II.—*Synthetical Formation of Closed Carbon-chains in the Aromatic Series.* Part II.

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AMONG the vast number of aromatic hydrocarbons, there are many which have been proved to contain two or more benzene nuclei condensed together, that is to say, they are compounds in which certain carbon-atoms are common to both rings, as for example, naphthalene, anthracene, and phenanthrene.

Other substances are known in which one or more atoms of nitrogen displace one or more atoms of carbon in the closed chain, without producing any alteration in the fundamental constitution of the compound; for instance, quinoline, acridine, and pseudoanthroline.

Quinoline.

Acridine.

Pseudoanthroline.

Now, in examining the formulæ which, according to the present theoretical views, have been proved, both by synthetical and analytical methods, to represent the constitution of the compounds mentioned, it is at once evident that the carbon-atoms which are common to any two rings are situated in the ortho- or 1.2-position; up to the present time no compound has been obtained in which two carbon-atoms, occupying the meta- or para-position in one closed chain, enter into the formation of the adjoining one; although in the present state of our knowledge of the formation of closed chains there is no *à priori* reason why such compounds should not exist, and why, for instance, isomeric naphthalenes having the formulæ—

could not be formed. In formula I, two carbon-atoms in the meta-position would be common to both rings, and in formula II this would be the case with two carbon-atoms in the para-position. It seemed an interesting subject for research to attempt to synthesise

either such hydrocarbons themselves, or some derivatives of them, in order to obtain experimental evidence as to the possibility of the existence of compounds so constituted.

In Part I of this paper (this vol., p. 1), W. H. Perkin, jun., has described the synthesis of naphthalene from ortho-xylene by a series of reactions, which forms an additional proof that condensation of the benzene-rings takes place in the ortho-position; if isomeric naphthalenes, or derivatives of such compounds, can be produced, it seemed probable that they would be obtained in an exactly similar manner when meta- or para-xylene was used in place of the ortho-compound. Acting on the kind suggestion of Perkin, I undertook to work out this research, and proceeded in the following manner: meta-xylene was treated with bromine, and the meta-xylylene bromide thus obtained was acted upon, in ethereal solution, with ethylic chloromalonate and sodic ethylate when ethylic meta-xylylenedichlorodimalonate was formed, the reaction being expressed by the following equation:—

By treating this product with reducing agents, the chlorine is displaced by hydrogen, and ethylic meta-xylylenedimalonate formed, thus:—

On adding sodic ethylate to an ethereal solution of this ethylic salt, a disodium-derivative is produced, thus:—

By appropriate treatment with iodine or bromine, it was thought that the sodium would be eliminated, and from this compound a tetrahydrometanaphthalene-derivative obtained according to the following equation:—

from which, by hydrolysis and removal of two carboxyl-groups, tetrahydrometanaphthalenedicarboxylic acid would be obtained—

A dicarboxylic acid was in fact obtained, which was at first thought to be the desired compound; on careful examination, however, it was found that it contained no meta-ring, but was simply metaphenylenedipropionic acid—

It will be seen that this acid differs in composition from the hypothetical metanaphthalene-derivative only by two atoms of hydrogen, and that, therefore, analysis alone would be insufficient to distinguish between them with certainty; it can be proved beyond doubt, however, that no closed ring has been formed in the above reactions, for when ethylic meta-xylylenedimalonate is directly hydrolysed without previous treatment with sodic ethylate and iodine (or bromine), the dicarboxylic acid which is ultimately obtained is identical with that which was supposed to be a tetrahydrometanaphthalene-derivative.

It is difficult to explain what takes place when the above-mentioned sodium-derivative is treated with iodine (or bromine), but it would seem that the halogen destroys a portion of the substance, with formation of hydriodic (or hydrobromic) acid, which then reacts on the remainder, reproducing the ethereal salt and the respective haloïd sodium compound.

In spite of the failure of these experiments to produce a meta-closed ring, the conclusion was not justified that a para-ring could not be formed, since, according to the present theories held regarding the constitution of the numerous compounds containing a pyridine-ring, and of the paraquinones, a union of two atoms in the para-position either directly or through the interposition of other atoms is assumed.

Para-xylene was therefore prepared, and submitted to a series of reactions exactly in the same way as in the case of the meta-hydrocarbon; the sodium compound of ethylic para-xylylenedimalonate was obtained, and treated with iodine (or bromine) in the hope of forming a tetrahydroparanaphthalene-derivative.

But here again no closed ring could be produced; when iodine is used the reaction which takes place appears to be similar to that suggested as the most probable in the case of the meta-compound, and the dicarboxylic acid which is the ultimate product is not a

tetrahydroparanaphthalene-derivative, but simply paraphenylenedipropionic acid—

This was proved in a manner similar to that already described. When bromine is used, the reaction is quite different; substitution takes place, and ethylic para-xylylenedibromodimalonate is formed, most probably as expressed by the equation—

From these experiments, then, the conclusion may be drawn that compounds containing rings condensed together in the meta- or para-position are incapable of existence, otherwise they would have been formed by the methods which have been described; now this may be so for one of two reasons—either on account of the relative positions of the two rings, or because of the number of carbon-atoms which would form the reduced ring; in tetrahydrometanaphthalene, as will be seen from the figures already given, there would be seven, in tetrahydroparanaphthalene there would be eight carbon-atoms in the larger closed chain.

To help to a decision on this point, experiments were made with the object of obtaining a derivative of a compound having the formula—

which, like naphthalene itself, would contain six atoms in each ring; a compound of this character should be obtained by treating meta-xylylene bromide with 2 mols. of sodic ethylate and 1 mol. of ethylic malonate, according to the equation—

in a manner exactly similar to that in which hydrindonaphthene-

derivatives were prepared by Perkin (see Part I, this vol., p. 7). But, although the experiment was repeated several times under varied conditions, no such compound could be obtained; the reaction was evidently of a very complicated nature, and yielded a resinous mass from which no definite product could be isolated. It seems, therefore, that the non-formation of a meta- or para-ring in any of these cases is due, not entirely to the number of atoms which would go to form the ring, but also, and perhaps wholly, to its relative position.

It is a general law in the chemistry of the aromatic compounds that no substance can be obtained in which a ring of any sort is joined to the benzene nucleus in other than the ortho-position, *e.g.*, the coumarins, carbostyryle-derivatives, quinoxaline, &c.; the simplest bibasic acid—phthalic—is readily converted into the anhydride, whilst the isomeric meta- and para-anhydrides have not yet been prepared.

The two isomeric meta- and para-phenylenedipropionic acids obtained in this research by reactions already described, were of considerable theoretical interest, owing to the fact that if anhydrides could be obtained from them they would contain a closed ring in the meta- and para-position respectively, as shown by the formulæ

Attempts were therefore made in this direction, but without success, and it was thought that perhaps this was owing to the large number of atoms which would have to take part in the formation of the closed ring: in the fatty series, as is well known, many dicarboxylic acids can be converted into anhydrides, but whether this is possible or not depends on the relative positions of the carboxyl-groups, that is, on how many carbon-atoms go to form the anhydride-ring. To throw some light on this question, meta- and para-xylylene cyanides were prepared, and from them, by hydrolysis, the corresponding phenylene-diacetic acids; it seemed possible that these compounds, containing as they do one atom of carbon less in each of the side chains, would be more capable of forming anhydrides; these would have the formulæ

No anhydride, however, could be obtained from either of these acids, and the conclusion drawn from all the experiments briefly described above confirms the general law that no exterior ring in the meta- or para-position can be formed.

Meta-xylylene bromide was first obtained by Colson (*Compt. rend.*, **99**, 40), by brominating boiling meta-xylylene; in preparing large quantities of this substance, I have found that the following method gives the best results:—50 grams of pure meta-xylylene, placed in a retort connected with a long reflux condenser, are heated in an oil-bath to 125—130°, 160 grams of bromine are then added by means of a dropping funnel inserted into the tubulus of the retort; at first the bromine may be added tolerably quickly, but later on, when the meta-xylylene is partially converted and red fumes escape up the condenser, the halogen must be added slowly, otherwise loss is incurred. The hydrogen bromide, which is evolved in large quantities during the reaction, is absorbed by conducting it into a concentrated solution of caustic soda.

When all the bromine has been added, the contents of the retort, which ought to be only slightly coloured, are poured out and left 24 hours in a cool place to crystallise; the mother-liquor is drained off, and the crystals, after lying for some time on a porous plate, are purified by recrystallisation from light petroleum; meta-xylylene bromide is thus obtained in the pure state as a colourless solid melting at 77°, the melting point given by Colson (*loc. cit.*). From 50 grams of meta-xylylene the quantity of pure bromide obtained is not very large, the mother-liquor can, however, be worked up for a less pure product. In consequence of the painful effect of the vapour on the eyes, it is best when using meta-xylylene to work as much as possible in the open air.

This compound is obtained by the action of ethylic chloromalonate and sodic ethylate on meta-xylylene bromide; 4.4 grams of sodium, dissolved in as small a quantity of alcohol as possible, are mixed with about 10 volumes of pure ether, and a solution of 37.8 grams of ethylic chloromalonate in 500 c.c. pure ether slowly added; after well cooling the mixture, 25.5 grams of finely-powdered meta-xylylene bromide are thrown in, and the whole well shaken. The white precipitate which is at first formed is the sodium-derivative of ethylic

chloromalonate, but as the meta-xylylene bromide dissolves, a lively reaction commences and the ether begins to boil, the sodium-derivative being decomposed with formation of ethylic meta-xylylene dichlorodimalonate and sodium bromide. The mixture is then heated on a water-bath for a couple of hours, great care being taken to shake occasionally, otherwise there is considerable danger of the ether boiling over from the bumping which always occurs; water is subsequently added, the ethereal solution washed and separated, dried over calcium chloride, and the ether distilled off.

Ethylic meta-xylylene dichlorodimalonate remains as a thick, yellowish oil, which even after long standing over sulphuric acid in a vacuum shows no signs of crystallising; on analysis the following results were obtained :—

- I. 0.1615 gram substance gave 0.1015 gram AgCl.
 II. 0.2805   "   "   0.1660   "   "

	Calculated for $C_{22}H_{28}O_8Cl_2$.	Found.	
		I.	II.
Cl	14.4 p. c.	15.5	14.6 p. c.

The second analysis was made from a different sample, the ethereal salt used in (I) having been found to contain a trace of unchanged meta-xylylene bromide.

When the calculated quantities of ethylic chloromalonate and meta-xylylene bromide are carefully weighed, the resulting ethylic meta-xylylene dichlorodimalonate is almost pure and the yield quantitative.

Ethylic Meta-xylylenedimalonate, $C_6H_4[CH_2 \cdot CH(COOC_2H_5)_2]_2$.

When the chlorine-compound described above is dissolved in about 15 volumes of glacial acetic acid and a small quantity of zinc-dust added, reduction at once commences, the mixture becoming quite warm.

The process is best carried out by adding the zinc-dust in very small quantities at a time for about an hour, the whole being constantly shaken in a long-necked flask; at the end of this time, the solution becomes very thick, owing to the formation of zinc acetate, and reduction proceeds only very slowly; water is therefore added, the mixture warmed on the water-bath, and the ethereal salt extracted with ether, not only from the solution but also from the undissolved zinc-dust, which retains a considerable quantity of the substance; the ethereal solution after washing, first with water, and then with sodium carbonate solution to get rid of acetic acid, is dried over anhydrous

potassium carbonate and the ether distilled off. The oil which remains still contains a considerable proportion of the unchanged chlorinated derivative, the reduction is therefore repeated in exactly the same manner; it was found, however, that even after three such treatments a trace of chlorine is still present; the best results are obtained when only small quantities at a time are operated upon.

In order to prepare this substance pure for analysis, use is made of the sodium-derivative; when the calculated quantity of sodium, dissolved in absolute alcohol and mixed with about 10 volumes of ether, is added to a weak ethereal solution of ethylic meta-xylylene dimalonate, a white precipitate of the disodium-derivative is formed. This is washed with ether on the filter-pump as quickly as possible, and then thrown into water or dilute sulphuric acid, when it is at once decomposed, yielding ethereal salt and sodium hydrate (or sulphate). The oil which separates is extracted with ether, and after drying the ethereal solution with calcium chloride, it is treated again, exactly as before, with the calculated quantity of sodic ethylate; the precipitate is washed as above, decomposed with dilute sulphuric acid, the solution extracted with ether, and the product isolated in the usual manner.

Ethylic meta-xylylenedimalonate is thus obtained in the pure state as a thick, colourless oil, which, however, could not be obtained in the crystalline form; it is readily soluble in ether, alcohol, acetic acid, &c., but insoluble in water.

The following results were obtained on analysis:—

0.1550 gram substance gave 0.3522 gram CO_2 and 0.1016 gram H_2O .

	Calculated for $\text{C}_{22}\text{H}_{30}\text{O}_8$.	Found.
C.....	62.56 per cent.	61.97 per cent.
H.....	7.11 ,,	7.28 ,,
O.....	30.33 ,,	30.75 ,,

The sodium-derivative of this ethereal salt is a white solid, which, however, on account of its extremely hygroscopic nature, soon decomposes on exposure to the air. To prepare a sample for analysis, a few grams of ethylic meta-xylylenedimalonate are dissolved in a large volume of dry ether, and the calculated quantity of sodic ethylate, mixed with about 10 volumes of ether, added to the solution. The flask is tightly corked, and the mixture after being well shaken is allowed to stand, in order that the precipitate may settle; when it has completely subsided, it is washed twice by decantation with pure ether (the air being excluded as much as possible), and after draining

off the ether as far as possible, quickly transferred to a tared stoppered weighing-bottle.

After standing in a vacuum over sulphuric acid, a sodium determination was made, from which the following result was obtained :—

0.4055 gram substance gave 0.1215 gram sodic sulphate.

	Calculated for $C_{22}H_{28}Na_2O_8$.	Found.
Na	9.9 per cent.	9.7 per cent.

Experiments were now made to obtain a tetrahydrometanaphthalene-derivative from the disodium malonate.

The following is a description of the methods employed:—The calculated quantity of sodium, dissolved in alcohol and mixed with about 10 volumes of ether, is added to a weak ethereal solution of ethylic meta-xylylenedimalonate, and after allowing the sodium-derivative to separate out, which takes but a very few moments, a very slight excess of the calculated quantity of iodine, also dissolved in ether, is added and the mixture vigorously shaken. The dark-brown colour of the iodine rapidly disappears, and in a few minutes the reaction is completed, the slightly brown colour of the solution being due to the small excess of the halogen used; after adding water to dissolve the sodic iodide, and removing the trace of iodine by means of dilute sulphurous acid, the colourless ethereal solution is washed with water, dried, and the ether distilled off, when the ethereal salt of a tetracarboxylic acid remains behind as a thick, brown oil. This salt is hydrolysed by boiling it for two hours on the water-bath with a solution of potash in methyl alcohol; the alcohol is then evaporated and the potassium-compound dissolved in water; on acidifying this solution with dilute sulphuric acid, a small quantity of impurity is precipitated, this is filtered off and the filtrate extracted repeatedly with ether. The acid obtained on distilling off the ether is a thick, brown oil, which, as it could not be obtained crystalline was, without purifying, converted into the dicarboxylic acid; this is effected by heating it in a flask in a metal-bath at 180—200°, a considerable amount of decomposition taking place, with a copious evolution of carbonic anhydride. When no more gas is given off, the process is at an end, and, on cooling, the contents of the flask become solid. To purify the product, it is now converted into the ethylic salt; for this purpose it is dissolved in dilute ammonia, the excess of the latter removed by standing in a vacuum over sulphuric acid, and the solution filtered to get rid of a small quantity of oil which is present; silver nitrate is then added to the filtrate, and the silver salt thus formed is washed with water on the filter-pump. After careful drying, it is suspended

in ether, treated with an excess of ethyl iodide, and boiled on the water-bath with reflux condenser for about two hours, whereby the silver salt is completely decomposed. The silver iodide is filtered off and well washed with warm ether, the washings added to the filtrate, and the ethereal salt obtained by distilling off the ether; it is, however, still impure, and is therefore submitted to fractional distillation under diminished pressure. A trace of ethyl iodide first comes over, the thermometer then rapidly rises, and the whole distils between 200° and 250° (60 mm. pressure); the high boiling portion is again fractioned, when almost the whole distils over without decomposition constantly at $247-250^{\circ}$ as a colourless, mobile oil. An analysis was now made, which, however, agreed equally well for either of the two formulæ—

As the acid itself would probably crystallise, and could therefore be more easily obtained in a high degree of purity, further attempts to purify the ethereal salt were considered unnecessary, and it was converted into the acid by boiling with a solution of pure potash in methyl alcohol; when hydrolysis was complete, the solution was evaporated to dryness, the potassium salt dissolved in water, dilute sulphuric acid added in excess, and the organic acid extracted with ether. After isolating the product in the usual way, and recrystallising it from boiling water, it was obtained in beautiful glistening plates; an analysis was made which again did not decide whether the ring formation had taken place or not, and other means had therefore to be employed to settle this point beyond doubt. Metaphenylenedipropionic acid was prepared according to the methods described later on, and as this substance, which must have the formula

is identical with the acid obtained above, it is quite clear that no meta-ring had been formed by the action of iodine on the sodium-derivative of ethylic meta-xylylenedimalonate.

Another attempt to obtain a tetrahydrometanaphthalene-derivative was therefore made; in this case, bromine was used instead of iodine, and since there was a considerable loss from decomposition on heating the tetracarboxylic acid in the metal-bath, another method for eliminating the two carboxyl-groups was adopted. The following is an account of the manner in which the experiment was carried out: to a solution of 1.4 grams of sodium dissolved in 15 grams of absolute alcohol, and mixed with 50 c.c. of pure ether, 12 grams of ethylic meta-xylylene-

dimalonate in ethereal solution were added, and the mixture allowed to stand in a freezing mixture until the sodium compound had completely subsided; 4·6 grams of bromine were then gradually dropped in, the whole being kept well cooled. Each drop of bromine was immediately absorbed, the few last only causing the solution to assume a slightly yellow colour.

The product of this reaction was separated as already described in the experiment with iodine, and the ethereal salt hydrolysed by boiling it for two hours with alcoholic potash; 9 grams of the tetracarboxylic acid were thus obtained in the form of a brown oil which could not be got to crystallise; it was therefore mixed with about three times its weight of water, and heated in a sealed tube, first at 110°, then, after opening the capillary to get rid of the carbonic anhydride, at 150°, and finally again at 180° until the evolution of gas entirely ceased.

The contents of the tube, when cool, consisted of two layers; the undermost after standing for some time solidified almost completely, whilst the upper one was filled with colourless crystals. After purification, these crystals were found to be identical with the acid obtained before—viz., metaphenylenedipropionic acid. The solid mass which formed the lower layer was dissolved in boiling water, and, after filtering, allowed to crystallise; again the same acid was proved to have been formed, and the quantity obtained was from $1\frac{1}{2}$ —2 grams. About 3 grams of a black resinous mass from which no crystalline product could be isolated remained on the filter; the mother-liquor from the acid yielded nothing but a further quantity of impure metaphenylenedipropionic acid, which took the form of a slightly yellow oil.

The result of these two experiments showed, therefore, that by acting on the sodium compound of ethyl meta-xylylenedimalonate with bromine or iodine no meta-ring is produced, and the same compound is ultimately obtained after hydrolysis and elimination of two carbonyl-groups, whether this reaction is carried out or not; the possibility that such a ring can exist is thereby rendered improbable.

Meta-xylylenedimalonic Acid, $C_6H_4[CH_2 \cdot CH(COOH)_2]_2$.

When the crude ethylic salt of this acid (see p. 27) is boiled with excess of potash in methylic alcohol until no oil is precipitated on addition of water, hydrolysis is complete; this is the case after about two hours.

The alcohol is distilled off, and the potassium salt which is obtained on evaporation to dryness is dissolved in water; the addition of sulphuric acid in excess produces a slight turbidity, the solution is

therefore filtered, and the product extracted from the filtrate by shaking out about 10 times with pure ether. When the ether is distilled off, meta-xylylenedimalonic acid remains behind as a thick, slightly brown oil, which is readily soluble in water, alcohol, and ether. Unfortunately it could not be obtained in the crystalline form, so no analysis of it was made; that its constitution is that represented by the above formula is, however, proved by its method of formation and by its decompositions, also by a comparison with the isomeric para-acid described later on, to which it is strictly analogous.

Metaphenylenedipropionic Acid, $C_6H_4(CH_2 \cdot CH_2 \cdot COOH)_2$.

On heating the tetracarboxylic acid just described, it is readily converted into metaphenylenedipropionic acid with elimination of 2 mols. of carbonic anhydride.

This conversion may be effected in two different ways:—First, meta-xylylenedimalonic acid is heated in a small flask in a metal-bath; as soon as the temperature rises above 100° carbonic anhydride begins to be evolved, the evolution becoming more rapid as the temperature rises; after keeping the bath at about 180° for some time, no more carbonic anhydride is given off, and the change is complete. On cooling, the dark-brown oil solidifies to an almost solid cake, which is dissolved in hot water, boiled with animal charcoal, and the solution filtered; the new acid crystallises from the filtrate in beautiful colourless plates, and is obtained pure by three recrystallisations from boiling water.

The second method for the preparation of this substance takes up far more time, but it is preferable as the yield is far better: meta-xylylenedimalonic acid is dissolved in about three times its volume of water, and heated in a sealed tube for one hour at 100 – 120° ; the tube is then allowed to cool, and the capillary opened to permit of the escape of the carbonic anhydride; after re-sealing, it is heated again at 150° for an hour, the gas formed allowed to escape, and the contents of the tube raised to a temperature of about 180° for some considerable time. The tetrabasic acid is now completely decomposed, and the liquid which was at first homogeneous is found, after cooling, to have separated into two layers; the bottom one solidifies completely whilst the top one is filled with leaf-like crystals. To purify the product, the whole is collected, and the residue, after spreading on a porous plate to remove traces of oil, is dissolved in boiling water, and the solution filtered. On cooling, pure metaphenylenedipropionic acid separates in magnificent, lustrous, colourless plates. It was dried

over sulphuric acid, then at 100° , and analysed with the following result:—

0.1690 gram substance gave 0.4010 gram CO_2 and 0.0985 gram H_2O .

	Calculated for $\text{C}_{12}\text{H}_{14}\text{O}_4$.	Found.
C	64.86 per cent.	64.71 per cent.
H	6.31 ,,	6.47 ,,
O	28.83 ,,	28.82 ,,

Metaphenylenedipropionic acid when pure melts at $146\text{--}147^{\circ}$; it is moderately soluble in hot, but almost insoluble in cold water, and dissolves easily in ether and alcohol. On precipitating a neutral solution of the ammonium salt with silver nitrate, the silver salt falls down as a white amorphous precipitate; after washing well and drying over sulphuric acid in a vacuum, it was analysed with the following result:—

0.3318 gram substance gave 0.1638 gram Ag.

	Calculated for $\text{C}_{12}\text{H}_{12}\text{Ag}_2\text{O}_4$.	Found.
Ag	49.54 per cent.	49.37 per cent.

This salt is very stable, and does not darken when exposed to diffused light.

In an aqueous neutral solution of the ammonium salt, lead acetate gives a white, amorphous precipitate, copper sulphate a light, bluish-green precipitate, and zinc sulphate a white, crystalline precipitate. Barium chloride gives no reaction.

An experiment was made to try and obtain the anhydride of this acid by heating a small quantity for half an hour in a metal-bath at a temperature of 250° . The acid darkened in colour, traces of water were evolved, and a slight amount of decomposition took place; on heating more strongly over the naked flame, a brown oil distilled and almost immediately solidified. After washing the product with ether on a porous plate, an almost colourless substance was obtained which showed the same melting point as the original acid; no anhydride was therefore formed.

Methylic Metaphenylenedipropionate.

This ethereal salt is obtained in the usual manner by treating argentic metaphenylenedipropionate with methyl iodide.

The pure dry silver salt is mixed with an excess of methyl iodide dissolved in 10 volumes of ether, and the mixture heated on the

water-bath with reflux condenser for about five hours; at the end of this time, the silver salt will be entirely decomposed. To isolate the product, the silver iodide is filtered off, washed with ether, and the washings added to the filtrate; on distilling off the ether, a thick colourless oil remains behind, which in a short time solidifies to a hard cake of crystals; it is purified by spreading on a porous plate and recrystallising from dilute methyl alcohol. Methylic metaphenylenedipropionate is thus obtained pure in the form of colourless plates, and on analysis the following results were obtained:—

0.1570 gram substance gave 0.3865 gram CO_2 and 0.1065 gram H_2O .

	Calculated for $\text{C}_{14}\text{H}_{18}\text{O}_4$.	Found.
C	67.2 per cent.	67.14 per cent.
H	7.2 „	7.53 „
O	25.6 „	25.33 „

This substance is very easily soluble in ether, alcohol, and benzene, but only sparingly in cold methyl alcohol; it melts at 51° , and when heated in small quantities at a time distils at a high temperature almost without decomposition.

Ethyllic Metaphenylenedipropionate.

This is obtained in a manner exactly similar to that used in the preparation of the methyl salt just described; it is a colourless oil, which boils at $247\text{--}250^\circ$ (60 mm. pressure) without decomposition. The analysis gave the following results:—

0.1243 gram substance gave 0.3171 gram CO_2 and 0.0866 gram H_2O .

	Calculated for $\text{C}_{16}\text{H}_{22}\text{O}_4$.	Found.
C	69.07 per cent.	69.55 per cent.
H	7.91 „	7.74 „
O	23.02 „	22.71 „

Para-xylylene Bromide, $\text{C}_6\text{H}_4(\text{CH}_2\text{Br})_2$.

This is prepared by brominating para-xylylene in the same way as described under the meta-compound. When the reaction is finished, the product is allowed to stand for a short time; it then solidifies, and is purified by simply spreading on a porous plate. The yield obtained ranges from $85\text{--}90^\circ$ of the theoretical. The action of the vapour of this substance on the eyes is extremely painful, it is advisable, therefore, to work as much as possible in the open air.

Ethylic Para-xylylenedichlorodimalonate, $C_6H_4[CH_2 \cdot CCl(COOC_2H_5)_2]_2$.

36·8 grams of ethylic chloromalonate are dissolved in about 500 c.c. of ether, the calculated quantity of sodium dissolved in absolute alcohol and mixed with 10 volumes of ether added, and then 25 grams para-xylylene bromide thrown in and the mixture vigorously shaken. The sodium-derivative of ethyl chloromalonate first forms, but on continued shaking the para-xylylene bromide dissolves and the reaction commences; no appreciable warming of the mixture, however, is noticed.

After heating on the water-bath with reflux condenser for about four hours, care being taken on account of the great tendency of the mixture to bump, water is added to dissolve the sodium bromide, and the ethereal solution is then separated and dried. When the ether is distilled off, ethyl para-xylylenedichlorodimalonate remains as a thick, brownish oil, the amount obtained being in accordance with theory. On standing for some hours, this oil is converted into a crystalline solid mass; the adhering mother-liquor is removed by spreading on a porous plate, and the product purified by recrystallisation from alcohol. In this way the ethereal salt is obtained in large, colourless, six-sided plates; it melts at 86—87°, is readily soluble in alcohol, ether, light petroleum, acetic acid, &c., but is insoluble in water. A chlorine determination gave the following result:—

0·3715 gram substance gave 0·2200 gram AgCl.

	Calculated for $C_{22}H_{28}Cl_2O_8$.	Found.
Cl.	14·4 per cent.	14·6 per cent.

Ethylic Para-xylylenedimalonate, $C_6H_4[CH_2 \cdot CH(COOC_2H_5)_2]_2$.

To prepare this substance, the chlorine-compound just described is reduced with zinc-dust and acetic acid in exactly the same way as the corresponding meta-ethereal salt. About 15 grams are dissolved in 15 c.c. of glacial acetic acid, and a small quantity of zinc-dust added; as the reduction commences, the mixture becomes warm. After constant shaking for about an hour with frequent addition of small quantities of zinc-dust, water is added and the mixture warmed on the water-bath in order to dissolve the zinc acetate; the whole is then shaken out with ether several times, the ethereal solution washed with water and sodium carbonate to get rid of the acetic acid, dried over anhydrous potassium carbonate, and the ether distilled off. Ethyl para-xylylenedimalonate remains behind: as in the case of the

meta-derivative, however, a very considerable quantity of the chlorine compound still remains unreduced; it is necessary, therefore, to repeat the treatment with zinc-dust and acetic acid, and it was found best to work with only small quantities of the substance, and submit it to at least three reductions. It is thus obtained as a slightly yellow oil, which if allowed to remain over sulphuric acid in a vacuum, in a few days deposits a quantity of colourless crystals; these are freed from oil by spreading them on a porous plate and washing with a trace of alcohol, when the substance is obtained quite pure; after drying in a vacuum, an analysis was made with the following results:—

0·2285 gram substance gave 0·5215 gram CO_2 and 0·1495 gram H_2O .

	Calculated for $\text{C}_{22}\text{H}_{30}\text{O}_8$.	Found.
C	62·56 per cent.	62·24 per cent.
H	7·11 „	7·27 „
O	30·33 „	30·49 „

Ethylc para-xylylenedimalonate is a fine, white, crystalline substance, which melts at 51° ; it is very readily soluble in ether, far less so in alcohol, and insoluble in water. This ethereal salt, like the corresponding meta-derivative, forms a compound with sodium, which is obtained as a white precipitate when the calculated quantity of sodic ethylate and ethyl para-xylylenedimalonate are mixed together in ethereal solution. The precipitate is washed with pure dry ether, by decantation, the same precautions being taken to exclude the air as were described in the preparation of the meta-compound, thrown on to a filter and transferred as quickly as possible to a tared stoppered weighing bottle; after standing in vacuum over sulphuric acid, a sodium estimation was made, of which the following was the result:—

0·5010 gram substance gave 0·1520 gram Na_2SO_4 .

	Calculated for $\text{C}_{22}\text{H}_{28}\text{Na}_2\text{O}_8$.	Found.
Na	9·9 per cent.	9·8 per cent.

This sodium-derivative is white and extremely hygroscopic, in consequence of which it decomposes quickly on exposure to the air, and immediately on the addition of water or acids, the ethereal salt being regenerated.

It was thought that if this compound were treated with iodine or bromine a tetrahydropara-naphthalene-derivative would be formed, as shown by the following equation:—

The experiment was carried out thus: 12 grams of ethyl para-xylylenedimalonate, dissolved in about 50 c.c. of ether, were mixed with an ethereal solution of sodic ethylate, containing 1·4 grams of sodium, and then 5 grams of bromine slowly added. The colour of the bromine disappeared instantly on coming into contact with the sodium-compound, the last few drops, however, causing a yellow coloration. Water was then added to dissolve the sodium bromide, and after separating and drying the ethereal solution, the ether was distilled off; 16 grams of a heavy oil remained, which on examination was found to contain bromine. On standing for 24 hours in a cool place, crystals were deposited; these were partially separated from the mother-liquor by spreading on a porous plate, and while still on the plate purified by washing with a trace of methyl alcohol, in which the oil is readily soluble, whilst the crystals are hardly dissolved at all. After crystallising from hot methyl alcohol, 4·5 grams of a fine, colourless substance were obtained, and on analysis numbers were found agreeing with the formula—

- I. 0·2370 gram substance gave 0·3990 gram CO_2 and 0·1090 gram H_2O .
 II. 0·2900 gram substance gave 0·1820 gram bromide of silver.

		Found.	
		I.	II.
C	Calculated. 45·6 p. c.	45·9	—
H	4·8 „	5·1	—
Br	27·5 „	—	26·5 per cent.

This substance is, therefore, ethylic para-xylylenedibromodimalonate; it is only sparingly soluble in cold, but readily in hot methyl alcohol, from which it crystallises on cooling in magnificent, glittering plates, which melt at 107—108°. In order to prove that it really had the constitution assigned to it above, it was treated with zinc-dust and acetic acid, when it was reduced to ethyl para-xylylenedimalonate, and far more readily than the corresponding chlorine-compound. On extracting with ether, a quantity of a crystalline product was obtained, which melted at 51°, and possessed all the properties of ethylic para-xylylenedimalonate, there can therefore be no doubt that this substance is para-xylylenedibromodimalonate.

Since bromine acted on the sodium-compound of ethylic para-xylylenedimalonate in this manner, an experiment was made in exactly the same way, using the calculated quantity of iodine, however, instead of bromine; the product of the reaction was a thick brown oil, which owing to the impurities present could not be got to crystallise; on heating a few drops in a test-tube, violet vapours were evolved, and traces of iodine sublimed. The analysis of the impure substance showed that it contained only from 2 to $2\frac{1}{2}$ per cent. of iodine, which was present in the combined state, so that ethylic para-xylylenediiododimalonate was either not formed at all or only in very small quantities, as this compound would contain 38 per cent. of iodine. The oil was, therefore, hydrolysed and converted into the dicarboxylic acid by heating it in a sealed tube at 180° until there was no further evolution of carbonic anhydride; the product was isolated, recrystallised, and when pure its melting point was found to be $223\text{--}224^\circ$ (the melting point of para-phenylenedipropionic acid). In this case, also, it is clear that no ring formation had taken place.

Para-xylylenedimalonic Acid, $\text{C}_6\text{H}_4[\text{CH}_2\cdot\text{CH}(\text{COOH})_2]_2$.

When the ethereal salt of this acid, which has been already described, is boiled for about four hours on a water-bath, with excess of potash in methyl alcohol, hydrolysis is complete. The solution is then evaporated to dryness to drive off the alcohol, the residual potassium salt is dissolved in water, and the solution after acidifying with sulphuric acid is extracted repeatedly with ether. When the ethereal solution has been dried over calcium chloride, and the ether distilled off, para-xylylenedimalonic acid is obtained as a thick syrup, which on standing solidifies to a hard cake. This is spread on a porous plate in order to get rid of traces of oil, and is then warmed with water and a small quantity of animal charcoal; the filtered solution when allowed to evaporate over sulphuric acid in a vacuum, slowly deposits a finely divided crystalline powder; this is collected and dried, first on a porous plate, and then in a vacuum over sulphuric acid. The analysis gave the following results:—

0.1982 gram substance gave 0.3905 gram CO_2 and 0.0885 gram H_2O .

	Calculated for $\text{C}_{14}\text{H}_{14}\text{O}_8$.	Found.
C	54.2 per cent.	53.7 per cent.
H	4.5 „	4.9 „
O	41.3 „	41.4 „

On heating, para-xylylenedimalonic acid melts at about 195° with

slight decomposition and evolution of carbonic anhydride; the whole mass then suddenly becomes solid, and on continuing to heat melts again at 223° (the melting point of para-phenylenedipropionic acid, see below).

The silver salt was prepared by precipitating a neutral solution of the ammonium salt with silver nitrate; it is a white amorphous substance, and on analysis gave the following result:—

0.5843 gram substance gave 0.3393 gram silver.

	Calculated for $C_{14}H_{10}Ag_4O_8$.	Found.
Ag	58.47 per cent.	58.07 per cent.

The neutral solution of the ammonium salt gives with lead acetate, barium chloride, and calcium chloride, white precipitates of the respective salts.

Paraphenylenedipropionic Acid, $C_6H_4(CH_2CH_2COOH)_2$.

Para-xylylenedimalonic acid when heated is easily decomposed yielding paraphenylenedipropionic acid and 2 mols. of carbonic anhydride. This decomposition is best effected by heating a solution of the acid in about 3 parts of water at 180° in a sealed tube until the evolution of gas ceases, exactly as is described in more detail under the corresponding meta-compound. The reaction in this case goes beautifully, and after cooling, the tube is found to be filled with hard white nodular masses of almost pure paraphenylenedipropionic acid. To purify the product, it is collected and spread on a porous plate to remove traces of oil, and is then dissolved in boiling methyl alcohol; this solution on standing for 24 hours deposits the pure acid in curious nodular aggregates, which after washing with a little alcohol and drying at 100° , were analysed and the following results obtained:—

0.1770 gram substance gave 0.4200 gram CO_2 and 0.1010 gram H_2O .

	Calculated for $C_{12}H_{14}O_4$.	Found.
C	64.86 per cent.	64.73 per cent.
H	6.31 ,,	6.34 ,,
O	28.83 ,,	28.93 ,,

Paraphenylenedipropionic acid melts at 223 — 224° ; it is only sparingly soluble in cold methyl or ethyl alcohol, and almost insoluble in water.

The silver salt is a white, apparently amorphous precipitate which does not blacken on exposure to diffused light; it was obtained in the

usual way by precipitating the neutral solution of the ammonium salt, and, after drying at 100° , analysed.

0.4300 gram substance gave on ignition 0.2125 gram silver.

	Calculated for $C_{12}H_{12}Ag_2O_4$.	Found.
Ag	49.54 per cent.	49.42 per cent.

The following reactions are shown by a neutral solution of the ammonium salt:—Copper sulphate gives a faint greenish-white amorphous precipitate, sparingly soluble in cold, more readily in hot water; lead acetate throws down the lead salt as a white compound insoluble in water; zinc sulphate and mercuric chloride also give white precipitates, whilst barium chloride and calcium chloride give no precipitate.

The following experiment was then made in the hope of obtaining an anhydride of this acid:—0.3 gram of the pure substance was heated in a test-tube in a metal-bath for half an hour at 300 — 320° , the acid darkened slightly but no appreciable quantity of water was given off; on raising the temperature considerably and as quickly as possible, the whole distilled over in the form of a thick oil, which, however, at once solidified on the colder parts of the tube, while a very small quantity of carbonaceous matter remained behind. The solid distillate was scraped out of the tube and washed on a porous plate with a small quantity of ether, when an almost colourless substance was obtained which melted at 221 — 224° ; it is therefore clear that no anhydride was formed, but that, on heating, paraphenylenedipropionic acid (m. p. 223 — 224°) distils unchanged.

Methylic Paraphenylenedipropionate.

By boiling the silver salt of the acid, suspended in ether, with excess of methyl iodide, for about four hours on a water-bath, methylic paraphenylenedipropionate is formed. The solution is filtered, the residual iodide of silver washed well with warm ether, the washings added to the filtrate, and the whole distilled, when the ethereal salt remains behind as a white, crystalline mass. It was purified by spreading on a porous plate and then recrystallising from hot methyl alcohol. The analysis gave the following results:—

0.16225 gram substance gave 0.3995 gram CO_2 and 0.1050 gram H_2O .

	Calculated for $C_{14}H_{18}O_4$.	Found.
C	67.20 per cent.	67.14 per cent.
H	7.20 „	7.19 „
O	25.60 „	25.67 „

Methylic paraphenylenedipropionate is only sparingly soluble in cold methyl alcohol, and separates out from the hot solution, on cooling, in beautiful glittering plates which melt at 115° .

Paraphenylenediacrylic Acid, $C_6H_4(CH : CH \cdot COOH)_2$.

Ethylic ortho-xylylenedichlorodimalonate is readily decomposed on heating it with alcoholic potash into hydrochloric acid, carbonic anhydride, and orthophenylenediacrylic acid.

It was thought interesting to try a similar reaction with an analogous para-derivative. 2 grams of ethylic para-xylylenedibromodimalonate were mixed with a solution of 3 grams of caustic potash in a little alcohol, and the mixture boiled on a water-bath for four hours. After addition of water, the solution was evaporated to dryness, in order to expel the alcohol, and the residual potassium salts dissolved in water; on acidifying with dilute sulphuric acid, a yellowish flocculent substance, probably consisting of impure paraphenylenediacrylic acid, was precipitated; this was not filtered off but the whole extracted with ether, the ethereal solution dried and the ether distilled off. The semi-solid mass which remained was mixed with about 10 c.c. of water and heated in a sealed tube for eight hours at 180° , in order to decompose any tetrabasic acid which might be present. The slightly yellow flocculent substance thus obtained was purified by dissolving it in ammonia, boiling with animal charcoal, and reprecipitating; lastly the substance was well washed with water, dried at 100° and analysed, when the following results were obtained:—

0.2010 gram substance gave 0.4840 gram CO_2 and 0.0892 gram H_2O .

	Calculated for $C_{12}H_{10}O_4$.	Found.
C	66.05 per cent.	65.67 per cent.
H	4.59 ,,	4.96 ,,
O	29.36 ,,	29.37 ,,

Paraphenylenediacrylic acid has been already obtained by Loew (*Annalen*, **231**, 361—384) by the action of sodic acetate and acetic anhydride on terephthalic aldehyde; the product obtained from ethylic para-xylylenedibromodimalonate is identical with Loew's compound, its properties agreeing with those already given by him.

Meta-xylylene Cyanide, $C_6H_4(CH_2 \cdot CN)_2$.

The method used in the preparation of this substance is as follows:—13 grams of meta-xylylene bromide are dissolved in alcohol

and a slight excess of the calculated quantity of potassium cyanide, in aqueous solution, added. No reaction takes place at first, but, on warming, potassium bromide begins to crystallise out on the sides of the flask, the reaction being as follows:— $\text{C}_6\text{H}_4(\text{CH}_2\text{Br})_2 + 2\text{KCN} = \text{C}_6\text{H}_4(\text{CH}_2\text{CN})_2 + 2\text{KBr}$.

By boiling on a water-bath with reflux condenser for a considerable time, the change is completed, the alcohol is then distilled off, and the residue treated with water, whereby the crude meta-xylylene cyanide is precipitated as a brown oil; after separating it from the aqueous solution by means of a separating funnel, it is dried over calcium chloride and fractioned in a vacuum.

Thus purified, it is obtained as a colourless oil, which on cooling almost immediately solidifies to a white crystalline mass; the analyses gave the following results:—

- I. 0.2410 gram substance gave 0.6775 gram CO_2 and 0.1120 gram H_2O .
 II. 0.2195 gram substance gave 0.6155 gram CO_2 and 0.1095 gram H_2O .
 III. 0.22425 gram substance gave 34.75 c.c. Nitrogen. Bar. 718 mm. T. 17° .

	Calculated for $\text{C}_{10}\text{H}_8\text{N}_2$.	Found.		
		I.	II.	III.
C	76.92 p. c.	76.48	76.67	—
H	5.13 „	5.54	5.16	—
N	17.95 „	—	—	17.75 p. c.

Meta-xylylene cyanide is a colourless, crystalline substance melting at $28-29^\circ$; it boils under 300 mm. pressure at $305-310^\circ$, a certain amount of decomposition taking place. Ether, alcohol, and chloroform dissolve it readily; it is insoluble, however, in water and light petroleum.

Metaphenylenediacetic acid, $\text{C}_6\text{H}_4(\text{CH}_2\text{COOH})_2$.

To obtain this acid, the crude oil formed by the action of potassium cyanide on meta-xylylene bromide is, without further purification, hydrolysed by boiling it on a water-bath with an excess of alcoholic potash solution, whereby it is converted into the potassium salt of metaphenylenediacetic acid.

Hydrolysis does not take place at all readily, and it is necessary to boil for about six hours before the cessation of the evolution of ammonia shows that the reaction is at an end. When this is the case, the alcohol is distilled off and the residue dissolved in water; on acidifying with dilute sulphuric acid, a small quantity of a brown

resinous substance is precipitated and is filtered off; the clear solution is then extracted about 20 times with ether, and after drying the ethereal solution over calcium chloride and distilling off the ether, the acid is left in slightly yellowish crystalline crusts. The product is spread on a porous plate, and while still on the plate, the traces of oil are washed away with a few drops of ether; after two crystallisations from water, it is obtained pure in the form of colourless needles.

It was dried at 100°, and analysed with the following results:—

0.1697 gram substance gave 0.3830 gram CO₂ and 0.0800 gram H₂O.

	Calculated for C ₁₀ H ₁₀ O ₄ .	Found.
C	61.86 per cent.	61.54 per cent.
H	5.15 „	5.24 „
O	32.99 „	33.22 „

Metaphenylenediacetic acid melts at 170°; it is easily soluble in water, alcohol, and ether, but almost insoluble in light petroleum or chloroform: it crystallises from water in beautiful clusters of concentric needles. The yield obtained by hydrolysing the cyanide with alcoholic potash is almost theoretical.

On adding silver nitrate to a neutral aqueous solution of the ammonium salt, the silver salt is obtained as a white amorphous precipitate; after washing well with water, and drying first on a porous plate, and then at 100°, analysis gave the following result:—

0.1305 gram substance gave 0.0685 gram Ag.

	Calculated for C ₁₀ H ₈ Ag ₂ O ₄ .	Found.
Ag	52.8 per cent.	52.5 per cent.

In an aqueous solution of the ammonium salt, lead acetate gives a white amorphous precipitate, but with sulphate of zinc a crystalline substance is produced; barium and calcium chlorides do not give any reaction.

No anhydride of the acid was obtained although an experiment was made as follows:—0.2 gram of the pure acid was heated in a metal-bath for 40 minutes at 300—320°, and then distilled by quickly raising the temperature: a small amount of carbonaceous residue was left, but almost the whole of the acid passed over as a slightly yellowish oily distillate, which condensed on the cooler parts of the tube and immediately solidified; it was purified by washing with a small quantity of ether, and a melting point taken, which was found to be 170—172°; metaphenylenediacetic acid melts

at 170° , and it is therefore clear that no anhydride had been formed.

Para-xylylene Cyanide, $C_6H_4(CH_2CN)_2$.

15 grams of para-xylylene bromide are dissolved in alcohol, and 8 grams of potassium cyanide dissolved in as little water as possible are added to the solution; no reaction takes place at first, but on heating the mixture double decomposition commences, a large quantity of a bright-yellow flocculent substance separating; this is, however, not para-xylylene cyanide, but a resinous compound formed by some more complicated secondary reaction: after boiling on the water-bath with reflux condenser until the penetrating odour of the bromide is no longer perceptible, the alcohol is distilled off and water added to the residue, when the cyanide is precipitated as a dirty-white solid. On shaking with ether, it is dissolved while the insoluble resinous impurities are left; after drying, the ether is evaporated and the para-xylylene cyanide is obtained crystallised on the sides of the flask.

It may be purified by redissolving it in ether, boiling with a little animal charcoal, filtering, and allowing the filtrate to evaporate slowly: by this means well-defined crystals are obtained which after recrystallisation are quite pure. On analysis, the following results were obtained:—

I. 0.1690 gram substance gave 0.4755 gram CO_2 and 0.0820 gram H_2O .

II. 0.12425 gram substance gave 19.7 c.c. Nitrogen. Bar. 718 mm. $T = 7^{\circ}$.

	Calculated for $C_{10}H_8N_2$.	Found.	
		I.	II.
C	76.90 per cent.	76.73	—
H	5.13 „	5.39	—
N	17.95 „	—	18.16 per cent.

Para-xylylene cyanide is a colourless substance which crystallises in long three-sided prisms and melts at 96° ; in whatever manner the conditions are varied, it seems impossible to avoid the formation of a large amount of the yellow resinous substance alluded to above; the yield of cyanide is, therefore, a poor one, being only about 50 per cent. of the theoretical.

Paraphenylenediacetic Acid, $C_6H_4(CH_2COOH)_2$.

When the preceding compound is hydrolysed, paraphenylenediacetic acid is obtained; for its preparation, 2 grams of the cyanide

were added to an excess of the calculated quantity of potash dissolved in methyl alcohol, and boiled on the water-bath with reflux condenser, until no further evolution of ammonia could be observed.

After evaporating the alcohol, the residue was taken up with water and dilute sulphuric acid until the solution showed a strongly acid reaction; paraphenylenediacetic acid was thus partially precipitated together with a small quantity of brown impurity; the whole was shaken out well with ether, when the acid dissolved, leaving most of the impurities. The ethereal solution was dried and the product obtained as a crystalline crust when the ether was distilled off; the yield was almost theoretical. To purify the acid, it was dissolved in alcohol, boiled with a little animal charcoal, the filtered solution evaporated to dryness on the water-bath, and the residue twice recrystallised from water containing a trace of alcohol. Para-phenylenediacetic acid is thus obtained in fine, colourless needles, which are very readily soluble in alcohol, far less so in water or ether, and melt at 240—241°. The analysis gave the following results:—

0.1730 gram substance gave 0.3920 gram CO_2 and 0.08850 gram H_2O .

	Calculated for $\text{C}_{10}\text{H}_{10}\text{O}_4$.	Found.
C	61.86 per cent.	61.80 per cent.
H	5.15 „	5.46 „
O	32.99 „	32.74 „

The silver salt is precipitated on adding nitrate of silver to a neutral solution of the ammonium salt as a white amorphous mass; it was collected, well washed with water, and dried, first on a porous plate, then at 100°, and analysed with the following result:—

0.2805 gram substance gave 0.1473 gram silver.

	Calculated for $\text{C}_{10}\text{H}_8\text{Ag}_2\text{O}_4$.	Found.
Ag.	52.8 per cent.	52.6 per cent.

Paraphenylenediacetic acid is not converted into its anhydride even on heating at 300—320° for half an hour, since, by quickly raising the temperature, a product distils over which after washing with a little ether showed the same melting point as the original acid.

NOTE ON THE PREPARATION OF ISOPHTHALIC ACID.

Meta-xylylenediethyl Ether, $\text{C}_6\text{H}_4(\text{CH}_2\text{OC}_2\text{H}_5)_2$.

The preparation of isophthalic acid by the oxidation of meta-xylene with potassium dichromate and dilute sulphuric acid (Fittig, Velguth,

Annalen, **148**, 11), is known to be very tedious owing to the extreme stability of this hydrocarbon, the greater portion of which remains unchanged even after continued boiling for days together. The following method was therefore worked out and found to give excellent results: meta-xylylene is treated with the requisite quantity (2 mols.) of bromine at 125°, and the dibromide formed, without purification, is boiled with alcoholic potash, and thus converted into meta-xylylene diethyl ether. When this is treated with potassium dichromate and sulphuric acid, a quantitative yield of isophthalic acid is obtained; the ether was, however, first prepared in the pure state and investigated a little more closely; for this purpose pure meta-xylylene bromide was boiled for six hours with a solution of alcoholic potash which contained twice the calculated quantity of alkali, water was then added, and the oil which settled to the bottom separated from the aqueous solution, dissolved in ether, and allowed to stand over calcium chloride; after distilling off the ether, the product remained as a dark-brown oil which was found still to contain bromine, either owing to the presence of a trace of undecomposed meta-xylylene bromide, or of an intermediate compound having the formula $C_6H_4Br \cdot CH_2 \cdot OC_2H_5$. It was therefore treated with zinc-dust and acetic acid, and the ether, thus freed completely from bromine, was isolated in the usual manner, and submitted to fractional distillation, when almost the whole distilled over between 235° and 255°; this process was twice repeated and meta-xylylene diethyl ether obtained in the pure state in the form of a colourless, mobile, pleasant-smelling oil; it was analysed with the following results:—

0·1392 gram substance gave 0·3805 gram CO_2 and 0·1153 gram H_2O .

	Calculated for $C_{12}H_{18}O_2$.	Found.
C	74·23 per cent.	74·53 per cent.
H	9·28 ,,	9·19 ,,
O	16·49 ,,	16·28 ,,

This compound boils at 246—247° (712 mm. pressure, uncorr.), and does not solidify even when cooled to 0°; it is isomeric with the ortho-derivative prepared by Leser (*Ber.*, **17**, 1825), which boils at 247—249° (720 mm. pressure).

Of course, when this ether is required for the preparation of isophthalic acid, it is quite unnecessary to purify it, the crude product of the action of alcoholic potash on the xylylene bromide is mixed directly with an excess of potassium dichromate in a large flask and sulphuric acid added; the reaction is very energetic and great heat is evolved, so that in working with large quantities it is advisable to add the acid very slowly or the mixture will be apt to froth over.

When the oxidation is completed, which is the case in a very short time, the isophthalic acid seen as a white sandy powder on the bottom of the flask is collected and washed with water; it is, however, very difficult to get rid of the last traces of the green mother-liquor, and to obtain the product quite pure, it is dissolved in sodium carbonate, and the filtered solution acidified with sulphuric acid. After washing the precipitated isophthalic acid and drying it at 100° , an analysis was made with the following result:—

0.1477 gram substance gave 0.3128 gram CO_2 and 0.0500 gram H_2O .

	Calculated for $\text{C}_8\text{H}_6\text{O}_4$.	Found.
C	57.77 per cent.	57.75 per cent.
H	3.61 „	3.76 „
O	38.62 „	38.49 „

In this way, an almost theoretical yield of isophthalic acid can be obtained from meta-xylene with comparative ease and in a short time, whereas by the old method, several days were required to prepare a few grams.

This work was carried out in the laboratory of Professor A. v. Baeyer in Munich, and, before closing, I desire to express my gratitude for the kindness which was invariably shown to me, and for the interest which he took in this research.