

CCXLI.—*The Action of Diazo-salts on Aromatic Sulphonamides. Part I.*

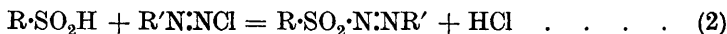
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HINSBERG (*Ber.*, 1894, **27**, 598), by the action of benzenediazonium chloride on benzenesulphonamide in very dilute alkaline solution, obtained a yellow, crystalline product, which in the crude state melted at 102° with decomposition and on analysis gave 15.63 per cent. of nitrogen. From this, the author assigned to it the structure $\text{SO}_2\text{Ph}\cdot\text{NH}\cdot\text{N}\cdot\text{NPh}$, which requires 16.09 per cent. of nitrogen. On warming with dilute acids or alkalis, it decomposed into benzenesulphonamide, phenol, nitrogen, and a resinous product.

In repeating Hinsberg's reaction with molecular quantities of *p*-toluenesulphonamide and benzenediazonium chloride, we obtained a yellow, crystalline product which, however, smelt strongly of phenylazoimide. On recrystallisation from dilute alcohol, it melted at 95° (with decomposition), and its analysis agreed with the formula $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{N}\cdot\text{NPh}$. A similar compound isomeric with the above, *p*-toluenediazobenzenesulphinate, $\text{SO}_2\text{Ph}\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Me}$, had previously been prepared by Hantzsch and Singer (*Ber.*, 1897, **30**, 312) by the action of *p*-toluenediazonium chloride on benzenesulphinic acid, and the lower homologue, $\text{SO}_2\text{Ph}\cdot\text{N}\cdot\text{NPh}$, by Königs (*Ber.*, 1877, **10**, 1531) by the action of benzenediazonium chloride on the same substance. On the other hand, when the crude yellow product was crystallised from benzene and light petroleum, it melted sharply at 87—88°, with decomposition, and its analysis agreed with the formula $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{NH}\cdot\text{N}\cdot\text{NPh}$.

Assuming that the diazo-sulphinate, $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{N}\cdot\text{NPh}$, had been formed in a similar way to that of Königs and of Hantzsch and Singer, we concluded that the diazoamino-compound, first formed, must have decomposed in presence of alkali into *p*-toluenesulphinic acid and phenylazoimide, and the sulphinic acid thus formed must have combined with the benzenediazonium chloride. This has been verified by carrying out the condensation in presence of a large excess of alkali, when no solid but phenylazoimide was obtained in very good yield. The sulphinic acid present in the alkaline aqueous portion was converted into the insoluble ferric salt (Thomas, T., 1909, **95**, 342). The yield was almost quantitative, according to equation (1). In another experiment the sulphinic acid was condensed with a molecular proportion of the diazonium salt, when

the diazosulphinate was obtained in very good yield, the reaction taking place according to equation (2).



Hinsberg's product may therefore be regarded as a mixture of the diazoamino-compound, $R \cdot SO_2 \cdot NH \cdot N:NR'$, and the diazo-sulphinate, $R \cdot SO_2 \cdot N:NR'$. This reaction has been studied with both benzene- and *p*-toluene-sulphonamides on the one hand, and aniline, *o*-, *m*-, and *p*-toluidines, and *p*-chloroaniline on the other. The products in all cases are similar and the reaction may be represented by equations (1) and (2). The reaction, therefore, can conveniently be utilised for the preparation of aromatic azoimides and sulphinic acids.

EXPERIMENTAL.

Action of Benzenediazonium Chloride on p-Toluenesulphonamide.

Experiment I.—Benzenediazonium chloride (made from aniline, 4.6 grams, hydrochloric acid, 15 c.c., and water, 25 c.c., diazotised with sodium nitrite, 3.5 grams in water, 15 c.c.) was slowly added to a well-cooled solution of 8.5 grams of *p*-toluenesulphonamide and 6 grams of sodium hydroxide in 175 c.c. of water. The mixture was stirred for about ten minutes and filtered, and the yellow, crystalline product washed with water and dried in a vacuum desiccator. The filtrate was slightly alkaline and smelt strongly of phenylazoimide. The crude product melted and decomposed at 83—85° (Found: N = 13.9 per cent.). The yield was 8 grams. A portion, recrystallised from aqueous alcohol, formed yellow needles, m. p. 95° with decomposition (Found: C = 59.78 by the wet method; N = 10.98; S = 12.34. *Benzenediazo-p-toluenesulphinate*, $CH_3 \cdot C_6H_4 \cdot SO_2 \cdot N:NPh$, requires C = 60.00; N = 10.77; S = 12.31 per cent.). The sulphur was estimated by fusion with potassium carbonate and potassium nitrate, as an attempt by the Carius method resulted in an explosion just after the tube had been sealed.

The diazo-sulphinate, on reduction with zinc dust and acetic acid in alcoholic solution (Königs, *loc. cit.*), gave the colourless dihydro-derivative. This, when recrystallised from alcohol, formed needles, m. p. 154° with decomposition (Found: N = 10.9. $CH_3 \cdot C_6H_4 \cdot SO_2 \cdot NH \cdot NPh$ requires N = 10.7 per cent.).

A small portion of the crude condensation product, m. p. 83—85°, mentioned above, was dissolved in a large volume (1 gram in 50 c.c.)

of benzene at about 30° and filtered. The pale yellow, crystalline precipitate that separated on adding light petroleum to the cooled filtrate was quickly collected and dried in the dark; it melted sharply with decomposition at $87-88^{\circ}$ (Found: N = 15.55. The diazoamine, $\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{NH} \cdot \text{N} \cdot \text{NPh}$ requires N = 15.27 per cent.). When warmed with sodium hydroxide solution, contrary to Hinsberg's statement, it liberated phenylazoimide. In alcoholic solution, it gave a deep red coloration with a solution of β -naphthol.

Experiment II.—In this experiment the reaction was carried out in presence of a large excess of alkali. Benzenediazonium chloride (made from 9.3 grams of aniline) was slowly added to a solution of 17 grams of *p*-toluenesulphonamide and 15 grams of sodium hydroxide in 350 c.c. of water. In this case no precipitate was formed, but an orange, opalescent liquid was obtained smelling strongly of phenylazoimide. A drop of the liquid produced a deep red coloration on β -naphthol test-paper. A few c.c. of the liquid were acidified with cold dilute acetic acid and gave a pale yellow precipitate, which, after being filtered, washed, and dried, melted with decomposition at $85-86^{\circ}$ (Found: N = 15.28 per cent.). The reaction mixture, which evidently contained the diazoamine in solution, showed no appreciable decomposition even after being stirred for two hours. The mixture having been kept overnight in the ice box, a considerable amount of oil had accumulated at the bottom of the vessel, but the liquid still gave the red coloration with β -naphthol test-paper. Sodium hydroxide (15 grams) was then added and the mixture stirred until no colour reaction was obtained with β -naphthol paper. It was then extracted with ether, the ether distilled off, and the residue distilled in steam. The steam distillate was again extracted with ether, and the extract dried over calcium chloride and distilled in a vacuum from a water-bath. The yield of phenylazoimide was 9 grams, the calculated yield being 11.9 grams according to equation (1). It is a clear yellow liquid, having a characteristic, penetrating, but not unpleasant smell. It explodes when heated in a test-tube over a Bunsen flame, but distils at 81° under 44 mm. pressure. To identify the product further, it was condensed with ethyl acetate, a substance, melting at 115° , being produced identical with that obtained by Dimroth (*Ber.*, 1902, **35**, 4057) from phenylazoimide and ethyl acetate.

The aqueous solution left after the phenylazoimide had been removed was divided into two equal portions. One portion was acidified with hydrochloric acid. The brick-red precipitate obtained by the addition of ferric chloride to the acid solution was collected (yield 8.5 grams, the calculated yield being 8.7 grams), treated with a slight excess of aqueous ammonia, and filtered. On the

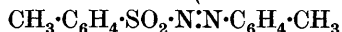
addition of concentrated hydrochloric acid to the cooled filtrate, colourless, crystalline *p*-toluenesulphinic acid was precipitated. It was recrystallised from water and melted at 86—87° (Thomas gives m. p. 86—87°, *loc. cit.*). It gave the characteristic blue colour reaction of aromatic sulphinic acids with concentrated sulphuric acid and anisole (Smiles and Rossignol, T., 1906, **89**, 696) (Found : S = 20·54. Calc., S = 20·51 per cent.).

The other portion of the aqueous solution mentioned above was treated with half the quantity of benzenediazonium chloride, when a yellow, crystalline precipitate was obtained. This was filtered off, washed with water, and dried; the yield of crude product was 13 grams (m. p. 91°), the theoretical yield being 14 grams. On recrystallisation from dilute alcohol it formed yellow needles, m. p. 95°, and proved to be identical with the benzenediazo-*p*-toluenesulphinate described in experiment I.

Action of o-Toluenediazonium Chloride on p-Toluenesulphonamide.

In this and the following experiments with *p*-toluenesulphonamide, 17 grams of the substance were dissolved in an alcoholic solution of 20 grams of potassium hydroxide, the alcohol was distilled off in a vacuum, and the residue dissolved in 150 c.c. of water. This process has the advantage that the bulk of the solution is smaller than in the previous experiments, and in spite of the large concentration of alkali the potassium salt of the sulphonamide does not separate out. *o*-Toluenediazonium chloride (made from 10·7 grams of *o*-toluidine) was then added, when a dark oil was formed. This was extracted with ether and purified as in experiment II. The yield of pure *o*-tolylazoimide was 10 grams (b. p. 90·5° at 31 mm.), the theoretical yield being 13·3 grams.

The aqueous solution was divided into two equal portions; one was treated with ferric chloride and the other with half the quantity of *o*-toluenediazonium chloride, as described in experiment II. The yield of ferric *p*-toluenesulphinate was 8 grams [Found : Fe = 10·6. $(\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2)_3\text{Fe}$ requires Fe = 10·74 per cent.]. The yield of the crude *o*-toluenediazo-*p*-toluenesulphinate (m. p. 74° with decomposition) was 11 grams, the theoretical yield being 13·7 grams. On recrystallisation from alcohol, it formed deep yellow needles and melted at 95° (Found : N = 10·26.



requires N = 10·22 per cent.).

Action of m-Toluenediazonium Chloride on p-Toluenesulphonamide.

The same quantities were used as in the previous experiment. The yield of pure *m*-tolylazoimide was 11 grams (b. p. 92·5° at 31 mm.), that of ferric *p*-toluenesulphinate 8·5 grams (Found: Fe = 10·65 per cent.), and that of the crude diazo-sulphinate (m. p. 62—66°) 11·5 grams. The last, on recrystallisation from alcohol, formed bright yellow needles, m. p. 72—73° (Found: N = 10·16 per cent.).

Action of p-Toluenediazonium Chloride on p-Toluenesulphonamide.

The same quantities were used. The yield of pure *p*-tolylazoimide (b. p. 93° at 32 mm.) was 10 grams. It has a characteristic aniseed smell. The yield of ferric *p*-toluenesulphinate was 8 grams (Found: Fe = 10·7 per cent.), and that of the crude diazo-sulphinate (m. p. 96—99°) was 12 grams. The latter, on recrystallisation from alcohol, formed bright yellow needles which melted at 100° with decomposition (Found: N = 10·59 per cent.).

Action of p-Chlorobenzenediazonium Chloride on p-Toluene-sulphonamide.

The yellow, crystalline precipitate formed on the addition of *p*-chlorobenzenediazonium chloride (made from 12·7 grams of *p*-chloroaniline) to the solution of the sulphonamide decomposed very slowly with the separation of an oil. After remaining overnight, the mixture was extracted with ether and the extract purified as before. The yield of *p*-chlorophenylazoimide (b. p. 90—91° at 15 mm.) was 8 grams, the calculated yield being 15 grams. The aqueous portion was divided into two equal parts and treated as before. The yield of ferric *p*-toluenesulphinate was 5 grams (Found: Fe = 10·67 per cent.), that of the crude *p*-chlorobenzenediazo-*p*-toluenesulphinate, m. p. 112—117°, was 8 grams, the calculated yield being 14·7 grams. The latter, on recrystallisation from alcohol, formed golden-yellow plates, m. p. 118° with decomposition (Found: N = 9·7 per cent. $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_4\text{Cl}$ requires N = 9·5 per cent.).

Action of Benzenediazonium Chloride on Benzenesulphonamide.

In this and the following experiments 15·7 grams of the sulphonamide were dissolved in alcoholic potassium hydroxide, and the aqueous solution was prepared as before. Molecular quantities

of the various diazo-salts were used. With benzenediazonium chloride, the yield of pure phenylazoimide was 8 grams. The aqueous portion was also treated as before. The yield of ferric benzenesulphinat was 7 grams, the calculated yield being 8 grams (Found: Fe = 11.48. Calc., Fe = 11.69 per cent.). The free sulphinic acid obtained from it melted at 83—84° (Thomas gives m. p. 85°; *loc. cit.*).

The yield of the crude benzenediazobenzenesulphinat was 12 grams, the theoretical yield being 14.7 grams. On recrystallisation from dilute alcohol, it formed orange plates which melted at 75—76° with decomposition (Königs gives m. p. 75—76°; *loc. cit.*) (Found: C = 58.37; N = 11.8. Calc., C = 58.54; N = 11.38 per cent.). On reduction with zinc dust and acetic acid, it gave the dihydro-derivative, which, on recrystallisation from alcohol, formed colourless needles and melted at 158° (Königs gives m. p. 148°) (Found: N = 11.7. Calc., N = 11.3 per cent.).

Action of o-Toluenediazonium Chloride on Benzenesulphonamide.

The yield of pure *o*-tolylazoimide was 10 grams, that of ferric benzenesulphinat 6.5 grams (Found: Fe = 11.47 per cent.), and that of the crude *o*-toluenediazobenzenesulphinat 9.6 grams, the calculated yield being 13 grams. The last, on recrystallisation from alcohol, formed salmon-coloured, small prisms which melted with decomposition at 59—60° (Found: N = 10.6. $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{SO}_2\text{Ph}$ requires N = 10.77 per cent.).

Action of m-Toluenediazonium Chloride on Benzenesulphonamide.

The yield of pure *m*-tolylazoimide, b. p. 78° at 14 mm., was 9 grams, that of ferric benzenesulphinat 6.4 grams (Found: Fe = 11.48 per cent.), and that of the crude diazo-sulphinat 9.6 grams. The last, on recrystallisation from alcohol, formed yellow prisms which melted at 58° with decomposition (Found: N = 10.78 per cent.).

Action of p-Toluenediazonium Chloride on Benzenesulphonamide.

The yield of pure *p*-tolylazoimide was 9 grams, that of ferric benzenesulphinat 5.6 grams (Found: Fe = 11.48 per cent.), and that of the diazo-sulphinat 9.2 grams. The last, on recrystallisation from alcohol, formed golden-yellow prisms which melted at 85—86° with decomposition (Found: N = 10.8 per cent.); Hantzsch and Singer give m. p. 90° (*loc. cit.*).

Action of p-Chlorobenzenediazonium Chloride on Benzene-sulphonamide.

The yellow, crystalline diazoamine formed in this experiment appeared to be rather stable. After stirring for two hours, it was filtered, washed, and dried. It melted indefinitely at about 85° (Found: N = 14.41. $\text{SO}_2\text{Ph}\cdot\text{NH}\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_4\text{Cl}$ requires N = 14.21 per cent.).

In another experiment, the reaction mixture was stirred for two days, when an oily liquid separated, which was extracted and purified in the usual way. The yield of pure *p*-chlorophenylazoimide was 7 grams. The aqueous portion was divided into two equal parts and treated as before. The yield of ferric benzenesulphinate was 5 grams, and that of the crude diazo-sulphinate 7 grams, the theoretical yield of the latter being 14 grams. On recrystallisation from alcohol, it formed deep yellow prisms, m. p. 106° with decomposition; Hantzsch and Singer give m. p. $102\text{--}103^{\circ}$ (Found: N = 10.2. Calc., N = 9.98 per cent.).

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