LXX.—On the Action of Diazonaphthalene upon Salicylic Acid.

By PERCY F. FRANKLAND, Ph.D.

ALTHOUGH numerous azo-bodies have been prepared of late years, many even upon a manufacturing scale, yet only few thereof are compounds of the hydroxybenzoic acids; these are hydroxybenzoëdiazobenzoic acid,

and oxybenzoëbidiazobenzoic acid,

prepared by Griess (*Journ. f. Prakt. Chem.* [2], **1**, 106) at first by the decomposition of diazobenzoic acid, and later (*Ber.*, 1876, 629) also directly from hydroxybenzoic acid and diazobenzoic acid. Griess has further prepared a parazosulfoxybenzeneazosalicylic acid (*Ber.*, 1880, 716) from paradiazosulfobenzoic acid and salicylic acid, possessing the formula—

Finally, azobenzeneoxybenzoic acid has quite recently been prepared by Stebbins (*Ber.*, **13**, 716), by acting with diazobenzene upon salicylic acid.

As yet the above compounds have been but little examined, and in none of them has the position of the phenylazo-group been ascertained.

At the suggestion of Professor Wislicenus, I undertook the following work, the object of which was, besides the preparation of a new azo-compound, the determination of the place of entry of the diazo-group into the benzene nucleus of salicylic acid. The diazo-group was introduced in the form of diazonaphthalene, naphthylazosalicylic acid being formed. The naphthylazosalicylic acid, on treatment with tin and hydrochloric acid, yielded naphthylamine and amidosalicylic acid; the latter was then converted, by means of its diazo-compound, into iodosalicylic acid, which, by its melting point and characteristic reactions, was identified as the iodosalicylic acid already known. To render the proof of its identity still more positive, the iodosalicylic

acid was further converted into hydroxysalicylic acid, which proved to be the quinolcarboxylic acid.

Bye-products of some interest were formed in the action of diazonaphthalene upon salicylic acid, which will be referred to below.

Naphthylazosalicylic Acid.

The following numbers show the proportions in which the ingredients were used for its preparation:—

8.98 grams of naphthylamine hydrochloride were dissolved in 500 grams of water, to which was added 1.85 gram of hydrochloric acid; this solution, after filtration, was cooled by immersion in ice, and then treated with 3.45 grams of sodic nitrite dissolved in a little water. The solution assumed a dark-brown colour, and a small quantity of a reddish-brown powder was precipitated; the latter was filtered off as quickly as possible, and the clear solution of diazonaphthalene was run into 6.9 grams of salicylic acid and 6 grams of sodic hydrate dissolved in 500 grams of water. The liquid became orange-coloured, a considerable evolution of nitrogen took place, and a dark-brown precipitate was formed. The mixture was then heated upon the water-bath and filtered hot. The brown residue was several times extracted with boiling water, its further treatment being referred to later under the title of the "brown product." The clear yellow filtrate contains the sodium salt of naphthylazosalicylic acid, which is formed according to the equations:—

Common salt was then added to the solution, causing the dissolved sodium salt of the naphthylazosalicylic acid to separate out as a light-yellow bulky precipitate, which was then filtered off. On acidulating the filtrate with dilute hydrochloric acid, a white precipitate was formed, which was identified as salicylic acid, and its appearance in a quantity equal to about half of that employed shows that the reaction between diazonaphthalene and salicylic acid is only a very partial one, and hence but a small yield of naphthylazosalicylic acid was obtained.

The sodium salt of the naphthylazosalicylic acid was then crys-

tallised from boiling water, and, on analysis, yielded the following numbers:—

Calculated for $C_{10}H_7N_2 \cdot C_6H_3 < \begin{smallmatrix} Ho \\ CONaO \end{smallmatrix}$

	Theory.	Found.	
N.....	8.92 per cent.	9.25	9.75
Na	7.32 ,,	7.17	

This sodium salt is nearly insoluble in water (1 part requiring 1,420 parts of cold and 644 parts of hot water). The solution dyes silk a light-yellow colour. Hydrochloric acid precipitates from its aqueous solution free naphthylazosalicylic acid as a grey gelatinous mass, which can be crystallised from boiling benzene. On analysis it yielded the following results:—

Calculated for $C_{10}H_7N_2 \cdot C_6H_3 < \begin{smallmatrix} Ho \\ COHo \end{smallmatrix}$.

	Theory.	Found.		
C	69.86 per cent.	69.52	68.91	69.50
H	4.11 ,,	4.57	4.37	4.48
N	9.59	—	9.45	—

Decomposition of Naphthylazosalicylic Acid by Tin and Hydrochloric Acid.

The sodium salt was gradually introduced into a mixture of granulated tin and concentrated hydrochloric acid, the mixture being finally heated on the water-bath until all had passed into solution. The products of this reduction are naphthylamine and amidosalicylic acid. The solution containing the tin double salts was first freed from tin by precipitation with sulphuretted hydrogen, and then, after filtration, evaporated down in a stream of carbonic anhydride. The concentrated solution was then rendered alkaline with sodic carbonate, and the precipitated naphthylamine filtered off, the remainder of the naphthylamine being removed by shaking out with ether. The solution (now only containing amidosalicylic acid) was then again rendered acid and evaporated further until the amidosalicylic acid, or rather its hydrochloric acid compound, crystallised out in fine brownish needles.

The naphthylamine obtained possessed the correct melting point, and a chlorine determination was made with its hydrochloric acid salt:—

Calculated for $C_{10}H_7NH_2HCl$.

	Theory.	Found.
Cl	19.77 per cent.	19.94

Conversion of the Amidosalicylic Acid into Diazo- and Iodo-salicylic Acids.

The solution containing the hydrochloric acid compounds of naphthylamine and amidosalicylic acid was evaporated down to crystallisation in a stream of carbonic anhydride, and the crystals were stirred up with a small quantity of water, and a stream of nitrous anhydride was then passed through the mixture, which was cooled by immersion in ice. By this means the naphthylamine was converted into diazonaphthalene, which, being very soluble in water, remained in solution; whereas the amidosalicylic acid was transformed into insoluble diazosalicylic acid, which separated out as a yellow flocculent precipitate—

The precipitated diazosalicylic acid was filtered off and treated with a concentrated solution of hydriodic acid; a violent reaction, accompanied by abundant evolution of nitrogen, took place. The mixture was finally heated for half-an-hour on the water-bath. When cool, it was filtered; the precipitate remaining on the filter was iodosalicylic acid—

After being washed free from excess of hydriodic acid, the residue was dissolved in ammonia, reprecipitated with hydrochloric acid, and then repeatedly crystallised out of boiling water. The melting point of the colourless acid so obtained was 193.5° ; this is 2.5° lower than that given by Goldberg (*Dissertation*, Wurzburg, 1878) as the melting point of paraiodosalicylic acid; but in all other respects the above acid agrees with his. Moreover, I prepared, for the sake of comparison, some paraiodosalicylic acid according to his directions, viz., from paranitrosalicylic acid by means of the amido- and diazo-compounds, and also obtained for it the melting point 193.5° . The iodosalicylic acid gave with a solution of ferric chloride the characteristic violet coloration. There can be no doubt that paraiodosalicylic acid and the iodosalicylic acid obtained from naphthylazosalicylic acid are identical. Analysis gave:—

Theory.	Found.	
I = 48.11 per cent.	47.76	47.77

Conversion of the Iodosalicylic Acid into Hydroxysalicylic Acid.

The iodosalicylic acid was fused with an excess of caustic potash, the temperature being maintained at 200°. The fused mass was then dissolved in water, acidulated with hydrochloric acid, and then repeatedly shaken out with ether. On evaporating the ether, dark-coloured needles in rosette-like groups were left behind. The hydroxysalicylic acid so obtained, after purification by recrystallisation, gave on analysis :—

Calculated for $C_6H_3 \begin{matrix} \swarrow Ho \\ \swarrow Ho \\ \searrow COHo \end{matrix}$.		
	Theory.	Found.
C.....	54.54 per cent.	55.18
H	3.90 ,,	4.26

The melting point was 195—197°. Ferric chloride gave with the acid a deep-blue coloration, becoming dirty-red on addition of sodic carbonate. On dry distillation at 215° it yielded hydroquinone.

From the above evidence, the hydroxysalicylic acid obtained is proved to be identical with parahydroxysalicylic acid, and as the latter possesses the formula

it is thus shown that the diazo-group of the diazonaphthalene attached itself to the benzene-ring of the salicylic acid, just as in the case of most other substitutions suffered by the latter, in the para-position to the hydroxyl, and in the meta-position to the oxatyl.

Examination of the "Brown Product."

It has already been mentioned that in the preparation of naphthylazosalicylic acid, an amorphous brown body insoluble in water is simultaneously formed. It was found that the salicylic acid takes no part in the formation of the latter, but that the same body may also be obtained by simply neutralising a solution of chloride of diazonaphthalene with sodic carbonate.

The brown product consists of a mixture of two bodies; one of which is insoluble in caustic alkalis, whilst the other, which is formed in far smaller quantity, dissolves in sodic hydrate to a deep-crimson solution, from which it is precipitated even by carbonic acid. These two bodies are extremely difficult to obtain in a pure state, but the

one insoluble in alkalis can be got in a minutely crystalline form by precipitating with alcohol from a benzene solution. Both these bodies dissolve in alcohol, ether, benzene, and glacial acetic acid to dark crimson-coloured solutions. The brown body, soluble in alkalis, gave on analysis numbers pointing to the formula $C_{10}H_8NO$:—

	Theory.	Found.
C.....	75.95 per cent.	74.79
H	5.06 „	4.88
N	8.86 „	8.46

On the other hand, the brown body insoluble in alkalis gave, on analysis, results corresponding with the formula $C_{50}H_{33}N_5O_2$:—

	Theory.	Found.
C.....	81.63 per cent.	81.58
H	4.49 „	4.91
N	9.52 „	9.51

The oxygen does not appear to be combined in the form of hydroxyl, as all attempts to obtain a sodium compound failed.

In order to throw light upon the constitution of these brown bodies, a comparative experiment was made with diazobenzene; but, as will be seen below, the reactions in the two cases are not quite analogous. An aqueous solution of chloride of diazobenzene, on being almost neutralised with sodic hydrate, gave rise to a light-brown precipitation. On extracting the precipitate with boiling sodic hydrate, it was found to consist of two bodies; the one soluble, and the other insoluble in caustic alkalis. Both were obtained in a minutely crystalline state by allowing their saturated boiling alcoholic solutions to cool.

For the body insoluble in alkalis numbers were found, on analysis, agreeing not very closely with any formula, $C_{30}H_{23}N_5O$ being, however, the nearest :—

	Theory.	Found.
C.....	76.76 per cent.	75.90
H	4.90 „	4.91
N	14.93 „	14.58

For the light-brown body soluble in alkalis, analysis gave numbers corresponding with the formula $C_{18}H_{14}N_4O$:—

	Theory.	Found.	
C	71.52 per cent.	71.19	71.04
H	4.64 „	5.10	4.92
N	18.54 „	18.62	18.73

For the formula $C_{18}H_{14}N_4O$, there are two principal isomerides, viz. :—

and—

In order to ascertain which of these formulæ belonged to the body in question, the latter was submitted to the reducing action of tin and hydrochloric acid. The only products of decomposition obtained were aniline and a phenol, which was identified as the diamidophenol described by Hemilian (*Ber.*, **8**, 768), and these are precisely the products that should be formed if the second formula be the correct one. A body possessing this formula was prepared many years since by Griess (*Jahresb.*, 1864, 435; *Ber.*, **9**, 627) under the name of phenol-bidiazobenzene; firstly, by the treatment of nitrate of diazobenzene with barium carbonate, and later by the action of diazobenzene upon phenylazophenol.

Naphthylazo-(α)-naphthol.

The portion of the "brown product," soluble in alkalis, formed in the preparation of naphthylazosalicyclic acid, was at first thought to be naphthylazo-(α)-naphthol, and some of this new azo-compound was therefore prepared in order to compare with the brown body above-mentioned. Naphthylazo-(α)-naphthol is obtained by introducing a solution of chloride of diazonaphthalene into a sodic hydrate solution of α-naphthol; the mixture assumes a deep crimson colour, and on acidulating with hydrochloric acid, the naphthylazo-(α)-naphthol falls out as a dark crimson powder.

The following numbers were obtained on analysis:—

Calculated for $\text{C}_{10}\text{H}_7\text{N}=\text{NC}_{10}\text{H}_6\text{H}_0$.

	Theory.	Found.	
C	80·53 per cent.	80·85	80·42
H	4·69 „	4·57	4·47
N	9·39 „	8·75	8·70

In conclusion, I wish to express my sincerest thanks to Professor Wislicenus for his kind assistance and invaluable advice in the carrying out of this investigation.