XCII.—*The Competitive Interaction of Alkyl and Aryl Halides with Magnesium.*

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MEASUREMENTS of the reactivity of alkyl halides have hitherto been made using five different types of reagent: (1) Sodium meth-, eth-, or *n*-prop-oxide (Hecht, Conrad, and Brückner, *Z. physikal. Chem.*, 1889, **4**, 273), sodium phenoxide (Segaller, J., 1913, **103**, 1154), sodium α- and β-naphthoxides (Cox, J., 1918, **113**, 666) and sodium benzyloxide (Heywood, J., 1922, **121**, 1904). (2) Ethyl sodiomalonate or -acetoacetate (Wislicenus, *Annalen*, 1882, **212**, 239). (3) Various tertiary bases (Menschutkin, *Z. physikal. Chem.*, 1890, **5**, 589; Wedekind, *Annalen*, 1901, **318**, 90; Preston and Jones, J., 1912, **101**, 1930). (4) Alcoholic silver nitrate (Burke and Donnan, J., 1904, **85**, 555; *Z. physikal. Chem.*, 1909, **69**, 148). (5) Sodium thiosulphate (Slator, J., 1904, **85**, 1286).

Although these different reagents would not be expected to give a similar order of reactivity for a series of alkyl halides, a number of general conclusions may be drawn. Methyl iodide is far more reactive than ethyl iodide, and the latter much more reactive than *n*-propyl iodide (Menschutkin, Segaller, Cox, Heywood, and Hecht, Conrad, and Brückner). Burke and Donnan found that methyl and *n*-propyl iodides reacted at approximately the same rate, which was less than that for ethyl iodide, and not much greater than that for *n*-butyl iodide. The reaction between iodides and alcoholic silver nitrate is, however, complicated, as Burke and Donnan pointed out. Wislicenus found that ethyl and *n*-propyl iodides were respectively very much more reactive than the corresponding bromides, and that benzyl bromide was much more reactive than the chloride. Menschutkin found ethyl, *n*-propyl, *n*-butyl, *n*-heptyl and *n*-octyl iodides to be more reactive than the bromides. Slator concluded that bromides and iodides were almost equally reactive, and very much more reactive than the corresponding chlorides.

No measurements have hitherto been made of the reactivities of simple halogen derivatives of aromatic hydrocarbons. Indeed, there are very few reactions which could be used for such measurements. Certain facts were known, *e.g.*, that iodobenzenes react with copper bronze (Ullmann reaction), whereas bromo- and chloro-compounds do so much less readily; further, that whereas bromo- and iodo-benzene readily combine with magnesium, chlorobenzene does not. The formation of the Grignard reagent has now been found to afford a convenient method for comparing "reactivities" of both aliphatic and aromatic halogen compounds.

Our procedure has been to allow a mixture of two different halogen derivatives (1 mol. of each) to compete, under certain definite conditions, for one atom of magnesium, and to analyse the product when complete dissolution of the metal had occurred. Ordinary " Grignard " magnesium turnings were used. The slight difference in surface area and condition between one sample and another introduces no material error, since after the first few minutes of reaction the condition of the metallic surface in one experiment is little different from that in another, and moreover, both halides will presumably benefit or suffer to the same extent.

By using specially standardised magnesium, even more accurate results would possibly be attainable. Our purpose, however, has been, not to obtain absolute values of the reactivities, but to compare reactivities to a reasonably quantitative degree. The method is capable of general application, and is being extended.

In discussing our results, the fact must not be overlooked that two other reactions may accompany the formation of a Grignard reagent : (*a*) $RMgX + RX = MgX_2 + R{\cdot}R$ and (*b*) $2RX + Mg = MgX_2 + R{\cdot}R$. It seems probable that (*b*) is realised usually through (*a*). Di-alkyl and di-aryl hydrocarbons are formed to any large extent, however, only with particular types of halogen compound when conditions such as have been used for the present work obtain.

A trace of iodine was sometimes necessary to start the reaction. This vitiates the results to the extent only of 0·02% (see Experimental).

It is possible that the reactivity of one halide may be affected by the presence of another more reactive halide. We found as a limiting case that magnesium did not react with chlorobenzene even when a vigorous combination of the metal with bromobenzene was in progress.

The results obtained are in Tables I and II. The figures given under " %Br," " %Cl," etc., refer to the percentage of bromine and chlorine respectively which, at the completion of a reaction, had combined with the magnesium.

These figures show many interesting features. In the first place, when bromide–chloride pairs compete for magnesium, the bromide, at first the more reactive, becomes relatively more reactive as one passes from ethyl to butyl. A mixture of methyl chloride and bromide could not be made to react with magnesium. On the other hand, with iodide–chloride pairs, the initially more reactive iodide decreases in reactivity with ascent from methyl to butyl, and with bromide–iodide pairs an alternation is observed.

TABLE I.

	% Br.	% Cl.		% I.	% Cl.		% Br.	% I.
MeBr–MeCl	—	—	MeI–MeCl	73	27	MeBr–MeI	71	29
EtBr–EtCl	76	24	EtI–EtCl	71	29	EtBr–EtI	46	54
$Pr^{\alpha}Br$–$Pr^{\alpha}Cl$	81	19	$Pr^{\alpha}I$–$Pr^{\alpha}Cl$	56	44	$Pr^{\alpha}Br$–$Pr^{\alpha}I$	57	43
$Bu^{\alpha}Br$–$Bu^{\alpha}Cl$	91	9	$Bu^{\alpha}I$–$Bu^{\alpha}Cl$	54	46	$Bu^{\alpha}Br$–$Bu^{\alpha}I$	27	73

	% Br.	% I.		% Br.	% Cl.
PhBr–PhI	52	48	$Bu^{\alpha}Br$–CH_2PhCl	73	27
o-C_6H_4MeBr–o-C_6H_4MeI	94	6			
m-C_6H_4MeBr–m-C_6H_4MeI	88	12			
p-C_6H_4MeBr–p-C_6H_4MeI	84	16			

TABLE II.

Analysis of results for aliphatic compounds. Relative reactivities.

Alkyl radical present.	Br.	I.	Br.	Cl.	I.	Cl.
Me	2·5	1	—	—	2·7	1
Et	0·8	1	3·2	1	2·5	1
Pr^{α}	1·3	1	4·3	1	1·3	1
Bu^{α}	0·4	1	9·9	1	1·2	1

Consideration of the results obtained with the four aromatic pairs suggests that the introduction of a methyl group into the nucleus of bromobenzene increases the reactivity of the halogen atom, and that the reverse effect occurs with iodobenzene. We hope to elaborate this point later and correlate the results with such facts as the greater speed of nitration of toluene as compared with benzene, etc. (compare Wibaut, *Rec. trav. chim.*, 1915, **34**, 241).

The effect of a methyl group on the reactivity of a halogen atom appears to be little dependent on the relative positions of the two atoms, although the bromine/iodine reactivity ratio decreases in the order $o > m > p$.

In view of the greatly increased activity associated with the introduction of a methyl group into bromobenzene, the three chlorotoluenes might be expected to react with magnesium. We find that they do react to some extent with magnesium which has previously been treated with iodine or with ethereal methyl iodide, but that the reaction soon becomes very slow. Moreover, from the fact that the resulting solution does not decolorise ethereal iodine solution, it may be inferred that what reaction does occur is of type (*b*) above (ditolyl formation). *cyclo*Hexyl halides were also found to react to a considerable extent in the sense of equation (*b*), although Grignard reagent formation occurs to a large extent in addition.

One of the most interesting results obtained is that bromine compounds appear on the whole to combine more readily with magnesium than do the corresponding iodine compounds.

EXPERIMENTAL.

Preparation and Purification of Reagents.—The liquid alkyl halides were purified by routine processes and distilled at least twice just before use, the first and last runnings being rejected. The aromatic halogen compounds were prepared for the purpose and purified by routine processes.

Method.—In most cases, the quantities used were 1/40 molar. Equimolecular amounts of each halide were taken, magnesium in the same proportion, *i.e.*, 1 : 1 : 1, and a fixed amount of ether (50 c.c. in a 1/40 molar experiment). The magnesium was placed in a litre round-bottom flask, fitted with a reflux condenser and dropping-funnel, suitable precautions being taken against the ingress of water and carbon dioxide. The halides were washed into the funnel with a little ether and run into the flask, and the rest of the ether was added in the same way. Iodine (not more than 1·5 mg., corresponding to 1/200,000 mol. of Grignard reagent) was added after a short time if the reaction did not start spontaneously. The flask was kept well shaken until no further reaction occurred, and the solution was at no time allowed to boil vigorously. The reactions were complete in 2—4 hours. The mixture was then treated with water, and with very dilute sulphuric acid. The ethereal layer was separated and washed with water, and the aqueous part together with the washings boiled to expel dissolved ether. This solution was then analysed.

For very volatile halides, the reaction was carried out in a stout glass bottle of about 400 c.c. capacity, fitted with a ground glass stopper, the halides being introduced, and the stopper then tightly closed. It was not removed until the mixture was decomposed with water.

The gaseous halides were stored over brine. The required volume of gas, 560 c.c. at *N.T.P.* corresponding to 1/40 mol., corrected to prevailing conditions, was measured in a gas pipette, and displaced through two phosphoric oxide drying tubes into a spiral condenser surrounded with ice and salt or with ether and solid carbon dioxide according to the halides in use. The condensed halide passed straight into the reaction bottle, the latter having a protected air exit. The ether was added subsequently. When two gaseous halides were being used together (*e.g.*, methyl chloride and bromide), a two-way tap introduced into the system enabled measurement to be made of each gas independently. The reaction bottle was kept at a suitable temperature during the reaction.

The results obtained are shown below. The meaning of x may be explained by considering a bromide–iodide pair; x_{Br} is the fraction of 1 mol. of bromide attacked by the metal, so that $(1 - x_{\mathrm{Br}})$ mol. of iodide (shown as x_{I}) is attacked (per 1 mol. of magnesium).

Chloride–bromide pairs.

	Mixed silver			Mean.	
Radical.	halides (g.).	x_{Br}.	x_{Cl}.	x_{Br}.	x_{Cl}.
Methyl	—	—	—	—	—
Ethyl	0·2221	0·772	0·228	0·76	0·24
	0·2210	0·752	0·248		
n-Propyl	0·2263	0·848	0·152	0·81	0·19
	0·2223	0·776	0·224		
n-Butyl	0·1850	0·937	0·063	0·91	0·09
	0·1812	0·878	0·122		

Iodide–chloride pairs.

	Mixed silver			Mean.	
Radical.	halides (g.).	x_{I}.	x_{Cl}.	x_{I}.	x_{Cl}.
Methyl	0·2653	0·753	0·247	0·73	0·27
	0·2598	0·705	0·295		
Ethyl	0·2589	0·697	0·303	0·71	0·29
	0·2623	0·727	0·273		
n-Propyl	0·2440	0·570	0·430	0·56	0·44
	0·2410	0·541	0·459		
n-Butyl	0·2409	0·540	0·460	0·54	0·46
	0·2412	0·542	0·458		

Bromide–iodide pairs.

	Mixed silver			Mean.	
Radical.	halides (g.).	x_{Br}.	x_{I}.	x_{Br}.	x_{I}.
Methyl	0·2503	0·710	0·290	0·71	0·29
	0·2513	0·718	0·282		
Ethyl	0·2647	0·490	0·510	0·46	0·54
	0·2685	0·426	0·575		
	0·2666	0·458	0·542		
n-Propyl	0·2605	0·562	0·438	0·57	0·43
	0·2601	0·568	0·432		
n-Butyl	0·2764	0·291	0·709	0·27	0·73
	0·2790	0·247	0·753		

Aromatic compounds.

	Mixed silver			Mean.	
Radical.	halides (g.).	x_{Br}.	x_{I}.	x_{Br}.	x_{I}.
Phenyl	0·5227	0·505	0·495	0·52	0·48
	0·5233	0·542	0·458		
	0·5244	0·534	0·466		
o-Tolyl	0·2371	0·961	0·039	0·94	0·06
	0·2396	0·916	0·084		
m-Tolyl	0·2400	0·911	0·089	0·88	0·12
	0·2431	0·858	0·142		
	0·2405	0·902	0·098		
p-Tolyl	0·2445	0·834	0·166	0·84	0·16
	0·2440	0·843	0·157		

Benzyl chloride–butyl bromide. By using 0·05 molar quantities, 0·4395 g. and 0·4406 g. of mixed silver halides were obtained in two experiments, whence x_{Br} is 0·730 and 0·740, respectively, and the mean x_{Br} is 0·73 and x_{Cl} 0·27.

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