266. *The Interaction of Arylsulphonylphenylhydrazines with Bromine.*

By Frank Bell.

Although phenylhydrazine is converted by the action of bromine in alcoholic or acetic acid solution into benzenediazonium bromide (Chattaway, J., 1908, **93**, 852), acetylphenylhydrazine undergoes substitution to give progressively the 4-bromo- and then the 2 : 4-dibromo-derivative (Humphries and Evans, J., 1925, **127**, 1676). The interaction of arylsulphonylphenylhydrazines with bromine has now been examined under various conditions.

Both benzene- and *p*-toluene-sulphonylphenylhydrazines are sparingly soluble in cold solvents, and therefore bromination was first attempted in boiling chloroform suspension. In both cases a poor yield of the corresponding 2 : 4-*dibromo*-derivative was obtained. Use of warm acetic acid as solvent led to still smaller yields. In cold pyridine, oxidation and not bromination occurred, resulting in the production of the corresponding diazonium compounds.

Benzene- and p-*toluene-sulphonyl-*4-*bromophenylhydrazines,* from 4-bromophenylhydrazine, showed a similar behaviour on bromination, the corresponding 2 : 4-*dibromo*-derivatives being produced in chloroform, and the *diazonium sulphinates* in pyridine.

Experimental.

Experiments with p-*Toluenesulphonylphenylhydrazine.*—(a) 8 G. suspended in hot chloroform were treated with bromine (5 g.) in chloroform. The mixture was filtered hot from the solid (A), and the filtrate evaporated to dryness. The residue after crystallisation from alcohol gave needles (1·8 g.) of p-*toluenesulphonyl*-2 : 4-*dibromophenylhydrazine,* m. p. 166° (Found : C, 37·1; H, 2·8. $C_{13}H_{12}O_2N_2Br_2S$ requires C, 37·1; H, 2·9%). By treatment of a pyridine solution with bromine, this compound gave 2 : 4-*dibromobenzenediazonium* p-*toluenesulphinate,* which crystallised from alcohol in yellow needles, decomp. 128° (Found : C, 37·3; H, 2·3. $C_{13}H_{10}O_2N_2Br_2S$ requires C, 37·8; H, 2·4%), and was alternatively prepared by the addition of diazotised 2 : 4-dibromoaniline to an alkaline solution of sodium *p*-toluenesulphinate. The 2 : 4-dibromoaniline was obtained as follows. 2 : 4-*Dibromobenzenesulphonanilide* (Found : N, 3·7. $C_{12}H_9O_2NBr_2S$ requires N, 3·6%), needles, m. p. 128°, from alcohol, was obtained in poor yield by the bromination of 4-bromobenzenesulphonanilide in chloroform solution, and dissolved in cold sulphuric acid. Much 2 : 4 : 6-tribromoaniline was obtained as by-product.

Crop (A), above, recrystallised from alcohol, gave plates (1 g.), m. p. 212°, of *4-bromophenylhydrazine* p-*toluenesulphonate* (Found: C, 43·6; H, 4·2. $C_{13}H_{15}O_3N_2BrS$ requires C, 43·4; H, 4·2%), converted by trituration with ammonium hydroxide into 4-bromophenylhydrazine and by bromine in pyridine into 4 : 4′-dibromoazobenzene. The latter was compared with a sample prepared by the distillation of 4 : 4′-dibromoazoxybenzene with iron filings.

(b) Bromine (2·5 g.) was added slowly to 4 g. of *p*-toluenesulphonylphenylhydrazine in pyridine, the mixture kept for 1 hour, and poured into water. The resultant yellow gum was recrystallised first from warm acetic acid and then from alcohol, yielding *benzenediazonium* p-*toluenesulphinate* in long yellow needles, decomp. 93° (Found: N, 10·7. $C_{13}H_{12}O_2N_2S$ requires N, 10·8%). This was very readily obtained by oxidation of the hydrazine in hot chloroform suspension with mercuric oxide.

(c) Bromine (4 c.c.) was added slowly to 20 g. of *p*-toluenesulphonylphenylhydrazine in pyridine (25 c.c.), the mixture kept for 2 days, and poured into water. The precipitated dark brown viscous mass was separated and added to warm alcohol. On cooling, *di*-p-*toluenesulphonylphenylhydrazine* separated; after recrystallisation from alcohol or acetic acid it gave colourless glistening needles, m. p. 194° (Found: C, 57·4; H, 4·9; N, 7·0. $C_{20}H_{20}O_4N_2S_2$ requires C, 57·7; H, 4·8; N, 6·7%). The yield was variable, but five such experiments gave a total yield of 10·5 g. This compound is rather soluble in chloroform, and was recovered unchanged after treatment with mercuric oxide in this solvent; it did not react with bromine in boiling carbon tetrachloride or cold pyridine, and crystallised out unchanged after heating in alcoholic hydrogen chloride for 1 hour. 4 G. were rapidly dissolved in 4 c.c. of cold concentrated sulphuric acid, and the solution was poured into water, giving a precipitate of crude phenylhydrazine sulphate. This was dissolved in alcohol containing the appropriate quantity of potassium acetate, and the filtered solution used for the preparation of the phenylhydrazones of benzaldehyde and anisaldehyde. Fission of the di-*p*-toluenesulphonyl derivative with piperidine was tried under various conditions, but in only one experiment was any solid material isolated. Piperidine (3 c.c.) was added to 3·5 g. and the resultant deep red solution, which was slowly evolving nitrogen, left over-night. About 10 c.c. of water were then added, and the black sticky precipitate was separated and dissolved in alcohol. On cooling, *p*-toluenesulphonylhydrazine separated; recrystallisation from alcohol gave 0·25 g. of pure material. The mode of origin of the di-*p*-toluenesulphonyl derivative is still obscure. It could not be present in the initial material as impurity for two reasons. (i) 10 G. of the initial material were extracted with cold chloroform; the extract on evaporation furnished 1 g. of highly crystalline material of unchanged decomposition point. (ii) *p*-Toluenesulphonylphenylhydrazine did not react with *p*-toluenesulphonyl chloride in pyridine or in warm aqueous sodium carbonate, showing that there is little tendency for direct combination to occur.

Benzenediazonium *p*-toluenesulphinate was recovered unchanged after standing in pyridine solution over-night, but after ½ hour's boiling in alcohol or after addition of bromine to the solution in pyridine, it was so completely decomposed that no crystalline material could be isolated. It did not react with either *p*-toluenesulphonyl chloride or *p*-toluenesulphinic acid in pyridine solution.

Interaction of 4-bromophenylhydrazine with *p*-toluenesulphonyl chloride in pyridine solution gave mainly p-*toluenesulphonyl-4-bromophenylhydrazine*, needles, m. p. 144° (Found: C, 45·7; H, 3·8. $C_{13}H_{13}O_2N_2BrS$ requires C, 45·7; H, 3·8%), fairly soluble in hot benzene, and some 4-bromophenylhydrazine *p*-toluenesulphonate, almost insoluble in benzene. *p*-Toluenesulphonyl-4-bromophenylhydrazine (3 g.) with bromine in pyridine for 1 hour gave on decomposition with water *4-bromobenzenediazonium* p-*toluenesulphinate* (1·6 g. of purified material). This was alternatively prepared by the oxidation of the hydrazine in chloroform solution with mercuric oxide or by the addition of diazotised *p*-bromoaniline to alkaline sodium *p*-toluenesulphinate; it crystallised from alcohol in bright yellow needles, decomp. 124° (Found: C, 46·0; H, 3·3. $C_{13}H_{11}O_2N_2BrS$ requires C, 46·0; H, 3·3%). The diazonium sulphinate underwent decomposition on boiling in alcoholic solution for some time, and on cooling 4 : 4′-dibromoazobenzene (0·1 g. from 1·8 g.) crystallised out (compare Hantzsch and Blagden, *Ber.*, 1900, **33**, 2556, for the formation of azo-compounds in about 10% yield by the decomposition of diazo-compounds). 4-Bromobenzenediazonium *p*-toluenesulphinate was reconverted into the hydrazine by treatment with zinc dust in acetic acid solution or by sulphur dioxide in alcohol. With bromine in chloroform it gave an immediate crystalline deposit of the diazonium perbromide, decomposed by warm ethyl alcohol to give *p*-dibromobenzene.

p-Toluenesulphonyl-4-bromophenylhydrazine with bromine (1 mol.) in chloroform gave the 2 : 4-dibromo-derivative (above).

Experiments with Benzenesulphonylphenylhydrazine.—(a) On addition of bromine (6·5 g.) in chloroform (6 c.c.) to 10 g. suspended in boiling chloroform (100 c.c.) a deep red colour developed. After ½ hr. the mixture was filtered from a deposit (4 g.) of hydrobromide, which after solution in alcohol gave needle crystals, m. p. 177°, of *benzenesulphonyl-2 : 4-dibromophenylhydrazine* (Found : C, 35·6 ; H, 2·6. $C_{12}H_{10}O_2N_2Br_2S$ requires C, 35·5 ; H, 2·5%). The chloroform mother-liquor furnished further small crops of the same material. It was converted by the action of bromine in pyridine or by mercuric oxide in chloroform into 2 : 4-*dibromobenzenediazonium sulphinate*, orange-yellow needles, decomp. 98° (Found : C, 35·6 ; H, 2·0. $C_{12}H_8O_2N_2Br_2S$ requires C, 35·6 ; H, 2·0%).

(b) Interaction with bromine in pyridine was tried under a variety of conditions (concentration, length of standing, decomposition with water or acids) but in each case a dark oil was isolated from which no crystalline material could be obtained. This failure is attributed to the fact that this diazonium sulphinate has a lower m. p. than any of the others studied, rather than to any difference in the nature of the reaction.

4-Bromophenylhydrazine with benzenesulphonyl chloride in pyridine gave a product of highly indefinite m. p., from which, by repeated crystallisation, pure *benzenesulphonyl-4-bromophenylhydrazine* was obtained in needles, m. p. 140° (Found : C, 44·4 ; H, 3·4. $C_{12}H_{11}O_2N_2BrS$ requires C, 44·0 ; H, 3·4%). By bromine in pyridine or by mercuric oxide in chloroform it was converted into 4-bromobenzenediazonium benzenesulphinate, identical with an authentic specimen (Hantzsch and Singer, *Ber.*, 1897, **30**, 314). These authors describe also the reduction, by zinc dust in acetic acid, of this compound to give a benzenesulphonyl-4-bromophenylhydrazine of m. p. 162°, although the result is not supported by analytical data. Attempts to repeat this experiment failed, only zinc benzenesulphinate being isolated in every case. This formed shining plates, decomp. 205°, difficultly soluble in alcohol but readily recrystallised from acetic acid (Found : C, 37·5 ; H, 3·75 ; residue, 20·5. Calc. : C, 37·6 ; H, 3·7 ; ZnO, 21·2%) (compare Schiller and Otto, *Ber.*, 1876, **9**, 1586). 4-Bromobenzenediazonium benzenesulphinate was decomposed by boiling with alcohol for ½ hour, and on cooling, 4 : 4′-dibromoazobenzene crystallised out (0·1 g. from 2 g.).

Benzenesulphonyl-4-bromophenylhydrazine with the calculated quantity of bromine in chloroform gave the 2 : 4-dibromo-derivative (above).

The analyses were carried out by Dr. A. Schoeller of Berlin.

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