V. — *On a General Method of Substituting Iodine for Hydrogen in Organic Compounds, and on the Properties of Iodopyromeconic Acid.* By Mr JAMES F. BROWN,* Assistant to Professor ANDERSON, Glasgow.

(Read 3d April 1854.)

In a paper on pyromeconic acid read before this Society, and since published in the Philosophical Magazine for September 1852, I have detailed the preparation and properties of a compound obtained by the substitution of an equivalent of bromine for an equivalent of hydrogen in that acid. Having observed that this substitution was very easily effected, I was induced to attempt the formation of an iodopyromeconic acid, in the hope of adding one to the very few instances in which the direct substitution of iodine for hydrogen has been found possible. For this purpose, I digested pyromeconic acid with tincture of iodine, but no success attended the experiment, the acid remaining entirely unchanged. The failure of this attempt led me to speculate as to its cause, and to contrive a method of producing the required substitution which has proved entirely successful, and has the further advantage of being perfectly general, so that its application will enable chemists to obtain iodine substitution compounds in cases in which they have hitherto failed.

A few preliminary observations on the cause of substitution will render intelligible the nature of the method in question. Selecting the production of bromopyromeconic acid and of trichloracetic acid, as characteristic examples of substitution, we have the following formulæ representing the changes which occur :—

$$\underbrace{C_{10}\,H_4\,O_6}_{\text{Pyromeconic Acid.}} + Br_2 = \underbrace{C_{10}\,H_3\,Br\,O_6 + H\,Br}_{\text{Bromopyromeconic Acid.}}$$

$$\underbrace{C_4\,H_4\,O_4}_{\text{Acetic Acid.}} + Cl_6 = \underbrace{C_4\,H\,Cl_3\,O_4 + 3\,H\,Cl}_{\text{Trichloracetic Acid.}}$$

In these, as in every other case of substitution, the chlorine and bromine obviously perform a twofold function, one portion entering into the complex atom in the place of an equivalent quantity of hydrogen, which is eliminated in combination with another quantity either of chlorine or bromine ; and the new product contains the same number of atoms, and is commonly said to belong to the same type. In talking of such substitution, it is not unfrequently said, that the

* It is with deep regret I have to record here the early death of Mr JAMES BROWN, who, in this and a previous communication read before this Society, had given such high promise of future eminence. He died at Glasgow on the 2d July, after an illness of only twelve hours' duration.—T. A.

atom of chlorine simply displaces or pushes out the atom of hydrogen, and so comes to occupy its place, but a very slight consideration enables us to see that it is really dependent, not so much on the quantity of chlorine which remains in the compound as on that which escapes in combination with hydrogen. The original substance in all cases of substitution, forms a perfect molecular group in which the individual affinities of the different elementary atoms are properly balanced, and the whole remains in a quiescent state. But when another element, such as chlorine, comes in contact with this complex group of atoms, it immediately exerts its affinity for the hydrogen, with which it easily combines, and withdraws the whole or part of it from the compound. In this way a gap is produced in what was before a perfect group, the balance of the affinities of its elements is destroyed, and there must either be a complete readjustment of its molecular arrangements, or some other element must stop the gap and produce another perfect molecule not differing from the original substance in the arrangement of its parts, but only in the presence of one or more atoms of a different sort from those which it previously contained. Considered in this point of view, it becomes at once obvious that we fail to produce the substitution of iodine for hydrogen, not from any inability of the former to occupy the place of the latter, but simply because it has not a sufficiently powerful affinity for hydrogen to withdraw it from the compound, so as to leave an empty space into which another portion may enter. It occurred to me that as chlorine and bromine in causing a substitution exercise the two different functions already alluded to, one quantity withdrawing hydrogen, and the other simply slipping into the vacant space, it might be possible to produce an iodine substitution by associating that element with some substance having a sufficiently powerful affinity for hydrogen, to open the door as it were, and leave nothing for it to do but to step into the place prepared for it.

For this purpose I selected the bromide of iodine, as being most likely to fulfil the required conditions. It was prepared by agitating bromine water with a considerable excess of iodine, and decanting the reddish-brown solution from the undissolved residue. When this bromide was added to pyromeconic acid, a change rapidly occurred, the solution became colourless, and iodopyromeconic acid was produced. Having succeeded in this way, I then tried the chloride of iodine, and having found it to act equally well, I made use of it in all my subsequent experiments. The chloride of iodine was prepared by passing a rapid current of chlorine through finely-pounded iodine suspended in a small quantity of water, and kept in continual agitation, care being taken to stop the process before the iodine was entirely dissolved. A moderate heat is produced during the combination, and the fluid should be kept as cool as possible.

In order, therefore, to obtain iodopyromeconic acid, a freshly-prepared solution of the chloride of iodine is mixed with a cold saturated solution of pyrome-

conic acid. The solution is instantly decolorized, and the new acid is deposited in the form of fine delicate plates, which are so abundant as to render the fluid almost semisolid. The only precautions necessary are to avoid the use of a hot solution of the acid, and an excess of the chloride, as the product, under such circumstances, becomes coloured, owing to the occurrence of a further decomposition, to be afterwards referred to. The change which first takes place is represented by the equation:—

$$C_{10} H_4 O_6 + I Cl = C_{10} H_3 I O_6 + H Cl.$$

The crystals of iodopyromeconic thus precipitated are in a short time filtered off and washed with cold water; they are then finally dissolved in boiling alcohol, from which they again deposit themselves, upon cooling, in perfectly colourless plates, having a high degree of lustre. The acid is sparingly soluble in cold water; but at a boiling heat it dissolves more readily, and crystallizes again from the solution in long, slender needles, possessing a slightly acid reaction. Acids and alkalies increase its solubility in water, but it is easily decomposed, if boiled with strong caustic potash. It is also decomposed by concentrated nitric acid, with the separation of free iodine. It gives a yellowish-white precipitate with nitrate of silver, soluble in ammonia, and with perchloride of iron it produces a deep purple colour, but no precipitate. It suffers no loss of weight at 212°, but heated to a higher temperature, it first fuses to a black fluid, and is then suddenly decomposed, with the evolution of a large quantity of iodine.

The combustion of iodopyromeconic acid was attended with some difficulty, for it was found that not only the acid itself, but even its lead salt permitted the iodine to escape in the free state, when burned either with chromate of lead, or with a mixture of oxide of copper and litharge. This would have been of little moment in determining the constitution of a substance such as iodopyromeconic acid, where the mode of its formation sufficiently indicates its composition, and the determination of the carbon and iodine would have been quite sufficient to fix its formula; but having observed the same peculiarity in another substance afterwards to be described, in which the exact determination of the hydrogen was essential to the establishment of its formula, I was compelled to devise some method by which the iodine might be retained, and the following is that which I found most successful.

The substance to be analysed was mixed with chromate of lead, and a small quantity of fused litharge reduced to a fine powder; the mixture was then introduced into a long combustion tube, held with its point downwards, and at the same time there were dropped into it small pieces of metallic lead, which remained at the under-side of the tube, and so arranged as to be about three inches apart. After the whole of the mixture had been introduced, and the remaining space in the interior of the tube filled up with chromate of lead, the point was turned

upwards, and by slight tapping a passage opened throughout the whole length of the tube, while the pieces of lead projecting above the surface melted on the application of heat, and by exposing a metallic surface during the time combustion was going on, served to retain all the iodine.

The results of analysis are as follows: The hydrogen of No. 1 *was not weighed*, as, from its combustion being effected in the ordinary way without lead, the small end of the chloride of calcium tube was completely covered with small plates of iodine.

No. 1. 4·893 grains substance burned with chromate of lead, gave
4·620 ... carbonic acid.

No. 2. 7·298 grains substance burned with chromate of lead, litharge, and metallic lead, gave
6·759 ... carbonic acid, and
·975 ... water.

No. 3. 6·85 grains substance heated with carbonate of potash, gave
6·707 ... iodide of silver.

	No. 1.	No. 2.	Calculation.		
Carbon, . . .	25·750	25·25	25·19	C_{10}	60
Hydrogen, . .	...	1·48	1·26	H_3	3
Oxygen, . . .	...	...	20·17	O_6	48
Iodine, ...	52·909	...	53·38	I	127·1
	100·000	100·00	100·00		238·1

These results correspond exactly with the formula, $C_{10} H_2 I O_5 + HO$.

Iodopyromeconic acid is monobasic, and forms salts, of which I have minutely examined only those of baryta and lead. It does not appear to form an ammonia salt.

Iodopyromeconate of baryta is readily prepared by mixing together alcoholic solutions of acetate of baryta, and of the acid made slightly alkaline with ammonia. After a short time it deposits a fine network of delicate crystals, of little solubility either in cold or hot water or alcohol. It is alkaline to litmus paper, and at 212° it suffers no loss of weight.

The following result was obtained on igniting the salt with sulphuric acid:—

4·49 grains substance gave
1·63 ... sulphate of baryta.

which corresponds to the formula, $Ba O C_{10} H_2 IO_5 + HO$, as shown by the following calculation:—

	Experiment.	Calculation.		
Carbon, . . .	...	19·068	C_{10}	60
Hydrogen, . .	...	·954	H_3	3
Oxygen, . . .	...	15·255	O_6	48
Iodine, . . .	...	40·394	I	127·10
Baryta, . . .	23·84	24·329	Ba O	76·55
	100·00	100·000		314·65

Iodopyromeconate of lead is readily obtained as a fine colourless amorphous precipitate, on mixing alcoholic solutions of the acid and acetate of lead, with the addition of a small quantity of ammonia. As thus prepared, it is apt to carry down an excess of oxide of lead, which is easily removed by warm acetic acid. It is of sparing solubility in alcohol or water, and becomes highly electrical when rubbed. This salt, contrary to expectation, evolves free iodine, like the acid itself, when burned with chromate of lead; but the phenomenon is probably owing to the decomposition of the salt taking place at a temperature much lower than that sufficient to enable the iodine to combine with lead. For this reason I contented myself with a determination of its oxide of lead, which was effected by igniting the salt, after the addition of a few drops of concentrated sulphuric acid:—

6·15 grains substance, dried in the air, gave
2·76 ... sulphate of lead.

corresponding to the formula, $PbO, C_{10} H_2 I O_5$, as shown by the subjoined calculation:—

	Experiment.	Calculation.		
Carbon, . . .	...	17·612	C_{10}	60
Hydrogen, . . .	...	·587	H_2	2
Oxygen, . . .	...	11·743	O_5	40
Iodine, . . .	...	37·309	I	127·1
Oxide of lead, . .	33·03	32·749	PbO	111·56
	100·00	100·000		340·66

I have already mentioned, that when the quantity of chloride of iodine employed is larger than is requisite for the production of iodopyromeconic acid, the fluid acquires a yellow colour, due to the presence of another compound, of very remarkable characters, produced by a further decomposition of pyromeconic acid, and to which I gave the name of iodomecone. When potash is gradually added to the fluid, after separation of the iodopyromeconic acid, a blackish precipitate immediately falls, which rapidly dissolves on agitation of the fluid, while a peculiar odour is evolved. After the addition of the potash has been continued for some time, a point is reached at which the precipitate assumes a lighter colour, is no longer dissolved, and is not increased by further addition of the alkali. The precipitate is then filtered from the alkaline fluid, washed with cold water, and purified by repeated crystallization from boiling alcohol. By subsequent experiments, I ascertained that it was easy to convert pyromeconic acid entirely into this compound, by adding a large quantity of chloride of iodine, when the crystals of iodopyromeconic acid at first formed rapidly disappeared, and carbonic acid was evolved. Exactly similar effects are produced by bromide of iodine.

Iodomecone is obtained in large hexagonal plates of a bright yellow colour

and brilliant lustre, and having an odour resembling that of saffron. It is insoluble in water, soluble in alcohol, especially on boiling, and in ether. It is insoluble in hydrochloric acid, and may be boiled with that reagent, without suffering decomposition. Strong nitric acid attacks it with great violence, but does not effect a complete oxidation of all the iodine. It is unacted on in the cold by strong sulphuric acid, but if heated, it is decomposed with the liberation of iodine. Caustic potash when long boiled with it, removes a very small quantity of iodine. It does not affect litmus paper, and seems to possess neither acid nor basic properties. It sublimes unaltered at a temperature greatly below that of boiling water.

These characters closely approximate to those of iodoform, and I at first considered it to be that substance. The analysis, however, made with every care, and on specimens prepared at different times, gave results which cannot be made to agree with the formula of that substance.

The analysis are as follows :—

No. 1. 7·141 grains substance, air-dry, gave
0·913 ... carbonic acid, and
... ... water.

No. 2. 4·365 grains substance, air-dry, gave
... ... carbonic acid, and
0·164 ... water.

No. 3. 8·153 grains substance, air-dry, gave
0·958 ... carbonic acid, and
0·346 ... water.

No. 1. 5·697 grains substance, air-dry, gave
9·706 ... iodide of silver.

No. 2. 3·611 grains substance, air-dry, gave
6·140 ... iodide of silver.

	No. 1.	No. 2.	No. 3.
Carbon,	3·48	lost.	3·204
Hydrogen,	...	0·417	0·471
Oxygen,	...	...	4·440
Iodine,	...	92·060	91·885
	100·000	100·000	100·000

	Mean.	Calculation.		
Carbon,	3·337	3·258	C_6	36
Hydrogen,	0·444	0·364	H_4	4
Oxygen,	4·247	4·344	O_6	48
Iodine,	91·972	92·034	I_8	1016·8
	100·000	100·000		1104·8

The formula is therefore $C_6\ H_4\ I_8\ O_6$.

The decomposition by which iodomecone is produced from pyromeconic acid, now becomes obvious. It is represented by the following equation :—

$$C_{10} H_4 O_6 + 8 I Cl + 8 HO = C_6 H_4 I_8 O_6 + 4 CO_2 + 8 HCl$$

This being the mode of its formation, it seemed probable that meconic and comenic acids, which differ from pyromeconic acid only by the elements of carbonic acid, would yield the same substance, when acted on by chloride of iodine. Accordingly, I have found that it is immediately produced with all its characteristic properties from these acids, by the same process. The relations of this substance to meconic and pyromeconic acids, are of a very remarkable character, and cannot at present be distinctly brought out. It obviously belongs to the same class as the very curious product obtained by CAHOURS, by the action of bromine on citric acid, and which he has called bromoxaform. According to this chemist, when bromine is added to citrate of potash, effervescence takes place from the evolution of carbonic acid, and on the addition of potash, an oily matter is thrown down, which consists of three substances, one bromoform, the other a crystalline solid bromoxaform, and the third apparently an accidental product, for it is obtained in too small quantities to admit of examination. It can scarcely be doubted that bromoxaform would be the only product, if the action could be properly moderated, and that the bromoform is a secondary product of the former substance, from which indeed it is readily obtained, by treatment with caustic potash. If this be the case, the decomposition of citrate of potash would be quite analogous to that of pyromeconic acid, as represented in the equation :—

$$\underbrace{C_{12} H_5 K_3 O_{14}}_{\text{Citrate of Potash.}} + 2 HO + Br_{14} = \underbrace{C_6 H Br_5 O_4}_{\text{Bromoxaform.}} + 6 CO_2 + 3 K Br + 6 H Br.$$

The relation which these curious substances bear to their parent acids is very obscure, and cannot be elucidated without further experiments. In regard to iodomecone, the small quantity in which I was able to obtain it, has prevented my following out its decompositions as I could have wished, but I propose extending this investigation to some of the stronger acids by which means some light may probably be thrown upon the constitution of these bodies.

It was my desire to have extended my examination of the iodine substitution products obtained by chloride of iodine, to some other substances. As yet, however, I have only tried codeine; but the instability of the compound produced has occasioned such difficulties, that I have hitherto been unable to arrive at satisfactory results. When chloride of iodine is added to a concentrated solution of hydrochlorate of codeine, a fine yellow crystalline precipitate makes its appearance. It is insoluble in water, but readily soluble in boiling alcohol. If this solution is carefully effected, and too much of the substance be not added, it crystallizes on cooling in stellar groups, of a fine red colour, but if a large quantity is dissolved,

it is deposited as a perfectly amorphous mass. Unfortunately, the iodine is retained with a very feeble affinity, and I have found that at every crystallization, a small quantity is separated and remains in the fluid, so that results of a satisfactory character could not be obtained on its analysis. It is soluble in hydrochloric acid, and if the solution be made hot, it deposits at first an oily substance, which aftewards concretes to a flocky mass. Both ammonia and potash precipitate it from its solution in hydrochloric acid, the former giving a slightly coloured substance. With chloride of platinum it yields a bright yellow precipitate, one determination of the platinum in which gave 12·20 per cent.; 11·95 corresponds to the formula, $C_{36}\ H_{19}\ I_2\ N\ O_6\ H\,Cl\ Pt\,Cl_2 + H\,O.$, which represents the hydrated salt of a base, which may be called di-iodocodeine, as being derived from codeine by the substitution of two atoms of iodine for two of hydrogen.

These experiments were conducted in the laboratory of Professor ANDERSON, to whom I am much indebted for assistance during their prosecution.