CXV.—*The Diazo-derivatives of the Mixed Aliphatic Aromatic ω -Benzenesulphonylaminobenzylamines.*

By GILBERT THOMAS MORGAN and FRANCES MARY GORE
MICKLETHWAIT.

THE acylsulphonyl derivatives of the purely aromatic ortho- and para-diamines give rise to two characteristic series of diazo-anhydrides. The compounds of the ortho-series are very stable substances produced even in the presence of mineral acids and not hydrolysed by hot acids or alkalis. The para-diazoimides, on the other hand, are formed only when the mineral acid present is replaced by a weaker organic acid, and the change is readily reversed by treating the diazo-anhydride with cold concentrated hydrochloric acid. The para-diazoimides are further characterised by their colour, all the members of the series hitherto prepared being distinctly yellow (Trans., 1905, **87**, 73, 921, 1302). In the ortho-series, the appearance of colour is exceptional, and the acyl-*o*-diazoimides are generally described as being colourless substances.

In their last communication on this subject (this vol., p. 4), the authors described benzenesulphonyl-1:8-naphthylenediazoimide and showed that this heteronuclear peri-derivative was similar in all respects to the para-diazoimides. As these facts indicated that the production of a coloured diazoimide occurs even when the aminic nitrogens are situated in different aromatic rings, it seemed of interest to ascertain whether similar compounds would be formed from mixed aliphatic aromatic diamines containing the acylamino-group in an open chain. Accordingly, the ω -benzenesulphonyl derivatives of the three aminobenzylamines were examined from this point of view, and the results obtained are recorded below.

The structural relationship between ω -benzenesulphonyl-*o*-amino-benzylamine (II) and benzenesulphonyl-1:8-naphthylenediamine (I) is indicated by the following formulæ:

The two bases behave similarly when their hydrochlorides are treated with nitrous acid; they both yield soluble diazonium salts which do not undergo condensation in the presence of excess of the mineral acid, and in each case the addition of excess of sodium acetate to the acid solution determines the formation of a diazoimide, but whereas the peri-diazoimide (III) is yellow, the new ω -benzenesulphonyl-*o*-benzylenediazoimide (IV) is colourless.

In other respects the two compounds are similar, both undergo fission on treatment with cold concentrated hydrochloric acid, regenerating the original diazonium chlorides. In spite of its lack of colour, there seems no reason to doubt that the new mixed diazoimide is a diazo-compound and not a diazonium derivative, and accordingly it may be represented by the more expanded formula V, this view of its constitution agreeing with the configuration ascribed to the analogous colourless β -phenylphenylenedihydrotriazine (VI) obtained by M. Busch from *o*-aminobenzylaniline (*Ber.*, 1892, 25, 448).

In the case of ω -benzenesulphonyl *m*-aminobenzylamine (VII), it was found that the tendency to form a diazo-anhydride had greatly diminished. The diazonium chloride of this base is not appreciably affected by excess of aqueous sodium acetate, but when the solution is treated with excess of potassium hydrogen carbonate a pale yellow precipitate slowly separates. The yield of this compound is, however, somewhat small, representing only about 10 per cent. of the diamine employed. The remainder of the diazo-compound remained uncondensed, and was recognised by combining it with β -naphthol in alkaline solution. This formation of diazo-anhydride, which is therefore very incomplete, differs markedly from the reaction taking place with ω -benzenesulphonyl-*o*-aminobenzylamine, where the condensation is quantitative.

o-Benzenesulphonyl-*p*-aminobenzylamine (VIII), when subjected to the action of nitrous acid under similar conditions, furnishes a diazonium chloride, which does not undergo condensation on treatment with aqueous sodium acetate or potassium hydrogen carbonate, the solution, after the addition of these reagents, still yielding the calculated amount of azo- β -naphthol derivative.

VII.

VIII.

In the two cases where condensation had occurred, the reaction was shown to depend on the presence of the hydrogen atom of the benzenesulphonylamino-group ($\text{NH}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_5$), for when this was replaced by methyl, no formation of insoluble diazoimide took place :

IX.

X.

o-Benzenesulphonyl-*o*-methyl-*o*-aminobenzylamine (IX) and its meta-isomeride (X) are both readily diazotised to soluble diazonium chlorides, which are not affected by aqueous alkali acetates or bicarbonates and yield insoluble, red azo- β -naphthol derivatives.

EXPERIMENTAL.*

The three phthalaldehydnitrobenzylimides,

required in this research were obtained by condensing potassium phthalimide with *o*-, *m*-, and *p*-nitrobenzyl chlorides in the manner indicated by Gabriel (*Ber.*, 1887, 20, 2227). The hydrolysis of the three substituted imides was most effectively carried out by Wolff's method (*Ber.*, 1892, 25, 3031), in which an intimate mixture of the imide with concentrated acetic and hydrochloric acids is heated under pressure at 180° for three to five hours. Equal parts by weight of the two acids were employed, and about seven parts of this mixture were used for three parts of the imide. In this way, the hydrochlorides of the three nitrobenzylamines were obtained and converted into their benzenesulphonyl derivatives by the Schotten-Baumann reaction. The main product of the reaction consists of the mono-benzenesulphonyl

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derivative, providing that only a slight excess of benzenesulphonic chloride is employed ; with larger proportions of this reagent, a certain amount of the disulphonyl compound is formed. The crude benzenesulphonyl derivatives were dissolved in aqueous caustic alkalis, reprecipitated with dilute acetic acid, and recrystallised from alcohol or benzene.

Benzenesulphonyl-o-nitrobenzylamine, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{SO}_2 \cdot \text{C}_6\text{H}_5$, separated from benzene in well-defined, hard, amber-yellow, prismatic crystals melting at 92° .

0.3568 gave 30 c.c. nitrogen at 18° and 755 mm. $N = 9.65$.

$\text{C}_{13}\text{H}_{12}\text{O}_4\text{N}_2\text{S}$ requires $N = 9.58$ per cent.

Benzenesulphonyl-m-nitrobenzylamine crystallised readily from benzene in colourless needles or pale yellow prisms and melted at $123\text{--}124^\circ$.

0.3627 gave 32.7 c.c. nitrogen at 19° and 768 mm. $N = 10.28$.

0.1855 „ 0.1554 BaSO_4 . $S = 11.50$.

$\text{C}_{13}\text{H}_{12}\text{O}_4\text{N}_2\text{S}$ requires $N = 9.58$; $S = 10.97$ per cent.

Benzenesulphonyl-p-nitrobenzylamine crystallised from benzene in lustrous, light orange leaflets melting at 118° .

0.2284 gave 19.4 c.c. nitrogen at 23° and 759 mm. $N = 9.57$.

Reduction of the Benzenesulphonylnitrobenzylamines.

The foregoing benzenesulphonylnitrobenzylamines were readily reduced by iron filings and dilute acetic acid.

ω -Benzenesulphonyl-o-aminobenzylamine (II),

was obtained by reducing 5 grams of the corresponding nitro-compound with 10 grams of iron, 5 c.c. of glacial acetic acid, and 100 c.c. of hot water. After boiling for one hour, the mixture was rendered alkaline with 5 grams of sodium carbonate and filtered, when a small portion of the diamine separated from the aqueous solution as a white powder ; the greater part was extracted by alcohol from the residue and crystallised from dilute alcohol in well-defined, colourless, elongated plates melting at $108\text{--}110^\circ$.

0.2462 gave 23.0 c.c. nitrogen at 20° and 767 mm. $N = 10.76$.

$\text{C}_{13}\text{H}_{14}\text{O}_2\text{N}_2\text{S}$ requires $N = 10.68$ per cent.

This substance crystallises from benzene in colourless plates melting at 95° and containing solvent of crystallisation.

0.1964 gave 14.1 c.c. nitrogen at 18° and 758 mm. $N = 8.27$.

$\text{C}_{13}\text{H}_{14}\text{O}_2\text{N}_2\text{S} \cdot \text{C}_6\text{H}_6$ requires $N = 8.23$ per cent.

This specimen, when crystallised from dilute alcohol, lost its benzene and separated in lustrous, colourless leaflets having the composition $C_{13}H_{14}O_2N_2S$ and melting at 109° .

ω-Benzenesulphonyl-m-aminobenzylamine (VII) was prepared by treating 4 grams of the nitro-compound with 8 grams of iron, 4 c.c. of glacial acetic acid, and 150 c.c. of water. After boiling for thirty minutes, 4 grams of sodium carbonate were added, the mixture was then filtered, the residue extracted with alcohol, the combined filtrates evaporated nearly to dryness, and the final residue dissolved in 50 per cent. acetic acid, from which solution the diamine was deposited as a pale yellow solid (m. p. $85-87^\circ$) on the addition of ammonia. When crystallised either from benzene or very dilute alcohol, this base separated in yellow, tabular crystals having a resinous appearance, which contained solvent of crystallisation and melted at $76-78^\circ$. When kept in a desiccator over sulphuric acid or when heated in the steam-oven, these crystals lost their combined solvent and also their lustre, becoming appreciably viscous; finally, they hardened again and then melted indefinitely at $80-85^\circ$.

0.3198 gave 29.3 c.c. nitrogen at 19.5° and 766 mm. N = 10.59.

$C_{13}H_{14}O_2N_2S$ requires N = 10.68 per cent.

ω-Benzenesulphonyl-p-aminobenzylamine (VIII) was obtained when 4 grams of nitro-compound, 8 grams of iron filings, 4 c.c. of glacial acetic acid, and 100 c.c. of water were boiled for forty minutes, the remainder of the preparation being carried out as in the case of the ortho-isomeride. The base, when crystallised from benzene, separated in colourless needles melting at $131-133^\circ$.

0.1180 gave 11.1 c.c. nitrogen at 19° and 768 mm. N = 10.93.

0.1808 „ 0.1671 $BaSO_4$. S = 12.68.

$C_{13}H_{14}O_2N_2S$ requires N = 10.68; S = 12.21 per cent.

Action of Nitrous Acid on the ω-Benzenesulphonyl-aminobenzylamines.

Benzenesulphonyl-o-benzylenediazoimide, $C_6H_4 \begin{smallmatrix} <CH_2 \\ N:N \end{smallmatrix} > N \cdot SO_2 \cdot C_6H_5$.

One gram of *ω*-benzenesulphonyl-o-aminobenzylamine was diazotised with 9 c.c. of concentrated hydrochloric acid and 2 c.c. of 20 per cent. aqueous sodium nitrite; 3 grams of ice were added during the process and the mixture was cooled externally with ice and salt. A colourless solution of diazonium chloride was obtained, which remained perfectly clear on dilution and yielded the colourless diazoimide on the addition of excess of aqueous sodium acetate. The precipitate consisted of minute, colourless leaflets; the filtrate gave no coloration with

alkaline β -naphthol, showing that the condensation was complete. This diazoimide decomposed violently at about 130° .

0.2650 gave 0.5569 CO_2 and 0.1070 H_2O . $\text{C} = 57.31$; $\text{H} = 4.49$.

0.2509 „ 33.7 c.c. nitrogen at 19.5° and 767 mm. $\text{N} = 15.56$.

0.2370 „ 0.2090 BaSO_4 . $\text{S} = 12.11$.

$\text{C}_{13}\text{H}_{11}\text{O}_2\text{N}_3\text{S}$ requires $\text{C} = 57.10$; $\text{H} = 4.03$; $\text{N} = 15.38$; $\text{S} = 11.72$ per cent.

The diazoimide when treated in the cold with a mixture of concentrated hydrochloric and acetic acids dissolved, leaving only a slight viscid, brown residue; the solution, when diluted considerably and poured into alkaline β -naphthol, yielded at once a light red, granular precipitate of *benzenesulphonyl- ω -aminotoluene-2-azo- β -naphthol*,

which, when crystallised from benzene, separated as a bright scarlet, microcrystalline powder melting at $161-163^{\circ}$.

0.1860 gave 16.0 c.c. nitrogen at 20° and 769 mm. $\text{N} = 9.96$.

$\text{C}_{23}\text{H}_{19}\text{O}_3\text{N}_3\text{S}$ requires $\text{N} = 10.07$ per cent.

This azo-derivative was also prepared directly from the diazonium chloride of ω -benzenesulphonyl-*o*-aminobenzylamine.

Benzenesulphonyl-m-benzylenediazoimide.

ω -Benzenesulphonyl-*m*-aminobenzylamine was diazotised in hydrochloric acid solution according to the method adopted in the case of the ortho-base. The pale yellow solution thus obtained, which contained only a slight brown turbidity, was diluted considerably, filtered, and treated with excess of aqueous sodium acetate. The solution then became slightly turbid, but no further change occurred until excess of potassium hydrogen carbonate was added, when an amorphous, pale yellow precipitate slowly separated, and was collected after three hours, washed successively with water, alcohol, and light petroleum, and finally dried in the desiccator; 4 grams of the meta-base yielded 0.6 gram of the diazoimide. The compound could not be obtained crystalline, as it decomposed on warming with solvents.

0.2192 gave 0.4538 CO_2 and 0.0838 H_2O . $\text{C} = 56.46$; $\text{H} = 4.25$.

0.1144 „ 14.2 c.c. nitrogen at 20° and 764 mm. $\text{N} = 14.29$.

0.1131 „ 0.0979 BaSO_4 . $\text{S} = 11.88$.

$\text{C}_{13}\text{H}_{11}\text{O}_2\text{N}_3\text{S}$ requires $\text{C} = 57.14$; $\text{H} = 4.03$; $\text{N} = 15.38$; $\text{S} = 11.72$ per cent.

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These data indicate that the substance has the composition of a diazoimide. It is insoluble in aqueous alkalis or acids, and is decomposed by the concentrated mineral acids (30 per cent. HCl or 50 per cent. H₂SO₄) even in the cold, evolving two-thirds of its nitrogen, and leaving a dark brown, resinous product. When this experiment was performed in the volumeter with cold sulphuric acid, 9·5 per cent. of nitrogen was eliminated, the calculated value for

namely, two-thirds of the total amount, being 10·24. This compound differs so much from the well-defined, crystalline ortho-diazoimide (p. 1162), and also from the aromatic para-diazoimides, that it is by no means certain that it has the foregoing simple configuration. Its reactions would be equally well indicated by the more complex formula $\text{C}_6\text{H}_4 \left\langle \begin{array}{c} \text{CH}_2 \cdot \text{N}(\text{SO}_2 \cdot \text{C}_6\text{H}_5) \cdot \text{N}:\text{N} \\ \text{N}:\text{N} \cdot \text{N}(\text{SO}_2 \cdot \text{C}_6\text{H}_5) \cdot \text{CH}_2 \end{array} \right\rangle \text{C}_6\text{H}_4$, in which the condensation is assumed to occur between two molecules of the diazonium base. The hydrogen of the acylamino-group, $\text{NH} \cdot \text{SO}_2 \cdot \text{C}_6\text{H}_5$, is certainly involved in the condensation, for when it is replaced by methyl, no diazo-anhydride is produced (compare p. 1166).

Benzenesulphonyl-ω-aminotoluene-3-azo-β-naphthol,

The filtrate from the preceding condensation product, when poured into alkaline β-naphthol containing a moderate excess of caustic alkali, immediately gave a scarlet precipitate of the azo-derivative, the amount of which showed that the greater portion of the diazonium chloride had not undergone condensation or any other radical change. The compound, when recrystallised from benzene, separated in small, red, flattened needles melting at 170—172°.

0·1130 gave 10·2 c.c. nitrogen at 17° and 764 mm. N = 10·62.

C₂₃H₁₉O₃N₃S requires N = 10·09 per cent.

Benzenesulphonyl-ω-aminotoluene-4-azo-β-naphthol,

ω-Benzenesulphonyl-p-aminobenzylamine, when diazotised like its

isomerides, gave rise to a soluble diazonium chloride, the solution of which, when diluted and treated successively with sodium acetate and potassium hydrogen carbonate, yielded no insoluble condensation product and, on mixing with alkaline β -naphthol, furnished sufficient of the azo- β -naphthol derivative to show that the diazo-compound had not been affected by the acetate or bicarbonate. The azo-derivative was quite insoluble in water and crystallised from glacial acetic acid, benzene, or alcohol, separating from the last of these solvents in orange-red needles or prismatic crystals; its solutions in the other media deposited minute, felted needles.

0.2034 gave 18.2 c.c. nitrogen at 19.5° and 765 mm. $N = 10.34$.

$C_{23}H_{19}O_3N_3S$ requires $N = 10.09$ per cent.

This compound, which melts at 188°, varies considerably in colour and crystalline form, sometimes separating from its solvents in dark red prisms. The three foregoing azo-derivatives all develop intense purple colorations with cold concentrated sulphuric acid; they dissolve in a moderate excess of caustic alkali to form sparingly soluble alkali salts which are precipitated by a large excess of the alkali. The ortho- and para-salts are readily hydrolysed by water, regenerating the free azo- β -naphthol; the meta-derivative is dissociated much less readily.

*Preparation of ω -Benzenesulphonyl- ω -methyl- o - and
 m -aminobenzylamines.*

Benzenesulphonylmethyl- o -nitrobenzylamine,

was prepared by heating together in alcoholic solution benzenesulphonyl- o -nitrobenzylamine (1 mol.), potassium hydroxide (1 mol.), and methyl iodide (1.5 mols.). During two and a half hours, no appreciable change occurred, but subsequently the contents of the flask became nearly solid. The alcohol was removed by evaporation, the solid product extracted with dilute aqueous caustic soda, and the residue, which consisted of almost colourless needles, crystallised with extreme readiness from either benzene or alcohol. The methylated nitro-compound was thus obtained in colourless, lustrous needles melting at 140–141°. The yield was practically quantitative.

0.2572 gave 20.6 c.c. nitrogen at 23° and 762 mm. $N = 9.06$.

$C_{14}H_{14}O_4N_2S$ requires $N = 9.15$ per cent.

Benzenesulphonylmethyl- m -nitrobenzylamine was obtained in quantitative yield by heating benzenesulphonyl- m -nitrobenzylamine in alcoholic solution with the calculated amounts of caustic potash and methyl iodide.

After boiling the solution for six hours in a reflux apparatus, the liquid was cooled, when the whole became nearly solid owing to the separation of almost colourless needles of the methylated product; this compound when recrystallised from dilute alcohol separated in fern-like aggregates of colourless, transparent plates melting at 128° .

0.1959 gave 15.5 c.c. nitrogen at 22° and 769 mm. $N = 9.07$.

$C_{14}H_{14}O_4N_2S$ requires $N = 9.15$ per cent.

ω -Benzenesulphonyl- ω -methyl-o-aminobenzylamine (IX),

was prepared by reducing 2 grams of nitro-base with 4 grams of iron, 2 c.c. of glacial acetic acid, and 50 c.c. of hot water. After boiling for thirty-five minutes and neutralising with sodium carbonate, the reduction was quite complete, the insoluble residue on extraction with alcohol yielding an almost theoretical amount of the diamine. The base is very soluble in alcohol, although dissolving only sparingly in hot water; it crystallises best from dilute alcohol, separating from this solvent in colourless, nacreous leaflets or transparent plates melting at $108-110^{\circ}$.

0.2594 gave 23.0 c.c. nitrogen at 21° and 771 mm. $N = 10.24$.

0.2596 „ 0.2320 $BaSO_4$. $S = 12.27$.

$C_{14}H_{16}O_2N_2S$ requires $N = 10.14$; $S = 11.60$ per cent.

ω -Benzenesulphonyl- ω -methyl-m-aminobenzylamine (X), when obtained from the corresponding nitro-compound by the method described for its ortho-isomeride, crystallised from both aqueous and alcoholic extracts in colourless, glistening leaflets, the yield being practically quantitative. It is much less soluble in alcohol than the unmethylated base, and separates from this solvent in lustrous, lath-like crystals melting at $128-129^{\circ}$. This melting point is practically identical with that of the nitro compound, but a mixture of the two substances melts at 110° .

0.1413 gave 12.8 c.c. nitrogen at 22° and 769 mm. $N = 10.37$.

0.2342 „ 0.2114 $BaSO_4$. $S = 12.39$.

$C_{14}H_{16}O_2N_2S$ requires $N = 10.14$; $S = 11.60$ per cent.

Diazotisation of the ω -Benzenesulphonyl- ω -methylaminobenzylamines.

—The two foregoing ω -benzenesulphonyl- ω -methylaminobenzylamines behave similarly when treated with excess of cold concentrated hydrochloric acid and sodium nitrite, colourless solutions of soluble diazonium chlorides being obtained in both cases. These solutions are quite stable on dilution, and furnish no precipitate on successive treatment with sodium acetate and potassium hydrogen carbonate, but on pouring into alkaline β -naphthol solution the azo-derivatives are at once produced as orange-red precipitates.

Benzenesulphonylmethyl- ω -aminotoluene-2-azo- β -naphthol,

This azo-derivative crystallises well from benzene in scarlet lamellæ melting at 188—189°.

0.2128 gave 18.7 c.c. nitrogen at 21° and 772 mm. $\text{N} = 10.11$.

$\text{C}_{24}\text{H}_{21}\text{O}_3\text{N}_3\text{S}$ requires $\text{N} = 9.74$ per cent.

Benzenesulphonylmethyl- ω -aminotoluene-3-azo- β -naphthol,

This substance, which separates from alkaline solutions as a somewhat viscid, orange-red precipitate, crystallises readily from benzene in transparent, brownish-red, massive plates containing benzene of crystallisation; the solvent is expelled at 100° and the residue melts very indefinitely at 150—160°.

0.6395 lost 0.0983 in the steam oven. $\text{C}_6\text{H}_6 = 15.37$.

0.3322 gave 23.7 c.c. nitrogen at 20° and 769 mm. $\text{N} = 8.26$.

$\text{C}_{24}\text{H}_{21}\text{O}_3\text{N}_3\text{S} \cdot \text{C}_6\text{H}_6$ requires $\text{C}_6\text{H}_6 = 15.32$; $\text{N} = 8.25$ per cent.

The two foregoing azo-derivatives develop intense crimson colorations with cold concentrated sulphuric acid.

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ROYAL COLLEGE OF SCIENCE, LONDON,
SOUTH KENSINGTON, S.W.