OXIDATIONS WITH SILVER IODIDE DIBENZOATE

Part II. Preparation of $s$-Azo Compounds from Some Aromatic Primary Amines

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Received December 18, 1956

(Communicated by Dr. K. N. Menon, F.A.Sc.)

In a recent paper from this laboratory the use of the Sinomini complex formed from iodine and silver benzoate for the scission of $\alpha$-glycols was reported. The present communication deals with the oxidation of some substituted anilines. Aromatic primary amines are rapidly oxidised by the reagent with the production of deeply coloured products. A detailed investigation of the action of this reagent on $p$-toluidine, $p$-chloraniline, $p$-bromaniline, $p$-nitroaniline and 2-chloro-4-nitro-aniline has shown that the main product of the oxidation in each case is the corresponding symmetrical azo compound when molar proportions of silver iodide dibenzoate and the aromatic primary amine are employed. The reaction thus proceeds according to the general equation

$$2R-NH_2 + 2(C_6H_5-COO)_2 AgI \rightarrow R-N = N-R + 2 Ag I + 4 C_6H_5-COOH.$$ 

Silver iodo dibenzoate thus constitutes another useful member of a group of oxidising agents like permanganate, ferricyanide, chromic acid anhydride, sodium hypobromite, phenyl iodosoacetate and lead tetraacetate for the oxidation of aromatic primary amines to the corresponding $s$-azo compounds.

The reaction probably involves a free radical mechanism and proceeds through the highly reactive intermediate radical $R-NH^*$ which undergoes dimerisation to the hydrazo compound followed by further oxidation to the azo compound.

$$2R-NH_2 (C_6H_5-COO)_2 AgI \rightarrow 2 R-NH^* \rightarrow R-NH-NH-R \rightarrow R-N = N-R.$$

The intermediate $R-NH^*$ may enter into side reactions and this probably accounts for the formation of dark coloured products encountered in the oxidations. This mechanism finds support in the work of Pausacker.
and others on the oxidation of aromatic primary amines to azo compounds with phenyl iodosoacetate and lead tetra-acetate for which analogous reaction mechanisms have been proposed by them. The mechanism is also partially supported by the fact that hydrazo benzene is very rapidly oxidised to azo benzene in very high yields (94%) by the action of silver iodide dibenzoate. But aniline itself, on treatment with the complex under mild conditions, gave a dark, gummy product from which only traces of azo benzene could be isolated.

Although the conditions for the maximum yield of the azo compounds were not investigated, the yields obtained in the different cases were fairly good, excepting in the case of p-toluidine. The oxidation of p-toluidine was very rapid whereas it was relatively slower in the case of p-nitroaniline and still slower in the case of 2-chloro-4-nitroaniline. The yields of azo compounds were somewhat widely different in the case of the different amines; those amines containing electron-attracting groups tend to give relatively higher yields of azo compounds. Thus p-toluidine gave 28%, p-nitroaniline 44% and 2-chloro-4-nitroaniline 56% of the corresponding azo compound. Benzoic acid, arising from the oxidising agent, was obtained in high yields in all cases after the oxidation.

**EXPERIMENTAL**

Silver iodide dibenzoate was prepared by warming 9.2 g. (0.04 mole) of silver benzoate and 5 g. (0.04 atom) of iodine in 140 c.c. of dry benzene, with exclusion of moisture. This was cooled to room temperature and the amine (0.02 mole) added either as such or in benzene solution. The mixture in almost all the cases became warm and was afterwards shaken at room temperature and then heated on the water-bath for a short time. By this time the bulky silver iodide dibenzoate got replaced by the heavier silver iodide and the benzene solution became deeply coloured. The hot benzene solution was filtered, the residual silver iodide washed with warm benzene and the combined benzene filtrate worked up for the isolation of the azo derivatives as indicated under the different compounds. The identity of the different azo compounds was established by mixed m.p. determinations with authentic specimens prepared according to the general method of Bogoslovskii.9

4, 4'-Dimethyl azo benzene.—After adding the p-toluidine dissolved in dry benzene to the complex, the mixture was shaken for 10 mins. and then heated on the water-bath for about 15 mins. The colour of the benzene solution which was brownish yellow at first turned dark brown by this time. The benzene solution from the reaction was concentrated to small bulk
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under reduced pressure, cooled and the crop consisting mostly of benzoic acid was filtered off. The benzene filtrate was brought to dryness and the residue triturated with alcohol. The portion insoluble in alcohol was brown in colour and melted at 135–40°. Wt. 0·6 g. (28%). Crystallisation from alcohol gave pure 4, 4'-dimethyl azo benzene, yellow crystals, m.p. and mixed m.p. 143–44°.

4, 4'-Dichloro azo benzene.—p-Chloraniline in benzene solution was added to the silver iodide dibenzoate complex, mixture shaken for 15 mins. and then heated on the water-bath for 10 mins. Concentration of the dark brown benzene filtrate under reduced pressure to about 40 c.c. and cooling in ice gave the azo compound mixed with benzoic acid. The azo compound (yield 1 g.; 40%; m.p. 180–85°) separated by bicarbonate, crystallised from alcohol and then acetone (charcoal) gave yellow needles, m.p. and mixed m.p. 184–85°.

4, 4'-Dibromo azo benzene.—The oxidation of p-bromaniline was done exactly as in the case of p-chloraniline. The colour of the benzene solution which was brown initially changed to almost dark towards the end. The benzene filtrate, worked up as above, gave 1·4 g. (41%) of the azo compound as a yellowish brown solid, m.p. 197–200°. Crystallisation from acetone (charcoal) gave yellow needles, m.p. and mixed m.p. 203–05°.

4, 4'-Dinitro azo benzene.—Powdered p-nitroaniline was added to the complex and the mixture heated on the water-bath for 75 mins. The deep red benzene filtrate on concentration to small bulk, gave the azo compound mixed with benzoic acid. Separation by bicarbonate gave the azo compound (1·2 g.; 44%) which on crystallisation from acetone (charcoal) gave orange-red needles, m.p. 223–24°.

2, 2'-Dichloro-4, 4'-dinitro azo benzene.—After addition of 2-chloro-4-nitroaniline to the complex, the mixture was very gently boiled on the water-bath for 1½ hrs. The benzene solution was brought to dryness under reduced pressure, residue treated with bicarbonate solution and then triturated with cold alcohol. Filtration gave a brown product (1·9 g.; 56%) melting at about 270°. Crystallisation from benzene gave the azo compound as fine, brownish red crystals, m.p. and mixed m.p. 275–76°.

Azo benzene from hydrazo benzene.—Hydrazo benzene (3·7 g.) was added to the complex prepared as above and after shaking the warm mixture for 15 mins., it was heated on the water-bath for 10 mins. The colour of the benzene layer which immediately changed to yellow, turned reddish yellow and finally reddish brown. The filtered benzene solution was brought to
dryness, the residue taken up in ether, washed with bicarbonate solution and then water, the ether solution dried with anhydrous sodium sulphate and the solvent removed. The residue on a single crystallisation from dil. alcohol gave 3·45 g. of azo benzene as orange-red crystals, m.p. and mixed m.p. 67–68°.

ACKNOWLEDGMENT
My thanks are due to Prof. K. N. Menon for his valuable help and suggestions in this work.

SUMMARY
The formation of $s$-azo compounds by the oxidation of some aromatic primary amines by silver iodide dibenzoate is described. The reaction probably proceeds through a free radical mechanism in which the highly reactive $R\text{-}NH^*$ radical plays a part.

REFERENCES