

XLVI.—*The Comparative Reactivities of Some Chloro-,
Bromo-, and Iodo-nitrobenzenes.*

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IN an attempt to determine the relative degrees to which chlorine, bromine, and iodine atoms are activated by nitro-groups, present in the same aromatic nucleus, we chose piperidine as reagent for reasons already stated (Le Fèvre and Turner, J., 1927, 1113), and first tried to compare the reactivities of different halogenonitro-compounds by allowing them to compete, two at a time, for piperidine in benzene solution. The results, however, did not lend themselves to simple interpretation, and we therefore made quantitative measurements of the reactivity of individual halogeno-nitro-compounds towards piperidine. The reactivity of *p*-chloronitrobenzene, the least reactive compound used, being expressed by unity, the compounds mentioned below have reactivities for this one reagent, and under the present definite conditions, represented by the attached figures :

<i>o</i> -Chloronitrobenzene	36.3	1-Chloro-2 : 4-dinitrobenzene	56.9
<i>o</i> -Bromonitrobenzene	43.5	1-Bromo-2 : 4-dinitrobenzene	56.4
<i>o</i> -Iodonitrobenzene	17.9	1-Iodo-2 : 4-dinitrobenzene ...	34.4
<i>p</i> -Bromonitrobenzene	2.38	4-Chloro-3-nitrobenzonitrile	56.1
<i>p</i> -Iodonitrobenzene	2.24	4-Bromo-3-nitrobenzonitrile	55.1
2 : 5-Dichloronitrobenzene	55.9		
2 : 5-Dibromonitrobenzene	56.0		

The results show that, whereas *o*-chloronitrobenzene is about 36 times as reactive as the corresponding *p*-compound, the *o*-bromo- and *o*-iodo-compounds are respectively only 18 and 8 times as reactive as the *p*-analogues. They also seem to show that iodine is incapable of activation to the extent possible with chlorine and bromine.

Competitive Experiments.—In the first series of experiments, a pair of halogenonitro-compounds (1 mol. of each) was allowed to react with piperidine in 100 c.c. of benzene, at 15° for 60 hours (dinitro-compounds) or in the boiling solvent for 8 hours (*o*-nitro-compounds). The results are in Tables I and II.

TABLE I.

w = g. of silver halide from 50 c.c. of solution; v = c.c. of 0.1038N-AgNO₃ required by 50 c.c. of solution; r = molecular ratio of piperidine salts in the mixture.

Pair of 1-halogeno- 2 : 4-dinitrobenzenes.	w .	v .	r .
Cl, Br	0.1860	11.23	Cl : Br = 1.75 : 1
Br, I	0.1661	7.26	Br : I = 1 : 2.22
I, Cl	0.1115	6.95	I : Cl = 1 : 6.83

In each of these cases the mixed piperidine salts, made up to 1 litre with water, were analysed in the usual manner, but in experiments 2 and 3, where iodine ions were present, more accurate results were obtained by adding excess of silver nitrate and titrating the final excess with ammonium thiocyanate.

TABLE II.

w' = g. of mixed piperidine hydrohalides; w = g. of mixed silver halides from 50 c.c. of solution; r = molecular ratio of piperidine salts in the mixture.

Pair of 1-halogeno- 2-nitrobenzenes.	w' .	w .	r .
Cl, Br	2.3488	0.1344	Cl : Br = 0.6 : 1
Br, I	2.0249	0.1130	Br : I = 1.5 : 1
I, Cl	0.9033	0.0523	I : Cl = 1 : 5.4

In these experiments the mixture of piperidine salts was collected in a Gooch crucible, washed with benzene, dried to constant weight at 100°, and then analysed gravimetrically.

From the first two experiments in Table I and in Table II iodine would be expected to be a little more reactive than chlorine; it appears from the third experiment in each table to be considerably less so.

Direct Method of Measurement.—The halogenonitro-compound (0.02468 g.-mol., equiv. to 5 g. of 1-chloro-2 : 4-dinitrobenzene) was allowed to react for 8 hours in boiling benzene solution (50 c.c.) with piperidine (1 mol.); the precipitated piperidine salt was then

collected in a Gooch crucible and dried at 100°. The results are in Table III.

TABLE III.

	Substance.	Percentage reaction.		Mean.	Ratio (Cl = 1).
		Series 1.	Series 2.		
ortho-	$C_6H_4Cl \cdot NO_2$	59.7	60.1	59.9	1
	$C_6H_4Br \cdot NO_2$	71.6	72.0	71.8	1.20
	$C_6H_4I \cdot NO_2$	29.6	29.4	29.5	0.49
para-	$C_6H_4Cl \cdot NO_2$	1.6	1.7	1.65	1
	$C_6H_4Br \cdot NO_2$	3.9	3.85	3.93	2.38
	$C_6H_4I \cdot NO_2$	3.9	3.5	3.7	2.22
1 : 2 : 4-	$C_6H_3Cl(NO_2)_2$	95.8	92.2	94.0	1
	$C_6H_3Br(NO_2)_2$	94.8	91.2	93.0	0.99
	$C_6H_3I(NO_2)_2$	56.8	56.5	56.7	0.60
1 : 2 : 4-	$C_6H_3Cl(NO_2) \cdot CN$	92.85	92.1	92.5	1
	$C_6H_3Br(NO_2) \cdot CN$	90.5	91.4	91.0	0.98
1 : 2 : 5-	$C_6H_3(NO_2)Cl_2$	92.9	91.7	92.3	1
	$C_6H_3(NO_2)Br_2$	93.1	91.7	92.4	1
1 : 4-	$C_6H_4Cl \cdot NO_2$		1.65	1.65	1
1 : 3 : 4-	$C_6H_3(NO_2)Cl_2$	3.9	3.9	3.9	2.36

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