

361. *The Direct Conversion of Iodic Acid and Aromatic Hydrocarbons into Iodonium Compounds.*

By IRVINE MASSON and EDWARD RACE.

Iodic acid in suitable concentrations of sulphuric acid attacks aromatic compounds C_6H_5X (where $X = H, CH_3, Cl, Br, I$) to give the iodonium radical $(C_6H_4X)_2I^{\cdot}$. The reaction is of a new type, and its mechanism is studied. The yields are high and the method is in these cases the simplest for preparing iodonium compounds; it incidentally furnishes a quick and delicate test for aromatic hydrocarbons in paraffins. The case of chlorobenzene has chiefly been investigated. Accompanying the iodonium radical, there is produced an iodine-free reducing agent, apparently an open-chain unsaturated acid, the product of oxidation of part of the organic reagent. A by-product, the formation of which may be largely suppressed under proper working conditions, is the iodo-derivative of the aromatic reagent.

The mechanism of the process is dealt with experimentally; various hypotheses are thus excluded, and evidence is given that it consists of a primary deoxidation of the iodic acid to the iodous stage by a fraction of the aromatic reagent (which is thereby converted into the open-chain unsaturated substance), followed by the direct interaction of the "iodous acid" and the aromatic reagent to give the diaryliodonium radical. The latter interaction is also new; it is shown experimentally to proceed, quantitatively, with an inorganic iodous compound, independently prepared; and by considering the properties of iodous iodine it is concluded that this is an ionic reaction: $I^{+++} + 2RH \longrightarrow 2H^+ + R_2I^+$ or alternatively $IO^+ + 2RH \longrightarrow H_2O + R_2I^+$. The need for a sulphuric acid medium is at the same time explained.

Facts are mentioned which are thought to relate to the condition of the ions in iodonium salts $R_2I^+X^-$, and to the mechanism of their known thermal decomposition into $RI + RX$.

Full analytical data are stated, with notes of precautions.

IN a paper on the chemistry of iodoxy-compounds (Masson, Race, and Pounder, J., 1935, 1669) it was mentioned that that work had arisen from a reaction, discovered by one of us, in which benzene derivatives and iodic acid in sulphuric acid formed diaryliodonium salts in high yield. This reaction, for which we have not found any precedent or analogy, is the subject of the present paper.

For the better control of the reaction, and for the sake of a closer diagnosis of its nature, the bulk of this work has been done with chlorobenzene in preference to benzene itself or other derivatives, which have, however, been partly studied; and an explanation of the reaction has been reached. In a number of cases, this reaction affords much the simplest and most economical way to make iodonium compounds; it also affords a very quick, easy, and decisive test for the presence of traces (or more) of aromatic hydrocarbons in other hydrocarbon oils (see p. 1719).

If benzene, toluene, chloro-, bromo-, or iodo-benzene is shaken, at or below room temperature, with a suspension of iodine pentoxide in concentrated sulphuric acid, a rapid reaction occurs which in a few minutes forms a dark solution. When this is diluted with ice or cold water, an oily flocculus is precipitated; this, which is essentially the iodo-

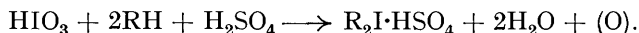
substitution product of part of the aromatic reagent, is a by-product, mainly avoidable under the controlled conditions to be described. The acid liquor separated from it gives, when treated with sulphur dioxide or sodium iodide or both, a bulky whitish or yellow precipitate which is the diaryliodonium iodide. Alternatively, the acid liquor may be diluted so as to make the sulphuric acid in it 8*N.*, whereupon an oil separates, which crystallises later and is the iodonium hydrogen sulphate, a substance with interesting physico-chemical characteristics. In all these cases the linkage between the aromatic nucleus and the iodine of the iodonium radical is exclusively in the *para*-position to the methyl or halogen substituent.

With anisole and other highly reactive or oxidisable benzene derivatives, it is difficult to obtain more than traces of an iodonium product; even under carefully controlled conditions, drastic decompositions predominate. On the other hand, when the substituent is *meta*-directing, as with nitrobenzene, scarcely any reaction is observed, though a little iodonium derivative is slowly formed.

The practical success of the reaction depends, as in nitrations, upon choosing the proper degree of hydration of the sulphuric acid, upon maintaining this despite the water set free by the action itself, and upon keeping the temperature from rising. For instance, for benzene, the concentration of the acid should not be weaker than $\text{H}_2\text{SO}_4 : 2\text{H}_2\text{O}$, and should not exceed $\text{H}_2\text{SO}_4 : 1 \cdot 2\text{H}_2\text{O}$; and the temperature should be below 10° , preferably 0° . For chlorobenzene, a less vigorous reagent, the acid should be $2\text{H}_2\text{SO}_4 : 1\text{H}_2\text{O}$, and the temperature should be between 15° and 25° . (In using the reaction as a test for aromatic impurity in paraffins, ordinary concentrated sulphuric acid, $3 \cdot 5\text{H}_2\text{SO}_4 : 1\text{H}_2\text{O}$, is safe; powdered sodium iodate can be used in place of iodine pentoxide; and the volume of oil so tested need not exceed 2 or 3 c.c. The product is poured into water, separated, and filtered, and the solution treated with sulphur dioxide; the flocculent iodonium iodide precipitates at once or, with only minute traces, after some time.)

Using chlorobenzene (2 mols. to 0.5 mol. of iodine pentoxide), and working strictly quantitatively under a variety of conditions of temperature, of concentration of sulphuric acid, and of the mode of mixing the reagents, we can account for as much as 98% of the initial iodine and 85% of the initial chlorophenyl groups, in the yield of bis-(*p*-chlorophenyl)iodonium salt, with some of its decomposition product *p*-chloroiodobenzene, and a trace of free iodine. No oxidising agent is left.

It will be seen that, besides the missing 15% of chlorophenyl groups, one-third of the initial oxygen atoms are also unaccounted for:



This "disappearance" of one oxygen atom per iodonium radical formed has a parallel in the interaction of iodosobenzene and concentrated sulphuric acid:



in which Meyer and Hartmann first discovered the existence of iodonium compounds. They showed (*Ber.*, 1894, 27, 426) that the oxygen did not survive in any oxidising agent, and that it was not evolved as such; but they did not further pursue the point, remarking "offenbar wird der Sauerstoff zur Oxydation eines kleinen Theiles der Substanz verbraucht." In our reaction, although we have not yet finally identified the dissolved substance which accounts for the missing oxygen, we have been able to disentangle its reactions from the complications which occur when it is in the presence of iodonium salts; and the evidence makes it most probable that the missing oxygen atom has broken the aromatic ring in the 15% of the organic reagent, to form (in the case of chlorobenzene) a chlorinated unsaturated aliphatic acid. The following facts from this section of the work bear upon the main reaction.

The main reaction liquor from experiments with chlorobenzene was deprived of most of its iodonium product as the crystalline hydrogen sulphate, the remainder was precipitated from the mother-liquor with sodium iodide, and the excess of iodide removed with excess of silver sulphate. The resulting solution contained a non-phenolic substance which reduces dilute permanganate strongly, absorbs bromine, is neither steam-volatile nor

extractable with benzene from acid or from alkaline solution, is destroyed (as a reducing agent) by alkali, but is precipitated with sulphate by barium carbonate. Oxidised in acid solution by permanganate in presence of silver sulphate, it yields hydrochloric acid (as silver chloride) and carbon dioxide; the oxygen content of the latter is 1.57 times that in the permanganate used to produce it (calc., *e.g.*, for chlorofumaric acid, 1.60). It is a remarkable fact, which we have not explained, that if the permanganate oxidation is done without previous removal of the iodonium product from solution, the latter is at once wholly decomposed at the same time as the reducing agent, forming *p*-chloriodobenzene, and so also is additional iodonium salt if it is deliberately put into the liquor in limited quantity; yet the pure iodonium salt in the absence of the reducing agent is not at all affected by permanganate under conditions otherwise identical.

In the main reaction between iodic acid and chlorobenzene, the production of some carbon dioxide was observed; experiments were made in which this was collected quantitatively and weighed. It proved to represent no more than a few units % of the initial material, unless high reaction temperatures were allowed. It appears to be formed in a side reaction between some of the primary reducing agent just described and a small part of the iodic acid, which therefore acts in this secondary reaction much in the same way as did the permanganate in the tests above mentioned. The evidence also makes it probable that when low yields of iodonium salt occur, through the sulphuric acid being too concentrated or the temperature too high, the increase in aromatic iodo-compound at the expense of iodonium is largely due to the same peculiar breakdown of iodonium in the presence of the reducing agent and an oxidiser, as was noted in the permanganate oxidations.

The equation on p. 1719, together with the information given about the destination of the oxygen atom and the causes of iodonium loss, state adequately the balance sheet of substances, but they do not give a dynamically satisfying explanation of the sequence of action. Two hypotheses for this present themselves. One is that iodic acid and hydrocarbon first interact to form a complex, which then, or in analysis, undergoes fission into the diaryliodonium radical and organic degradation products. Such an initial interaction might, for instance, produce the sulphate of the diaryliodol radical whose existence was disclosed in our earlier paper: $2RH + HIO_3 + H_2SO_4 \longrightarrow 2H_2O + R_2IO \cdot HSO_4$; or $3RH + HIO_3 + H_2SO_4 \longrightarrow 2H_2O + R_3IO \cdot H_2SO_4$, a possible analogue of the tertiary phosphine or stibine oxides; or even $4RH + HIO_3 + H_2SO_4 \longrightarrow 3H_2O + R_4I \cdot HSO_4$, a possible quaternary iodonium salt.

We did, in fact, find suggestions of the formation and survival of some such precursor of iodonium; for example, the quantity of iodonium salt analytically got from the diluted reaction liquor was considerably greater than would be allowed by the solubility of the pure iodonium salt in acid of the same concentration, as found in separate measurements. But it is clear that the complex, if one were present, could not be a diaryliodol compound, for the characteristic oxidising reactions of this were wholly lacking; and careful experiments have shown us that the analytical precipitation of actual diaryliodonium, from the solutions which would contain a supposed tertiary oxide or quaternary radical, did not release any other discoverable substance, such as would represent the organic remainder of the molecule of the hypothetical complex. Further, iodic acid did not react with more than 2 mols. of the aromatic reagent. Hence, plausible hypotheses of this kind are, on the experimental evidence, scarcely tenable, notwithstanding the initial indications in their favour.

The other hypothesis is that iodic acid produces iodonium only in virtue of its being first wholly reduced to "iodous acid," HIO_2 or I_2O_3 , by its oxidising a part (*e.g.*, 15%) of the initial aromatic reagent so as to open the ring and form the unsaturated iodine-free acids already mentioned. The resulting iodous acid, as its iodine is already in the requisite condition of tervalency, might then be supposed to react: $2RH + OIOH \longrightarrow R_2I \cdot OH + H_2O$. This hypothesis has been fully borne out by the experiments in which we put it to the test; for, on preparing iodine sesquioxide (as a sulphate) we found that, in the appropriate sulphuric media, it at once attacks chlorobenzene or benzene very smoothly and cleanly and without noticeable heat, giving simply the pure iodonium radical in

quantitative yield. Further experiments on this and allied matters are in progress (cf. Masson, *Nature*, 1937, **139**, 150).

The known properties of iodine sesquioxide, however, enable us to understand its attack upon aromatic reagents (above) and consequently the course and the conditions of the reaction of iodic acid under discussion; for the inorganic preparative work of Fichter and Kappeler (*Z. anorg. Chem.*, 1915, **91**, 134), following Chrétien's original isolation of $I_2O_3 \cdot SO_3 \cdot 0.5H_2O$ (*Ann. Chim. Phys.*, 1898, **15**, 358), has clearly shown that I_2O_3 is a basic oxide towards powerful and concentrated acids. Accordingly, in our main reaction, all the iodic acid is gradually reduced by a fraction of the organic reagent (which thereby is degraded), but the reduction goes no further than to the iodous state, because the sulphuric acid stabilises this as an iodous sulphate; and the immediately ensuing reaction between this solute and the aromatic reagent, forming the iodonium salt which is the most obvious product of the reaction as a whole, is to be considered as a cationic attack. For instance, if the iodous cation is simply I^{+++} , corresponding to $I(HSO_4)_3$, the reaction is $I^{+++} + 2RH \longrightarrow 2H^+ + (R_2I)^+$, and if it is the univalent iodyl radical, as Chrétien's salt would suggest, the reaction is $IO^+ + 2HR \longrightarrow H_2O + (R_2I)^+$. The former alternative would entail a change in the electronic number of the iodous atom from 50 to 54; the latter need not call for any change from 54. These matters will be dealt with in the light of other experimental evidence, to be produced in later papers.

Notes on the Iodonium Salts.—Crystalline bis-(*p*-chlorophenyl)iodonium hydrogen sulphate undergoes, on treatment with water, a strikingly evident conversion into the crystalline anhydrous normal sulphate; as seen under the microscope, the process seems to go by way of a metastable oily form (also observed during the initial preparation of the hydrogen sulphate). The change is reversed in sulphuric acid, and the concentration of acid in which both solid phases are in equilibrium is near 6N. : $2 R_2I \cdot HSO_4 \rightleftharpoons (R_2I)_2SO_4 + H_2SO_4$.

Organic solvents such as alcohols and acetone dissolve appreciable amounts of iodonium salts, particularly those in which the phenyl groups of the cation are already substituted; while water is commonly weaker as a solvent. Chloroform, whether freed from alcohol or not, has a notably specific effect upon the hydrogen sulphates (and possibly some other salts) which carbon tetrachloride has not; the salt partly dissolves as such, and to some extent undergoes fission, producing the aromatic iodo-compound. This is reminiscent of the specific effect of chloroform on the most heavily substituted quaternary ammonium halides, which are not only highly soluble in it (Peddle and Turner, *J.*, 1913, **103**, 1202) but also, if they are optically active, are racemised by it, apparently by fission and re-union (Wedekind, Paschke, and Mayer, *Ber.*, 1911, **44**, 1406).

That a salt of an alkali-forming cation with a strong oxy-acid should have an oily form, besides solubilities such as are here indicated, points to marked polarisability of the anion by the cation. This interpretation is in no way inconsistent with the study of diphenyl-iodonium iodide by Juliusburger, Topley, and Weiss (*J.*, 1935, 1295), wherein by using radioactive iodine they showed that the covalent iodine and the anionic iodine do not exchange places during aqueous reactions, or even during incipient thermal decomposition; nor does it conflict with the evidence from *X*-rays, by which Medlin showed that the distance between the two iodine atoms in the crystals of the same compound is compatible with an ionic structure, not with a covalent link (*J. Amer. Chem. Soc.*, 1935, **57**, 1026). Fletcher and Hinshelwood (*J.*, 1935, 596) have shown the thermal decomposition of the iodide to be unimolecular, and have also measured the activation energies of the process in the solid state and in solution in iodobenzene. It seems clear that any strong interionic polarisation, the effects of which are to induce, as has been mentioned, properties tending towards those of covalent compounds, must play an important part in initiating the wholly irreversible fission which all iodonium salts undergo when they are heated, $R_2I \cdot X \rightleftharpoons RI + RX$, wherein the hitherto anionic *X* becomes covalently attached to one of the radicals *R*.

EXPERIMENTAL.

For lack of a more accurate word, and for the sake of brevity, we use the term "iodylation" for the operation in which iodic acid acts on an aromatic compound.

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Conduct of an Iodulation.—The following characteristic example with chlorobenzene gives the practical directions; in any departure from these, we find it important to attend to the principles outlined on p. 1719, and particularly to calculate beforehand the range of hydration of the sulphuric acid during the proposed iodulation.

25 Millimols. of iodine pentoxide (= 8.38 g. of 99.4% material) are dissolved in 5.0 c.c. of water, and the solution is added to 20 c.c. of 95% sulphuric acid, a fine suspension thus being obtained. This is cooled, and is well shaken with 100 millimols. of pure chlorobenzene (*ca.* 10.3 c.c.), the temperature being 15–20°. With continual shaking, 30 c.c. more of the same sulphuric acid are run in from a burette in 2 c.c. doses, the temperature being kept between 15° and 25° by external cooling; this addition necessarily occupies some hours, but might be accelerated if a very efficient internal cooling arrangement were used. During the addition the mixture becomes very dark; the pentoxide eventually disappears, and the reaction is then over. To the mixture, chilled in a freezing mixture, are added 150 g. of chilled pure ice, in order to make the sulphuric acid about 8*N*. From this point, the treatment varies according to the object of the experiment, but it must be adapted to the somewhat inconvenient properties of iodonium salts, and to the presence of the by-product, the aromatic iodo-compound.

An oil deposits which crystallises on standing, and should then be crushed under its liquor. The crystals contain about nine-tenths of the total iodonium yield, and consist of anhydrous $R_2I \cdot HSO_4$ with some intermixed *p*-chloriodobenzene, coloured dark by small traces of other substances. The solid is collected on a sintered-glass filter and washed free from iodic acid, if any is left, with 8*N*-sulphuric acid. To isolate the hydrogen sulphate as such, it must be washed free from water, acid, and the by-product by being rubbed repeatedly on the filter with dry ether, water vapour from the air and water-pump being excluded by appropriate fittings. Chloroform should not be used, for reasons only discovered at a late stage of our work; benzene may be used, if preceded by sufficient ether. For the final cleaning of the yield, a little dry acetone is advantageous. The best yields are *ca.* 14–15 g. From the filtrate and acid washings, the remaining iodonium is precipitable as iodide by aqueous hydriodic acid or sodium iodide, with the help of sulphur dioxide if necessary. The results of working up the final aqueous filtrate and the organic extracts (which have both been extensively studied) have been sufficiently outlined above; apart from pure *p*-chloriodobenzene (about 2.5 g.), the extractable organic residues were insignificant—they yielded with alkali rose-purple phenolic substances, and may have contained isomeric chloriodo-compounds.

The quantities obtained in one such operation (in which, however, chloroform had been used as well as ether for washing the crystals) were :

| Taken : I_2O_5 , 24.9; H_2SO_4 , 919; C_6H_5Cl , 97.0; H_2O , 460 | Millimols. | | Yields, %. | |
|---|------------|---|----------------|-------------|
| | | | On PhCl taken. | On I taken. |
| Obtained : $(C_6H_4Cl)_2I$, in crystals | 31.9 | } | 74.3 | 72.3 |
| from soln. | 4.1 | | | |
| <i>p</i> -Cl- C_6H_4 -I | 10.8 | | 11.1 | 21.6 |
| Free I_2 | 1.0 | | — | 4.0 |
| Totals : | | | 85.4 | 97.9 |

Methods and Results of Analyses.—The aqueous solubilities of the nitrates, sulphates, etc., of some of the substituted iodonium radicals are so slight, even in hot water, that exceptional care has to be used in simple precipitations in order to ensure complete reaction and the purity of the precipitate. This applies to precipitations either of the iodonium as iodide, or of the anion with Ag^+ , Ba^{++} , etc. It cannot be assumed, without prior disproof, that a given iodonium salt $R_2I \cdot X$ will not undergo some fission to RI and products representing RX when it is treated with warm reagents. Upon this change is based one method of determining the equivalent weight of an iodonium radical, the salt being boiled with standard alkali, of which the residual excess, including the phenoxide, is then titrated. Other methods for determining the iodonium radical as its iodide are as described in our former paper, supplemented in some cases by determinations as chloride gravimetrically. In determining total chlorine and iodine in a chlorophenyliodonium salt, the decomposition by Stepanow's method (a twelve-fold excess of sodium being used) is followed by the usual determination of total halogen in one part of the filtrate, and in the other, the iodide is separately determined by titration with standard iodate in 5*N*-sulphuric acid containing acetone with starch as indicator (Berg, *Z. Anal. Chem.*, 1926, 69, 369), the accuracy of which for our compounds we have tested and found highly satisfactory. The methods of micro- or semi-micro-analysis would at present appear to be somewhat less

reliable for the halogens of these iodonium salts than are the foregoing full-scale methods, upon which alone we have therefore depended.

| Product. | $(C_6H_4Cl)_2I \cdot HSO_4$. | | $[(C_6H_4Cl)_2I]_2SO_4$. | | $(C_6H_4Cl)_2I \cdot I$. | | $C_6H_4Cl \cdot I$. | |
|-----------------------|-------------------------------|-------|---------------------------|-------|---------------------------|-------|----------------------|-------|
| | Found. | Calc. | Found. | Calc. | Found. | Calc. | Found. | Calc. |
| Total I | 28.27 | 28.39 | 31.94 | 31.90 | 54.01 | 53.24 | 52.84 | 53.24 |
| „ Cl | 15.84 | 15.86 | 17.60 | 17.82 | 14.72 | 14.87 | 14.89 | 14.87 |
| Ions : R_2I^+ | 78.86 | 78.28 | 87.96 | 87.94 | — | — | — | — |
| H^+ | 0.228 | 0.226 | — | — | — | — | — | — |
| $SO_4^{''}$ | 21.73 | 21.48 | 12.05 | 12.07 | — | — | — | — |
| I^- | — | — | — | — | 26.75 | 26.62 | — | — |

The iodonium iodide formed from the hydrogen sulphate or from the sulphate was that of which the analyses are shown in col. 6, and was wholly identical with the iodide precipitated from the iodylation filtrate whence the hydrogen sulphate had crystallised. Col. 8 gives the analysis of the product of its complete thermal decomposition in a sealed tube. The orientation was proved by the m. p. of this solid chloriodobenzene after its dissolution in alcohol (to free it from a trace of iodine) and complete recovery and drying : m. p. 52.9° ; synthetic *p*-chloriodobenzene, m. p. 52.1° ; mixed m. p. 52.3° . The chloriodobenzene obtained as a by-product of iodylation had m. p. 51.2° , mixed m. p. 50.7° .

Action of Iodous Sulphate on Chlorobenzene.—In one of several experiments, iodine and iodine pentoxide in nearly theoretical proportion were first allowed to interact in sulphuric acid of composition $1.99H_2SO_4 : H_2O$, in which they form a solid sulphate of the trioxide; this reaction has been described in outline by one of us (*Nature, loc. cit.*), and details will be published later. When this had occurred, and without separation of any of the ingredients, a minute excess of chlorobenzene was added, and the whole was sealed up and shaken on a wheel at 0° for 2 hours, and then kept overnight at 0° . The reaction mixture was worked up quantitatively by the methods described for iodylations, the products were identified by analyses and, as to orientation, by mixed m. p., as before, and the results were :

Taken : I_2 , 0.513 g. = 2.02 millimols.;
 I_2O_5 , 1.005 g. of 98.8% = 2.97 millimols.
 calculated to form
 I_2O_3 , 4.95 millimols.; I_2 , 0.035 millimol. (excess).

| | Millimols. | Yield, %, on calc. I_2O_3 . |
|--|------------|-------------------------------|
| Obtained : $(C_6H_4Cl)_2I^+$, in crystals | 7.99 | 91.6 |
| „ „, from soln. | 1.08 | |
| <i>p</i> - $C_6H_4Cl \cdot I$ | 0.45 | 4.5 |

Since in any case the preliminary formation of iodous sulphate from the initial reagents is, in this particular acid medium, not quite quantitative, whereas the above yields of iodonium, etc., are nevertheless calculated as if it were, it is clear that we have to do with an iodonium-forming reaction of very satisfactory completeness.

Addendum (Received, September 23rd, 1937).—Meyer and Wachter (*Ber.*, 1892, 25, 2632), in describing iodosobenzoic acid, the first iodoso-compound, include the following passage which had escaped our notice : “ Ferner ist zu prüfen, ob man durch Behandlung von aromatischen Substanzen mit Schwefelsäure und Jodsäure— JO_2OH , entsprechend der Reaction der Salpetersäure NO_2OH —Verbindungen mit der Gruppe $-JO_2$ erhalten kann. Wir können vorläufig nur mittheilen, dass Benzol beim Zusammenbringen mit Jodsäure und Schwefelsäure äusserst heftig reagiert und auf Zusatz von Wasser einen festen Körper abscheidet, welchen wir noch näher untersuchen werden.”

It does not appear that the experiment was followed up either then or after 1894, when the iodoxy- and the iodonium group were discovered; but we should not like to omit reference to this early trial of the same idea which initiated our own work described in this and in our previous paper.