CCXCI.—*Benzoic Esters and Electronic Affinities of Radicals. Part II. The Halogenoalkyl Benzoates.*

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IN Part I (J., 1928, 983) comparison was made between the orienting powers of various alkyl radicals as exhibited in the alkyl benzoates. The effect of a halogen atom in the alkyl group is now considered.

When the halogens are separated from the benzene nucleus by one or more saturated carbon atoms, the phase in which they exercise their free electrons by increasing their covalency with the α-carbon of the nucleus, causing *op*-substitution, cannot exist. The intrinsic negativity of these elements, instigated by their strong nuclear charges and transmitted by electrostatic induction along a chain, becomes the controlling factor. The periodic table gives the clue to their order of negativity. For meta-orientation the order becomes : $F > Cl > Br > I$.

This principle gains support from the following comparisons, the percentages referring to the amount of *m*-compound obtained on nitration :

Toluene	3%	Holleman, " Die direkte Einführung, etc.," p. 96.
Benzyl chloride	4%	Holleman, *Rec. trav. chim.*, 1924, **33**, 1.
Benzal chloride	35%	,, ,, ,, ,,
Benzotrichloride	64%	,, ,, ,, ,,
Benzal fluoride	65%	Hove, *Bull. Acad. roy. Belg.*, 1913, **3**, 1082.
Benzotrifluoride	99%	Schwartz, *Bull. Acad. roy. Belg.*, 1920, **6**, 389.

Chlorine therefore functions as an attractor of electrons, and the more atoms of it there are present the greater is the attraction. Fluorine functions as chlorine does, but to a much greater extent, and it may be presumed that bromine, for which no data could be found, will function in the same way, only in a less degree. The same applies to iodine.

It was anticipated that the nitration of the halogenoalkyl benzoates would provide evidence of the same kind. The radicals chosen were chloromethyl, β-chloro-, β-bromo-, and β-iodo-ethyl, and the three corresponding γ-halogenopropyls. On nitration, however, the iodoalkyl benzoates liberated practically all their iodine directly they came in contact with nitric acid. The bromo-compounds gave very little bromine, and the chlorine proved to be firmly held in the molecule. The following results were obtained :

Radical.	% Meta.	Radical.	% Meta.	Diff.
CH_2Cl	81·9	Me	72·6	9·3
$CH_2Cl{\cdot}CH_2$	75·8	Et	69·9	5·9
$CH_2Cl{\cdot}CH_2{\cdot}CH_2$	77·3	Pr^{α}	71·8	5·5
$CH_2Br{\cdot}CH_2$	71·5	Et	69·9	1·6
$CH_2Br{\cdot}CH_2{\cdot}CH_2$	72·8	Pr^{α}	71·8	1·0

The effect due to the chlorine is evident from comparisons with the corresponding unsubstituted alkyl benzoates. γ-Chloropropyl benzoate, when compared with its lower homologues, shows the same alternation as *n*-propyl benzoate in comparison with methyl and ethyl benzoates (see Part I, *lcc. cit.*). Alternation there was considered to be due to the steric influence of the carbonyl group on the odd carbon atoms of the chain and it was shown that the influence disappeared with the disappearance of the cause; and the same reasoning applies here. The differences in the last column give a measure of the effect due to the chlorine atom in its various positions in the chain. The effect is greater the nearer the chlorine is to the nucleus, the view that the transmission of these effects is governed by electrostatic laws thus being plainly illustrated.

The bromo-esters occupy a place between the corresponding normal and chloro-esters and show the alternation exhibited by the other two series.

EXPERIMENTAL.

The nitration of the esters, the hydrolysis of the products, and the subsequent analyses were carried out as described in Part I. Attempts to attain saturation at 25° in less than 3 days by first warming the solutions above 25° failed owing to supersaturation.

Chloromethyl Benzoate.—This was obtained from benzoyl chloride and paraformaldehyde with anhydrous zinc chloride as a catalyst (Ulich and Adams, *J. Amer. Chem. Soc.*, 1921, **43**, 662); b. p. 104—106°/2 mm.

The nitration product (yield, 98·2%) was hydrolysed by boiling with *N*-potassium hydroxide in a current of air free from carbon dioxide. The subsequent hydrolyses were all performed in this way.

β-*Chloroethyl Benzoate.*—This was prepared in 90% yield by boiling benzoyl chloride and β-chloroethyl alcohol together for 3 hours; b. p. 255—257°/762 mm. and 138·8°/18 mm.

The yield of nitration product was 96·9%.

Trimethylenechlorohydrin.—The pure glycol (52 g.) was saturated with dry hydrogen chloride in a bottle in cold water and then kept under pressure in boiling water; after 5 hours, all the gas had been absorbed. When the product was distilled, only 6 g. of the required compound were obtained, between 155° and 165°, the remainder being trimethylene dichloride or unchanged trimethylene glycol (concentrated hydrochloric acid gave a similar result). The products from two such experiments were fractionated and the alcohol was collected at 158—159°.

γ-*Chloropropyl Benzoate.*—Equivalent quantities of trimethylenechlorohydrin and benzoyl chloride were heated together for 3 hours. The yield of ester, b. p. 155—156°/15 mm., was 75% (Found: C, 60·2; H, 5·6. Calc.: C, 60·4; H, 5·5%).

The yield of nitration product was 98·5%.

Ethylenebromohydrin.—This was prepared by saturating ethylene glycol with dry hydrogen bromide and heating it under pressure in a water-bath for 5 hours; b. p. 47—48°/15 mm. The yield was poor.

β-*Bromoethyl Benzoate.*—This was prepared by heating benzoyl chloride and ethylenebromohydrin in molecular proportion (Auwers, *Annalen*, 1904, **332**, 209); b. p. 147—149°/15 mm. An attempt to prepare it by heating ethylene dibromide with sodium benzoate under pressure (von Braun, *Ber.*, 1913, **46**, 1784) gave only ethylene dibenzoate. In an attempt to convert β-chloroethyl benzoate into the bromo-compound by heating it with sodium bromide in alcohol (compare β-iodoethyl benzoate) the chloro-ester was wholly unattacked.

The yield of nitration product was 98·7%.

γ-Bromopropyl Benzoate.—This was obtained by heating trimethylene dibromide (b. p. 162—165° ; prepared from trimethylene glycol and hydrobromic acid in about 90% yield; "Organic Chemical Reagents," vol. II, p. 19) with sodium benzoate at 200° for 10 hours (von Braun, *Ber.*, 1913, **46**, 1784); b. p. 164·5—165·5°/16 mm.

The yield of nitration product was 99·0%.

In the nitration of this ester and the previous one, a little bromine separated, distinguishable by its smell and by the slight coloration of the aqueous mixture obtained when the product was poured on ice. Before extraction with ether a current of carbon dioxide was passed through and every trace of bromine removed.

β-*Iodoethyl Benzoate.*—β-Chloroethyl benzoate (100 g.) was boiled with 160 g. of sodium iodide (2 mols.) in 100 c.c. of 90% alcohol for 6 hours. Alcohol was then distilled off, water added, the product extracted with ether, and the extract washed with water containing sulphur dioxide and dried over calcium chloride. The oil left after the removal of the solvent was fractionated in a vacuum, air not being admitted until the fractions had cooled (the hot ester gives up iodine easily in air); b. p. 161—163°/17 mm. The yield was about 80% (Found: C, 39·0; H, 3·3. Calc.: C, 39·1; H, 3·3%).

γ-Iodopropyl Benzoate.—This was prepared from γ-bromopropyl benzoate and sodium iodide (von Braun, *Ber.*, 1913, **46**, 1784), precautions similar to those described for the previous ester being taken in fractionating the product; b. p. 177—179°/15 mm.

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