156. *Benzoic Esters and Electronic Affinities of Radicals. Part III.*

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IN Part II (J., 1930, 2269) the orienting power of halogenoalkyl radicals in benzoic esters was examined. The directive influences in glycol dibenzoates, in *cyclo*hexyl, aryl, and benzyl benzoates, and in benzamides are now considered.

Glycol Dibenzoates.—The glycol dibenzoates supply evidence for the order Cl>O>H with regard to meta-nitration induced by substitution in a saturated chain. The results are :

	m-Nitro-compound, %.		
	$n = 1$.	$n = 2$.	$n = 3$.
$Ph\cdot CO\cdot O\cdot[CH_2]_n\cdot O\cdot COPh$	80·8	74·8	75·8
$Ph\cdot CO\cdot O\cdot[CH_2]_nH$	72·6	69·9	71·8
$Ph\cdot CO\cdot O\cdot[CH_2]_nCl$	81·9	75·8	77·7

These dibenzoates can be regarded as acyloxyalkyl benzoates. The oxygen atom shows a greater attraction for electrons than the hydrogen atom in every case, as shown by comparison with the corresponding alkyl benzoates. Alternations such as those found for unsubstituted and halogen-substituted alkyl groups are also evident here. Nitration of the chloroalkyl esters demonstrates the lower negativity of oxygen as compared with chlorine.

A benzoyl radical, or in fact any other radical, carried by an oxygen or a nitrogen atom increases the pull of the latter on the electrons in the rest of the molecule. This is due to the conjugation of the oxygen or nitrogen with the carbonyl group and is shown by the decrease in the basic character of these atoms and by their decreased orienting powers. Notwithstanding the assistance given by the benzoyl radical to the oxygen in the glycol dibenzoates, its pull falls short of that of the chlorine atom.

cyclo*Hexyl Benzoates.*—On nitration, benzylpiperidine gives a much higher proportion (72%) of *m*-nitro-compound than benzyldiethylamine (51%), and β-phenylethylpiperidine a higher proportion (22%) than β-phenylethyldimethylamine (13%). An explanation of the differences, based on the difference in dissociation of the salts which the bases form with the acid medium, has been given by Pollard and Robinson (J., 1927, 2770), who, however, admit the possibility that the increase in the proportion of *m*-nitro-compound may be due to the composition difference of two hydrogen atoms brought about by closure of the ring.

The nitration of the *cyclo*hexyl benzoates was examined to test the possibility, as in this case no salt formation is possible to complicate the issue. The figures obtained were :

Benzoate.	*m*-Nitro-compound, %.	Benzoate.	*m*-Nitro-compound, %.
*cyclo*Hexyl	67·0	3-Methyl*cyclo*hexyl	67·2
2-Methyl*cyclo*hexyl	65·4	4-Methyl*cyclo*hexyl	67·3

The figures are lower than those obtained for the lower alkyl benzoates (methyl benzoate gives 72·6% of *m*-nitro-compound), confirming the hypothesis that the repulsion of electrons is increased by increasing carbon substitution. Compared with that for *n*-hexyl benzoate (63·7%), however, all the figures are appreciably higher. This can only be due to the closure of the ring. One might object to the value 63·7% being taken as representing the true influence of the *n*-hexyl radical after it had been shown that the steric influence of the carbonyl group affected the carbon atoms in the chain. This objection is, however, met by the consideration that in the absence of that steric influence the percentage of *m*-nitro-compound formed from *n*-hexyl benzoate would be lower still, making the difference more pronounced.

Ring closure alone, however, which produces but a small effect (3%), can be responsible for only a small fraction of the differences (20%) observed in the benzylamine bases.

The presence of a 2-methyl group in the *cyclo*hexyl radical diminishes, as expected, the amount of meta-substitution. Similar replacements in the 3- and the 4-position should produce similar but smaller effects : their non-production may be due to the greater distances of the methyl groups from the benzoyl radical in so far as the transmission of effects through the bonds is concerned.

Aryl Benzoates.—Aryl groups present special difficulties because they may be nitrated at the same time as the phenyl group of the benzoyl radical and the result will then be due only in part to the aryl group originally present. It was thought, however, that, by starting with nitrophenyl benzoates, nitration of the benzoyl radical might be completed before the other phenyl group had time to be nitrated appreciably. Nitration of *p*-nitrophenyl benzoate at 0° and at −15° resulted in the nitrophenyl group being further nitrated, to some extent even to the trinitro-stage. The products were nevertheless separated in the usual way and hydrolysed. The phenols formed were soluble in alkali, but it was found that ether extracted all the *p*-nitrophenol from an alkaline solution of the hydrolysis products saturated with carbon dioxide (carbon dioxide does not decompose sodium 2 : 4-dinitrophenoxide). The usual procedure was then adopted and the phenols that could not be isolated were treated as foreign acidity and allowed for in the titrations. The percentage of meta-nitration thus found, namely, 88%, must be approximate and shows only more or less qualitatively that electrons are attracted away from the benzoyl residue by conjugation of the phenolic oxygen with the phenyl ring, assisted by the effects due to the nitro-groups. Account being taken of the ease with which nitrophenyl benzoates are hydrolysed, the degree of meta-nitration obtained must have been depressed owing to benzoic acid being liberated before nitration and being nitrated as such. Benzoic acid under these conditions of nitration gives 80% of *m*-nitrobenzoic acid.

Nitrobenzyl Benzoates.—As the nitrophenyl group in *p*-nitrophenyl benzoate was nitrated to some extent owing to conjugation of the oxygen atom with the phenol ring, it was thought probable that, if these two were separated by a saturated carbon atom, such nitration would be impeded. *p*-Nitrophenyl acetate was subjected to nitration under the usual conditions : it suffered little if any change. Nitrobenzyl benzoates would be less liable to nitration. The possibility of hydrolysis before or during nitration was also excluded, as *o*-nitrobenzyl benzoate is not changed by heating with fairly concentrated sulphuric acid under pressure (Paal and Bodewig, *Ber.*, 1892, **25**, 2963). This was confirmed by the comparative resistance to hydrolysis shown later by the esters after nitration.

The three isomeric nitrobenzyl benzoates were accordingly nitrated, but when the products were hydrolysed the alkali partly oxidised the nitrobenzyl alcohols to the corresponding nitrobenzoic acids. The percentage of *m*-nitrobenzoic acid in the products of hydrolysis was therefore bound to be higher for the *m*-nitrobenzyl benzoate and lower for the *o*- and the *p*-nitrobenzyl ester. *m*-Nitrobenzyl alcohol, *o*-nitrobenzyl chloride, and *p*-nitrobenzyl bromide were therefore subjected to the action of alkali under exactly the same conditions as in the hydrolysis, and the extent to which oxidation occurred was determined in each case and used to correct the results obtained in the nitration experiment. *o*-Nitrobenzyl benzoate was thus found to give 76% of the *m*-nitrobenzoate, the *m*-nitrobenzyl ester 73%, and the *p*-nitrobenzyl ester 75%. These results show sufficiently well that all the nitrobenzyl radicals are less directive than methyl, the *m*-nitrobenzyl radical being the nearest to it (72·6%).

Benzamide Derivatives.—Benzodiethylamide and benzoylpiperidine were nitrated with excess of fuming nitric acid under the same conditions as those used by Cooper and Ingold (J., 1927, 836) for the nitration of benzamide. The hydrolysis accompanying nitration was about 3%, compared with 10% for the benzamide, and the degree of mono-nitration was estimated to be 95% (for both amides), compared with 97—100% for benzamide. Calculations on this basis placed the amount of meta-nitration between the following limits :

Benzodiethylamide	27—32%;	mean 29·5%
Benzoylpiperidine	29—33%;	,, 31%
Benzamide		69%

Meta-nitration is therefore considerably lowered by the substitution of the hydrogen atoms of the amino-group. The pentamethylene of the piperidyl radical and the two ethyl radicals have a greater repulsion for electrons than the two hydrogen atoms and accordingly produce more *o,p*-activation in the nucleus.

The nitration of both amides was repeated with the addition of enough beryllium nitrate to saturate the nitric acid, but this had little if any influence on the proportion of *m*-nitro-isomeride formed. The view is thus confirmed that in the nitric acid solution the amides exist only to a small extent as salts, otherwise the nitrate ion would have electrostricted the kations and increased *o,p*-nitration (compare Goss, Ingold, and Wilson, J., 1926, 2440; Pollard and Robinson, *loc. cit.*).

The percentage of *m*-nitration of benzoylpiperidine is a little higher than that of the diethylamide, and this, according to a previous argument, must be taken as due to the closure of the ring.

The yields obtained in the four nitrations were comparatively low, and were all practically the same, namely, 85%.

EXPERIMENTAL.

The nitration of the compounds, the hydrolysis of the products, and the subsequent analyses were carried out as described in the previous parts.

Methylene dibenzoate, obtained together with chloromethyl benzoate in the preparation of the latter, crystallised from alcohol and then melted constantly at 97—98°.

The yield of nitration product was 96·8%.

Ethylene dibenzoate was prepared by gently boiling benzoyl chloride (2 mols.) and ethylene glycol (1 mol.) for 4 hours. When the oil finally obtained from the ethereal extractions was fractionated at 14 mm., a portion, presumably the monobenzoate, came over at 135—200°, and then the dibenzoate at 225—227°. Crystallised from alcohol, the latter had m. p. 73°.

The yield of nitration product was 97·3%.

Trimethylene dibenzoate was obtained together with γ-bromopropyl benzoate in the preparation of the latter. The fraction, b. p. 233—241°/16 mm., melted at 57° after crystallisation from alcohol.

The yield of nitration product was 96·8%.

*cyclo*Hexyl benzoate was prepared by gently boiling *cyclo*hexanol and benzoyl chloride for 4 hours; b. p. 160°/18 mm. (yield, over 90%).

The yield of nitration product was 94·0%.

4-Methyl*cyclo*hexyl benzoate, prepared in the same way as the previous ester, had b. p. 174—175°/20 mm. (yield, over 90%) (Found : C, 77·0; H, 8·5. Calc. : C, 77·1; H, 8·3%).

The yield of nitration product was 93·8%.

3-Methyl*cyclo*hexyl benzoate, similarly prepared, had b. p. 169·5—170°/17 mm.

The yield of nitration product was 94·8%.

The yield of nitration product from 2-methyl*cyclo*hexyl benzoate (b. p. 167—168°/16 mm.) was 94·0%.

During the hydrolysis of the four *cyclo*hexyl and the three nitrobenzyl esters a by-product was formed in considerable amount; it was soluble in ether and acid in nature, but insoluble in water in comparison with the nitrobenzoic acids. The nitrobenzoic acid product was therefore heated with sufficient water to dissolve it wholly (determined by a blank experiment on an artificial mixture), and the solution filtered hot, neutralised with ammonia, concentrated, acidified, and extracted in the usual way.

m-Nitrobenzyl benzoate was prepared by heating equivalent quantities of *m*-nitrobenzyl alcohol and benzoyl chloride for 3 hours. The cooled product was dissolved in hot glacial acetic acid and poured into water. Crystallised twice from alcohol, the ester melted at 69—69·5° (yield, theoretical) (Found : N, 5·4. Calc. : N, 5·4%).

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