

123. *Influence of Directing Groups on Nuclear Reactivity in Oriented Aromatic Substitutions. Part VI. Nitration of Ethyl Phenylacetate and of Benzyl Chloride.*

By CHRISTOPHER K. INGOLD and FLORENCE R. SHAW.

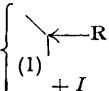



The nitration in acetic anhydride of ethyl phenylacetate and of benzyl chloride has been studied. In each case the rate of nitration of the benzene derivative, relatively to that of benzene itself, has been measured by the competition method; and in each case the proportions have been determined in which *o*-, *m*-, and *p*-nitro-isomereides are formed under corresponding conditions. From these results the factors are calculated by which either side-chain increases or decreases the rate of nitration at each nuclear carbon atom. Both compounds show predominating *op*-orientation, but this result is produced in quite different ways. In ethyl phenylacetate the *o*- and *p*-positions are activated, and the *m*-position is unaffected, by the side-chain. In benzyl chloride the *o*- and *m*-positions are deactivated, and the *p*-position is unaffected. These results are discussed theoretically, and are shown to be intelligible if we take account of polarisability effects arising from hyperconjugation.

THE appearance of Bordwell and Rohde's paper (*J. Amer. Chem. Soc.*, 1948, **70**, 1191) on the effect of a "negatively" substituted vinyl side-chain on aromatic nitration rate, their example being the nitration of cinnamic acid, reminded us that we have not yet published our results, obtained in 1928, on the effect on nitration rate of "negatively" substituted methyl side-chains, our examples being benzyl chloride and ethyl phenylacetate. This work constitutes the fulfilled part of a programme of research on the effect of halogen- and carboxyl-substituted methyl and vinyl side-chains on rate of nitration. We had intended to complete the scheme and present the results together, but now it seems unnecessary further to delay our report, since by good fortune Bordwell and Rohde's results and ours are complementary.

In our first paper (*J.*, 1927, 2918) we pointed out that the effect of a substituent on aromatic reactivity in an electrophilic substitution such as nitration is more usefully described if we can

state how the substituent influences the rates at which the different nuclear positions are attacked, than if we know only the proportions in which the isomeric substitution products are formed. We instituted a general method of obtaining information concerning such effects on rate by what is called the competition method: a benzene derivative and benzene itself, in known proportions, and both in excess, are allowed to compete for a limited amount of a nitrating agent in the same homogeneous solution; and from the proportions in which the aromatic compounds are nitrated, the ratio of the specific rates at which they are attacked by the nitrating entity is computed. A group was said to activate or deactivate a given nuclear position with respect to nitration when its presence increased or decreased, as the case may be, the rate of nitration in that position.

Having examined a number of benzene derivatives by this method, we set up a framework of theory, which has been the main guide for subsequent investigations (Ingold, Lapworth, Rothstein, and Ward, *J.*, 1931, 1959; Ingold and Smith, *J.*, 1938, 905; Bird and Ingold, *J.*, 1938, 918). Orienting substituents were divided into four types:

Type :				
	(1) + I	(2) - I	(3) - I + T	(4) + I + T
Example :	Toluene	Ethyl benzoate	Chlorobenzene	Phenoxide ion
Effect :	$\left\{ \begin{array}{l} \textit{op}\text{-Orientation} \\ \text{Activation} \end{array} \right.$	$\left\{ \begin{array}{l} \textit{m}\text{-Orientation} \\ \text{Deactivation} \end{array} \right.$	$\left\{ \begin{array}{l} \text{As} \mid \textit{op}\text{-Orientation} \mid \text{As} \\ (2) \mid \text{Deactivation} \mid (4) \end{array} \right.$	$\left\{ \begin{array}{l} \textit{op}\text{-Orientation} \\ \text{Activation} \end{array} \right.$

In type 1, activation is general, extending even to the *m*-positions. In type 2, deactivation is similarly general. Type 3 comprises a range of cases, having a central section in which the rule associating *op*-orientation with activation and *m*-orientation with deactivation is broken through. Type 4 is characterised by intense *op*-activation.

The interpretation given was that the inductive effect ($\pm I$) is an activating or deactivating polarisation, present in the normal state of the aromatic molecule, a polarisation which therefore affects the *op*-positions directly, and the *m*-positions by relay; whilst the tautomeric effect ($+T$) is an activating polarisability effect, which is developed essentially in the course of reaction, and cannot therefore be relayed, being tied by the structures of the transition states to the *op*-positions exclusively. It is because the tautomeric effect arises from the demand of the reagent, because it is electromeric rather than mesomeric, that we have no need to take account of the other possible form of it ($-T$) in the (approximate) treatment of substitution by electrophilic reagents.

In substituents of type 3, the $-I$ -effect signifies a permanent electron-withdrawing polarisation, which deactivates, not only the *op*-positions, but also, though to a smaller extent, the *m*-positions. The $+T$ -effect represents an activating electron supply to the *op*-positions only, which is operative during reaction. In the central band of groups belonging to type 3, this activating effect is strong enough to raise the reactivity of the *op*-positions above that of the *m*-positions; but it is not strong enough to raise the reactivity of the *op*-positions above that of the nuclear positions in unsubstituted benzene; and thus the normal correlation between orientation and reactivity becomes abrogated. Hitherto this interesting situation could be exemplified only by means of the four halogenobenzenes (Bird and Ingold, *loc. cit.*): thus chlorobenzene is wholly *op*-orienting, but its rate of nitration, as measured by the competition method, is only 0.033 times that of benzene. Bordman and Rohde have now shown that cinnamic acid is a further example (*loc. cit.*): although it is exclusively *op*-orienting, its nitration rate, as given by the competition method, is only 0.111 times that of benzene. One can picture a wider separation between the origins of the two effects, $-I$ and $+T$, in the case of cinnamic acid than for chlorobenzene, where both must originate in the chlorine atom. In cinnamic acid the carboxyl group, permanently acting on the ring through the ethylenic double bond, deactivates all the nuclear positions; but, during reaction, the ethylenic bond itself will partly counteract this effect by supplying, to the *op*-positions only, the electrons required by the nitrating agent.

Today we understand that hyperconjugation will occasionally blur the clear distinctions which were at one time made between the inductive and tautomeric effects. For instance, toluene certainly exhibits a permanent polarisation which it is convenient to label $+I$. But neither toluene nor any benzyl compound can be completely free from a polarisability effect $+T$, originating in the CH-electrons of the side-chain. Where in some comparison such an effect is weak enough to be neglected, the substituent of the benzyl compound might still be

classified with type 1 or type 2, rather than with type 3 or type 4; but this would be recognised as a simplifying approximation. It is with such marginal cases, involving weak effects, that we are now concerned.

We have studied the nitration of ethyl phenylacetate, and of benzyl chloride, in acetic anhydride at 25°. We have also studied the nitration of ethyl phenylacetate at 45°, but not so fully, since the results appeared to be rather closely duplicating those obtained for 25°. The differences were too small to be interesting. For each substance the rate of nitration, relatively to that of benzene, was determined (k'/k) by competition between the substance and benzene. For each substance the proportions were determined in which the *o*-, *m*-, and *p*-nitro-isomerides are formed in nitration under similar conditions (but without the benzene). By combining these results, according to the principles set down in our first paper, we have calculated the partial rate factors (F) for the benzene derivatives, *i.e.*, the factors by which the original substituent increases or decreases the rate of nitration at each nuclear carbon atom. The principal results are in Table I.

Ethyl phenylacetate shows predominating *op*-orientation, accompanied by a weak activation of the *op*-positions; but the side chain has no significant effect on the reactivity of the *m*-positions. We interpret the last result as meaning that the permanent $+I$ -effect, which may be ascribed to the methyl group of toluene, is almost exactly neutralised, when one hydrogen atom is replaced by a carboxyl substituent, by the relayed $-I$ -effect of the latter; so that the complete side-chain in ethyl phenylacetate exerts only a negligibly small inductive polarisation. The principal polar effect which is left is the weak polarisability effect, $+T$, which arises through the hyperconjugation of the hydrogen electrons of the methylene group. It is this which produces the weak *op*-activation, and the consequent *op*-orientation. The side-chain of ethyl phenylacetate might be placed on the junction between types 1 and 2, but it would more correctly be regarded as being on the boundary between types 3 and 4, *i.e.*, on the horizontal line, and not far from the origin, in the annexed diagrammatic scheme.

The permanent polarisation of the ring by the carboxyl group is evidently much weaker in ethyl phenylacetate than in cinnamic acid, no doubt because of the absence from the former of an appropriate conjugation. On the other hand, the polarisability effect due to the methylene electrons of ethyl phenylacetate is much weaker than the polarisability effect originating in the ethylenic π -electrons of cinnamic acid, because, of course, hyperconjugation normally produces weaker polar effects than conjugation.

Representation of polar effects in aromatic substitution.

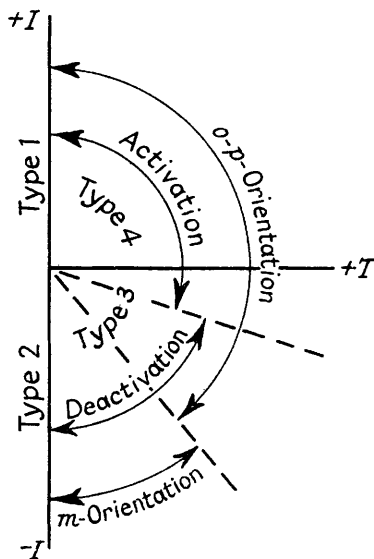


TABLE I.

Rates and Orientations for Nitration in Acetic Anhydride at 25°.

Substance.	Relative rate (k'/k).	Proportions of isomerides (%)*			Partial rate factors.		
		Ortho.	Meta.	Para.	$F_{ortho.}$	$F_{meta.}$	$F_{para.}$
$C_6H_5-CH_2-CO_2Et$	3.66	42.0	10.6	47.4	4.62	1.16	10.41
$C_6H_5-CH_2Cl$	0.302	32.0	15.5	52.5	0.290	0.140	0.951

* The proportion of ethyl *m*-nitrophenylacetate here recorded (10.6%) may be compared with the value (9.4%) derived by Baker and Ingold for the nitration of ethyl phenylacetate by nitric acid in the absence of acetic anhydride (*J.*, 1927, 832).

Our value for the proportion of *m*-nitrobenzyl chloride (15.5%) formed by nitration of benzyl chloride differs largely from the figure (4.2%) deduced by Holleman from results of thermal analysis (*Rec. Trav. chim.*, 1914, **33**, 1); and it differs appreciably from the value (12.0%) obtained by Flürscheim and Holmes by an oxidation method (*J.*, 1928, 1611). The cause of Holleman's low result is not known, though the result has always seemed anomalous. Flürscheim and Holmes record a single nitration experiment without controls, and probably would not claim high accuracy for the recorded result.

In the case of benzyl chloride the predominating *op*-orientation is accompanied by an incomplete deactivation of the aromatic nucleus: the deactivating effect is most pronounced in

the *m*-positions, weaker in the *o*-positions, and insignificant in the *p*-position. We interpret the effect on the *m*-positions as meaning that the permanent $+I$ -effect of the methyl group of toluene is over-compensated, when one hydrogen atom is replaced by chlorine, by the relayed $-I$ -effect of the latter; so that an appreciable inductive polarisation, $-I$, is exerted by the complete side-chain of benzyl chloride. The nuclear deactivation due to this cause is opposed in the *op*-positions, but not in the *m*-position, by an activating polarisability effect, $+T$, originating in the methylene electrons. This counter-effect depends on hyperconjugation, and is expected to be somewhat weak. Our results show that it can compensate the $-I$ -effect sufficiently to give a predominating *op*-orientation, but that it is just not quite strong enough to produce *op*-activation.* Evidently the side-chain of benzyl chloride falls into the central series of groups belonging to type 3, *i.e.*, those which disobey the usual rule correlating orientation with reactivity. In our diagram we should place the group not very far from the origin, and quite near to the upper of the two sloping lines by which the area assigned to groups of type 3 is divided.

The polarisation of the ring by the chlorine atom is clearly much smaller in benzyl chloride than in chlorobenzene, doubtless because the effect has to be relayed through the methylene group in the former compound. On the other hand, the polarisability effect of the methylene electrons of benzyl chloride is likewise much smaller than that of the unshared halogen electrons of chlorobenzene; for the former effect depends on hyperconjugation, and the latter on conjugation. On the whole, the polar effects of benzyl chloride bear to those of chlorobenzene a relation similar to that subsisting between the polar effects of ethyl phenylacetate and those of cinnamic acid.†

EXPERIMENTAL.

Nitration of Benzyl Chloride.

Method and Control Experiments.—The materials employed were purified by standard methods. Benzyl chloride was nitrated in acetic anhydride solution at 25°, both in the presence of benzene and alone. In the former case, varying quantities of nitric acid, always in deficit, were employed, and the product after isolation in the usual way was distilled (Dufton column) to remove benzene. The residual mixture of nitrobenzene, benzyl chloride, and nitrobenzyl chlorides was distilled under reduced pressure. Control experiments on the isolation of nitrobenzene, benzyl chloride, nitrobenzyl chlorides, and mixtures of these, from artificial mixtures equivalent to the diluted nitration solution, showed that the small experimental loss was mechanical and not selective.

Theoretically the above mixture can be analysed (apart from the determination of individual isomerides) by determination of any two elements (as Cl and N), but applications to artificial mixtures showed that methods of this type gave unsatisfactory results owing to the large magnification undergone by the experimental errors during the calculations. The method which was ultimately found to be the most satisfactory was as follows. Chlorine was first determined. The mixture (1 part) was treated with 10% aqueous potassium carbonate (100 parts), and oxidised by gradual addition of very slightly more than the theoretical amount of a 3% potassium permanganate solution which also contained 10% of potassium carbonate (Ingold and Ingold, *J.*, 1928, 2261), the object of the carbonate being to facilitate the oxidation of benzyl chlorides by their prior hydrolysis to benzyl alcohols. From the acid oxidation products, isolated as usual, nitrobenzene was removed, and the benzoic, and total nitrobenzoic, acids determined by volatilisation of the former. As a control, benzyl chloride and the three nitrobenzyl chlorides were separately oxidised by the same method; each gave the corresponding acid in $93 \pm 1\%$ yield, wherefore the oxidation is not appreciably selective. The whole process was then repeatedly checked on artificial mixtures of benzyl chloride, nitrobenzene, and the three nitrobenzyl chlorides, and shown to yield satisfactory results; thus (control expt. 1) a mixture of *o*-nitrobenzyl chloride 3.65%, the *m*-isomeride 0.40%, the *p*-isomeride 5.04% (total 9.1%), nitrobenzene 19.5%, and benzyl chloride 71.4%, gave, on analysis, nitrobenzyl chlorides 9.4%, nitrobenzene 19.5%, and benzyl chloride 71.1% (errors within 0.3%). The internal consistency of the results tabulated below shows that the method is equally satisfactory in its application to the mixtures obtained by nitration.

The calculation of the quantities of benzyl chloride and benzene nitrated involves the following considerations. In view of the non-selectivity of the oxidation (above), the ratio of the mols. of benzoic acid to those of nitrobenzoic acids is equal to the ratio of the mols. of benzyl chloride to the mols. of nitrobenzyl chlorides. The chlorine content depends essentially on the sum of the quantities of benzyl and nitrobenzyl chlorides, whence these are individually calculable, and the nitrobenzene follows by difference. From the high yield and non-selectivity of the process of isolation of the mixture of benzyl and nitrobenzyl chlorides and nitrobenzene (above) it follows that the determined proportions of these are the proportions in which they were present before isolation; but since unchanged benzene, owing to its volatility, cannot conveniently be isolated in satisfactory yield, it is necessary to know the yield of the mixture of constituents isolated. For this purpose the ratio of the sum of the molecules of benzyl

* Steric hindrance may retard *ortho*-substitution, but it does not seem profitable at present to attempt an assessment of that factor in relation to the observed differences of reactivity between the *o*- and *p*-positions of either of the compounds treated in this paper.

† Our original plan for this research included the examination of ω -chlorostyrene: the above comparison would have been closer if we could have referred to this substance, instead of the most nearly analogous available example, that of chlorobenzene.

and nitrobenzyl chlorides obtained to the molecules of benzyl chloride used is taken to represent the yield of the whole mixture including the nitrobenzene, this assumption being again based on the established absence of selection during isolation.

The determination of the proportions of the isomeric nitrobenzyl chlorides obtained by nitration was carried out as described by Baker and Ingold (*J.*, 1926, 2462) except that the method of oxidation was that mentioned above. The results were controlled in two ways, namely, (1) by oxidation of individual nitrobenzyl chlorides followed by application of the analytical methods to artificial mixtures of nitrobenzoic acids, and (2) by application of the complete process to artificial mixtures of the nitrobenzyl chlorides.

Results.—The relationship connecting the molecular ratio (R) in which two aromatic substances, x_0 and y_0 mols. of which were originally present, are simultaneously nitrated by a deficit of nitric acid, with the ratio of the velocity coefficients, was given in Part I as

$$\frac{k_y}{k_x} = \log \left\{ 1 - \frac{z_0}{y_0} \left(\frac{R}{1+R} \right) \right\} / \log \left\{ 1 - \frac{z_0}{x_0} \left(\frac{1}{1+R} \right) \right\}$$

where $R = (y_0 - y_\infty)/(x_0 - x_\infty)$ and $z_0 = x_0 + y_0 - x_\infty - y_\infty$. Since this is based on the assumption that both reactions follow the same mechanism, and since the data representing nuclear activation depend *inter alia* on the accuracy of this supposition, the present experiments were carried out to test the matter. As z_0 , the amount of nitric acid used, tends towards zero, k_y/k_x tends to equality with R ; otherwise, k_y/k_x always has a value on the side of R remote from unity. The meaning of this property is, of course, that when z_0 is small, z is the sole effective concentration variable, whence the velocities will bear, at every moment, a constant ratio, which is that in which the products are formed; whereas, when $0 < z_0 < x_0 + y_0$ the slower reaction can partly catch up the other during the tail-period of the latter; and when $z_0 = x_0 + y_0$ the overtaking would be complete excepting for any disturbance due to dinitration. The test of the expression is therefore the constancy of k_y/k_x when a progressive variation of z_0 causes a drift in the value of R . That this test is satisfied is shown by the last three columns of Table II, in which y relates to benzyl chloride and x to benzene. The quantities originally present,

TABLE II.

Simultaneous Nitration of Benzyl Chloride and Benzene with Different Proportions of Nitric Acid in Acetic Anhydride at 25°.

No.	Yield (%).	$x_0 - x_\infty$.	$y_0 - y_\infty$.	z_0 .	R .	k_y/k_x .
1	90.7	0.172	0.0560	0.228	0.326	0.305
2	90.0	0.173	0.0555	0.228	0.321	0.300
3	87.0	0.235	0.0795	0.315	0.337	0.307
4	93.1	0.257	0.0855	0.343	0.332	0.301
5	92.2	0.307	0.104	0.411	0.339	0.300
6	91.1	0.376	0.132	0.508	0.351	0.301
						Mean 0.302

x_0 and y_0 (for actual weights see Table III), were equivalent to the necessary order of accuracy, and are in each case taken as 1.000 mol. The yields recorded in the second column are those of the mixture of unchanged benzyl chloride and nitration products isolated (see above). The actual weights and analytical data necessary for the determination of $x_0 - x_\infty$ and $y_0 - y_\infty$ are given in Table III.

TABLE III.

Data for the Calculations given in Table II.

No.	Benzyl chloride (g.).	Benzene (g.).	Distilled product (g.).	Cl-determinations (%).	Mean Cl (%).	Mixture oxidised (g.).	Benzoic acid (g.).	Nitrobenzoic acids (g.).
1	15.10	9.31	16.269	{23.44, 23.77}	23.65	1.3317	1.1420	0.0925
2	15.05	9.28	16.060	{23.53, 23.87}	23.59	1.0803	0.7898	0.0611
3	13.82	8.52	15.112	{22.15, 22.43}	22.29	1.0226	0.7876	0.0940
4	13.35	8.23	15.90	{22.01, 21.95}	21.93	1.5218	0.9540	0.1219
5	12.85	7.92	15.79	{21.87, 21.89}	21.00	0.9924	0.5827	0.0934
6	13.60	8.39	17.49	{20.86, 21.13}	19.87	1.8591	1.0010	0.2102
				{19.85, 19.88}				
				{19.77, 20.19}				

Thus the effect of doubling z_0 is to cause the observed ratio R to increase by about 10%, whilst the value of k_y/k_x calculated from the formula remains constant to $\pm 1\%$. (The *mean* value of k_y/k_x is given as k'/k in the introduction.)

The proportions of the isomerides formed when benzyl chloride is nitrated as above except for the absence of benzene were determined by methods which have been employed previously (*e.g.*, *J.*, 1926, 2462; 1927, 813; 1928, 2249). The results are recorded in Table IV, and the experimental data necessary for the correction of the mean values (A), by the two methods (1 and 2) mentioned above, are given in Table V. This table also contains the two corresponding sets of corrected mean values (A_1 and

A_2); these ought to be identical, and their divergence indicates the order of the error. The mean values (A_{12}) of the two sets of corrected means are in the bottom line, and these are the values which have been employed, in conjunction with the data of Table II, to calculate the partial rate factors recorded in Table I.

TABLE IV.

Nitration of Benzyl Chloride Alone in Acetic Anhydride at 25°.

No.	Yield of distilled mononitro-derivs. (%)	Found Cl (theory 20.8%). (%)	Yield of acids by oxidation (%)	Meta (%)	Para (%)
1	87	21.0	93.0	14.1	50.3
2	86	21.0	93.0	14.4	51.3
3	86	21.0	94.3	14.0	51.3
4	89	20.9	93.6	14.4	50.7
			Means 14.2	50.9	(A)

TABLE V.

Data for Correcting the Results in Table IV.

	Ortho (%)	Meta (%)	Para (%)	Method of correction.
Composition of artificial mixture of acids	35.0	15.0	50.0	(1)
Composition found (i)	—	13.0	49.2	
Composition found (ii)	—	13.4	49.6	
Composition found (mean)	—	13.2	49.4	
Corrections to (A) for oxidation (see p. 578)	—	± 0.0	± 0.0	
Corrections to (A) for analysis of acids	—	+ 1.8	+ 0.6	
Means (A) corr. by (1) (o- by difference)	32.4	16.0	51.5	(A ₁)
Composition of artificial mixture (a) of chlorides	25.0	16.7	58.3	(2)
Composition of acids from (a): Found (ia)	—	15.9	55.8	
Composition of acids from (a): Found (iia)	—	16.0	—	
Composition of artificial mixture (b) of chlorides	32.3	14.6	53.1	
Composition of acids from (b): Found (ib)	—	13.9	50.5	
Corrections to (A) for oxidation and analysis	—	+ 0.8	+ 2.5	
Means (A) corr. by (2) (o- by difference)	31.6	15.0	53.4	(A ₂)
Means of corr. means A ₁ and A ₂	32.0	15.5	52.5	(A ₁₂)

Nitration of Ethyl Phenylacetate.

Method and Control Experiments.—The method of nitration, the control experiments, and the methods of analysis and calculation, were generally similar to those employed for benzyl chloride, and therefore only the more important differences are mentioned.

The nitrations, with and without benzene, were carried out both at 25° and at 45°; 24 hours were allowed to ensure completion.

For the analysis of the mixtures of phenyl- and nitrophenyl-acetic esters and nitrobenzene, isolated by distillation, determinations of OEt by saponification replaced the Cl-determinations of the experiments on benzyl chloride, and the determination of phenylacetic acid in the acidic hydrolysis products replaced the determination of benzoic acid in the acidic oxidation products in the other series. After saponification, the nitrobenzene was removed by extraction with ether from alkaline solution; the mixture of phenyl- and nitrophenyl-acetic acids was then quantitatively reduced with titanous chloride, and the phenylacetic acid removed from the acid solution. In one experiment, the results were checked by oxidation to benzoic and nitrobenzoic acids and then proceeding as in the experiments on benzyl chloride.

TABLE VI.

Simultaneous Nitration of Ethyl Phenylacetate and Benzene in Acetic Anhydride at 25° and 45°.

No.	Temp.	Yield (%)	$x_0 - x_\infty$	$y_0 - y_\infty$	z_0	R.	Mean R.	k_y/k_x	Mean k_y/k_x
1	25°	92.1	0.139	0.418	0.557	3.01	3.01	3.64	3.65
2	25	94.5	0.142	0.421	0.563	2.97	3.03	3.60	3.66
			0.141	0.422		3.00		3.63	
			0.137*	0.426*		3.11		3.75	
3	25	98.9	0.160	0.476	0.636	2.97	2.97	3.68	3.68
								Mean 3.66	
4	45	87.4	0.129	0.383	0.512	2.98	2.97	3.52	3.52
			0.129	0.382		2.97		3.53	

* By oxidation.

TABLE VII.
Data for the Calculations in Table VI.

No.	Ethyl phenylacetate (g.).	Benzene (g.).	Distilled product (g.).	OEt determinations (%).	Mean OEt (%).	Acids reduced (g.).	Phenylacetic acid (g.).	Nitrophenylacetic acid (g.).
1	10.11	4.81	11.344	{ 22.23 22.62, 22.79 }	22.55	1.3397	0.6872	0.6525
2	11.15	5.30	12.857	22.25, 22.75	22.50	1.5305 1.3527 1.8310 *	0.7786 0.6838 0.5202 †	0.7519 0.6689 0.5462 ‡
3	10.25	4.88	12.630	22.11, 21.85	21.98	1.2351	0.5612	0.6739
[45°] 4	10.82	5.15	11.396	{ 23.32 22.71, 22.67 }	22.90	1.3060 1.2450	0.7207 0.6893	0.5853 0.5557

* Acids oxidised. † Benzoic acid. ‡ Nitrobenzoic acids.

The nitrations of ethyl phenylacetate alone were carried out in exactly the same way, except for the absence of the benzene and the use of sufficient nitric acid to complete the nitration. The distilled mononitration products (pale-yellow and semi-solid) were treated just as were those obtained from benzyl chloride, except that the results were corrected by method (2) only. Ethyl *o*-nitrophenylacetate was prepared by Reissert and Scherk's method (*Ber.*, 1898, **31**, 395), ethyl *m*-nitrophenylacetate (Found: C, 56.8; H, 5.1. C₁₀H₁₁O₄N requires C, 57.4; H, 5.2%) by a similar process, and the *p*-isomeride by Maxwell's method (*Ber.*, 1879, **12**, 1767).

Results.—The symbols in Table VI have the same meaning as in Table II, excepting that γ now relates to ethyl phenylacetate. The values marked with an asterisk were obtained by the oxidation method (see above), and may be less exact than the others, since the complete set of controls (compare expts. on benzyl chloride) were not performed: the object of the experiment was to provide a rough check only. The results of the experiment at 45° are not utilised in the introduction since they are regarded as insufficiently established by the single set of data given in the Table. Table VII records the weights and analytical results by means of which the values of $x_0 - x_\infty$ and $y_0 - y_\infty$ given in Table VI have been calculated. As before, the initial quantities of ethyl phenylacetate and benzene were equivalent, and x_0 and y_0 are taken as unity.

TABLE VIII.
Nitration of Ethyl Phenylacetate Alone in Acetic Anhydride.

No.	Temp.	Yield of distilled nitration product (%).	C (%) (calc., 57.4%).	H (%) (calc., 5.2%).	Yield of acids by oxidation (%).	Meta (%).	Para (%).
1	25	89	56.4	5.2	93.6	8.3	49.9
2	25	92	57.2	5.3	92.1	9.0	48.9
3	25	90	57.3	5.2	93.3	9.1	49.1
			57.0	5.3	94.0	8.9	49.5
					Means (B)	8.8	49.3
4	45	97	56.4	5.0	81	10.5	47.6
			56.6	5.1	89	10.2	49.8
					Means (B')	10.4	48.7

TABLE IX.
Data for Correcting the Results in Table VIII.

	Ortho (%).	Meta (%).	Para (%).
Composition artificial mixture (a) of nitrophenylacetic esters...	42.7	11.2	46.1
Composition artificial mixture (b) of nitrophenylacetic esters...	44.1	11.7	44.2
Composition artificial mixture (c) of nitrophenylacetic esters...	40.2	10.6	49.2
Found for mixture (a)	—	9.6	53.4
Found for mixture (b)	—	9.4	46.6
Found for mixture (c)	—	9.0	50.4
Corrections to be applied to means (B and B')	—	+ 1.8	- 1.9
Means (B) corrected (B ₁ ; temp. 25°) (o- by difference)	42.0	10.6	47.4
Means (B') corrected (B ₁ '; temp. 45°) (o- by difference)	41.0	12.2	46.8

The proportions in which the isomerides are formed when ethyl phenylacetate is nitrated as above excepting for the absence of benzene are recorded in Table VIII, with yields and analytical figures. The data required for the correction of the means values (B and B') given in Table VIII, together with the corresponding corrected means (B₁ and B₁'), are in Table IX. The corrected means (B₁) are those which have been used, with the mean given in Table VIII, to calculate the values recorded in Table I.