ther of our phenyl results appear particularly inconsistent with our picture.

Finally, a series of k_H/k_D ratios for halogen atom attack on toluene are collected in Table V. Results for photochlorination in no solvent, vapor, benzene and *o*-dichlorobenzene are experimentally indistinguishable from each other and from the sulfuryl chloride reaction, in accord with our other data on relative reactivities, but the value in CCl_4 is significantly lower, further evidence for some difference in this solvent.

Our value of 3.08 for photobromination is larger than for chlorination, as might be anticipated for a process of higher activation energy,[32] but is actually too low,[33] since photobromination is significantly reversible. Accordingly, the measurement actually involves the complex process

$$RH + Br\cdot \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R\cdot + HBr \xrightarrow[k_2]{Br_2} RBr + \cdot Br \quad (18)$$

in which k_2 and k_{-1} have roughly comparable values.[27] A similar complication necessarily attends Kooyman's[15a] and our studies of competitive brominations, so, in spite of the good agreement, it may well be that both sets of data here represent values which are slightly different from, and probably smaller than, the actual ratios of k_2's.

---

[32] An admirable review of the relation between reaction properties and isotope effects is given by K. B. Wiberg, *Chem. Revs.*, **55**, 713 (1955); *cf.* also G. S. Hammond, THIS JOURNAL, **77**, 334 (1955).

[33] K. B. Wiberg, private communication, the actual value (in the absence of HBr) is 4.6–4.9.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Displacement of Aromatic Substituents by Halogen Atoms[1]

BY BERNARD MILLER[2] AND CHEVES WALLING

RECEIVED JANUARY 23, 1957

The reaction of chlorine with bromobenzene to give chlorobenzene and bromine is apparently a radical chain process on the basis of the following evidence: (1) the reaction is light catalyzed; (2) the analogous reaction using sulfuryl chloride is accelerated by benzoyl peroxide; (3) the reaction is inhibited by nitro-, azo- and azoxybenzene; (4) reactions run in competition with the side-chain chlorination of toluene yield comparable ratios of products in light and dark. Similar reactions of substituted bromobenzenes have been studied and competitive experiments show that the displacement is retarded by electron withdrawing groups. Benzenesulfonyl chloride and diphenylsulfone also undergo ready photochemical reaction with chlorine to give chlorobenzene and SO_2, and the photochemical exchange of bromobenzene and Br_2^{82} has been demonstrated. Radical chain sequences are proposed, and the critical step, $Cl\cdot + C_6H_5Br \rightarrow C_6H_5Cl + Br\cdot$, is suggested as possibly involving the rearrangement of an intermediate radical–substrate "pi complex."

The difficulty with which aromatic halogen is replaced by polar reagents is well known[3] and chlorination of bromobenzene in the presence of ferric or aluminum chloride proceeds smoothly to give chiefly *o*- and *p*-chlorobromobenzene.[4] However, in 1903 Eibner[5] reported that bromobenzene, on standing with chlorine at room temperature in the absence of catalysts, gave 50% chlorobenzene, together with polyhalogenated products. Molecular bromine was produced, and the reaction was stated to be favored by moisture and direct light.

Similar displacements have been reported in attempts to chlorinate bromotoluenes. Although the successful preparation of *ortho*-,[6] *meta*-[7] and *para*-bromobenzyl chlorides[8] by this route have all been claimed, in 1890 Srpek[9] reported that room temperature chlorination of *p*-bromotoluene gives an inseparable mixture of products with chlorine and bromine in both ring and side-chain. These reactions have been reinvestigated by Asinger,[10] who found that extensive nuclear substitution of chlorine for bromine occurred in all cases.

More recently, Goerner and Nametz reported similar nuclear displacement of bromine during the reaction of bromotoluenes with sulfuryl chloride and benzoyl peroxide at 93°.[11]

While our work was in progress, Voegtli, Muhr and Langer[12] have also described similar displacements on substituted bromobenzenes during photochlorination in refluxing carbon tetrachloride, the three isomeric chlorobromobenzenes giving 82–90% of the corresponding dichlorobenzenes. *p*-Fluorobromobenzene gave *p*-fluorochlorobenzene in similar yield, but under these conditions bromobenzene yielded only 68% chlorobenzene together with a dark residue.

Interestingly, iodine apparently is not replaced as is bromine, chlorination of iodobenzene producing only iodobenzene dichloride,[13] and similar dichlorides are reported from *p*-bromoiodobenzene and *sym*-tribromoiodobenzene.

---

[1] Taken from a portion of a dissertation submitted by Bernard Miller in 1955 to the Graduate Faculties of Columbia University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] University Fellow, Columbia University, 1954–1955.

[3] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter XV; thus nucleophilic displacements occur with ease only in the presence of strongly electron withdrawing substituents as in 2,4-dinitrochlorobenzene.

[4] M. A. F. Holleman and T. Van der Linden, *Rec. trav. chim.*, **30**, 253 (1911).

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

[6] W. A. Jacobs and M. Heidelberger, *J. Biol. Chem.*, **20**, 665 (1915).

[7] H. Berger, *J. prakt. Chem.*, **2**, 241, 346 (1932).

[8] M. J. Boeseken, *Rec. trav. chim.* **23**, 99(1904).

[9] O. Srpek, *Monatsh.*, **11**, 431 (1890).

[10] F. Asinger, *ibid.*, **64**, 153 (1934).

[11] G. L. Goerner and R. C. Nametz, THIS JOURNAL, **73**, 2940 (1951). A similar observation was made by C. W. in 1946 in an attempt to prepare *m*-bromobenzal chloride.

[12] W. Voegtli, H. Muhr and P. Langer, *Helv. Chim. Acta*, **37**, 1627 (1954)

[13] C. Willgerodt, *J. prakt. Chem.*, **2**, 33, 154 (1886).

The reported effect of light, and the efficacy of the sulfuryl chloride–peroxide, a well-recognized radical halogenating system,[14] in these displacements, made it appear very likely that they are radical processes, and this paper reports work intended to settle this point, and characterize this sort of reaction more fully.

Results and Discussion

Bromobenzene.—Preliminary experiments confirmed literature reports of the ease of the exchange. When chlorine was bubbled slowly through a slight excess of bromobenzene at 90° under strong illumination, bromine was liberated and chlorobenzene produced in 81% yield based on the equation

$$2C_6H_5Br + Cl_2 \longrightarrow 2C_6H_5Cl + Br_2 \qquad (1)$$

In the dark under similar conditions, but using excess chlorine, the yield was only 39%. The photoinduced reaction also occurs at room temperature, but is accompanied by the formation of a small amount of halogen addition to give mixed polychlorobromocyclohexanes. The presence of bromine at the start of a reaction leads to no reduction in yield, but the photochemical reaction was found to be inhibited completely in the presence of nitrobenzene, azobenzene or azoxybenzene. With sulfuryl chloride, yields of chlorobenzene were low (12–20%) at room temperature or reflux, either in the presence or absence of benzoyl peroxide, but peroxide was observed to eliminate a marked induction period before the appearance of the bromine color.

All of these observations, notably the increase in yield in the presence of light, the accelerating effect of peroxide on the sulfuryl chloride reaction, and the inhibition of the reaction by nitrobenzene, azobenzene and azoxybenzene are consistent with a radical chain process involving halogen atoms. However, in order to obtain more conclusive evidence, and also get an idea of the rate of the displacement step, the competitive reaction of bromobenzene and toluene with chlorine was investigated. Fractionation of the products, and treatment of the data as arising from competitive processes first order in halogen atom and substrate, essentially as described in the preceding paper,[15] yielded a value of k_1/k_2 in the equation

$$\frac{d \ln [C_7H_8]}{d \ln [C_6H_5Br]} = \frac{k_1}{k_2} \qquad (2)$$

of 4.0 for a reaction run at 90° in the dark and 5.6 for one run under strong illumination. The difference is probably within experimental error, and, since the chlorination of toluene under these conditions yields almost entirely benzyl chloride by a strongly photocatalyzed radical chain process, in which chlorine atoms are the chain carriers,[15,16] we consider this a crucial experiment establishing that chlorine atoms are involved in the displacement on bromobenzene as well.

Substituted Bromobenzenes.—We have also investigated bromine displacement in the presence of chlorine and light in a number of substituted bromobenzenes, both alone and in competitition with bromobenzene. In the latter case, a deficiency of chlorine was used and relative reactivities (again calculated as arising from competitive first-order processes) calculated from product analyses. Results are summarized in Table I, and indicate that, while displacement still occurs in the presence of electron withdrawing groups, reactivity is reduced and the reaction fails with *p*-nitrobromobenzene.

TABLE I

REACTIONS OF BROMOBENZENES WITH CHLORINE AND LIGHT (IN CCl_4 OR $CHCl_3$ AT 65–70° UNDER ILLUMINATION)

Substituent	Yield, %[a]	k/k_0[c]
None	81	1.0
p-Cl	98	0.91
o-COOH	~100	.23
m-COOH	...	.26
p-SO_2Cl	97[b]	< .12
p-NO_2	0	....

[a] Of corresponding chlorobenzene. [b] Of *p*-dichlorobenzene (see below). [c] Relative reactivities compared with bromobenzene from competitive experiments.

Other Displacements.—In our investigation of the photochemical reaction of chlorine with *p*-bromobenzenesulfonyl chloride (Table I) we observed that both bromine and sulfonyl chloride groups were displaced to give a 97% yield of *p*-dichlorobenzene. A similar displacement of the sulfonyl chloride group occurs with benzenesulfonyl chloride to give chlorobenzene (97%). Since chlorine is regenerated in the over-all reaction

$$C_6H_5SO_2Cl + Cl_2 \xrightarrow{h\nu} C_6H_5Cl + SO_2 + Cl_2 \qquad (3)$$

less than stoichiometric quantities are required and slow passage of only 25 mole % of chlorine into benzenesulfonyl chloride at 70° in carbon tetrachloride under illumination gave chlorobenzene in 92% yield. This facile displacement was surprising since the only analogous cases in the literature involve reactions of *o*-toluenesulfonyl chloride and fluoride to give *o*-chlorobenzyl and benzal chlorides at higher temperatures, and have been attributed to the *ortho* orientation of the two reaction sites.[17]

Our results with sulfonyl chlorides led us to investigate the chlorine atom displacement of other groups, and we find that diphenylsulfone reacts smoothly with excess chlorine on illumination in carbon tetrachloride to give chlorobenzene[18]

$$C_6H_5SO_2C_5H_6 + Cl_2 \longrightarrow 2C_6H_5Cl + SO_2 \qquad (4)$$

However, phenyl and methyl benzenesulfonates showed no displacement, even at temperatures of

---

[14] M. S. Kharasch and H. C. Brown, THIS JOURNAL, **61**, 2142 (1939).

[15] C. Walling and B. Miller, *ibid.*, **79**, 4181 (1957).

[16] M. S. Kharasch and M. G. Berkman, *J. Org. Chem.*, **6**, 810 (1941).

[17] W. Davies and J. H. Dick, *J. Chem. Soc.*, 2042 (1932). The usual technique for conversion of a $-SO_2Cl$ group $-Cl$ involves the use of PCl_5 at 200–220°; C. M. Suter "The Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y. 1944, p. 500.

[18] The reaction at 120–130° to give chlorobenzene and benzenesulfonyl chloride has been described by R. Otto, *Ann.*, **141**, 93 (1867), who also noted the reaction of 1,2-dichlorosulfonylethane with chlorine at 180° to give 1,2-dichloroethane, chlorobenzene, benzenesulfonyl chloride and other products, R. Otto *J. prakt. Chem.*, [2] **30**, 179 (1884).

150–170°. Displacements also were attempted with N-phenylphthalimide, azobenzene and azoxybenzene. The first was chosen since displacement should yield a presumably rather stable phthalimide radical, and the latter two since the reaction might gain driving force by the elimination of nitrogen. However, in no case were we able to detect any trace of chlorobenzene in the products.

Using Br^{82} as a tracer, we have also been able to show that bromine atoms displace bromine from bromobenzene. At room temperature under strong illumination, exchange between molecular bromine and bromobenzene is approximately 30% complete in 17 hours, while in the dark the reaction is negligible. The ease of this sort of halogen exchange evidently decreases as one ascends the periodic table, iodine showing very little photochemical exchange at room temperature, although a thermal exchange occurs at elevated temperatures.[19]

Reaction Mechanism.—The properties of the reactions we have observed are certainly consistent with a radical chain process which, for the photochemical chlorine–bromobenzene reaction, we may write as

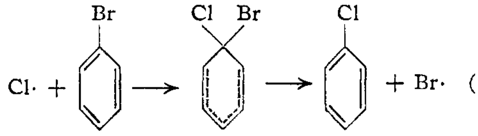
$$\mathrm{Cl_2} \overset{h\nu}{\rightleftarrows} 2\mathrm{Cl}\cdot \tag{5}$$

$$\mathrm{Cl}\cdot + \mathrm{C_6H_5Br} \longrightarrow \mathrm{BrCl} + \mathrm{Cl}\cdot \tag{6}$$

$$\mathrm{Br}\cdot + \mathrm{Cl_2} \longrightarrow \mathrm{BrCl} + \mathrm{Cl}\cdot \tag{7}$$

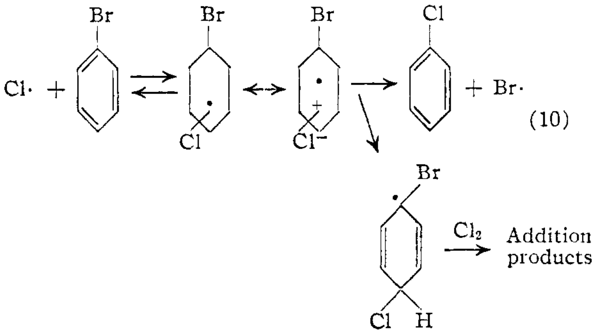
$$2\mathrm{BrCl} \rightleftarrows \mathrm{Br_2} + \mathrm{Cl_2} \tag{8}$$

with additional or alternative steps possible to account for the regeneration of chlorine atoms and the formation of molecular bromine. The interesting and critical step in the sequence is the displacement (6), which at first glance might be pictured either as addition to the aromatic ring followed by bromine atom loss, or as a direct displacement, analogous to the SN2 displacements observed with negatively substituted halobenzenes.[3] However, either formulation presents difficulties.[20] Addition appears well established as the usual path of attachment of halogen atoms or alkyl or aryl radicals on aromatic systems.[21] However, here, addition would have to occur to the already substituted carbon



(9)

actually the most unlikely point of attack, both on grounds of steric hindrance and resonance stabilization of the resulting radical. Conceivably, of course, addition could be essentially at random, but highly reversible (as actually appears to be the case in the first step of chlorine addition to benzene) with the result that only that fraction of addition which occurs as indicated in (9) leads to displacement. The alternative of direct displacement cannot be ruled out, but would represent one of the very few examples of a direct radical displacement on carbon, and is accordingly somewhat suspect. A third alternative also exists, namely, that both displacements of the sort described here and the more familiar halogen additions to aromatics arise through rearrangement of an initial loose "pi-complex," *i.e.* analogous to the complexes of aromatics with electrophilic reagents discussed by Brown.[22]



(10)

In the case of our sulfonyl chloride and sulfone displacements analogous chains are plausible

$$\mathrm{C_6H_5SO_2Cl} + \mathrm{Cl}\cdot \longrightarrow \mathrm{C_6H_5Cl} + \cdot\mathrm{SO_2Cl} \tag{11a}$$

$$\cdot\,\mathrm{SO_2\,Cl} \longrightarrow \mathrm{SO_2} + \mathrm{Cl}\cdot \tag{11b}$$

$$\mathrm{C_6H_5SO_2C_6H_5} + \mathrm{Cl}\cdot \longrightarrow \mathrm{C_6H_5Cl} + \mathrm{C_6H_5SO_2}\cdot \tag{12a}$$

$$\mathrm{C_6H_5SO_2}\cdot + \mathrm{Cl_2} \longrightarrow \mathrm{C_6H_5SO_2Cl} + \mathrm{Cl}\cdot \tag{12b}$$

or

$$\mathrm{C_6H_5SO_2}\cdot \longrightarrow \mathrm{C_6H_5}\cdot + \mathrm{SO_2} \tag{12c}$$

$$\mathrm{C_6H_5}\cdot + \mathrm{Cl_2} \longrightarrow \mathrm{C_6H_5Cl} + \mathrm{Cl}\cdot \tag{12d}$$

but we have no convincing explanation for the relative stability of benzene sulfonate esters.

Finally, two properties of these displacements need to be pointed out which must be accounted for in any complete reaction scheme. The first is the retarding effect of electron withdrawing groups (Table I) which is certainly consistent with a "pi-complex" scheme, but is actually a general characteristic of all chlorine atom processes.[15] The second is the extremely high *rate* of the displacement step, established by competition with the side-chain chlorination of toluene. Our results indicate that reaction 6 has approximately the same rate constant as that for the attack of a chlorine atom on a single benzyl C–H bond, a process which, as discussed further in our preceding paper,[15] probably has a rate constant of 10^{10}, and an activation energy of < 2 kcal. These displacements are thus extremely facile processes, with rates considerably higher than most radical–substrate reactions, and this, to us, makes them of particular interest.

Experimental

Reaction of Bromobenzene with Chlorine.—Fifty-nine grams (0.376 mole) of bromobenzene was placed in a 3-necked flask fitted with gas inlet tube, stirrer, reflux condenser and thermometer. The flask was illuminated by a 200 watt light bulb at a distance of three inches and maintained at 90°. Chlorine (0.156 mole, obtained by evapor-

---

[19] S. Levine, Thesis, Columbia University, 1955.

[20] An alternative scheme involving displacement on halogen

$$\mathrm{C_6H_5Br} + \mathrm{Cl}\cdot \longrightarrow \mathrm{C_6H_5}\cdot + \mathrm{ClBr} \tag{6a}$$

would be endothermic by ~19 kcal. and is accordingly ruled out by the high rate of the displacement step discussed below.

[21] For a discussion of this point, *cf.* J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1956, Ch. 22.

[22] H. C. Brown and J. D. Brady, THIS JOURNAL, **74**, 3570 (1952). The second step in the normal halogen addition process, in their terminology would correspond to the rearrangement of a π to a σ complex.

ating 3.5 ml. of liquid chlorine) was bubbled through the system during one hour. Within five minutes the reaction mixture turned orange and then red, and soon bromine refluxed in the condenser. The cooled reaction mixture was stirred with sodium bisulfite solution, extracted with ether, dried over NaOH pellets and fractionated through a 10-plate Fenske column. The yield of chlorobenzene was 31.5 g. (0.254 mole, 81% based on chlorine). A similar reaction carried out in the dark (with the system wrapped in aluminum foil) gave a yield of only 39%.

The photochemical reaction was carried out in a similar manner at room temperature employing 30 g. of chlorobenzene and excess chlorine, except that the bromine was removed by adding 100 ml. of chloroform at the end of the reaction and distilling off a mixture of chloroform and bromine. In addition to chlorobenzene (20.1 g.) the reaction mixture yielded 2.26 g. of intermediate fractions (b.p. 136–160°) and 4.41 g. of black crystalline residue. Recrystallization from acetic acid gave 2.00 g. of material, m.p. 126–127°. *Anal.* Calcd. for $C_6H_5Br_4Cl_3$: C, 14.3; H, 1.00; Br, 63.8; Cl, 20.9; for $C_6H_5Br_3Cl_4$: C, 15.8; H, 1.10; Br, 52.0; Cl, 30.8. Found: C, 14.62; H, 1.19; Br, 59.87; Cl, 22.90

A similar reaction carried out in the presence of approximately one mole equivalent of added bromine gave essentially identical results.

Attempts to carry out the displacement in carbon tetrachloride solution at 65–70° under illumination in the presence of nitrobenzene, azobenzene or azoxybenzene gave no material boiling between 125 and 135° or indication of the liberation of bromine.

Reaction of Bromobenzene with Sulfuryl Chloride.—Bromobenzene (35.1 g.) and freshly distilled sulfuryl chloride (20 ml.) were mixed and allowed to stand at room temperature. After two hours the initially light yellow solution turned light orange, and, 15 minutes later, dark red. After standing overnight the reaction mixture was poured into aqueous sodium bisulfite solution, extracted with ether, and the ether layer dried over calcium chloride and distilled to give a 12% yield of chlorobenzene and 85% recovered bromobenzene. A similar experiment carried out in the presence of 0.207 g. of benzoyl peroxide turned deep red within 11 minutes, but the yield of chlorobenzene was still only 15%. When the same quantities of bromobenzene and sulfuryl chloride were refluxed together the deep bromine color developed in 35 minutes, and, after 6 hours, the mixture yielded 12% chlorobenzene. Addition of benzoyl peroxide gave the bromine color within three minutes and 16% chlorobenzene after six hours.

Reaction of Substituted Bromobenzenes with Chlorine.—*p*-Chlorobromobenzene (31.0 g.) was dissolved in 200 ml. of carbon tetrachloride and heated to 70° under a reflux condenser. A rapid stream of chlorine was passed through the solution while it was illuminated by a 200 watt light bulb at a distance of three inches. The solution soon turned red, and after 90 minutes the solvent was evaporated to give 23.7 g. (98%) of *p*-chlorobenzene, m.p. 46–49°. Two recrystallizations from ethanol gave 20.0 g., m.p. 51–53°: other displacements on substituted bromobenzenes were carried out similarly using either chloroform or carbon tetrachloride as solvent with results listed in Table I. With *o*- and *p*-nitrobromobenzene, no bromine color developed, and starting materials were recovered unchanged.

Competitive Reaction of Toluene and Bromobenzene.—A mixture of 0.645 mole of toluene and 0.694 mole of bromobenzene was placed in a stirred reaction-flask and heated to 90° while illuminated by a 200 watt incandescent light. Chlorine (0.376 mole) was introduced over 90 minutes, and the mixture first turned yellow, but then became colorless. The product was fractionally distilled through a 12-plate glass helix packed column, using dicyclohexyl as a chaser, and the composition of intermediate fractions determined by index of refraction. In a parallel experiment in the dark, chlorine was introduced over two hours, and the product compositions shown in the following table were determined. Relative reactivities were calculated from the relation

$$\frac{k}{k_0} = \frac{\log [C_7H_8]_{\text{initial}}/([C_7H_8]_{\text{initial}} - [C_7H_7Cl])}{\log [C_6H_5Br]_{\text{initial}}/([C_6H_5Br]_{\text{initial}} - [C_6H_5Cl])} \tag{13}$$

Since material balances were not quantitative, the values of k/k_0 are subject to considerable uncertainty but it seemed that the best way of determining the amount of unreacted toluene and bromobenzene (the denominators in the fractions of eq. 13) was by subtracting the amount of isolated products from the accurately known initial quantities of reactants. Accordingly the values for k/k_0 reported are probably a little high. The alternate method of using values for recovered toluene and bromobenzene (corrected for the small amount of benzyl bromide formed), since it involves larger numerical quantities presumably subject to the same percentage error as those for chlorobenzene and benzyl chloride, appears less accurate and gives k/k_0's of 3.1 and 2.4 for the light and dark reactions, results which must be considerably too low.

	Light (moles)	Dark (moles)
Cl_2 (initial)	0.376	0.400
C_6H_5Br (initial)	.649	.720
C_7H_8 (initial)	.645	.747
C_6H_5Br (recovered)	.549	.572
C_7H_8 (recovered)	.264	.373
C_6H_5Cl	.069	.074
C_7H_7Cl	.297	.263
C_6H_5Br unaccounted for	.031	.074
C_7H_8 unaccounted for	.034	.054
k/k_0	5.6	4.0

Competitive reactions of bromobenzenes were carried out under illumination in chloroform solution at approximately 65° with over-all results summarized in Table I. In a typical experiment 0.175 mole of *m*-bromobenzoic acid and 0.185 mole of bromobenzene in 300 ml. of chloroform were treated with 0.095 mole of chlorine during two hours. The solution was cooled, the solid acids filtered off, and washed free of bromine with fresh chloroform. The filtrate and washings were stirred with aqueous sodium sulfite–sodium hydroxide, washed with water, and the aqueous extracts acidified. The resulting precipitate was combined with the acids originally isolated, and recrystallized from chloroform to give 33 g. of mixed acids containing 35.9% Br and 2.28% Cl by analysis. Bromobenzene and chlorobenzene were determined by fractionation of the chloroform layer, and the following material balance obtained

	Mole
C_6H_5Br (initial)	0.185
$C_6H_4BrCOOH$ (initial)	.175
C_6H_5Br (recovered)	.092
$C_6H_4BrCOOH$ (recovered)	.148
C_6H_5Cl	.074
$C_6H_4ClCOOH$	.021
C_6H_5Br unaccounted for	.019
$C_6H_4BrCOOH$ unaccounted for	.004

Relative reactivities were calculated in the same manner as for the toluene–bromobenzene experiment. The products from the competitive chlorination of bromobenzene and *o*-bromobenzoic acid were worked up in the same manner, while the products from bromobenzene–*p*-chlorobromobenzene were determined by fractional distillation. The reaction products from the competitive chlorination of bromobenzene and *p*-bromobenzenesulfonyl chloride were freed of bromine by distillation, diluted with additional chloroform, and treated with dry ammonia. The resulting precipitate was recrystallized from benzene and found to be chlorine-free *p*-bromobenzenesulfonamide, m.p. 165–166°. The difference between the amount obtained and the amount of *p*-bromobenzenesulfonyl chloride initially present was taken as the quantity of the former which underwent bromine displacement. Since some of the material was necessarily consumed by displacement of the sulfonyl chloride group, the resulting calculated reactivity for displacement of bromine represents merely an upper limit, and is so indicated in Table I.

Reaction of Chlorine with Benzenesulfonyl Derivatives.—*p*-Bromobenzenesulfonyl chloride (32.4 g.) was dissolved in 250 ml. of carbon tetrachloride and kept at 70° in an illuminated flask while a rapid stream of chlorine was passed through the solution for two hours. Evaporation of the solvent and bromine gave 18.1 g. (97%) of *p*-dichlorobenzene, m.p. 47–50°. A similar experiment using benzenesulfonyl chloride gave 97% chlorobenzene. When a limited amount of chlorine (0.078 mole for 0.308 mole of benzenesulfonyl chloride) was employed, the mixture at the end of the reaction showed no peak in the infrared spectrum at 8–9 μ, characteristic of sulfonyl chlorides, and gave 92% chlorobenzene on distillation.

Under the same conditions diphenylsulfone also gave chlorobenzene in essentially quantitative yield, but phenyl benzenesulfonate and methyl benzenesulfonate gave no chlorobenzene and good yields of starting material when treated with chlorine and light, either at 70° in carbon tetrachloride or at 150–170° in absence of solvent.

Other Attempted Displacements.—Treatment of azobenzene, azoxybenzene and N-phenylphthalimide with chlorine and light at 70° in carbon tetrachloride solution gave only starting material and no trace of chlorobenzene. Similarly no displacement was observed when iodobenzene was refluxed with sulfuryl chloride in the presence of benzoyl peroxide, or when benzenesulfonyl chloride or diphenylsulfone was illuminated in the presence of bromine.

Exchange of Br^{82}_2 with Bromobenzene.—Twenty-five ml. of bromine containing Br^{82}, 50 ml. of bromobenzene and 75 ml. of carbon tetrachloride were mixed and then divided into three equal portions placed in stoppered flasks. One flask was kept for 18 hours at room temperature while being illuminated at a distance of 8 inches by a 200 watt incandescent light, the others were stored in the dark. The contents of the illuminated flask and one other were washed with sodium bisulfite solution and then three portions of water, and the radioactivity of the organic layer determined, using a Geiger counter of the type described by Sibbett.[23] The contents of the third flask were used to determine total radioactivity. In a second experiment a similar mixture was irradiated for four hours at 50° and overnight at room temperature. The bromine was then washed out, and the radioactivity of the organic layer determined. In order to establish that the radioactivity was confined to bromobenzene, the organic layer was next carefully fractionated and the radioactivity of the bromobenzene fraction determined. Results of both experiments are shown below.

Run	Total	Activity (counts/min.) Organic	C_6H_5Br	Background
1 (light)	12,344	2272	...	50
1 (dark)	12,344	90	...	50
2 (light)	21,317	4211	4110	62

---

[23] D. L. Sibbett, Thesis, Columbia University, 1951, pp. 11–12.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE INSTITUTO DE QUÍMICA, UNIVERSIDAD NACIONAL AUTÓNOMA DE MÉXICO]

Structure and Properties of Cyclic Compounds. IX.[1] Hemiketal Formation of Cyclic Ketones

BY OWEN H. WHEELER

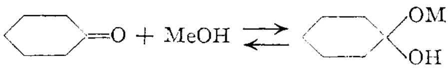
RECEIVED SEPTEMBER 20, 1956

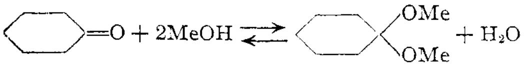
Cyclohexanone has been found to undergo acid-catalyzed hemiketal formation with methanol in dioxane solution. The extent of hemiketal formation of a number of cyclic ketones in pure methanol is in agreement with I-strain prediction, and is reduced by steric effects. Less reaction takes place with ethanol and no reaction is observed with isopropyl alcohol or water.

During the course of routine spectroscopic measurements,[2] it was observed that the intensity of absorption of cyclic ketones in methanol depended on the sample of methanol used as solvent. Addition of a drop of concentrated hydrochloric acid greatly reduced the intensity. The decreased absorption of aldehydes in polar solvents has been noted by many workers[3] and has been attributed to hemiacetal formation. This suggests that the above results may be due to a similar reaction. A decrease in the refractive index of solutions of acetone and cyclohexanone in methanol on the addition of acids has been noted[4] and is probably caused by the same effect.

The reaction between cyclohexanone and methanol was studied using dioxane as solvent. Solutions of cyclohexanone in dioxane showed λ_{max} 290 mμ (ϵ 15.8 ± 0.1, mean of five readings). In the presence of 0.05 M hydrogen chloride the absorption was unchanged. Similarly the absorption intensity of cyclohexanone in dioxane containing 0.07, 0.12 and 0.26 M methanol was ϵ 15.85, 15.75, 15.8, respectively, with the maxima at the same wave length. These solutions showed no change in absorption on standing. Thus the decrease in intensity in methanolic hydrogen chloride solution cannot be due to reaction between the ketone and the acid or to a non-acid-catalyzed reaction between the ketone and methanol.

The most probable reactions of cyclohexanone and methanol catalyzed by acids are those of hemiketal (1) and ketal (2) formation. Both reactions are first order in ketone but reaction 1 is first order


(1)


(2)

and reaction 2 second order in alcohol. The reaction was studied in dioxane containing 0.05 M hydrogen chloride using varying concentrations of ketone and alcohol (Table I). The concentration of unreacted ketone was calculated from the extinction coefficient of the solution and the known extinction of cyclohexanone in dioxane in the absence of acid. The concentration of the addition compound is then the difference between this and the initial ketone concentration. In the first case the final methanol concentration is the difference between the initial concentration and the concentration of addition compound and in the second the difference with twice the addition compound concentration. The dissociation constants K^1_D and

---

[1] Part VIII, *Chemistry & Industry*, 1388 (1956).

[2] *Cf.* O. H. Wheeler and J. L. Mateos, *Anal. Chem.*, **29**, 538 (1957).

[3] (a) W. Harold and K. L. Wolf, *Z. physik. Chem.*, **21**, 165 (1931); (b) A. M. Buswell, E. C. Dunlop, W. H. Rodebush and J. B. Swartz, THIS JOURNAL, **62**, 325 (1940); (c) I. L. Gaudity, *Z. physik. Chem.*, **48**, 228 (1941); (d) N. Melchior, THIS JOURNAL, **71**, 3647 (1949); (e) P. Rampf and C. Bloch, *Compt. rend.*, **223**, 1364 (1951); (f) C. D. Hurd and W. H. Saunders, THIS JOURNAL, **74**, 5324 (1952).

[4] T. Tomonari, *Angew. Chem.*, **46**, 269 (1933); *J. Soc. Chem. Ind. Japan*, **36**, 485 (1933)