[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

Halogenation Reactions. I. Some Regularities of Relative Rates of Reaction in Liquid Media[1]

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I. Introduction

Compounds of the type R_3MX, where R is an organic group, M an element of the carbon–lead group and X a halogen atom, react with halogens under suitable conditions, yielding R_2M derivatives according to the equation

$$R_3MX + X_2' = R_2MXX' + RX'$$

R_2Sn and R_2Ge derivatives are commonly prepared by means of such reactions, while the corresponding reactions of carbon and silicon compounds compete with hydrogen substitution.

In attempting to prepare a diethylgermanium derivative by the action of molecular bromine on triethylgermanium bromide, it was found that the reaction is very slow and difficult to control, while the bromination of triethylgermanium fluoride was found to be much faster and the diethylgermanium derivative readily obtained.[2]

It was thought that the halogenation of other compounds of the type R_3MX might be similarly influenced by the halogen X and that, if so, these reactions would constitute an interesting field for systematic study. Accordingly, a qualitative survey of reactions of this type was carried out, using a number of widely different compounds. While the study has not been exhaustive the results are consistent and indicate that the effect is indeed a general one.

II. Experimental

Materials.—Rates of bromination of the halides of the groups, $(C_6H_5)_3C$–, $(C_2H_5)_3Si$–, $(C_2H_5)_3Ge$– and $(C_6H_5)_3Ge$–, were compared; as well as the rates of iodination of the halides of the groups, $(C_2H_5)_3Sn$–, $(C_6H_5)_3Sn$–, $(C_6H_5)_3Pb$–. Hydroxides of the groups and tetraalkyl and tetraaryl compounds were included in some experiments.

All the compounds studied other than the silicon compounds were prepared and purified by previously described methods, minor modifications being used where deemed advantageous. The triethyl silicon halides were prepared by the action of concentrated sulfuric acid and sodium halide on $[(C_2H_5)_3Si]_2O$.[3]

The bromine used in the experiments was dried over phosphorus pentoxide and purified by fractional distillation. The ethyl bromide, ethylene dibromide and carbon tetrachloride were freshly dried and fractionally distilled before being used. The glacial acetic acid and iodine were of the commercial "Reagent Quality."

Method of Comparing Rates of Halogenation.—The relative rates of halogenation of all the compounds studied, with exception of triphenyllead and triphenylmethyl de-

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[1] This article is based on a thesis submitted by Leo Horvitz in May, 1932, to the Faculty of the Graduate School of Brown University, in partial fulfilment of the requirements for the degree of Master of Science.

[2] Flood, THIS JOURNAL, **54**, 1663 (1932).

[3] By this method, all the halides, including the fluoride, are easily obtained. [Flood, *ibid.*, **55**, 1735 (1933)].

rivatives, were determined in practically the same manner. The determination of the relative rates of bromination of triethylgermanium bromide, chloride and fluoride will be given in detail as an example of the general method.

A sample of each of the three triethylgermanium halides was weighed into three small capsules of about 5 ml. capacity. The necks of the capsules were constricted to facilitate subsequent sealing. The samples were cooled in liquid ammonia and to each sample a solution of bromine in ethyl bromide was added, the bromine corresponding to 30% of one mole of bromine per mole of germanium compound. The capsules were sealed at the constriction as quickly as possible and returned to the liquid ammonia bath. The three sealed capsules were then removed from the cooling bath and placed in a concentrated sulfuric acid bath which was maintained at a temperature of 140°. The time of immersion of the three capsules was noted, as well as the time when the color of the solution in each capsule reached that of a previously prepared color standard. The concentration of bromine in the color standard was one-hundredth of the initial concentration of bromine in the reaction mixtures. At the conclusion of the experiments the tubes were reweighed in order to determine more accurately the weight of bromine solution added. Thus the mole fractions of the various constituents were determined by weight. It was generally found that the error in measuring the solution by volume was not greater than 3%; moreover, it was found subsequently that considerable differences in the molar concentrations of the R_3M derivatives had no very marked influence on the relative rates of reaction. Consequently the final weighing was omitted in some of the experiments.

The details of other experiments were essentially the same, the temperatures of the bath, the concentrations of the constituents and the solvents used are indicated in the tables. In some of the experiments two color standards were used, one being very dilute while the other represented almost one-third of the bromine used for reaction. The relative rates were found to be essentially independent of the color standard. In practically all of the experiments the solutions became colorless very quickly after reaching the color of the dilute standard.

Rates of iodination were compared when the rates of bromination were too great to give reliable results. Where both bromination and iodination experiments were carried out consistent results were obtained.

When the rates of bromination of triphenylmethyl bromide, chloride and hydroxide were compared by the above method they were found to be almost identical. However, the small differences observed indicated that the order of the rates was reversed, the bromide reacting most rapidly. On opening the capsules at the conclusion of the experiment a considerable quantity of hydrogen bromide was evolved, indicating that a relatively large fraction of the bromine had substituted hydrogen in the phenyl groups rather than replacing them. However, relatively more hydrogen bromide was evolved from the capsule containing the bromide than from that containing the chloride, suggesting that relatively more phenyl group substitution had occurred with the latter. Had a phenyl group been substituted, a diphenylmethyl dihalide would be formed which, on hydrolysis, would yield benzophenone. Since benzophenone may be determined quantitatively by conversion to oxime,[4] the mixtures in the capsules were hydrolyzed and analyzed for benzophenone. While benzophenone was found present in each of the three mixtures, the quantities were too small to determine with accuracy. However, the yield from the carbinol was undoubtedly highest and that from the bromide the least. Since the total rate of consumption of bromine was practically the same in each of the three, the rates of substitution of the phenyl groups must have followed the usual order while the rates of hydrogen substitution followed the reverse order. The experiment

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(4) This method of determining benzophenone is due to Professor C. B. Wooster of Brown University and will be published shortly.

was repeated using larger quantities of materials and relatively more bromine in order to determine the yields of diphenylmethyl derivative more accurately. The experimental data appear in Table I.

Results.—The experimental results are summarized in the following tables. Individual peculiarities are pointed out where necessary.

TABLE I

BROMINATION OF TRIPHENYLMETHYL DERIVATIVES IN ETHYLENE DIBROMIDE SOLUTION AT 130°

Substance	Subs., g.	Br_2 soln., g.	Oxime, g.	Benzophenone yield, %.
$(C_6H_5)_3COH$	1.2412	1.448	0.2108	25
$(C_6H_5)_3CCl$	1.0121	1.111	.1387	22
$(C_6H_5)_3CBr$	1.0762	1.022	.0621	11

Concentration of Br_2 solution, 46.06% Br_2.

The reaction mixtures were heated during forty hours. Estimates of the relative reaction times were vitiated by the darkening of the solutions

TABLE II

RELATIVE RATES OF BROMINATION

Expt.	Solvent and temp.	Substance	Mole fraction Subs.	Mole fraction Br_2	Reaction time, minutes	Relative rates, chlorides 10
1	Ethylene	$(C_2H_5)_3SiF$	0.580(W)	0.087(W)	25	34.8
	dibromide	$(C_2H_3)_3SiCl$	.582	.087	87	10.0
	100°					
2	Ethylene	$(C_2H_5)_3SiF$	.716(V)	.107(V)	8	32.5
	dibromide	$(C_2H_5)_3SiCl$	.716	.107	26	10.0
	108°	$(C_2H_5)_3SiBr$	.714	.107	114	2.3
3	Ethylene	$(C_2H_5)_3GeCl$	.404(W)	.042(W)	55	10.0
	dibromide	$(C_2H_5)_3GeCl$(wet)	.398	.042	50	11.0
	112°	$(C_2H_5)_4Ge$	.360	.045	25	22.0
4	Ethylene	$(C_2H_5)_3GeF$	.667(V)	.204(V)	14	23.9
	dibromide	$(C_2H_5)_3GeCl$	.669	.201	31	10.0
	140°	$(C_2H_3)_3GeCl$(wet)	.662	.207	31	10.0
		$(C_2H_5)_3GeBr$	.654	.212	68	6.6
		$(C_2H_5)_4Ge$	.679	.195	2	115.5
5	Ethyl	$(C_2H_5)_3GeF$	.618(W)	.180(W)	6	60.0
	bromide	$(C_2H_5)_3GeCl$	.610	.184	36	10.0
	140°	$(C_2H_5)_3GeBr$	.624	.177	133	2.7
6	Carbon	$(C_2H_5)_3GeF$	.286(V)	.071(V)	18	25.0
	tetrachloride	$(C_2H_5)_3GeCl$	.285	.072	45	10.0
	118°	$(C_2H_5)_3GeBr$	.286	.071	140	3.2
7	Ethylene	$(C_6H_5)GeF$	.049(V)	.0077(V)	36	19.4
	dibromide	$(C_6H_5)_3GeCl$	.048	.0074	70	10.0
	90°	$(C_6H_5)_3GeBr$	.045	.0074	140	4.8
		$(C_6H_5)_4Ge$	.051	.0067	16	43.6

(W) Where the letter W appears the mole fractions were determined by weight. (V) The letter V indicates that mole fractions were calculated from volumetric measurements.

TABLE III

RELATIVE RATES OF IODINATION

Expt.	Solvent and temp.	Substance	Mole fraction		Reaction time, minutes	Relative rates, chlorides 10
			Subs.	I_2		
1	Glacial acetic acid 70°	$(C_2H_5)_3SnOH$	0.015(W)	0.0022(W)	64	21.8
		$(C_2H_5)_3SnF$	$<$.015[a]	$>$.0022[a]	99	14.1
		$(C_2H_5)_3SnCl$	.015	.0022	139	10.0
		$(C_2H_5)_3SnBr$	.014	.0022	334	4.2
		$(C_2H_5)_4Sn$	.015	.0022	3[b]	463.0
		$(C_2H_5)_2SnCl_2$	.015	.0022	$\gg$360	0.0
2	Glacial acetic acid 85°	$(C_2H_5)_3SnOH$	.016(V)	.0014(V)	35	22.4
		$(C_2H_5)_3SnF$	$<$.008[a]	$>$.0001[a]	25	22.4
		$(C_2H_5)_3SnCl$	.014	.0020	56	10.0
		$(C_2H_5)_3SnBr$	.021	.0032	97	5.8
		$(C_2H_5)_3SnI$	.013	.0020	136	4.1
		$(C_2H_5)_4Sn$	.025	.0038	3[b]	186.5
		$(C_2H_5)_4Sn$(wet)	.014	.0021	3[b]	186.5
3	Ethylene dibromide 110°	$(C_2H_5)_3SnOH$	$<$.035(V)[a]	$>$.0052(V)[a]	7	22.9
		$(C_2H_5)_3SnF$	$<$.037[a]	$>$.0055[a]	8	20.0
		$(C_2H_5)_3SnCl$	.022	.0036	16	10.0
		$(C_2H_5)_3SnBr$	.041	.0062	36	4.4
		$(C_2H_5)_4Sn$	.041	.0061	3[b]	53.4
4	Ethylene dibromide 88°	$(C_6H_5)_3SnF$	$<$.013(V)[a]	$>$.002(V)[a]	10	33.0
		$(C_6H_5)_3SnCl$	.017	.0038	33	10.0
		$(C_6H_5)_3SnBr$	.014	.0021	45	7.3
		$(C_6H_5)_3SnI$	.012	.0017	65	5.7
		$(C_6H_5)_4Sn$	.017	.0024	2[b]	165.0
5	Chloroform 24°	$(C_6H_5)_3PbCl$	6.50×10^{-4}(V)	1.81×10^{-4}(V)	2[c]	10
		$(C_6H_5)_3PbI$	6.58×10^{-4}	1.65×10^{-4}	2[c]	10

(W, V) See (W) (V), Table II.

[a] The substance was only partially dissolved. The concentration of substance is therefore considerably less than the figures given and the concentration of iodine slightly greater than that given in the table. [b] The observed time is probably somewhat low since some reaction undoubtedly must have taken place while the tubes were being sealed, etc. [c] The experimental procedure was adapted to the short reaction times. The observed reaction time is probably accurate within fifteen seconds.

toward the end of the reaction period. However, the color changes observed during the reaction indicated that the bromine concentrations in the three reaction mixtures, although differing during the final stages, were the same for the greater part of the reaction period. Hence it is improbable that bromine concentration differences can account for the different yields of diphenylmethyl derivative.

Water was found present toward the end of the reaction in the capsules containing $(C_6H_5)_3COH$, no doubt due to reaction of the carbinol with hydrogen bromide.

The yields of benzophenone are based on the weights of oxime and are probably somewhat low due to loss of oxime during purification.

III. Discussion of Results

For a general survey of these reactions it was necessary to study the halogenation of a number of widely different compounds; to determine the influence of specific experimental conditions such as the solvent media, temperature, concentration and systematic impurities; and finally to establish the nature of the common reaction.

Reaction Products.—The reaction common to all experiments is that yielding R_2M derivatives. While it seemed very probable that these reactions followed the equation

$$R_3MX + X_2 = R_2MXX' + RX' \quad (1)$$

group substitution might also be represented by

$$R_3MX + X_2' = R_2MX_2' + RX \quad (2)$$

It has been shown that bromination of triisobutyllead chloride yields diisobutyllead chlorobromide[5] supporting reaction 1. To obtain additional information triethyltin chloride was iodinated both in ethylene dibromide solution and in the absence of any solvent. The reactions were carried out in sealed tubes. Fractional distillation of the resulting mixtures gave no evidence of a product of lower boiling point than ethyl iodide. About 85% of the theoretical yield of ethyl iodide was obtained in both cases. Since less than five grams of triethyltin chloride was used in each of these experiments the yield of 85% indicated a probable quantitative reaction. Bromination of triphenylgermanium chloride was similarly found to yield bromobenzene, about 80% of the bromobenzene required by equation 1 being recovered. Bromination reactions of the ethylgermanium, silicon and triphenylmethyl compounds are complicated by hydrogen substitution, relatively more hydrogen substitution occurring with bromides than with chlorides. Partial bromination of triethylgermanium fluoride can be carried out without appreciable quantities of hydrogen bromide being formed, but in all attempts to carry out a complete reaction according to equation 1, hydrogen bromide was formed in considerable quantities. Where much hydrogen bromide was formed, the reaction mixtures consisted chiefly of ethylene dibromide, diethylgermanium derivatives and only very small quantities of ethyl bromide.

From the foregoing it is evident that R_2M derivatives are formed according to equation 1.[6]

Influence of Solvent, Temperature, Etc.—A glance at the tables will show that the sequence of the rates of halogenation is not dependent on the solvent. Comparing Experiments 4 and 5, Table II, it is evident, however, that the solvent does influence both the actual and relative rates of bromination. Temperature changes also affect the relative rates but do not change the sequence of the reaction rates of the R_3M halides.

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[5] Grüttner and Krause, *Ber.*, **50**, 278–85 (1917).

[6] In representing the reactions by equation 1, the authors do not exclude intermediate reactions consistent with the products.

It appears that conditions favoring rapid reactions tend to equalize the rates for a given set of halides. Considering Experiments 1, 2 and 3, Table III, it is clear that the rates of reaction are not affected materially by rather large concentration changes. The rates of reaction of carefully purified compounds were compared with those of the same compounds contaminated with probable impurities. Generally, no appreciable differences were detected. In Experiments 3 and 4, Table II, the effect of water, in concentrations far greater than could be present in carelessly purified materials, is seen to be negligible.

Extreme Cases.—It is clear from Experiment 5, Table III, that the difference in rates of iodination of the triphenyllead halides at room temperature is negligible. Attempts to carry out these reactions at lower temperatures were unsuccessful, due to the lack of a suitable solvent. It may be pointed out that the presence of ethyl alcohol or potassium iodide retards the rate of iodination of these compounds to a very marked degree.

Comparisons of the rates of bromination of tertiary butyl halides that are being carried out, indicate that the rates of substitution of hydrogen by bromine are influenced very markedly by the halogen atom of the butyl halide. The rate of hydrogen substitution is greater with the bromide than with the chloride. This is in harmony with observations described herein.

Range of Compounds Studied.—The compounds of the type R_3MX that have been used in these reactions vary widely in their physical and chemical properties; moreover, the physical properties of some R_3M halides do not vary in a regular manner. Thus the melting points of $(C_6H_5)_3SnI$, Br, Cl, F are 121, 121, 106 and 357°, respectively, while triethylsilicon fluoride is a low boiling liquid. The chemistry of the silicon and triphenylmethyl compounds is distinctly organic in character while the reactions of the tin derivatives are typical of amphoteric inorganic compounds. It is of special interest to compare the "strengths" of the bonds involved in these reactions. The C–C and the aliphatic C–Si bonds are particularly stable toward oxidation and reduction, while the C–Sn bond is easily broken by sodium in liquid ammonia or by iodine solutions. The reactivity of the C–Sn bond is illustrated by the ready reaction of $(C_2H_5)_3SnCl$ with $(C_2H_5)SnCl_3$ to form $(C_2H_5)_2SnCl_2$ and by similar reactions.

Summary

It is shown that the rate of group substitution by bromine and iodine in a number of compounds of the type R_3MX increases successively as X represents I, Br, Cl, F or OH, and that this effect is not due to specific experimental conditions.

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