

LXXV.—*The Nitration of 4-Chloro-4'-bromo-benzophenone and -diphenylsulphone, and the Attempted Nitration of 4-Chloro-4'-bromodiphenyl.*

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IN extension of our studies of nitration of diphenyl derivatives on the one hand (Le Fèvre and Turner, J., 1928, 963, etc.) and of mixed dihalogeno-derivatives on the other (Mayes and Turner, *ibid.*, p. 691), we have investigated the nitration of two compounds of the general formula $\text{Cl}-\text{C}_6\text{H}_4-\text{X}-\text{C}_6\text{H}_4-\text{Br}$. In both compounds, X is a meta-orienting group, *viz.*, carbonyl or sulphonyl, and therefore nitration occurs ortho to one halogen or to the other, but not elsewhere. In view of the improbability that the group X will transmit any influences from one nucleus to the other, the results supply information as to the relative rates of nitration in positions ortho to chlorine and to bromine in presence of a constantly acting meta-directing para-substituent.

4-Chloro-4'-bromobenzophenone is nitrated to the extent of 51% in position 3 and 49% in position 3'; the values for the nitration of 4-chloro-4'-bromodiphenylsulphone are 34 and 66%, respectively. These results are evidently connected with the facts that benzophenone is nitrated readily and diphenylsulphone tardily, and that bromobenzene is nitrated more rapidly than chlorobenzene (Ingold and Shaw, J., 1927, 2918), and has a higher *o/p* ratio than the latter (Holleman, *Rec. trav. chim.*, 1900, **19**, 188, 364; 1905, **24**, 146; 1913, **32**, 134).

We have also attempted to study the quantitative dinitration of 4-chloro-4'-bromodiphenyl, but this substance undergoes degradation when submitted to conditions which lead, in the case of 4:4'-dichloro- or -dibromo-diphenyl, to almost quantitative 2:3'-dinitration.

EXPERIMENTAL.

4-Chloro-4'-bromobenzophenone.—Chlorobenzene (32 g.) was slowly added to a gently boiling mixture of 100 g. of carbon disulphide, 50 g. of *p*-bromobenzoyl chloride, and 32 g. of anhydrous aluminium chloride, and boiling was continued for 2 days. Water and a little hydrochloric acid were then added and the mixture was freed from carbon disulphide and chlorobenzene by steam distillation. The residual solid (25 g.) was crystallised several times from alcohol. 4-Chloro-4'-bromobenzophenone forms very pale brownish plates,

m. p. 150° (corr.) (Found : AgCl + AgBr, 0.2230 g. $C_{13}H_8OClBr$ requires AgCl + AgBr, 0.2224 g.).

Nitration of 4-Chloro-4'-bromobenzophenone.—To a solution of 3.0 g. of the ketone in 15 c.c. of concentrated sulphuric acid kept at -5° , was slowly added a solution of 1 g. of potassium nitrate in 5 c.c. of concentrated sulphuric acid. When addition was complete, the cooling bath was removed, and the temperature of the nitration mixture rose slowly to 21° before reverting to the temperature of the room. The mixture was poured on ice, and the precipitated solid collected, washed with boiling water, and dried (3.3 g.) (Found : AgCl + AgBr, 0.2236 g. Calc. for $C_{13}H_7O_3NClBr$: AgCl + AgBr, 0.2235 g.).

The mixture of mononitro-derivatives so obtained (0.2472 g.) was heated at 100° for an hour with excess of piperidine. Water was then added, and the precipitated mixture of piperidino-derivatives was filtered off. The filtrate and washings were acidified with dilute nitric acid, and the mixed halogen displaced by piperidine was determined (Found : AgCl + AgBr, 0.1208 g.; atomic ratio of halogen displaced, Cl : Br = 48.8 : 51.2).

A second experiment with the same quantities of material gave AgCl + AgBr, 0.1191; Cl : Br = 53.8 : 46.2. Hence, in mean, 3-nitration = 51.3%, and 3'-nitration = 48.7%.

4-Chloro-4'-bromodiphenylsulphone.—Anhydrous aluminium chloride (1.3 mols.) was slowly added to a mixture of *p*-chlorobenzenesulphonyl chloride (1 mol.) and bromobenzene (2 mols.). The whole was heated on a steam-bath for 2 hours, cooled, poured on ice, and treated with hydrochloric acid. Bromobenzene was removed in a current of steam, and the residual solid thoroughly extracted with alkali to remove unchanged sulphonyl chloride; after being crystallised thrice from alcohol, it formed glistening white needles, m. p. 157° (corr.) (Found : AgCl + AgBr, 0.1896 g. $C_{12}H_8O_2ClBrS$ requires AgCl + AgBr, 0.1888 g.).

Nitration of 4-Chloro-4'-bromodiphenylsulphone.—A solution of 3.315 g. of sulphone in 40 c.c. of concentrated sulphuric acid was slowly treated at the ordinary temperature with a solution of 1.01 g. of potassium nitrate in 20 c.c. of concentrated sulphuric acid (1 c.c. of acid being used for washing). The temperature rose slowly to 22° , and when it had fallen, the solution was poured on ice and the precipitate was filtered off, washed repeatedly with warm water, and dried. It melted under hot water, but solidified on cooling (3.70 g.) (Found : AgCl + AgBr, 0.1550 g.; $BaSO_4$, 0.1101 g. Calc. for $C_{12}H_7O_4NClBrS$: AgCl + AgBr, 0.1559 g.; $BaSO_4$, 0.1098 g.).

The ratio of reactive chlorine to reactive bromine was determined

by the method used above. In one experiment, 0.3001 g. gave 0.1386 g. of $\text{AgCl} + \text{AgBr}$; $\text{Cl} : \text{Br} = 31.4 : 68.6$. In a second experiment, 0.4215 g. gave 0.1927 g. of $\text{AgCl} + \text{AgBr}$; $\text{Cl} : \text{Br} = 35.5 : 64.5$. Mean, $\text{Cl} : \text{Br} = 33.5 : 66.5$.

Dinitration of 4-Chloro-4'-bromodiphenylsulphone.—Nitric acid (d 1.5; 25 c.c.) was added to a solution of 5 g. of the sulphone in 25 c.c. of warm concentrated sulphuric acid. The mixture was heated on the steam-bath for an hour. 4-Chloro-4'-bromo-3 : 3'-dinitrodiphenylsulphone gradually separated, and in due course the solution was cooled, diluted, and filtered. The m. p., 219° (corr.), was not raised by crystallisation from glacial acetic acid, from which solvent the sulphone separated in pale yellow prisms (Found : $\text{AgCl} + \text{AgBr}$, 0.1231 g. $\text{C}_{12}\text{H}_6\text{O}_6\text{N}_2\text{ClBrS}$ requires $\text{AgCl} + \text{AgBr}$, 0.1235 g.). It reacted readily with boiling piperidine to give 3 : 3'-dinitro-4 : 4'-dipiperidinodiphenylsulphone, identical with an authentic specimen of this substance (Le Fèvre and Turner, J., 1927, 1113).

4-Chloro-4'-bromodiphenyl.—4-Chloro-4'-aminodiphenyl (Le Fèvre and Turner, J., 1928, 245) was diazotised in hydrochloric acid solution, and bromine, dissolved in hydrobromic acid, added. The perbromide separated as a bright red crystalline solid, which, after being washed, was suspended in glacial acetic acid. On heating, normal decomposition took place, and the solution on cooling deposited pale brownish needles of 4-chloro-4'-bromodiphenyl, which, after being crystallised three times from glacial acetic acid, had m. p. 147° (corr.) (Found : $\text{AgCl} + \text{AgBr}$, 0.2220, 0.2506 g. $\text{C}_{12}\text{H}_8\text{ClBr}$ requires $\text{AgCl} + \text{AgBr}$, 0.2216, 0.2476 g.).

When 2 g. of the chlorobromodiphenyl were added to 30 g. of nitric acid (d 1.5) at the ordinary temperature, a deep purple solution was obtained. On gentle warming, the colour faded. The resulting yellowish-brown solution was cooled and slowly diluted with water. About 1.2 g. of a gummy, pale yellow solid were obtained, the composition of which could not be determined. Similar products were obtained when different nitration conditions were employed.

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