423. *The Velocities of Reaction of Some β-Arylethyl Chlorides with Potassium Iodide.*

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In connexion with the discussion of the comparative influences of the various halogens as substituents on the velocities of reaction of aromatic compounds, in which it has been noted that the halogens often fall into an unexpected order, it seemed desirable to examine some substances in which the operation of electromeric effects would be either impossible or at least of only secondary importance as compared with the general polar (inductive) effects. In the substituted β-chloroethyl sulphides previously studied, the sulphur atom could act as a point of relay to which electromeric disturbances might arrive and be transmitted further by an inductive mechanism.

We have therefore prepared a series of seven β-phenylethyl chlorides and have determined the velocity of their reaction with potassium iodide in acetone solution by the method described in our earlier paper (J., 1933, 261).

The results are in the table, together with the approximate values of the energy of activation in three instances in which measurements were made at two temperatures. These values are of the same order of magnitude as those found for the substituted benzyl chlorides (preceding paper).

The figures for reaction velocity at 75° are, in general, in the familiar polar sequence for a reaction requiring electron-recession. The methoxy-group shows its true electron-attracting inductive effect, also evident from consideration of the strengths of methoxyacetic acid and *m*-methoxybenzoic acid. The four halogens do not appear, however, to have a decided order of diminishing effect in the group. These figures will be referred to in a general discussion contained in a separate paper.

Velocity Coefficients, k, *for the Reaction of Substituted* β-*Phenylethyl Chlorides,* Ar•CH_2•CH_2Cl, *with Potassium Iodide in Acetone.*

(Time in hours.)

Ar.	$k_{75\cdot0}$.	Ar.	$k_{55\cdot0^\circ}$.	$k_{75\cdot0^\circ}$.	*E*, kg.-cals.
Phenyl	0·735	*p*-Bromophenyl	0·237	1·63	17·9
p-Methoxyphenyl ...	1·04	*p*-Chlorophenyl	0·228	1·65	18·9
p-Iodophenyl	1·40	*p*-Fluorophenyl	0·208	1·55	19·4
		p-Nitrophenyl	—	3·76	—

EXPERIMENTAL.

β-Phenylethyl chloride and its *p*-nitro- and *p*-methoxy-compound (D.R.P. 234,795, Friedländer, X, 1232) were prepared as described in the literature.

Preparation of β-p-*Iodophenylethyl Chloride*.—*p*-Nitrophenylethyl alcohol (25 g.) was reduced by boiling for 1 hour with zinc dust (100 g.) and calcium chloride solution (10 g. $CaCl_2$ in 250 c.c.). The hot filtered solution was treated with sodium carbonate (10 g.), and the calcium carbonate filtered off. The amine solution was cooled, and diazotised by adding sulphuric acid (17 c.c. concentrated acid diluted with ice) and sodium nitrite (13 g.). A concentrated solution of potassium iodide (85 g.) was then added, and after standing for 1 hour the mixture was gently heated on the steam-bath until evolution of nitrogen ceased. Free iodine was removed by addition of thiosulphate, and when cold, the product solidified. β-p-*Iodophenylethyl alcohol* separated in almost colourless crystals, m. p. 46—47°, from light petroleum (b. p. 40—60°) (Found: I, 51·0. C_8H_9OI requires I, 51·2%).

This alcohol was converted by the action of thionyl chloride and pyridine into the required β-p-*iodophenylethyl chloride*, which solidified in a freezing mixture and was obtained in colourless crystals, m. p. 25°, from low b. p. paraffin (Found: total halogen calc. as Cl, 34·8; by analysis of silver halides, Cl, 13·4; I, 46·7. C_8H_8ClI requires 35·1, 13·3, and 47·6% respectively).

Preparation of β-p-*Chloro- and -Bromo-phenylethyl Chlorides*.—*p*-Aminophenylethyl alcohol (44 g.), diazotised with hydrochloric acid (80 c.c. concentrated acid and 52 c.c. water) and sodium nitrite (26 g.), was added to a cuprous chloride solution (from 5 g. $CuCO_3$ in acid with excess of metallic copper); the oil which remained after evolution of nitrogen had ceased was removed in ether, the extract dried over potassium carbonate and evaporated, and the residue distilled. The p-*chlorophenylethyl alcohol* was a colourless oil of b. p. 110°/0·5 mm. (Found: Cl, 22·5. C_8H_9OCl requires Cl, 22·7%). This substance was warmed with phosphorus pentachloride (1 mol.), and the product carefully fractionated with a column under reduced pressure. The p-*chlorophenylethyl chloride* was thus isolated as a colourless oil of b. p. 133°/35 mm. (Found: Cl, 40·5. $C_8H_8Cl_2$ requires Cl, 40·6%).

A repetition of this process using cuprous bromide in place of chloride yielded β-*p*-bromophenylethyl alcohol as a colourless oil solidifying at low temperatures and melting at 20°. This was converted by phosphorus pentachloride into β-p-*bromophenylethyl chloride*, a colourless oil of b. p. 137°/25 mm. (Found: total halogen calc. as Cl, 37·2; Cl, 16·8; Br, 35·2. C_8H_8BrCl requires 37·3, 16·2, and 36·4% respectively).

Preparation of p-*Fluorophenylethyl Chloride*.—*p*-Nitrophenylethyl benzoate (Ferber, *Ber.*, 1929, **62**, *B*, 183) (50 g.) was reduced with zinc dust (200 g.) in boiling aqueous-alcoholic calcium chloride solution (20 g. chloride in 500 c.c. 50% alcohol). After 1 hour, the solution was filtered, boiled with sodium carbonate (20 g.), and again filtered. The filtrate was distilled in steam to remove alcohol, cooled, and extracted with ether; on evaporation of the ether, the residue solidified. p-*Aminophenylethyl benzoate* formed almost colourless needles, m. p. 59—60°, from ligroin (Found: C, 74·4; H, 6·2. $C_{15}H_{15}O_2N$ requires C, 74·7; H, 6·3%).

To a diazotised solution of this amine (40 g., with 40 c.c. concentrated HCl, 26 c.c. water, 13·2 g. $NaNO_2$ in a little water) a saturated solution of sodium borofluoride was added, and the sandy precipitate of diazonium borofluoride was filtered off and dried in air. This salt was a buff-coloured crystalline powder; it was heated in a flask immersed in an oil-bath, and decomposed at 105—110° leaving a black oily residue. Extraction of this with paraffin of b. p. 60—80° yielded a colourless oil which solidified on cooling, and, after recrystallisation from paraffin of b. p. 40—60°, β-p-*fluorophenylethyl benzoate* was obtained as white aggregates of crystals, m. p. 43—44°, readily soluble in all organic solvents including the low b. p. paraffin (Found: C, 73·3; H, 5·3. $C_{15}H_{13}O_2F$ requires C, 73·7; H, 5·2%).

The ester was hydrolysed with alcoholic potassium hydroxide, the alcohol removed in a current of steam, the oil extracted in ether, and the solution distilled. *p*-Fluorophenylethyl alcohol, a colourless oil of b. p. 110°/20 mm., was heated with phosphorus pentachloride and the products carefully fractionated under diminished pressure. β-p-*Fluorophenylethyl chloride* was thus obtained as a colourless oil of pleasant odour, b. p. 80°/30 mm. (Found: Cl, 22·7. C_8H_8FCl requires Cl, 22·4%).

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