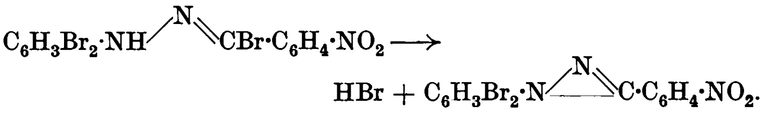
XLIX.—*The Reduction of* o-*Nitrophenyl*iso*diazomethanes.*

By FREDERICK DANIEL CHATTAWAY and ARTHUR JOHN WALKER.

IN previous papers it has been shown (J., 1925, **127**, 1687, 2407) that the direct action of halogens upon the nitrobenzaldehydephenylhydrazones leads to substitution in the ω-position; *e.g.*,

$$C_6H_5\cdot NH\cdot N\colon CH\cdot C_6H_4\cdot NO_2 \xrightarrow{3Br_2} C_6H_3Br_2\cdot NH\cdot N\colon CBr\cdot C_6H_4\cdot NO_2.$$

Of these ω-halogen derivatives, those derived from *o*-nitrobenzaldehydephenylhydrazone behave in an anomalous manner, easily splitting off halogen acid and forming explosive compounds. The α-hydrogen and the ω-halogen atom are eliminated in this change, which is simply accounted for by assuming the formation of a three-atom *iso*diazomethane ring thus:



A number of these *o*-nitrophenyl halogenophenyl *iso*diazomethanes have been described (*loc. cit.*, p. 2410) and the present paper is concerned with a further study of their properties, and notably of the products they yield on reduction.

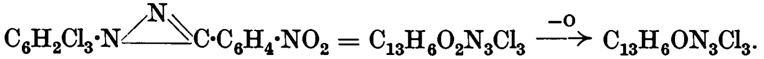
They are all well-crystallised, yellow substances which can be kept indefinitely at the ordinary temperature without change but explode with great violence when heated. In hot solution, they suffer decomposition to a greater or less extent. Those containing three halogen atoms in the nucleus are markedly more stable than those with less halogen. They are stable towards acids, and show feebly basic properties, dissolving in concentrated hydrochloric acid, for example, and being reprecipitated on dilution. When hydrogen chloride is passed into their dry ethereal solutions, colourless addition compounds are precipitated. These readily lose hydrogen chloride and revert to the original compounds on exposure to air, or on moistening with water.

They are all rapidly decomposed by alcoholic potash, or alcoholic ammonia, yielding as one of the products a halogen-substituted benzene (*e.g.*, *o*-nitrophenyl-2 : 4 : 6-trichlorophenyl*iso*diazomethane yields 1 : 3 : 5-trichlorobenzene).

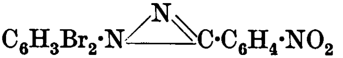
On oxidation with permanganate they yield *o*-nitrobenzoic acid.

Behaviour on Reduction.—When the *o*-nitrophenyl halogenophenyl *iso*diazomethanes are boiled for some time with alcohol they undergo reduction to almost colourless compounds, the alcohol being simultaneously oxidised to acetaldehyde. The same reaction can more conveniently be effected by the action of stannous chloride in the cold.

The products are well-crystallised compounds, and their analysis shows that in every case they are formed by loss of one atom of oxygen from the original *iso*diazomethane; *e.g.*,



$$C_6H_2Cl_3\cdot N\overset{N}{\diagup\!\overline{\quad\quad}\!\diagdown}C\cdot C_6H_4\cdot NO_2 = C_{13}H_6O_2N_3Cl_3 \xrightarrow{-O} C_{13}H_6ON_3Cl_3.$$

For the study of the constitution of these products, the one derived from *o*-nitrophenyl-2 : 4-dibromophenyl*iso*diazomethane,  $C_6H_3Br_2\cdot N\overset{N}{\diagup\!\overline{\quad\quad}\!\diagdown}C\cdot C_6H_4\cdot NO_2$ (which is typical of the series), was selected.

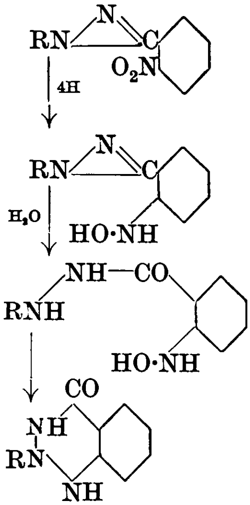
Prepared by reducing the *iso*diazomethane with stannous chloride, it crystallises in colourless needles, m. p. 176°. Under reduced pressure, it can be distilled unchanged, and it is unaffected by hot concentrated mineral acids. The halogens do not attack it at the ordinary temperature. It is, however, decomposed by alcoholic potash, giving a deep red solution. If this be effected in presence of silver nitrate, an amorphous, spontaneously explosive compound is produced.

The great stability of the original reduction product suggests that the *iso*diazomethane ring has been broken, and a larger, and more stable ring formed, in which the nitrogen of the original nitro-group is probably included.

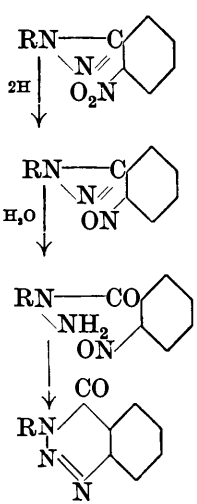
The compound still contains one oxygen atom, which is not removed on further reduction with tin and hydrochloric acid, indicating that this can no longer be attached to nitrogen, and is probably attached to carbon.

In representing the formation of such a compound, we may assume that reduction of the nitro-group occurs, and is followed by rupture of the three-atom ring by hydrolysis, the reduced nitro-group finally linking up to form the larger ring.

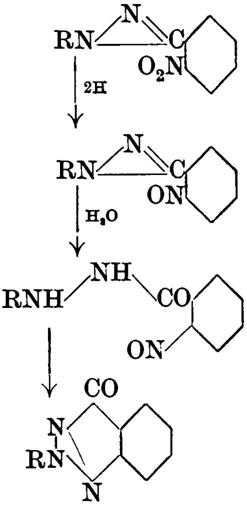
According to the extent to which reduction occurs in the nitro-group and the manner in which the three-atom ring is broken, we have the following possibilities ($R = C_6H_3Br_2$):



(I.) Dibromophenyl-dihydrobenztriazone.



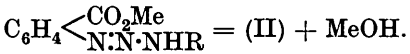
(II.) Dibromophenyl-benztriazone.



(III.) *cycloazi*-Dibromophenyl-benztriazone.

The first of these possibilities is excluded by the fact that the compound in question forms no acetyl derivative, and is unaffected by nitric or nitrous acid. Further, the minimum quantity of stannous chloride required for its production does not correspond with that required by this formula.

The second (II) of these was synthesised directly for comparison, by the method of Mehner (*J. pr. Chem.*, 1901, **63**, 279) from methyl 2 : 4-dibromodiazoaminobenzene-2′-carboxylate :

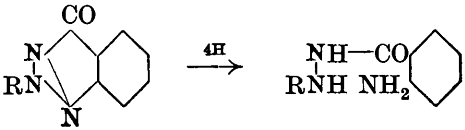


$$C_6H_4{<}\begin{matrix}CO_2Me\\ N{:}N{\cdot}NHR\end{matrix} = (II) + MeOH.$$

The product proved *not* to be identical with the reduction product of the *iso*diazomethane, and constitution (II) is therefore excluded.

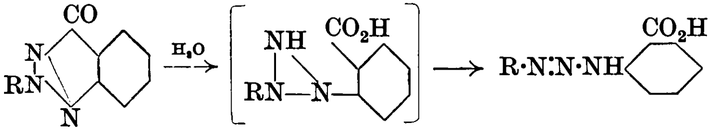
Formula (III) has been adopted, since it accounts in a satisfactory way for the products obtained when the compound is subjected to further reduction, and when it is decomposed by alkalis.

Reduction. On reduction in the cold with tin and hydrochloric acid, it yields o-*aminobenzoyl*-2 : 4-*dibromophenylhydrazine* :



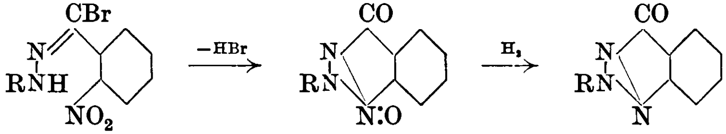
which yields dibromophenylhydrazine and anthranilic acid on hydrolysis and is identical with the compound obtained by reducing *o*-nitrobenzoyl-2 : 4-dibromophenylhydrazine.

Decomposition by potash. By the action of alcoholic potash in the cold, the compound yields 2 : 4-*dibromodiazoaminobenzene-2′-carboxylic acid*[*] identical with the acid obtained by coupling dibromobenzenediazonium chloride with anthranilic acid. The decomposition[†] may be represented :



The constitution of the reduction product is therefore well established, and there is no doubt that those obtained from similar *iso*diazomethanes are analogously constituted.

The preceding work suggests that an *alternative to the* iso*diazomethane structure* ought to be considered. By assuming an *iso*diazomethane structure for the explosive compounds we have a simple explanation of their formation from the ω-halogen derivatives (see p. 323). On the other hand it has to be borne in mind that the power to form these explosive compounds is limited to those ω-halogen derivatives containing the nitro-group in the ortho-position. This suggests that the reaction may be one in which the nitro-group (by virtue of its ortho-position) actually takes part, and the subsequent reduction to benztriazones lends support to this view. On this alternative theory the explosive compound might be represented as a nitrosoazi-compound, which would naturally pass into the triazone on reduction,



(explosive compound)
(alternative structure)

the formation from the ω-halogen derivative taking place by hydrolysis of the halogen, and ring closure involving the nitro-group :

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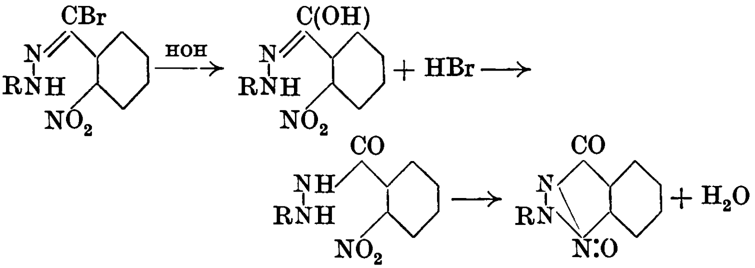
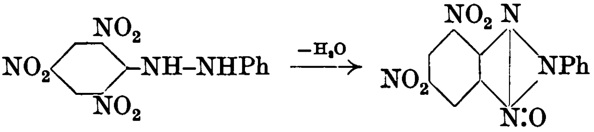
[*] At the same time, an isomeric acid is produced, which is probably the corresponding aminoazo-compound.

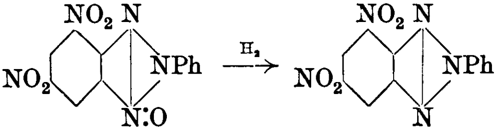
[†] The highly explosive compound formed when this is carried out in presence of silver nitrate (p. 328) may be a derivative of the intermediate compound (not isolated), written in brackets.



The work of Willgerodt (*J. pr. Chem.*, 1897, **55**, 375; compare also Werner and Stiasny, *Ber.*, 1899, **32**, 3266) on nitrohydrazobenzenes favours this interpretation. He finds that hydrazobenzenes containing a nitro-group in the ortho-position can lose water in the following way,



forming nitrosoazi-derivatives. These, like the explosive compounds here described, are easily reduced (by boiling alcohol) to the corresponding azimido-compounds.



EXPERIMENTAL.

Reduction of 1-2′ : 4′-*Dibromophenyl*-3-o-*nitrophenyl*isodiazo*methane to* cycloazi-*Dibromophenylbenztriazone* (III).—(a) *With alcohol.* 2 : 4-Dibromophenyl-*o*-nitrophenyl*iso*diazomethane (5 g.) was boiled under reflux with 100 c.c. of alcohol for 3—4 hours. The solution thus obtained was boiled for another hour, and a few c.c. were then distilled off. These contained acetaldehyde, detected by its smell, and by its action upon Fehling's solution, ammoniacal silver nitrate, and Schiff's reagent. The main bulk of the solution, on cooling, deposited colourless crystals of cycloazi-2 : 4-*dibromophenylbenztriazone*. Recrystallised from alcohol, in which it is moderately easily soluble, it forms long, colourless needles, m. p. 178° (yield, 3 g.) (Found: Br, 42·1. $C_{13}H_7ON_3Br_2$ requires Br, 42·0%).

(b) *With stannous chloride.* For the preparation of larger quantities, this method is more convenient. 2 : 4-Dibromophenyl-*o*-nitrophenyl*iso*diazomethane (10 g.) was ground to a paste with

60—70 c.c. of acetic acid, and 200 c.c. of concentrated hydrochloric acid added.

The whole formed a clear yellow solution, which was maintained at 10—15° while a solution of 15 g. (excess) of stannous chloride in 50 c.c. of concentrated hydrochloric acid was slowly run in with vigorous stirring. The reduction product, which meanwhile separated as a pale yellow precipitate, was washed with dilute hydrochloric acid and then with hot water and finally recrystallised from alcohol; m. p. 178° (yield, 7 g.).

General properties. The compound is remarkably stable, and when heated under reduced pressure above its melting point distils with only slight decomposition. It is insoluble in dilute mineral acids, but dissolves in hot concentrated sulphuric, hydrochloric, and nitric acids; from these solutions, it is precipitated unchanged by dilution.

It does not react with nitrous acid, and is recovered unchanged after 8 hours' boiling with acetic anhydride and a drop of sulphuric acid or with acetic anhydride and anhydrous sodium acetate. It is, however, decomposed by alcoholic potash, yielding a deep red solution (see p. 331).

When a solution of the compound in alcohol is warmed with a few drops of ammoniacal silver nitrate solution, and a little caustic potash, a black, amorphous precipitate is slowly formed. If this be touched with a glass rod, or in any way disturbed, under the supernatant liquid, it explodes sharply with great violence, invariably shattering the tube.

Analogous Reduction Products.—By the action of boiling alcohol, or of stannous chloride in the cold, other halogenophenyl-*o*-nitrophenyl*iso*diazomethanes yield reduction products, *cycloazi*-phenylbenztriazones, closely resembling the one described. For the sake of the additional analytical data which they afford, three of these were prepared and analysed.

cycloazi-p-*Bromophenylbenztriazone* was prepared from *p*-bromophenyl-*o*-nitrophenyl*iso*diazomethane by both methods. It crystallises from alcohol, in which it is moderately easily soluble, in pale yellow needles, m. p. 197° (Found : Br, 26·4. $C_{13}H_8ON_3Br$ requires Br, 26·5%).

cycloazi-2 : 4-*Dichlorophenylbenztriazone* was prepared from dichlorophenyl-*o*-nitrophenyl*iso*diazomethane by both methods. It exists in two polymorphic forms. The labile form separates from alcoholic solution in compact, yellow prisms, m. p. 167°; these, in contact with the mother-liquor, dissolve and the stable form appears as colourless needles, m. p. 157°. At the ordinary temperature, in contact with a saturated alcoholic solution, the yellow form slowly changes into the colourless (Found: C, 54·0; H, 2·6; N, 14·3; Cl, 24·2; *M*, in phenol, 272. $C_{13}H_7ON_3Cl_2$ requires C, 53·9; H, 2·5; N, 14·4; Cl, 24·3%; *M*, 292).

cycloazi-2 : 4 : 6-*Trichlorophenylbenztriazone* prepared from 2 : 4 : 6-trichlorophenyl-*o*-nitrophenyl*iso*diazomethane by both methods, crystallises from alcohol, in which it is only moderately readily soluble, in colourless needles, m. p. 258° (Found: C, 47·7; H, 2·1; N, 13·5; Cl, 32·4; *M*, in phenol, 300. $C_{13}H_6ON_3Cl_3$ requires C, 47·8; H, 1·9; N, 12·85; Cl, 32·6%; *M*, 326·5).

Synthesis of Isomeric Phenylbenztriazones for Comparison.—p-*Bromophenylbenztriazone* (II; R = *p*-C_6H_4Br). A solution of 3 g. (1 mol.) of methyl anthranilate in 5 c.c. (2·5 mols.) of concentrated hydrochloric acid and 30 c.c. of water was diazotised at 0° with 1·4 g. (1 mol.) of sodium nitrite. A solution of 3 g. of *p*-bromoaniline in dilute hydrochloric acid was added, and then excess of a cold solution of sodium acetate; methyl *p*-bromodiazoaminobenzene-*o*′-carboxylate slowly separated. It crystallised from alcohol, in which it is moderately easily soluble, in golden-yellow needles (yield, 4·5 g.), m. p. 120° (Found: Br, 24·9. Calc.: Br, 24·8%).

The conversion into p-*bromophenylbenztriazone* was effected by boiling for 2 hours with a mixture of 2 vols. of alcohol and 1 vol. of water; on cooling, the benztriazone separated in colourless crystals.

Recrystallised from alcohol, in which it is moderately easily soluble, it separated in colourless plates, m. p. 196°, which proved quite distinct in appearance and properties from the reduction product of *p*-bromophenyl-*o*-nitrophenyl*iso*diazomethane, m. p. 197°. A mixture of the two melted below 190° (Found: Br, 26·5. $C_{13}H_8ON_3Br$ requires Br, 26·5%).

2 : 4-*Dibromophenylbenztriazone* (II). Attempts to obtain methyl 2 : 4-dibromodiazoaminobenzene-2′-carboxylate from methyl anthranilate and dibromoaniline by diazotising and coupling in the usual way were unsuccessful, as the addition of sodium acetate to the acid solution of diazonium salt and amine simply reprecipitated the amine (dibromoaniline or methyl anthranilate) unchanged.

This difficulty was overcome by employing acetic acid as solvent in the place of water: To 5 g. (1 mol.) of dibromoaniline, dissolved in 50 c.c. of acetic acid, were added 10 c.c. (5 mols.) of concentrated hydrochloric acid and the mixture was cooled to 0° and diazotised by adding a saturated aqueous solution of 1·4 g. (1 mol.) of sodium nitrite. The diazo-solution was then mixed with a cold solution of 3 g. (1 mol.) of methyl anthranilate in 20 c.c. of acetic acid and 5 c.c. of water. On adding an excess of anhydrous sodium acetate, the diazoamino-compound slowly separated. After ½ hour, the mixture was diluted considerably with water, and the methyl 2 : 4-dibromodiazoaminobenzene-2′-carboxylate was filtered off and recrystallised from alcohol, in which it is moderately easily soluble, and from which it separates in bright yellow needles, m. p. 141° (Found : Br, 40·0. Calc. : Br, 39·9%).

The ester (1 g.) was heated at 100° for 2 hours in a sealed tube with 50 c.c. of alcohol and 10 c.c. of water (Mehner, *J. pr. Chem.*, 1901, **63**, 241). The *triazone* separated as a colourless solid when the cooled product was poured into water. It was crystallised from alcohol, in which it is moderately easily soluble, and from which it separates in compact prisms, m. p. 136° (Found : Br, 42·1. $C_{13}H_7ON_3Br_2$ requires Br, 42·0%).

The compound is quite distinct in appearance and properties from the reduction product of dibromophenyl-*o*-nitrophenyl*iso*diazomethane, m. p. 178° (see p. 327). On boiling for an hour with alcoholic potash it yielded, as the sole product of hydrolysis, 2 : 4-dibromodiazoaminobenzene-2′-carboxylic acid, m. p. 151° (see p. 332).

Reduction of cycloazi-2 : 4-*Dibromophenylbenztriazone to* o-*Aminobenzoyl*-2 : 4-*dibromophenylhydrazine*.—A solution of 5 g. of *cycloazi*-2 : 4-dibromophenylbenztriazone in 50 c.c. of boiling acetic acid was rapidly cooled with the addition of 40 c.c. of concentrated hydrochloric acid, so that a fine crystalline suspension was obtained. A considerable excess of granulated tin was added, and the whole kept at the ordinary temperature for 5 hours; the original solid had then completely dissolved. The solution was decanted from the tin, diluted with an equal volume of water, and extracted four times with 150—200 c.c. of ether. The ethereal layer was washed with water and dilute sodium carbonate solution, dried over potassium carbonate, and the ether distilled off. The colourless product, o-*aminobenzoyl*-2 : 4-*dibromophenylhydrazine*, exists in two polymorphic forms; when crystallised from alcohol, in which it is moderately easily soluble, it separates first in colourless needles, which in the solvent slowly transform to compact plates; both forms melt at 184°. Yield, 2 g. (Found : Br, 41·55; N, 11·2. $C_{13}H_{11}ON_3Br_2$ requires Br, 41·6; N. 10·9%).

The constitution of *o*-aminobenzoyl-2 : 4-dibromophenylhydrazine was determined by its hydrolysis to anthranilic acid and 2 : 4-dibromophenylhydrazine, and by its synthesis from *o*-nitrobenzoyl-2 : 4-dibromophenylhydrazine by reduction.

Hydrolysis. The substance, heated with concentrated hydrochloric acid in a sealed tube for 2 hours at 100°, yielded anthranilic acid, m. p. 144°, and 2 : 4-dibromophenylhydrazine; the latter was identified by conversion into its characteristic, bright red *o*-nitrobenzaldehydehydrazone, m. p. 205°.

Synthesis. β-o-*Nitrobenzoyl*-2 : 4-*dibromophenylhydrazine*, prepared by the Schotten-Baumann method from *o*-nitrobenzoyl chloride and dibromophenylhydrazine, crystallised from alcohol, in which it is moderately easily soluble, in yellow needles, m. p. 180° (Found : Br, 38·5. $C_{13}H_9O_3N_3Br_2$ requires Br, 38·55%).

The reduction of this compound with tin in a cold mixture of acetic and hydrochloric acids yielded the same product, *o*-aminobenzoyl-2 : 4-dibromophenylhydrazine, as the reduction of *cycloazi*dibromophenylbenztriazone, melting at 184° and crystallising in the same two polymorphic forms.

This identity was further established by the preparation and comparison of its mono- and di-acetyl derivatives. o-*Acetamidobenzoyl*-2 : 4-*dibromophenylhydrazine*, $C_6H_3Br_2{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}C_6H_4{\cdot}NHAc$, prepared by the action of acetic anhydride alone upon *o*-aminobenzoyldibromophenylhydrazine in the cold, forms colourless needles, m. p. 210° (Found : Br, 37·3. $C_{15}H_{13}O_2N_3Br_2$ requires Br, 37·5%).

o-*Acetamidobenzoyl*-α-*acetyl*-2 : 4-*dibromophenylhydrazine*,

$$C_6H_3Br_2{\cdot}NAc{\cdot}NH{\cdot}CO{\cdot}C_6H_4{\cdot}NHAc,$$

prepared by boiling *o*-aminobenzoyldibromophenylhydrazine with acetic anhydride and a drop of sulphuric acid, crystallises from alcohol, in which it is much more soluble than the monoacetyl derivative, in clusters of colourless needles, m. p. 184° (Found : Br, 34·2. $C_{17}H_{15}O_3N_3Br_2$ requires Br, 34·1%).

The Action of Potash on cycloazi-2 : 4-*Dibromophenylbenztriazone*. —A solution of 10 g. of *cycloazi*-dibromophenylbenztriazone in 150 c.c. of boiling alcohol was chilled to produce a fine crystalline pulp. A solution of 20 g. of caustic potash in 100 c.c. of alcohol and 5 c.c. of water was then added, and the whole kept at the ordinary temperature for 5—6 hours; the original crystals had then completely dissolved to give a deep red solution.

This solution contains the yellow potassium salt of 2 : 4-dibromodiazoaminobenzene-2′-carboxylic acid, and in addition, smaller quantities of the deep red potassium salt of another, more stable acid, of the same composition. The sparing solubility in aqueous alcohol of the former renders its isolation a comparatively easy matter.

To the red alcoholic solution was added a little more than its own volume of water; the potassium salt of dibromodiazoaminobenzene-2′-carboxylic acid then separated in an impure condition. It was redissolved in a small quantity of alcohol and again precipitated with an equal volume of water (yield, 2—3 g.). It may be recrystallised from alcohol, in which it is moderately easily soluble, and from which it separates in long, slender, pale yellow needles, m. p. 230—240° (decomp.). It is very sparingly soluble in water.

The free 2 : 4-*dibromodiazoaminobenzene-2′-carboxylic acid*, prepared from the potassium salt by treatment with acetic acid, was recrystallised from alcohol, in which it is moderately easily soluble, and from which it separates in yellow needles which melt at 151°, decomposing with a sharp puff. The crystallisations were effected as rapidly as possible, as the substance easily decomposes on prolonged boiling (Found: C, 39·5; H, 3·4; N, 10·1; Br, 40·1. $C_{13}H_9O_2N_3Br_2$ requires C, 39·1; H, 3·9; N, 10·5; Br, 40·2%).

On reduction with zinc in acetic acid, it yielded anthranilic acid and 2 : 4-dibromoaniline. Its constitution was further confirmed by its synthesis direct from anthranilic acid and 2 : 4-dibromobenzenediazonium chloride. The coupling was effected without difficulty in aqueous solution, and the insoluble diazoamino-compound, after recrystallisation from alcohol, melted at 151° and proved to be identical with the compound obtained from *cycloazi*dibromophenylbenztriazone.

The Isomeric Acid, $C_{13}H_9O_2N_3Br_2$.—The red mother-liquors remaining from the precipitation of potassium dibromodiazoaminobenzene-2′-carboxylate (see p. 331) were acidified with acetic acid, whereby a mixture of the free isomeric acids was precipitated as a brownish-red solid. This was separated, and the more easily soluble dibromodiazoaminobenzene-2′-carboxylic acid extracted with 100 c.c. of boiling alcohol. The sparingly soluble residue was crystallised from acetic acid, in which it is sparingly soluble, and separated in orange-red needles (yield, 1 g.), m. p. 275° (Found: C, 39·2; H, 3·7; Br, 40·1%).

The constitution of this acid has not yet been definitely settled, but its properties suggest that it is an aminoazo-derivative. Heated above its melting point, it sublimes in fine red needles. It is feebly basic, forming a colourless hydrochloride, whilst on boiling with acetic anhydride it yields an acetyl derivative, which crystallises from alcohol in yellow needles, m. p. 220°.

Its potassium salt dissolves in alcohol easily, and in water sparingly, forming deep red solutions. A small quantity boiled with zinc dust in acetic acid yielded 2 : 4-dibromoaniline.

The Action of Potash on cycloazi-2 : 4-*Dichlorophenylbenztriazone*.—The action of alcoholic potash on *cycloazi*-dichlorophenylbenztriazone is precisely similar to its action on the corresponding dibromo-derivative already described, and yields dichlorodiazoaminobenzene-2′-carboxylic acid, together with another more stable and deeply coloured acid of the same composition. These acids were separated in the manner described for the dibromo-derivatives.

2 : 4-*Dichlorodiazoaminobenzene-2′-carboxylic acid*,

$C_6H_3Cl_2{\cdot}NH{\cdot}N{:}N{\cdot}C_6H_4{\cdot}CO_2H$,

prepared from *cycloazi*-dichlorophenylbenztriazone by the action of potash and also directly from dichlorobenzenediazonium chloride and anthranilic acid, crystallises from alcohol, in which it is moderately easily soluble, in yellow needles, which melt at 163—167°, decomposing with a sudden puff (Found: Cl, 23·15; C, 50·2; H, 3·2; N, 13·2. $C_{13}H_9O_2N_3Cl_2$ requires Cl, 22·9; C, 50·3; H, 2·9; N, 13·5%).

On vigorous reduction with zinc in boiling acetic acid, the compound yielded 2 : 4-dichloroaniline, and anthranilic acid, m. p. 144°.

The potassium salt of this acid is almost insoluble in water, and moderately soluble in alcohol, crystallising from the latter in fine, pale yellow needles, m. p. 220° (decomp.).

The isomeric acid, $C_{13}H_9O_2N_3Cl_2$, separates from acetic acid, in which it is only sparingly soluble, in orange-red needles, m. p. 275° (Found: Cl, 23·0; N, 13·7%). In its properties it corresponds closely with the very stable, orange-red (dibromo) acid already described, m. p. 275° (see p. 332), subliming above its melting point in fine red crystals. Its potassium salt is sparingly soluble in water, but easily soluble in alcohol, giving a deep red solution.

THE QUEEN'S COLLEGE, OXFORD. [*Received, November 26th*, 1926.]