |
| 13·71 | 0·0707 | 0·5157 | 0·043 | 394 |
| " | 0·1480 | 1·079 | 0·090 | 394 |
| " | 0·2537 | 1·850 | 0·163 | 373 |
| 14·16 | 0·1170 | 0·8263 | 0·074 | 367 |
| " | 0·2233 | 1·577 | 0·134 | 387 |
| 12·44 | 0·1719 | 1·382 | 0·117 | 388 |
| 14·16 | 0·2364 | 1·669 | 0·152 | 361 |
| 13·24 | 0·2364 | 1·785 | 0·160 | 367 |
| " | 0·4401 | 3·324 | 0·275 | 398 |
| 12·53 | 0·2740 | 2·187 | 0·213 | 338 |
| 11·55 | 0·1775 | 1·537 | 0·145 | 349 |
| " | 0·3544 | 3·068 | 0·290 | 348 |
| 10·93 | 0·1936 | 1·771 | 0·145 | 402 |
| " | 0·3774 | 3·453 | 0·285 | 399 |
| 10·87 | 0·1902 | 1·749 | 0·140 | 412 |
| " | 0·3523 | 3·241 | 0·260 | 410 |
| 10·82 | 0·2542 | 2·349 | 0·197 | 392 |
| " | 0·4615 | 4·265 | 0·375 | 374 |
| Average .. | | | | 377 |

* This occurred on several occasions, and of course entirely vitiated the results.

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| Weight of solvent. | Weight of substance. | Grams substance in 100 grams solvent. | Rise in boiling point. | M. W. |
|---|----------------------|---------------------------------------|------------------------|-------|
| <i>Truxene</i> (C_9H_8) _n = 228 or 342. | | | | |
| II. Solvent phenol. | | | | |
| 11.16 | 0.2263 | 2.027 | 0.180° | 342 |
| 10.90 | 0.2636 | 2.418 | 0.217 | 339 |
| 12.19 | 0.1970 | 1.616 | 0.140 | 351 |
| " | 0.3264 | 2.677 | 0.223 | 365 |
| 12.52 | 0.2340 | 1.869 | 0.185 | 307 |
| " | 0.3896 | 3.112 | 0.267 | 355 |
| 12.42 | 0.1584 | 1.275 | 0.113 | 343 |
| " | 0.2935 | 2.363 | 0.218 | 329 |
| | | | Average .. | 341 |
| <i>"Tribenzylenebenzene"</i> (C_9H_4O) _n = 256 or 384. | | | | |
| I. Solvent aniline. | | | | |
| 13.36 | 0.1393 | 1.042 | 0.073° | 469 |
| " | 0.2833 | 2.120 | 0.140 | 498 |
| 13.71 | 0.1455 | 1.061 | 0.081 | 431 |
| " | 0.3488 | 2.544 | 0.182 | 460 |
| | | | Average .. | 464.5 |
| II. Solvent phenol. | | | | |
| 11.35 | 0.1644 | 1.448 | 0.095° | 463 |
| " | 0.3076 | 2.710 | 0.168 | 490 |
| 12.43 | 0.2048 | 1.647 | 0.110 | 455 |
| " | 0.2925 | 2.353 | 0.143 | 500 |
| 14.97 | 0.1823 | 1.218 | 0.083 | 446 |
| " | 0.3637 | 2.429 | 0.151 | 489 |
| | | | Average... | 474 |

Assuming that truxene is $C_{27}H_{18}$, the average value obtained in aniline solution is about 10 per cent. too high, whereas in phenol solution it agrees well with the calculated molecular weight; this difference can hardly be due to experimental error, and is possibly larger than it would have been if the constant for aniline had been determined with a greater variety of substances. There is apparently no regular increase in the deviation of the experimental from the calculated molecular weight with increasing concentration, as, in fact, could hardly be expected in such dilute solutions.

"Tribenzylenebenzene," which should have the molecular weight 384 if truxene be $C_{27}H_{18}$, gives an average value of 464.5 in aniline and 474 in phenol solution; the average deviation, taking the results of all the experiments, is, therefore, about 22 per cent. It would seem, however, that even in very dilute solutions the divergence from

the normal rapidly increases, and to about the same extent in both solvents; whether this is really the case or not cannot be stated with confidence, owing to the magnitude of the experimental errors, but assuming that it is so, the molecular weight in infinitely dilute solutions may be roughly calculated to be 408. This value is obtained by taking the average rise in boiling point of all the first, and also of all the last determinations of each series in aniline solution and plotting these against the average of the corresponding numbers for the molecular weight; the same process is then applied in the case of the determinations in phenol and the mean of the two values taken. Making this correction, which, however, can only be a very rough approximation, the deviation from the theoretical value becomes only about 6.4 per cent., so that the results would point decidedly to the trimolecular formula.

Oxidation of Truxene.

The hydrocarbon is slowly acted on by a hot mixture of potassium dichromate and sulphuric acid, and by a glacial acetic solution of chromic acid, being converted into a deep yellow compound; after boiling the pure, finely divided substance with the oxidising mixture for about 60 hours, portions of the insoluble powder being examined from time to time under the microscope, crystals of the hydrocarbon were no longer visible, and the powder appeared to be homogeneous. It was then separated by filtration, washed well with boiling water, and dried. The deep yellow product was then fractionally extracted with boiling xylene in the manner described in the case of the hydrocarbon; the yellow deposits from the second and third extracts were collected separately, washed with alcohol, dried and analysed. I = second extract, II = third extract.

- I. 0.1651 gave 0.5172 CO_2 and 0.0527 H_2O . C = 85.4; H = 3.5.
 II. 0.1577 „ 0.4918 „ „ 0.0501 „ C = 85.1; H = 3.5.
 $\text{C}_9\text{H}_4\text{O}$ requires C = 84.4; H = 3.1 per cent.

It will be seen that these results do not agree very well with the theoretical; this, however, is doubtless due to the difficulty of completely oxidising the hydrocarbon and of separating it from the oxidation product, and there is little doubt that the composition of the yellow substance is $\text{C}_9\text{H}_4\text{O}$. Lierbermann and Bergami experienced the same difficulty in purifying their "tribenzoylenebenzene," their analyses, like these, indicating the presence of hydrocarbon.

This oxidation product seems to be even more sparingly soluble in boiling xylene and nitrobenzene than the hydrocarbon, and separates from these solvents in long, deep-yellow filaments. It shows no sign of change at 300° , but when strongly heated it sublimes in orange

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needles, apparently undergoing decomposition, or melts to a yellow liquid; its melting point seems to be considerably higher than that of the hydrocarbon, as, on heating portions of the two substances on the bright surface of a metal-bath, the hydrocarbon liquefied some time before its oxidation product.

In order to ascertain whether this yellow oxidation product was identical with "tribenzoylenebenzene" the latter was prepared by heating phthalic anhydride with ethylic malonate and sodium acetate under the conditions specified by Gabriel.

A direct comparison of the compounds from the two sources left no doubt as to their identity. They both crystallised from boiling nitrobenzene in long, canary-yellow filaments, which to the naked eye, as well as under the microscope, were identical in appearance; portions of the two samples melted practically simultaneously when heated on a metal bath; both preparations dissolved in concentrated sulphuric acid, giving a brownish-red solution, and, on adding water, a light yellow flocculent precipitate was produced in both cases. With nitric acid of sp. gr. 1.5, the samples showed a slight difference in behaviour, "tribenzoylenebenzene" giving a yellow, the other preparation a greenish coloration; this, however, was probably due to the (known) presence of hydrocarbon in the latter sample, and may therefore be disregarded, especially as the "tribenzoylenebenzene" showed the same behaviour when it was mixed with a small quantity of the hydrocarbon.

Action of Nitrobenzene on Truxene.

In recrystallising the hydrocarbon from boiling nitrobenzene it was noticed that, even when the hydrocarbon was practically pure, the solvent became much darker in colour on boiling the solution for a short time, and the crystals deposited on subsequent cooling were dirty yellow, indicating that some decomposition had occurred; the following experiment shows that the hydrocarbon is slowly, but completely decomposed by boiling nitrobenzene.

The pure substance, about 1 gram, was dissolved in boiling nitrobenzene, about 10 grams, and the solution immediately cooled; apparently the whole of the hydrocarbon was deposited in beautiful yellow needles. After boiling for about two hours, the solution was reddish-brown, and only a very small quantity of crystals separated on cooling, whereas after four hours further boiling no crystals were deposited. On adding a considerable quantity of ether, a yellowish-brown, very bulky substance was precipitated, and this, after being separated by filtration, and washed with ether, retained its original form and appearance so long as it was covered with ether, but as soon as the latter evaporated it quickly changed to a black, sticky

mass, the bulk of which, compared with that of the original precipitate was very small; this curious change took place even when the brown precipitate was quickly spread on earthenware and transferred to a desiccator.

The ethereal nitrobenzene filtrate was shaken with soda and the alkaline extract acidified, but without result; the solution was therefore dried and the solvents distilled off until only 2—3 c.c. remained, but no definite product could be detected in the residue, only traces of a yellowish amorphous substance being precipitated on adding ether. Even on prolonged boiling with aniline, the hydrocarbon is partially converted into amorphous substances, the nature of which was not ascertained.

The comparatively rapid action of boiling nitrobenzene contrasts very strongly with that of boiling nitric acid of sp. gr. 1.5; in the latter case, although nitration probably occurs very soon, the hydrocarbon seems to be only slowly decomposed, and one of the products, at least, is a well-defined compound. The behaviour of other hydrocarbons with boiling nitrobenzene is being investigated.

Dibromotruzene.

On treatment with bromine, the hydrocarbon yields a substitution product of the composition C_9H_5Br . Since bromination could not well be effected in solution, owing to the slight solubility of the hydrocarbon, 1.6 grams of the pure substance were simply suspended in dry chloroform; on adding one drop of bromine a distinct reddish-brown coloration was produced, but after a short time the chloroform became colourless, and hydrogen bromide was evolved; the addition of small quantities of bromine was then continued until the brown coloration remained even after keeping for two days in a stoppered bottle. The chloroform was then evaporated at ordinary temperatures, and the residue washed with alcohol and dried; it weighed 2.62 grams, the theoretical yield being 2.76 grams.

The compound prepared in this way still contained a certain quantity of unchanged hydrocarbon, and on analysis gave 1 to 2 per cent. of carbon too much; as recrystallisation failed to get rid of the whole of this impurity a sample of the bromo-derivative which had been recrystallised was again treated with bromine in the manner described; an analysis then gave fairly satisfactory results.

0.1657 gave 0.3440 CO_2 and 0.0428 H_2O . C = 56.6; H = 2.9.

C_9H_5Br requires C = 56.0; H = 2.6 per cent.

This dibromo-derivative crystallises from boiling xylene or bromotoluene in microscopic needles, having a very faint yellowish tinge, which may be due to impurity; it is even more sparingly soluble

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than the hydrocarbon, and, like the latter, shows no sign of change at 300° ; when heated very strongly it slowly carbonises, but usually without melting. When gently warmed with ordinary concentrated sulphuric acid, it shows the same sequence of colours as the hydrocarbon, probably owing to the presence of the latter, as the purest samples gave only a very faint coloration. It is not visibly acted on by nitric acid of sp. gr. 1.3 at the ordinary temperature, but it seems to be slowly attacked by boiling nitrobenzene, as on recrystallisation from this solvent it is deposited in dark-yellow needles, a behaviour similar to that of the hydrocarbon.

Action of Nitric Acid on Truxene.

Nitric acid of sp. gr. 1.38 acts only slowly on the hydrocarbon, converting it into a yellow, amorphous substance of undetermined composition (compare p. 279). Acid of sp. gr. 1.5, however, dissolves it readily at ordinary temperatures with a hissing noise, dense ruddy fumes being given off. If water be added at once, an orange-yellow compound, probably a nitro-derivative, is precipitated.

Before the synthesis of the hydrocarbon from hydrindone had been accomplished, it was sought to obtain some clue to the constitution of the compound by studying its products of decomposition. For this purpose the pure hydrocarbon (6 grams) was dissolved in nitric acid of sp. gr. 1.5, and the solution heated on a sand-bath; oxidation rapidly set in, dense ruddy fumes being evolved; but, after boiling for a short time, the solution, which was previously clear, deposited a small quantity of a dark yellow, crystalline powder. After heating for about 40 hours, and adding fresh acid from time to time, the solution was decanted from the insoluble powder and diluted with water, when a bulky, canary-yellow substance was precipitated. This yellow product was separated by filtration, well washed with water, and then extracted with boiling glacial acetic acid, in which it dissolved freely, leaving, however, a small quantity of a deep yellow powder, probably identical with that separated from the concentrated nitric acid solution. The acetic acid extract was fractionally precipitated with water, and the precipitates washed with alcohol, and dried.

Analyses of two samples of the substance prepared in this way were made.

I. 0.1515 gave 0.2814 CO_2 and 0.0247 H_2O .

0.1619 ,, 14.2 c.c. moist nitrogen at 20° and 760 mm.

0.2035 ,, 17.9 ,, ,, ,, ,, ,, ,,

II. 0.1779 ,, 0.3321 CO_2 and 0.0305 H_2O .

Found: I. C = 50.8, H = 1.8, N = 10.1 per cent.

II. ,, 50.9 ,, 1.9 per cent.

As these two samples were obtained in two different oxidation experiments, the agreement between the analytical results indicates that the substance is homogeneous. Its composition may be represented by the formula $C_{18}H_7(NO_2)_3O_4$, which requires C = 50·8, H = 1·65, N = 9·9 per cent.

This oxidation product is readily soluble in glacial acetic acid and in ethylic acetate, being deposited from these solvents as a brown, transparent gum on evaporation at ordinary temperatures. On the addition of alcohol to the solutions, it is precipitated as a yellow, amorphous powder. It is only sparingly soluble in boiling chloroform and benzene, and insoluble, or nearly so, in alcohol, ether, and water; it dissolves, however, in dilute solutions of sodium carbonate, causing effervescence and giving a deep bluish-green solution, from which it is reprecipitated, on the addition of acids, in buff-coloured flocks. It also readily dissolves in ammonia and in soda. It has no definite melting point, but turns brown at about 220°, then blood-red, frothing up and decomposing at about 235°. It is readily acted on by phenylhydrazine at ordinary temperatures, heat being developed, and a reddish-brown, amorphous substance being formed.

Nitroptthalic acid.—The dilute acid mother liquors from the yellow nitro-compound just described were evaporated to dryness, and the pale yellow residue repeatedly taken up with water until free from nitric acid; when dried at 100° it weighed 8 grams. This product contained a small quantity of some compound which was soluble in benzene, but consisted for the most part of an acid insoluble in this liquid. On recrystallisation from a mixture of ethylic acetate and benzene, it was obtained in very pale yellow needles or prisms, melting at 162—163°. Analyses of samples dried at 100° were made.

0·1488 gave 0·2468 CO_2 and 0·0330 H_2O . C = 45·23; H = 2·46.

0·2024 „ 12·5 c.c. moist nitrogen at 17° and 750 mm. N = 7·2.
 $C_8H_3(NO_2)(COOH)_2$ requires C = 45·5; H = 2·3; N = 6·6 per cent.

On recrystallisation from hot water, it was deposited in small needles or prisms which contained water of crystallisation.

The *silver* salt was very sparingly soluble in boiling water, and decomposed very suddenly when gently heated; for this reason, the analyses came out rather too low, namely, 48·9 and 49·4 per cent. of metal respectively instead of 50·7 per cent. which is required by theory. The *methylic* salt was prepared by saturating with hydrogen chloride a solution of the acid in methylic alcohol; the oily product, isolated in the usual manner, quickly solidified, and, on recrystallisation from dilute methylic alcohol, was deposited in colourless needles.

0·1579 gave 0·2896 CO_2 and 0·0538 H_2O . C = 50·0; H = 3·8.

$C_{10}H_9NO_6$ requires C = 50·2; H = 3·8 per cent.

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It melted at 65—66°, and was readily soluble in alcohol and ethylic acetate, but only very sparingly soluble or insoluble in light petroleum.

The acid is, therefore, a nitrophthalic acid, and as it is identical with the compound obtained by Miller (*Annalen*, **208**, 224) and by Hönig (*Ber.*, **18**, 3448), its constitution is $[(\text{COOH})_2 : \text{NO}_2 = 1 : 2 : 4]$. The slight difference in melting point (Miller gives 161°) is probably due to a difference in observation only.

The formation of nitrophthalic acid from the hydrocarbon does not, of course, throw much light on the constitution of the latter; if, however, it be “tribenzylenebenzene,” it might have been expected to yield mellitic acid, $\text{C}_6(\text{COOH})_6$, on oxidation rather than nitrophthalic acid.

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