tion state does not give evidence of obedience to the Tait equation over the entire pressure range. If the curvature is really caused by a departure of the transition state from a Tait-like response to pressure, the basis for inferring its "structure" or other "molecular" properties from the pressure-dependence of the rate is seriously undermined. We conclude, therefore, that inferences regarding the volume of activation for the dimerization of isoprene are unjustified.

It is unfortunate that there are so few reliable data on pressure effects in liquid systems. While the apparatus for such measurements is not very difficult to obtain, the measurements themselves are fraught with many errors. A very appreciable error can arise from the heating effects due to adiabatic compression. Thus some experimenters have reported thermal explosions in systems containing reactive dienes when the pressures were raised too rapidly. This heating occurs both in the reaction liquid and the hydraulic fluid. Since the thermal conductivities of liquids are rather small, it takes appreciable time to dissipate this heat and the rates must be corrected for the initially high temperatures. For reactions with usual activation energies such corrections can be considerable.

A second source of error arises from the heat liberated in exothermic reactions. Benson[18] has made an analysis of such errors and shown that in small vessels containing liquids the temperature error can be of the order of a few tenths °C. These errors are most pronounced for reactions having large heats of reaction and half-lives of the order of 1 hr. To date, very little attention has been given to these sources of error by workers in the field, but it appears to us that they can introduce considerable uncertainty in the data on pressure effects where small changes in rate are being measured.

[18] S. W. Benson, *J. Chem. Phys.*, **22**, 46 (1954).

[CONTRIBUTION FROM THE VENABLE LABORATORY, THE UNIVERSITY OF NORTH CAROLINA, CHAPEL HILL, N. C., AND THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF MISSISSIPPI, UNIVERSITY, MISS.]

Photochemical Interchange of Halogens in Aromatic Compounds. I[1a]

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The series of reactions, $ArX + X' \rightarrow ArX' + X$, which are caused by light or peroxide–SO_2Cl_2, is discussed. Three new reactions of this type, the effects of some substituents on the rates of certain examples and the relative rates of displacement of bromine and iodine by a common reagent, chlorine, are reported.

Introduction

A number of investigators have reported that the side chain chlorination of the ring brominated toluenes proceeds anomalously,[2] with bromine appearing on the side chain and chlorine on the nucleus. Although Eibner's report, in 1903,[3] of the facile displacement of bromine from bromobenzene by chlorine clearly established that the methyl substituent is not required, Miller and Walling[4] were the first to report detailed further study of this simpler form of the displacement.

The experiments of Miller and Walling have demonstrated the intermediacy of halogen atoms in the reaction

$$Cl_2 + C_6H_5Br \xrightarrow{\text{light}} Br_2 + C_6H_5Cl$$

Because of the close analogy between displacement by a halogen atom and one by a free radical we are investigating in more detail this halogen displacement reaction and others closely related. Although the data now available are not extensive enough to shed light upon the nature of radical displacements on aromatic compounds, they have intrinsic interest.

Results

From consideration of the usual order of displacement in the halogen group, one might expect that a family of reactions analogous to the displacement of bromine from aromatic compounds by chlorine should be possible. In this family an halogen should be able to displace another of equal or higher atomic number

$$ArX + X' \longrightarrow ArX' + X$$
$$\text{at. no. } X' \leq \text{at. no. } X$$

giving rise to a total of ten reactions. Four of these involve fluorine and have not been investigated, but the remaining six have been observed. They are

$$ArCl + Cl^* \longrightarrow ArCl^* + Cl \qquad (A)$$
$$ArBr + Cl \longrightarrow ArCl + Br \qquad (B)$$
$$ArI + Cl \longrightarrow ArCl + I \qquad (C)$$
$$ArBr + Br^* \longrightarrow ArBr^* + Br \qquad (D)$$
$$ArI + Br \longrightarrow ArBr + I \qquad (E)$$
$$ArI + I^* \longrightarrow ArI^* + I \qquad (F)$$

Reaction B, of course, is well established, and reactions D and F have been reported by Miller and Walling[4] and by Noyes,[5] respectively. The remaining three reactions (A, C and E) are reported here for the first time.[6]

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[1] (a) Presented in part at the 138th National Meeting of the A.C.S., New York, N. Y., September, 1960. (b) To whom inquiries should be addressed, Department of Chemistry, The University of Mississippi.

[2] (a) O. Srpek, *Monatsh.*, **11**, 429 (1890); (b) S. C. J. Olivier, *Rec. trav. chim.*, **45**, 296 (1926); (c) F. Asinger, *Monatsh.*, **64**, 153 (1934); *J. prakt. Chem.*, **152**, 5 (1939); (d) G. L. Goerner and R. C. Nametz, *J. Am. Chem. Soc.*, **73**, 2940 (1951); (e) W. Voegtli, H. Muhr and P. Langer, *Helv. Chim. Acta*, **37**, 1627 (1954).

[3] A. Eibner, *Ber.*, **36**, 1229 (1903).

[4] B. Miller and C. Walling, *J. Am. Chem. Soc.*, **79**, 4187 (1957).

[5] R. M. Noyes, *ibid.*, **70**, 2614 (1948); R. M. Noyes and D. J. Sibbett, *ibid.*, **75**, 767 (1953).

Because chlorine reacts with iodobenzene to form iodobenzene dichloride,[7] the displacement of iodine by chlorine must be effected by means of ICl or SO_2Cl_2–peroxide.

All the reactions we have studied (A, B, C and E) proceed smoothly in carbon tetrachloride or other inert solvent at room temperature under illumination by visible wave lengths but do not take place at a noticeable rate in the dark. When a substituent is present, the entering halogen atom invariably occupies the position of the atom displaced. The likelihood that *cine* substitution occurs only in the unsubstituted case appears vanishingly small.

There are no indications that in the absence of complicating factors, such as the presence of methyl groups, very nearly a stoichiometric balance

$$2ArX + X'_2 \longrightarrow 2ArX' + X_2$$

(or suitable modification if an interhalogen reagent is used), does not exist in halogen interchange reactions in *dilute carbon tetrachloride solution at room temperature*. Although addition products have been isolated by other workers[3,4] from reactions at elevated temperatures, detectable amounts are not formed under the conditions we have used. Gas chromatographic analysis during the determination of substituent effects (*vide infra*) has in no case revealed unidentified or unexpected peaks. Furthermore, in preparative scale experiments involving solid non-volatile products, yields in excess of 90% have been realized.[2c] We have not established precise stoichiometry in all cases studied but have done so in a few (see Experimental) which we considered most likely to give difficulty.

In order to gain some insight into the nature of halogen interchange reactions, we have undertaken to compare the reactivities of several substituted halobenzenes with those of their unsubstituted analogs. Relative reactivities may be ascertained in two ways without recourse to complete kinetic analysis. First, one can allow two compounds to compete for a limited amount of reagent in the same solution and then analyze the products. Second, separate solutions of the compounds in question can be allowed to react side by side under identical conditions. The former method is far more precise, especially in cases such as ours which depend upon factors like light intensity that are not easily controlled. Nonetheless, before the advent of gas chromatography, the latter method (parallel reaction) offered the advantage of more convenient analysis. Our reason for presenting early results from the parallel technique stems from the fact that, in principle, the two methods can give different results. Both yield the same result only if the over-all rate of reaction is determined primarily by the substitution process. The currently available data are collected in Tables I and II.

TABLE I

SUBSTITUENT EFFECTS ON PHOTOCHEMICAL DISPLACEMENT OF AROMATIC BROMINE BY CHLORINE (REACTION B)

Substituent	Reagent	Reactivity ratio (substd./unsubstd.) Substituent position *o*	*m*	*p*
Cl	Cl_2	0.72	0.091[a]	1.28,[b] 0.9,[c] (>1)[d]
	ICl			1.71
F	Cl_2	0.74	0.12	1.23
	ICl			2.08
CO_2H	Cl_2	0.23[c]	0.26[c]	

[a] m-ClC_6H_4Br 5.0 *M*, C_6H_5Br 1.0 *M* (see Experimental). [b] p-ClC_6H_4Br 1.0 *M*, C_6H_5Br 1.0 *M* (see Experimental). [c] From ref. 4.[8] [d] Parallel technique. All aromatic concentrations 0.10 *M* except as noted.

TABLE II

SUBSTITUENT EFFECTS ON PHOTOCHEMICAL DISPLACEMENT OF AROMATIC IODINE BY BROMINE (REACTION E), Br_2 REAGENT AT 27°

Substituent	Reactivity ratio (substd./unsubstd.) Substituent position *o*	*m*	*p*
F	0.184	0.225	1.12 (0.9)[a]
Cl	1.43	.159	1.54 (1.3)
CF_3	0.0427	.0927	0.195
Br	1.99	.419	2.54
OCH_3	5.26		7.78 (7)

[a] Values in parentheses are from the parallel technique.

By means of parallel reaction experiments the following qualitative order of substituent effects has been observed for reaction B, p-phenyl > o-methoxy > p-chloro > unsubstd. > p-carbomethoxy > p-cyano.

Miller and Walling have reported[4] that the nitro substituent or the presence of nitrobenzene or azobenzene inhibits the displacement of aromatic bromine by chlorine. We have also observed such inhibition but find that it is not complete in the case of the m-nitro substituent, at least. A 40% yield (G.L.C.) of m-nitrochlorobenzene was obtained from m-bromonitrobenzene and chlorine in two weeks under conditions that cause bromobenzene to react completely in less than two hours. The 40% yield may be a minimum figure because chlorine displaces the nitro group, presumably as NO_2, although no m-dichlorobenzene was detected. In an experiment run parallel to the one just quoted a 60% yield (G.L.C.) of chlorobenzene was obtained from nitrobenzene.[9]

Because of the 14 kcal. difference between the aromatic carbon–iodine and carbon–bromine bond dissociation energies[10] and the fact that both bromine and iodine can be displaced by a common reagent, chlorine, the relative rates at which the two elements are displaced appeared to be of interest. We have, accordingly, compared the reactivities of iodo- and bromobenzenes toward chlorine (from ICl for the reasons given above). Difficulties in experiment and interpretation caused us to choose a more circuitous route than the obvious one of allowing iodo- and bromobenzenes to compete

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(6) T. Van derLinden [*Rec. trav. chim.*, **58**, 281 (1936)] isolated iodine and p-bromoiodobenzene but no bromobenzene from treatment of iodobenzene with bromine in sunlight.

(7) For example see L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **80**, 1723 (1958); R. M. Keefer and L. J. Andrews, *ibid.*, **80**, 5350 (1958).

(8) The discrepancy between our value for the effect of the p-chloro substituent and that of Miller and Walling is rather large to be ascribed to experimental error. Some of our recent data (to be reported later) suggest that the difference of conditions used may account for most, if not all, of the discrepancy.

(9) In both experiments aqueous washings were yellow suggesting that NO_2, which adds to aromatic compounds to give complex mixtures of polynitro phenol esters [A. I. Titov, *Zhur. Obshchei Khim.*, **22**, 1329 (1952)], was formed.

(10) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 50.

directly. The reactivity of iodobenzene relative to *p*-chlorobromobenzene was determined and then corrected for the effect of the *p*-chloro substituent from a separate experiment to give the ratio of the reactivity of iodobenzene to bromobenzene. As a check, an analogous experiment with the substituent "label" on the iodobenzene was carried out. The results are given in Table III. Although the 12% difference between the two results appeared justifiable as experimental error, we repeated the entire procedure using the *p*-fluoro substituent, which permits much more precise analysis by gas chromatography. The resulting reactivity ratios of iodobenzene to bromobenzene are also given in Table III.

TABLE III

PHOTOCHEMICAL COMPETITIVE DISPLACEMENTS OF IODINE AND BROMINE BY CHLORINE (FROM ICl) AT 27°

Iodo compound	Bromo compound	R reactivity ratio (iodo/bromo)	R' Substituent effect	R'' (RXR') $\frac{\text{Iodobenzene}}{\text{Bromobenzene}}$
C_6H_5I	*p*-ClC_6H_4Br	1.26	1.71	2.16
p-ClC_6H_4I	C_6H_5Br	3.00	0.806	2.42
C_6H_5I	*p*-FC_6H_4Br	1.10	2.08	2.28
p-FC_6H_4I	C_6H_5Br	6.92	0.322	2.23

Discussion

That none of the reactions under discussion, save the isotopic exchanges, is appreciably reversible can be verified by approximate thermodynamic calculations. We estimate that enthalpy changes exceed −10 kcal./mole for reactions B, C and E in the forward direction. Therefore, since entropy changes are small, no reversibility should exist under experimentally realizable conditions.

Inspection of the data in Tables I and II reveals that the customary linear free energy relationships do not hold. A plot of σ or σ^+ *vs.* log reactivity ratio (from Table II) for the *m*- and *p*-positions yields points in three quadrants. Because, by definition, either plot must pass through the origin, neither applies. The recent three parameter treatment of Knowles, Norman and Radda[11] is equally inapplicable. Using the data from Table II for the *p*-Cl and *p*-Br substituents a value of ϕ in their equation is established which predicts a reactivity ratio of 10^7 for the *p*-methoxy case, a substantial divergence from the observed value of 7.78.

Even a qualitative correlation of all the data in Tables I and II according to conventional steric and electronic factors cannot be formulated without highly contrived arguments. More data and more insight are required before substituent effects in these reactions can be unravelled.

The several aromatic halogen interchange reactions may take place by entirely different mechanisms, but we have adopted as a working hypothesis the assumption that all are closely related in mechanistic detail. The discussion that follows is based in large degree on that assumption, contrary to which no evidence has yet been discovered.

A number of mechanistic possibilities suggest themselves. Dissociation (mechanism 1) appears unlikely on the following grounds.

$$\begin{aligned} ArX + h\nu &\longrightarrow Ar\cdot + X\cdot \\ Ar\cdot + X'_2 &\longrightarrow ArX' + X' \qquad (1) \end{aligned}$$

The energy available in light of visible wave lengths, which proves effective, is insufficient to bring about the dissociation of either bromo- or chlorobenzene. Although the same is not true of iodobenzene, its extinction coefficient is extremely low in the visible region. The dissociation mechanism cannot apply to the displacements of iodine and bromine from aromatics by the chlorine of sulfuryl chloride–peroxide, and there is no reason to suspect that these reactions are fundamentally different from their photochemical analogs. Furthermore, the dissociation mechanism precludes a chain process which obtains in the aryl bromide–chlorine case at least.[4]

A mechanism involving displacement on halogen appears unlikely as well.

$$\begin{aligned} X'_2 + h\nu &\longrightarrow 2X'\cdot & \text{(a)} \\ ArX + X'\cdot &\longrightarrow Ar\cdot + XX' & \text{(b)} \\ Ar\cdot + X'_2 &\longrightarrow ArX' + X'\cdot\text{, etc.} & \text{(c)} \quad (2) \end{aligned}$$

If X is iodine and X′ is chlorine, step b is endothermic by 5 kcal./mole (the difference between the bond dissociation energies of ICl and iodobenzene), but if X is bromine and X′ chlorine, step b is endothermic by 17 kcal./mole. This mechanism, therefore, predicts that iodine would be displaced by chlorine at a rate several powers of ten faster than would bromine in a competitive experiment. Our experimental result, that iodine is displaced only 2.3 times as rapidly as bromine is, clearly belies this prediction.

Some sort of direct displacement on carbon, as others[4] have noted, is a more attractive possibility. Such a displacement could be a concerted one-step process, a two-step process involving a relatively stable σ-complex or some intermediate between these two extremes. In any event the transition state of the displacement step would not appear to involve appreciable bond breaking.

The formation of charge transfer (or π) complexes is a complicating but real possibility. The formation of complexes between aromatics and halogen *molecules* is well known and has been widely investigated.[12] Furthermore, the formation of complexes between aromatics and halogen *atoms* is indirectly supported by the selectivity studies of Russell[13a] and of Walling and Mayahi[13b] and more directly by the spectroscopic investigations of Strong, Rand and Britt.[14] Either type of complex could conceivably be a necessary precursor to the transition state of either of the extreme mechanisms mentioned above.

A point in favor of the incurrence of π-complex formation (of either type) is the unusual pattern of substituent effects. If π-complex formation were required or significant, a substituent effect observed by our experimental method would include not only alteration of the activation parameters of substitution but also of the stability and, possibly,

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[11] J. R. Knowles, R. O. C. Norman and J. K. Radda, *J. Chem. Soc.*, 4885 (1960).

[12] See for example, L. J. Andrews, *Chem. Revs.*, **54**, 713 (1954).

[13] (a) G. A. Russell, *Tetrahedron*, **8**, 101 (1960); (b) C. Walling and M. F. Mayahi, *J. Am. Chem. Soc.*, **81**, 1485 (1959).

of the extinction coefficient of the complex by the substituent.

We are continuing experiments to unravel some of the unanswered questions concerning photochemical interchange of halogens in aromatic compounds.

Experimental

Carbon Tetrachloride.—Reagent grade carbon tetrachloride was used in all experiments and was further purified by passing through a 120 × 1 cm. column of silica gel for competitive experiments. The column was repacked for each 3.7 l. purified.

Isotopic Chlorine Exchange.—Chlorine (5 mmoles) labeled with approximately 0.13 μc. of Cl^{36} was generated by the method of Brown, Gillies and Stevens[15] and condensed, by cooling with liquid air, from a stream of helium onto a mixture of 0.307 g. (2 mmoles) of *o*-chlorobenzoic acid (Eastman Kodak Co. white label) and 5 ml. of trifluoroacetic acid (Eastman Kodak Co. white label). The homogeneous solution obtained upon warming to room temperature was irradiated by a 275-watt mercury arc sunlamp 45 cm. away for 1 hour. The chlorine was then swept into 1 *M* Na_2SO_3 with a stream of helium. The solvent was evaporated at room temperature (24 hours) and the residue was sublimed *in vacuo* yielding 0.267 g. (93.5%) of material, m.p. 141–143° after one recrystallization from water. An unirradiated control was run simultaneously.

Radiochemical assay with a thin window G–M tube of samples plated on filter paper in 1-inch aluminum cups showed that 7.2% of the radioactivity was transferred to the *o*-chlorobenzoic acid (0.1% in the control). If exchange equilibrium had been reached 28.6% of the radioactivity would have been transferred.

Displacement of Iodine by Chlorine. (a) Sulfuryl Chloride Method.—A mixture of 54 g. of freshly distilled iodobenzene[16] and 16.7 g. of redistilled sulfuryl chloride was heated to reflux (liquid temperature 105°). Over a period of 3 hours. 15.5 g. of 4,4′-dichlorobenzoyl peroxide[17] of 85% assay[18] was added in small portions. An additional 16 g. of sulfuryl chloride was added in two portions to maintain the liquid temperature below 115°. The red-violet product mixture was washed with water, sodium sulfite and sodium hydroxide. Acidification of the sodium hydroxide washings yielded 15 g. (crude) of *p*-chlorobenzoic acid, m.p. 241–243° after recrystallization. The liquid remaining after washing was dried and fractionated at 58 mm. by means of a 1 × 60 cm. spinning band column with the results:

chlorobenzene, 2.32 g. (identified by distln. temp. and nitration prod.)
p-dichlorobenzene, trace (identified by infrared spectrum)
iodobenzene, 13.6 g. (identified by distln. temp.)
p-diiodobenzene, 7 g. (distln. residue); (identified by m.p. and nitration prod.)

Similar results were obtained in experiments using benzoyl peroxide and lauroyl peroxide.

(b) **Photochemical Method.**—To 8.20 g. of iodobenzene[16] dissolved in 4 l. of CCl_4 was added 10.7 ml. of 0.373 *M* ICl (10.0 mole%) in CCl_4. The solution was stirred and irradiated by a 275-watt mercury arc sunlamp 15 cm. away for 12 hours. The violet colored solution was washed with dilute thiosulfate and water and then dried with calcium carbide. The solvent was removed by distillation through a 1.5 × 75 cm. helix packed column until the residue was reduced to about 80 ml. The residue was transferred to a 100-ml. volumetric flask and was diluted to volume with CCl_4. Analysis of the solution by gas chromatography showed that a quantitative yield, based on ICl, of chlorobenzene was obtained. In a similar experiment substituting bromobenzene for iodobenzene a quantitative conversion of ICl to chlorobenzene was also obtained.

Displacement of Iodine by Bromine. (a) Vapor Phase.—A mixture of 50 g. of iodobenzene[16] and 40 g. of bromine (Merck C.P.) was passed drop by drop through a 60-cm. Pyrex air condenser which was heated to 200° by means of a resistance wire wound around it and which was illuminated by a 275-watt mercury arc sunlamp placed 2 cm. from the center. The effluent, which was condensed in two ice-cooled traps in series, was washed with dilute sodium hydroxide until the color of iodine had disappeared. After being dried the mixture was distilled through a 1 × 60 cm. spinning band column. There was isolated 4.17 g. (10%) of bromobenzene (identified by distillation temperature, refractive index and nitration product), unreacted iodobenzene and a crystalline residue containing bromine and iodine.

(b) **In Solution.**—An ampoule containing 0.406 g. of bromine (reagent) was broken under the surface of a solution of 8.30 g. of *p*-iodoanisole (m.p. 51–51.5°)[19] in 1 liter of CCl_4. The flask was closed with a glass stopper and stirred with a magnetic stirrer under illumination by a 200-watt incandescent lamp overnight at room temperature; reaction, as judged by color, was complete. The halogen present was titrated with standard thiosulfate. The organic layer was dried over anhydrous sodium carbonate and filtered. The entire process was repeated seven times. The total loss of halogen (from substitution, addition or volatilization) was 3.8%.

Substituent Effects by Parallel Reaction. (a) Displacement of Bromine by Chlorine.—In each run 10 mmoles of each of three bromo compounds (all Eastman Kodak Co. white label) was placed in a separate gas washing bottle with 50 ml. of CCl_4. Chlorine (Matheson) was bubbled through all three bottles at equal rates for several minutes, and then irradiation by a sunlamp equidistant from the samples was begun. The time of appearance of definite bromine color (1–60 min.) was noted. By means of several runs of this sort the order of substituent effects, $p\text{-}C_6H_5 > o\text{-}CH_3O > p\text{-}Cl > H > p\text{-}CH_3O_2C > p\text{-}CN$ was obtained.

(b) **Displacement of Iodine by Bromine.**—A 5.07×10^{-3} *M* solution of each of the following in CCl_4 was prepared; iodobenzene,[16] *p*-chloroiodobenzene (m.p. 55–56°),[19] *p*-fluoroiodobenzene[20] (b.p. 181–181.5°), and *p*-iodoanisole[19] (m.p. 51–51.5°). To a 5.00-ml. aliquot of each of two solutions was added a like amount of dilute bromine solution. Immediately after mixing, 3.00-ml. aliquots were transferred to matched spectrophotometer cells which were then sealed. After the bromine concentration in each was measured spectrophotometrically (Hilger ultraviolet spectrometer; solution pairs differing by more than 5% were discarded), the cells were irradiated side by side at room temperature for 1 hour by a 300-watt Hanovia quartz mercury arc lamp filtered by a Wratten 47 filter between soft glass plates (405 and 436 mμ lines transmitted). Spectrophotometric evaluation of the Br_2 and IBr present permitted calculation of the extent of reaction (always less than 20% and usually less than 10%) and the amount of halogen lost (less than 20% in all cases). Calculation of relative reactivities from the data of several pairs was made with the assumption of low conversion, *i.e.*, that

$$R = \mathrm{IBr}_{\mathrm{substd}}/\mathrm{IBr}_{\mathrm{unsubstd}}$$

Substituent Effects by Competitive Reaction.—All runs were made in a thermostat bath at 27.3° which was illuminated by two 275-watt mercury sunlamps which were filtered by 4 mm. of Corning glass 3060 (opaque below 400 mμ) and were 45 cm. from the bath. At least two runs were made in each case.

(a) **Displacement of Bromine by Chlorine.**—Except as noted below 2.50 mmoles each of bromobenzene and a substituted bromobenzene were weighed into a 25-ml. volumetric flask. After about 10 ml. of CCl_4 had been added, 2.0 ml. of a 0.12 *M* solution of Cl_2 in CCl_4 was discharged into the flask from an apparatus similar to that of Gillam and Morton.[21] The contents were quickly diluted to volume and mixed. The flask was placed in the bath

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(14) R. L. Strong, S. J. Rand and J. A. Britt, *J. Am. Chem. Soc.*, **82**, 5053 (1960).

(15) F. Brown, R. Gillies and W. H. Stevens, *Can. J. Chem.*, **31**, 768 (1953).

(16) H. J. Lucas and E. R. Kennedy, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 351.

(17) C. G. Swain, W. H. Stockmayer and J. P. Clarke, *J. Am. Chem. Soc.*, **72**, 5426 (1950).

(18) G. Braun, "Organic Syntheses," Coll. Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1951, p. 434.

(19) Prepared by the method of ref. 16 on commercial amine.

(20) Prepared by Schiemann reaction [G. Schiemann, *J. prakt. Chem.*, **140**, 97 (1934); A. Roe, "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 193] on *p*-iodoaniline [R. Q. Brewster, ref. 16, p. 347].

(21) A. E. Gillam and R. A. Morton, *Proc. Roy. Soc.* (*London*), **A124**, 604 (1929); **A132**, 152 (1951).

described above as quickly as possible and left for 2 hours, which sufficed for complete reaction. The contents were rapidly transferred to a separatory funnel containing 25 ml. of 10% aqueous KI, and the iodine liberated was titrated with standard thiosulfate. The lower layer was drawn off, washed with water, and dried over Drierite.

The dried solution was analyzed by gas chromatography (Perkin–Elmer 154B) either directly (as noted below) or after concentration by the following procedure. A sample was concentrated by depositing a 10-ml. aliquot on a 1 × 20 cm. column of 20–200 mesh silica gel which had been set up in CCl_4. Control experiments showed that all aromatics used (except *p*-dichlorobenzene) were quantitatively retained and could be quantitatively eluted by ethanol. The 0.5 ml. preceding and the 0.5 ml. succeeding the easily visible ethanol–CCl_4 front were collected together and analyzed. Because *p*-dichlorobenzene was not quantitatively concentrated by our procedure, runs involving *p*-bromochlorobenzene were made at ten times the usual concentration and analyzed without concentration. As a result of the low reactivity of *m*-chlorobromobenzene, the amounts formed were not accurately analyzable. Therefore, the result quoted was obtained with bromobenzene and *m*-bromochlorobenzene concentrations at 10 and 50 times, respectively, the usual concentrations. The products were analyzed without concentration.

All analyses except those of *o*-fluoro- and *p*-fluoro- runs were made on a 0.4 × 100 cm. column packed with 0.5% Flexol 10–10 (didecyl phthalate) on 200-mesh glass beads at 40–70°. Chlorobenzene and *o*- or *p*-chlorofluorobenzene were resolved on a 0.4 × 100 cm. column packed with 0.5% Ucon 50-HB-100 (polyalkalene glycol) on 200-mesh glass beads at 40°.

Bromofluorobenzenes were obtained from Pierce Chemical Co., *m*-bromochlorobenzene was Eastman Kodak Co. white label, *p*-bromochlorobenzene was Matheson highest purity and bromobenzene was Fisher reagent. These commercial materials gave single peaks on gas chromatography and were used as supplied. The *o*-bromochlorobenzene used was prepared by Sandmeyer reaction[22] of *o*-nitroaniline (Eastman Kodak Co. pract.) to produce *o*-bromonitrobenzene, which was reduced with iron and water.[23] The resultant *o*-bromoaniline was converted by Sandmeyer reaction[24] to *o*-chlorobromobenzene, b.p. 195–196°.

(b) **Displacement of Iodine by Bromine and of Iodine or Bromine by Chlorine from ICl.**—The procedure followed was the same as that described above with the following exceptions. Either bromine (reagent) or ICl (freshly distilled from $KClO_3$), 2.0 mmoles, was weighed into a 20.0-ml. aliquot of a CCl_4 solution which was 0.100 *M* in substituted and 0.100 *M* in unsubstituted compounds and was contained in a test-tube fitted with a ground joint. Oxygen was removed by attaching a stopcock to the joint on the tube and successively evacuating and bleeding to oxygen-free nitrogen.

Samples were irradiated for 3 to 5 days as described above, resulting in 5–7% reaction.

Iodobenzene, *o*-bromoiodobenzene, *m*-bromoiodobenzene and *p*-iodobromobenzene were Eastman Kodak Co. white label and were used as supplied.

The following compounds were prepared by Sandmeyer (Sa),[16,25] or Schiemann (Sc)[20] reactions on commercially available amines: (Sc) *p*-fluoroiodobenzene, b.p. 181–181.1°; (Sa) *m*-fluoroiodobenzene, b.p. 179–179.5°; (Sa) *o*-fluoroiodobenzene, b.p. 188–189°; (Sa) *p*-chloroiodobenzene, m.p. 55–56°; (Sa) *p*-iodobenzotrifluoride, b.p. 183–185°; (Sa) *m*-iodobenzotrifluoride, b.p. 179–180°; (Sa) *o*-iodobenzotrifluoride, b.p. 197–198°; (Sa) *p*-iodoanisole, m.p. 51–51.5°; *o*- and *m*-chloroiodobenzenes were prepared from the appropriate nitroanilines by the general method described above for *o*-chlorobromobenzene.

(c) **Calculations.**—Reactions were assumed to be first order in aromatics. Because only 5–7% conversion was obtained in the cases covered under (b) above, the ratios of chromatographic peak areas, corrected for thermal conductivity differences, were taken as reactivity ratios, $R = x/y$.

In those cases covered under (a) above, conversions were too high to use the simplifying assumption of low conversion. Therefore, the integrated rate expression

$$R = \frac{\log A/(A - x)}{\log B/(B - y)}$$

was used. The fact that all chlorine was converted to bromine permitted the titration data from the end of each run to be combined with product ratios obtained by gas chromatography to yield the actual concentrations of materials formed.

Displacement of the Nitro Group by Chlorine and the Displacement of Bromine by Chlorine with Nitro Group Present.—Chlorine (Matheson) was dried by bubbling through sulfuric acid and was passed into 2.0 g. of *m*-bromonitrobenzene (Eastman Kodak Co. white label) in about 80 ml. of CCl_4 until substantial chlorine color was visible. The solution was diluted to 100.0 ml. and tightly stoppered. A similar solution containing 1.50 g. of nitrobenzene/100 ml. was prepared. The solutions were irradiated for 16 days as described above at 27°. Each was then washed with dilute KI, $Na_2S_2O_3$, NaOH and water. After drying, the solutions were analyzed by gas chromatography. Conversions of *m*-bromonitrobenzene to *m*-chloronitrobenzene and of nitrobenzene to chlorobenzene were 40 and 60%, respectively.

All boiling and melting points are corrected.

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