CCCXLVI.—*The Reactivities of ω-Halogen Atoms in Acetophenone.*

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IN this paper is given a comparison of the reactivities towards aniline of chlorine, bromine, and iodine atoms in the ω-position of acetophenone, the reactions being carried out in alcohol at 40°. Under these conditions ω-chloroacetophenone shows little reactivity, but the bromo- and iodo-compounds are distinctly reactive, the order being $I>Br$. This order of reactivity is the reverse of that usually found for nuclear halogen; *e.g.*, Rheinlander (J., 1923, **123**, 3099) found for halogenonitrobenzenes and bases in alcohol the order $Br>Cl>I$, except for the one case of picryl iodide, which reacted more rapidly with methylaniline than did the chloride and bromide (see also *Ann. Reports*, 1929, 132, *et seq.*).

A reactive halogen is generally rendered negative, or given a tendency towards anionisation, by the influence of certain groups, *e.g.*, 2 : 4-nitro-groups in the case of nuclear halogen, and oxygen in the case of chlorodimethyl ether (Allan, Oxford, Robinson, and Smith, J., 1926, 404). The oxygen in ω-halogenoacetophenone has the opposite effect, however (Rây and Robinson, J., 1925, 1619; Lapworth and Manske, J., 1928, 2537; 1930, 1978), and Bennett and Berry (J., 1927, 1678) assumed a positive charge on the chlorine atom in ω-chloroacetophenone to account for its rapid reaction with potassium iodide, *via* the formation of a complex between the chloro-compound and the iodide ion.

In the first series of experiments equimolecular proportions of the halogen compound and aniline were used, the reaction being followed by titration of the halogen acid liberated. The reaction did not go to completion at 40° and it was assumed that the liberated halogen acid formed an unreactive salt with aniline. The termolecular equation was modified to account for the aniline removed in this way (compare Rheinlander, *loc. cit.*). In the second series the aniline was present in much greater concentration and the reaction was regarded as a unimolecular one, with constant concentration of aniline. This method had the advantage of removing the acid, which may have acted as a negative catalyst (compare Senter and Porter, J., 1911, **99**, 1053), and under these conditions ω-chloroacetophenone displayed distinct reactivity (in the first series no hydrogen chloride was liberated when ω-chloroacetophenone and aniline were kept at 40° for several days).

EXPERIMENTAL.

Absolute alcohol was used and was prepared by repeated drying over lime and distillation. Aniline was purified by fractional distillation and freezing. ω-Chloroacetophenone and ω-bromoacetophenone were prepared by adding the theoretical quantity of chlorine to, or aspirating bromine into, acetophenone dissolved in ligroin; this solvent was used because the products are not very soluble in it. ω-Iodoacetophenone was prepared by Collet's method (*Compt. rend.*, 1899, **128**, 312) except that the alcoholic solution of ω-chloro- or ω-bromo-acetophenone was kept over sodium iodide instead of potassium iodide. The sodium salt is the more soluble and the reaction is quickened and gives a purer product.

The reaction vessel was a three-necked Woulff's bottle, the central hole being fitted with a mercury-sealed stirrer. One side orifice was fitted with a condenser; the other with a stopper, being used for introduction of the reactants and withdrawal of the mixture. The solutions, 0·2*M*, of the reactants were made up separately, warmed to 40°, and mixed. 5 C.c. of the mixture were removed at definite intervals and run into 25 c.c. of 0·1*N*-silver nitrate solution. The whole was shaken with benzene, which removed organic matter from the aqueous layer and coagulated the silver halide precipitate. The excess of silver nitrate was titrated with ammonium thiocyanate without separation of the benzene and water layers. A typical experiment, for ω-iodoacetophenone, gave the following results.

Time (mins.).	$a - x$ (c.c. 0·1N-AgNO$_3$).	$a - 2x$.	$k \times 10^4$.	Time (mins.).	$a - x$ (c.c. 0·1N-AgNO$_3$).	$a - 2x$.	$k \times 10^4$.
13·25	4·40	3·80	22·1	46·25	3·62	2·24	20·8
22·25	4·15	3·30	20·8	74·50	3·27	1·54	20·8
33·50	3·85	2·70	21·1	89·25	3·11	1·22	21·0
						Mean	21·1

For ω-bromoacetophenone : mean $k \times 10^4 = 13·4$.
Ratio $k_I : k_{Br} = 1 : 0·67$.

There was no action with ω-chloroacetophenone.

When the experiments were repeated with 0·2M-halogen compound and 5M-aniline, the reaction was rapid. The results of typical experiments are given below.

ω-Iodoacetophenone.			ω-Bromoacetophenone.			ω-Chloroacetophenone.		
Time (mins.).	$a - x$.	$k \times 10$.	Time (mins.).	$a - x$.	$k \times 10$.	Time (mins.).	$a - x$.	$k \times 10$.
5	1·95	1·85	5	2·20	1·64	10	2·23	0·80
7·5	1·08	2·00	7·75	1·30	1·70	19	1·53	0·62
11	0·72	1·85	11·75	0·73	1·64	22	1·37	0·58
14	0·25	2·00		Mean	1·66		Mean	0·67
	Mean	1·9						

Ratio $k_I : k_{Br} : k_{Cl} = 1 : 0·88 : 0·35$.

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