CXXIX.—*Benzoic Esters and Electronic Affinities of Radicals. Part I.*

By Ahmad Zaki.

As a consequence of Robinson's ideas on orientation (*Chem. and Ind.*, 1925, **44**, 118, 563; J., 1926, 401, 1655), benzoic esters with alkyl or aryl radicals, repelling electrons more than the hydrogen they replaced in benzoic acid, should produce quantitatively, on nitration for instance, less *m*-compound than the free acid, whereas those attracting electrons should produce more of it. Nitration of benzoic esters, and estimation of the proportion of the *m*-isomerides afford a convenient auxiliary method for the estimation of the electron affinities of various groups, methyl benzoate being taken as the standard of reference.

The present paper records the results of an investigation of the alkyl benzoates. There is plenty of evidence to show that a methyl group has a smaller hold on electrons than a hydrogen atom (Lucas and Moyse, *J. Amer. Chem. Soc.*, 1925, **47**, 1459; Lucas, Simpson, and Carter, *ibid.*, p. 1462). It was accordingly anticipated (*a*) that as one ascended the series, normal alkyl benzoates would give, on nitration, a smaller percentage of the *m*-isomeride, (*b*) that aliphatic radicals with a branched chain would produce less *m*-compound than a normal-chain radical with the same number of carbon atoms, and (*c*) that the nearer the branching in the alkyl group to the benzoyl residue, the smaller would be the percentage of the *m*-isomeride.

Nitrations were first carried out at 25°, but with branched esters at that temperature nitric acid caused some decomposition with the formation of oxides of nitrogen. The nitrations were therefore carried out at 0°, with the following results.

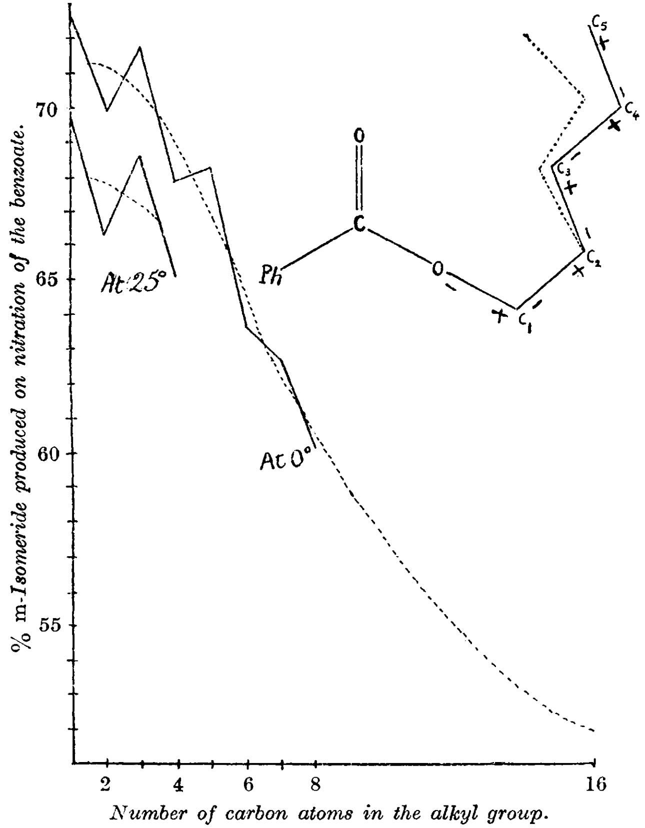
	At 0°.		At 25°.	
Benzoate.	Meta.	Ortho + para.	Meta.	Ortho + para.
Methyl	72·6	27·4	69·7	30·3
Ethyl	69·9	30·1	66·3	33·7
n-Propyl	71·8	28·2	68·6	31·4
n-Butyl	67·9	32·1	65·1	34·9
n-Amyl	68·3	31·7		
n-Hexyl	63·7	36·3		
n-Heptyl	62·8	37·2		
n-Octyl	60·2	39·8		
n-Cetyl	52 (*ca.*)	48		
*iso*Propyl	64·1	35·9		
*iso*Butyl	69·4	30·6		
sec.-Butyl	65·2	34·8		
tert.-Butyl	59·4	40·6		
sec.-Octyl	59·4	40·6		

The results clearly agree with (*b*) and (*c*) above, but the anticipation (*a*) concerning the normal chains is evidently not verified in the precise manner defined. The percentages of the *m*-isomeride obtained for the normal-chain benzoates are plotted in Fig. 1 as ordinates against the number of carbon atoms in the alkyl group as abscissæ.

The "general effect" due to a straight aliphatic saturated radical is the sum of the effects of all the carbon atoms it contains transmitted by electrostatic induction throughout the length of the chain (Allan, Oxford, Robinson, and Smith, J., 1926, 405; Lewis, *J. Amer. Chem. Soc.*, 1916, **38**, 762; Thomson, *Phil. Mag.*, 1923, **46**, 496; Lowry, *Trans. Faraday Soc.*, 1923, **18**, 293). According to the laws of electrostatic induction the further a carbon atom is removed from one end of the chain the less is its effect felt at that end. The curve anticipated for the normal alkyl benzoates as

FIG. 1.
Nitration of n-*alkyl benzoates.*

FIG. 2.



plotted in Fig. 1 would on these assumptions be expected to slope downwards continuously with the lengthening of the chain, the slope diminishing as the series is ascended. Now the dotted line joining the middle points on the straight lines forming the zigzag curve in the figure, Stark's " form line " of the curve (*Z. anorg. Chem.*, 1921, **119**, 293), has a definite continuous downward slope indicating the fundamental truth of the above conceptions. According to Pauly (*Z. anorg. Chem.*, 1921, **119**, 271) and Müller and Shearer (J., 1923, **123**, 3156) the alcoholic carbon chain has a uniplanar zigzag configuration. Fig. 2 would therefore represent the configuration of the carbalkyloxy-group in the benzoic esters. Carbons numbered 3 and 5, including the hydrogen atoms they carry, would fall more within the field of influence of the carbonyl oxygen, whereby neutralisation of affinities through space occurs, than carbons 2 and 4. While affinities are being transmitted in the normal way through the bonds of the chain, neutralisation of affinities on the odd carbons might proceed to such a degree as to absorb the greater part of the former transmission. As the chain lengthens further, the additional carbon atoms, both in the even and in the odd positions, would be very nearly equally out of the sphere of influence of the carbonyl group and bond transmission alone would be felt, and alternation disappears.

Another factor which would make the above steric influence still more pronounced is the effect of distribution of the electric charges within the chain. According to Thomson (*loc. cit.*) the replacement of a hydrogen atom by a different atom or group is equivalent to the introduction of an electrostatic doublet whose magnitude and signs are dependent on the electronic nature of that atom or group. The orientation of the signs of the doublets introduced by the successive substitution of a methyl group for a hydrogen atom in forming the aliphatic chains is represented in Fig. 2. An alkyl group with an odd number of atoms would contain an even number of such doublets, each pair of which would attract one another, and the angle between the carbon linkings in each pair would be smaller than 109° 28′, which is the angle normally existing in the tetrahedral carbon atom. The zigzag structure would fold up closer together inwards towards the molecule, at the same time curving slightly round the carbonyl group (Fig. 2, dotted lines). By this means the neutralisation of charges through space becomes more effective at shorter distances and more odd carbon atoms are brought within the steric influence of the carbonyl oxygen, so that the influence is felt up to the *n*-heptyl ester. Alkyls with an even number of carbon atoms would on the other hand have an odd number of doublets, with the result that the end unpaired doublet, which occupies a sort of *trans*-

position with respect to the benzoyl part, would actually lessen the folding up of the structure, thus diminishing the steric effect and giving a clearer expression to the electronic repulsion as transmitted through the bonds.

Meerwein (*Annalen*, 1919, **419**, 121), studying quantitatively the pinacolin transformation of various tertiary glycols, has determined approximately the " affinity demands " of alkyl groups with straight and with branched chains. Taking a group of a great affinity demand to mean a group of greater hold on its electrons, it is found that his results accord exactly with the results of the present work and can be similarly explained.

After nitration of the esters and hydrolysis of the products as described in the experimental part, a method of determining the percentage of the *m*-isomeride in a mixture of the three nitrobenzoic acids based on Holleman's method (*Rec. trav. chim.*, 1899, **18**, 267; *Z. physikal. Chem.*, 1899, **31**, 79) was worked out.* It is more accurate than Holleman's method, which degree of accuracy was necessary in the case under consideration in order to detect small differences in the orienting powers of the groups. Owing to its general usefulness in orientation problems, a detailed account of it is given in the practical part.

EXPERIMENTAL.

Nitration of the Esters.—Nitric acid (d^{14° 1·517) free from oxides of nitrogen was freshly prepared for each nitration. The ester (3—4 g.) was introduced during ¾ hour into the nitric acid (12 c.c.) at 25° (thermostat) or 0° (ice). After remaining a further ¾ hour at the same temperature, the product was poured on 100 g. of crushed ice. The esters separating were extracted three times with 200 c.c. in all of ether that had been kept boiling for an hour over sodium and then distilled. The ethereal extract was freed from nitric acid by twenty washings with water (10 c.c.). The complete removal of acid was generally indicated by a small amount of a green colouring matter, a by-product in the nitration, passing into the washings. The aqueous washings were neutralised, and extracted with two quantities of 100 c.c. of ether. The ethereal extract was similarly washed several times with small quantities of water to remove a small amount of adhering colouring matter. On evaporation of the solvent from the combined ethereal extracts, an ester was obtained which was free from nitric acid and colouring matter. The aqueous washings left no appreciable residue when they were evaporated slowly to dryness on a steam-bath.

Hydrolysis of Nitration Products.—Acid hydrolysis at various

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* Completed towards the end of March, 1927.

concentrations and temperatures either failed altogether or did not effect complete hydrolysis. Cold 50% caustic potash was effective when shaken with the esters of the lower alcohols. With the less readily hydrolysable esters, long heating on the water-bath with 10% caustic potash was found necessary, some alcohol being added to assist solution. Impurities and by-products were then extracted with ether (the ethereal extract always contained a small quantity of a greenish oily residue whose weight was of the order 10 to 20 mg.) and dilute hydrochloric acid was added. The precipitated nitrobenzoic acids were extracted very thoroughly with pure ether, and the extract was dried over sodium sulphate; on evaporation of the solvent a solid mixture of the nitrobenzoic acids was obtained in a slightly damp condition. This was kept at 50° at the pump for 2 hours, then in a vacuum over a mixture of solid sodium hydroxide and calcium chloride for 3 days. Though dry, it still occluded traces of alcohol and ether, so it was ground to a fine powder and kept in a vacuum desiccator for a few days longer. Only after constant weight was attained was the mixture considered ready for analysis.

Before analysis the absence of 3 : 5-dinitrobenzoic acid and benzoic acid was ascertained, the former microscopically and the latter by steam distillation of the products and artificial mixtures containing this acid, the acidity of the distillates being compared. In addition the amount of nitrogen present was determined by Pregl's micro-method, the correct percentage being obtained except in the case of the nitration product from cetyl benzoate.

Analysis of a Mixture of Nitrobenzoic Acids.—The mixture (0·7000 g.) together with pure *o*- and *p*-nitrobenzoic acids (3·0000 g. and 0·2000 g., respectively) was introduced into a bottle of about 250 c.c. capacity with exactly 175·0 c.c. of pure distilled water, a volume which is a little more than sufficient to dissolve all the *m*-nitrobenzoic acid expected to be present. With the omission of the mixture a control bottle of the same capacity was similarly filled. Both the analysis and the control bottles were rotated for 3 days at about 50 revolutions per minute in a thermostat, electrically controlled and kept at 25·00° ± 0·02°, and containing a minimum and a maximum thermometer to register any deviation in the temperature when the thermostat was not watched. At the end of that time the bottles were placed upright in the thermostat for 2 hours to allow the contents to settle, and 25·0 c.c. were drawn out from each bottle in the manner described below and titrated against $N/40$-baryta. Rotation was then continued for another day and the solutions were again titrated. The two titrations gave identical results within the error due to burette readings. A mean was taken of each and the difference between the two means represented the amount of *m*-nitrobenzoic acid present in 25 c.c. of solution, and the whole amount of meta in the 175 c.c. was calculated. However, the presence of the *m*-nitrobenzoic acid in the analysis bottle causes more of the *o*-isomeride to dissolve than in the control bottle (Holleman, *loc. cit.*). To correct for this, a graph was plotted from results of analyses carried out on artificial mixtures in exactly the same way as described, the amounts of meta found being plotted against the amounts found in excess. The nitration products also contained slight excesses of acidity whose origin could not be traced with certainty. To correct for this, 2·000 g. of pure *m*-nitrobenzoic acid were added to each of the two bottles directly after the former titrations and the whole procedure was repeated once more. The differences in the titres represent foreign acidity and had to be allowed for.

It is essential to rotate the bottles for the time prescribed. When rotation lasted only 2 hours, unsaturated solutions were produced. This is in agreement with the experience of Paul (*Z. physikal. Chem.*, 1894, **14**, 110), that solutions of nitro- and similarly substituted benzoic acids required from 3 to 4 days for saturation. In order to draw clear solutions a small glass tube about 10 mm. in diameter and 15 mm. in length was drawn out at one end to simulate the narrow end of the standardised pipette, to which it was attached by a small piece of thin pressure tubing. Before the pipette was dipped in the solution, this inverted funnel was stuffed with three short layers of clean cotton-wool, each being more tightly packed than the one below it.

The baryta solution (*N*/40) was drawn by suction into a well-standardised 100 c.c. burette capable of holding more than is required by any one titration and with a scale reading accurately to 0·01 c.c. and a thin outlet delivering drops of not more than 0·03 c.c. This method of analysis should theoretically give results accurate within ± 0·3%. In practice, repeated determinations of the same mixtures, artificial and otherwise, under standard conditions gave results agreeing within ± 0·3%. Holleman's original method claims an accuracy of ± 1%.

Most of the esters are already described in the literature. sec.-*Butyl benzoate*. Equivalent quantities of benzoyl chloride and alcohol were heated under reflux for 4 hours, a little moist powdered calcium carbonate was added, and the heating continued for a further 4 hours. From 16 g. of alcohol, 30 g. of ester, b. p. 148—151°/50 mm., were obtained (yield, 75%).

n-*Amyl benzoate*. The alcohol was heated with benzoyl chloride for 5 hours. B. p. 138—139°/15 mm. (Found : C, 75·1 ; H, 8·3. Calc. : C, 75·0 ; H, 8·3%). The ester was prepared by Blaise and Picard (*Ann. Chim. Phys.*, 1912, **25**, 261), but not analysed.

tert.-*Amyl benzoate.* Into a boiling solution of sodium (3·4 g.) in dry *tert.*-amyl alcohol (50 g.), a mixture of newly distilled methyl benzoate (20 g.) and *tert.*-amyl alcohol (26 g.) was introduced in drops during an hour. After boiling for another hour, the product was worked up in the usual manner and fractionated at 22 mm. The ester required was collected between 127° and 128° (yield, 17 g.; 60%) (Found: C, 75·2; H, 8·5. Calc.: C, 75·0; H, 8·3%). The nitration of this ester, however, proved a failure owing to decomposition.

n-*Hexyl benzoate.* Equivalent quantities of benzoyl chloride and the alcohol were boiled very gently for 5 hours. The yield of crude product exceeded 70%. B. p. 200—202°/100 mm.

n-*Heptyl benzoate.* This was prepared in the same way as the hexyl ester. B. p. 216—217°/100 mm. (Found: C, 76·5; H, 9·3. Calc.: C, 76·4; H, 9·1%).

sec.-*Octyl benzoate.* Same preparation as in the two previous esters with similar good yield. B. p. 218—219°/100 mm.

Cetyl benzoate. After the preparation of the ester (Becker, *Annalen*, 1857, **102**, 221) it was purified by distillation at 9 mm.; it came over steadily between 300° and 301° without decomposition. It was, however, difficult to separate all the cetyl alcohol from the mixture of nitrobenzoic acids obtained, and the result of analysis can only be taken as a very approximate one.

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