CCX.—*The Laws of Aromatic Substitution. Part VIII.**

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ACCORDING to the theory evolved by one of us, reactivity is governed by three *internal* factors: the *amount* of affinity available at the reacting atom (quantitative factor *q*); the *nature* of this affinity (polar factor *p*); and the degree of spatial obstruction (steric factor *s*). In so far as the problem of substitution in the benzene ring is concerned, the steric effect on positions 3 and 4 exercised by a substituent in position 1 may be neglected. On the other hand, its polar effects on positions 3 and 4 will generally not be the same, but until recently empirical evidence appeared to indicate that the *difference* of the polar effects on the nuclear carbon atoms in positions 3 and 4 was not large enough to produce an appreciable modification of their relative reactivities as determined by the quantitative effect.

On the other hand, Robinson has repeatedly stated that he regards the polar effect (which, according to his theory, would be an electrostatic effect) as one of the chief factors governing aromatic substitution. In Part V (J., 1926, 1562) we have shown that Robinson's view [but not the electrostatic mechanism on which it is based, against which we have adduced arguments (J., 1926, 1566) which have not been refuted] is justified when the quantitative effect is not very pronounced and when, at the same time, the polar effect is at its maximum through proceeding from an actual, undisputed, electrical charge, *viz.*, the charge on an electrolytic ion.† When, however, the polar effect originates in an accumulation

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* In Part VII (this vol., p. 453), two important *errata* in the proofs have escaped our attention: On p. 466, section V, first line, "bromomalonic" should read "bromonitromalonic"; and on p. 474, lines 5 to 3 from the bottom, a sentence describing the recovery of *pure* *m*-bromobenzoic acid from nitration 13 has been transposed: it should read "... 0·160 g. of *m*-bromobenzoic acid (m. p. 143—145°; 152·5—153° on further recrystallisation; mixed m. p.) and 0·045 g. melting at 148—156° (nitrobromo-acids. . . ."

† The first recognition of the effect of electrolytic dissociation on aromatic substitution, and its application to benzoic acid and salts of the benzylammonium series, are to be found in a publication by one of us in *Chem. and Ind.*, 1926, p. 43, issued on Jan. 15th, 1926. Since that date, papers by Soper and Smith and by Ingold and co-workers have been submitted in which the effect of electrolytic dissociation on aromatic substitution (*e.g.*, in phenols) has been further discussed.

of *uncharged* groups of strongly polar nature, our early experiments on the nitration of phenylbromocyanonitromethane appeared to indicate that it can be neglected. Since, however, substitution in this compound, as we now know it to be constituted (see Part VII), is favoured in one and the same position by *both* effects, it appeared desirable to examine the behaviour of substances containing lateral substituents the polar effect of which—if it preponderated—would cause substitution to occur mainly in positions other than those required by the quantitative factor.

Hitherto no examination of the directive effect has been made with a toluene derivative having all its methyl-hydrogen atoms replaced by such " negative " substituents as would, if directly attached to the nucleus, cause preponderating *m*-substitution and which, when attached to the α-carbon atom, should accordingly—if the quantitative (alternating) effect alone were considered—have an *o*-*p*-directive influence. Indeed, no such compounds appear to have been prepared hitherto, with the exception of tribenzoylphenylmethane (Meisenheimer and Weibezahn, *Ber.*, 1921, **54**, 3195)—an unsuitable material owing to the presence of several phenyl groups. We have succeeded in obtaining three such compounds. The preparation and nitration of one of them—*ethyl phenylmethanetricarboxylate* [*ethyl toluene-ααα-tricarboxylate*, $\mathrm{CPh(CO_2Et)_3}$]—are described below. For comparison, compounds have also been examined in which some or all of the lateral substituents are groups which in direct attachment to the nucleus would be *o*-*p*-directing. In the present communication we submit quantitative determinations, by our new method (compare Part VI), of the directive effects in the complete series
$\mathrm{CH_2PhCl}$, $\mathrm{CH_2Ph{\cdot}CO_2Et}$;
$\mathrm{CHPhCl_2}$, $\mathrm{CHPhCl{\cdot}CO_2Et}$, $\mathrm{CHPh(CO_2Et)_2}$;
$\mathrm{CPhCl_3}$, $\mathrm{CPhCl_2{\cdot}CO_2Et}$, $\mathrm{CPhCl(CO_2Et)_2}$, $\mathrm{CPh(CO_2Et)_3}$;
together with two bromo-compounds, $\mathrm{CH_2PhBr}$ and $\mathrm{CPhBr(CO_2Et)_2}$.

The theoretical conclusions suggested by these experiments will be discussed in detail in Part IX, in conjunction with those indicated by a further series of investigations. Meanwhile it may suffice to summarise the following general points :

1. Our results with ethyl phenylmethanetricarboxylate constitute the first case of preponderating *m*-nitration in the exclusive presence, at the α-carbon atom, of such substituents as would be *m*-directing if directly attached to the nucleus.*

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* Phenylnitromethane, which has long been known to be preponderatingly *m*-directing, might be supposed to come under this definition. But in Part X we shall adduce support for its formulation as an equilibrium, $\mathrm{PhCH_2{\cdot}NO_2} \rightleftharpoons \underset{\diagdown\mathrm{O}\diagup}{\mathrm{PhCH{-}NOH}}$, in which the bridge form must be regarded as responsible for most of the *m*-nitration.

2. Where the quantitative factor is not very pronounced—*e.g.*, at an α-carbon which neither forms part of an ethylenic or acetylenic group nor is linked to substituents possessing a *much* higher or lower affinity demand than hydrogen—and where at the same time the polar factor is very pronounced—*e.g.*, in the case of an α-carbon atom directly linked to an atom charged through electrolytic dissociation, or to several substituents of distinct and similar polarity—there the quantitative factor may be overborne by the polar effect.

3. But even in such extreme cases the quantitative factor can be distinctly traced. For instance, the electrolytic dissociation constants of aromatic acids and bases, substituted in the *m*- or *p*-positions by chlorine on the one hand, by carbethoxyl on the other, show that the polar effect transmitted from these positions is *greater* with carbethoxyl than with chlorine. The *m*-directive effect, however, as evidenced by the results given below, is *less* for carbethoxyl than for chlorine (with the exception of one case where it is equal within the experimental error). Since this quantitative factor—which, as will be shown in Part IX, is much more obvious where the postulated affinity demand is very high and polarity is less pronounced—appears to be capable only of a non-electronic interpretation (at any rate, when it is transmitted through a "single" bond), a non-electronic interpretation appears to be also involved for the polar effect.

4. We interpret * the polar effect as an influence of the *nature* of the chemical affinity of one atom on the *nature* of the chemical affinity of other atoms in the molecule. We regard chemical affinity as the resultant of a distinct chemical attractive force component (one of four different kinds of forces inherent in an atom, the other three being electrostatic, magnetic and gravitational) and an electropolar component. In a free atom both these components will emanate more or less evenly from the whole surface of the atom. Combination of atoms must produce a redistribution of these components along the atomic surface, resulting in an equilibrium; the density of the lines of force of components which attract each other being increased round the point of closest approach between the atoms, the reverse occurring in the case of components which repel each other. Round the point of closest approach, therefore, an increase of density must take place for the lines of force of the chemical component and for electropolar components of opposed sign; for electropolar components of the same sign there must result a decrease of density round the point of closest approach between the atoms, and an increase of density at remote points of

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* This should be read in conjunction with Part V (*loc. cit.*), pp. 1563—1564.

the surfaces of the atoms. In this way, the polar component, by a process of inductive transmission (see Flürscheim, *J. pr. Chem.*, 1907, **76**, 189, for comparison with electrostatic induction)—*without the participation of any electrons*—is propagated throughout a chain. This polar effect gradually falls off with the number of intervening atoms (a necessary consequence of the establishment of an equilibrium), and is transmitted from one atom to another (as postulated by one of us in previous papers) to an extent which is a direct function of the affinity content of (*i.e.*, the number of lines of force participating in) the bond between them.

According to our theory of aromatic substitution, this polar effect is, in an overwhelming majority of cases, transmitted to the *p*-position to a greater extent than to the *m*-position. This is due to the *direct* affinity exchange between *p*-atoms postulated by Werner's benzene formula (*Vierteljahrschr. Züricher Naturforsch. Ges.*, 1891, **36**, 1). Only where this residual affinity exchange has been considerably reduced is the reverse to be expected. The exact extent to which such reduction must take place in order to obtain a greater polarity transmission to the *m*-position is an empirical question; present indications suggest that to bring about this result a substituent with a pronounced affinity demand must be present at *each* end of the residual *p*-bond; in such cases (for instance in quinol) the molecule is more or less in a state approximating the quinonoid (compare Flürscheim, *J. pr. Chem.*, 1907, **76**, 203). At any rate, all compounds of the class examined below are well within this border line. At all their nuclear carbon atoms, electropolar components of the same sign as those of the lateral substituents are shifted in a direction away from the bonds leading to these substituents, and this shift is greater at the *p*- than at the *m*-carbon atoms. A nitric acid molecule, when approaching these atoms, will find at the accessible (unoccupied) portion of their surfaces more free affinity in the *p*- than in the *m*-position, but in this free affinity the electropolar component—of the same sign as that in the atoms constituting the nitro-group—will predominate more at the *p*- than at the *m*-carbon atom. The result is substitution at *either* atom, in a proportion determined by the relative preponderance of the two conflicting factors.

5. The fact remains, however, that the *existence* of a polar effect on the relative degree of *m*- and *p*-substitution was first postulated by Robinson. For *o*-substitution it had been postulated by one of us long ago.

Table I contains the results calculated from our experiments.

The numbers of the nitrations in Table I correspond to the numbers in Table II. The ratio $m/o + p$ has been adopted as the

TABLE I.*

No.	Compound nitrated.	Medium.	Nitration products (mols. %).			Hydrolysis during nitration (% of total halogen).	% Ratio, $m/o + p$.	Results previously recorded.		
			Unsubs.	$o + p$.	m.			m, % of total substn.	$m/o + p$, %.	Authors.
1	CH_2PhCl	HNO_3	0	88·4	11·6	3·2	13·1	—	—	—
			0	88·4	11·6					
2	CH_2PhCl	HNO_3 + Ac_2O	3·2	85·2	11·6	0·14	13·6	4·2	4·4	Holleman, *Rec. trav. chim.*, 1914, **33**, 1.
3	$CH_2Ph{\cdot}CO_2Et$	HNO_3	0	87·9	12·1	0	13·6	9	9·9	Baker and Ingold, J., 1927, 832.
4	$CH_2Ph{\cdot}CO_2Et$	HNO_3	0	88·2	11·8	0				
5	$CHPhCl_2$	HNO_3 + Ac_2O	3·2	63·5	33·3	1·0	52·25	33·8	51·05	Holleman, *loc. cit.*
			4·2	63·0	32·8					
6	$CHPhCl{\cdot}CO_2Et$	,,	51·3	33·9	14·8	0·28	43·35	—	—	—
			55·4	31·2	13·4					
7	$CHPh(CO_2Et)_2$	HNO_3	0	74·8	25·2	0	34·05	20	25	Baker and Ingold, *loc. cit.*
			0	74·4	25·6	0				
8	$CPhCl_3$	HNO_3 + Ac_2O	21·6	30·1	48·3	1·35	160·1	64·5	181·7	Holleman, *loc. cit.*
			21·2	30·2	48·6					
9	$CPhCl_2{\cdot}CO_2Et$	,,	46·9	20·6	32·5	2·15	156·8	—	—	—
			45·8	21·1	32·9					
10	$CPhCl(CO_2Et)_2$	,,	7·5	39·5	53·0	2·45	132·6	—	—	—
			6·9	40·3	52·8					
11	$CPh(CO_2Et)_3$	HNO_3	0	43·5	56·5	0	130·1	—	—	—
			0	43·4	56·6					
12	CH_2PhBr	HNO_3 + Ac_2O	4·7	88·7	6·6	0·38	7·45	—	—	—
			5·3	88·1	6·6					
13	$CPhBr(CO_2Et)_2$	HNO_3	0	60·4	39·6	3·2	65·05	—	—	—
			0	60·8	39·2					

* This table was communicated at the meeting of the Society on March 29th (see *Chem. and Ind.*, 1928, p. 369). Subsequently, Ingold and Shaw (this vol., p. 1278, footnote) obtained for benzyl chloride a *m*-proportion of 16%, which differs from our value (11·6%) by far more than the normal error of our method.

standard of comparison because it immediately indicates the relative degree of nitration in these positions, whereas the usual ratio $m/o + p + m$ does not. With the exception of benzal chloride, agreement with earlier results in the five cases where such were available is moderate to poor.

EXPERIMENTAL.

Methods.—(a) *Nitration.* Compounds containing no mobile halogen were nitrated in Kahlbaum's nitric acid, *d* 1·52. For the nitration of compounds containing mobile halogen, a mixture of this acid and acetic anhydride was used (compare Holleman, *Rec. trav. chim.*, 1914, **33**, 1). Benzyl chloride was nitrated both ways (see Nos. 1 and 2), and the results show that these two nitrating media yield values which are identical within the experimental error. Hydrolysed halogen was determined by treating the whole of the diluted and repeatedly extracted spent acid with excess of silver nitrate. The carbethoxy-group remained unaffected during nitration, apart from traces of hydrolysis which were determined by extraction of the products of nitration with bicarbonate. The yields on nitration, allowing for the determined amounts of unnitrated material, varied between 95·5% and 100% of the theoretical. In one case—benzyl chloride in nitric acid alone—the yield was calculated to be 101·8% of the theoretical for complete mononitration. This indication of the presence of a small quantity of dinitro-product was not contradicted by the result of the reduction and bromination of the corresponding acids, since the melting point of the tribromoaniline obtained was slightly low, which it would be if the base were contaminated with a little tribromo-*m*-phenylenediamine.

(b) *Determination of the isomerides.* Oxidation of the products of nitration to the acids was carried out according to the method described in Part V (*loc. cit.*), alkali being, however, added in proportions calculated for each compound so as fully to neutralise any acids produced from its side-chain by oxidation. The acids were then reduced, brominated, etc., as described in Part VI.

Preparation of the Substances used.—(a) *Ethyl phenylmethanetricarboxylate.* 25 G. of ethyl phenylmalonate were added, 2 g. at a time, to 100 c.c. of sodium-dried ether containing 2·5 g. of sodium wire. As much as possible of the ether was then decanted from the sodium salt which had separated, and a further 80 c.c. of dry ether and 15 c.c. of ethyl chloroformate were added with good water-cooling. The sodium salt disappeared and a gelatinous mass took its place. The mass was shaken for 7 hours (although the reaction appeared to be over at the end of 1 hour), and water then added. The ethereal layer, when dried and evaporated, left a residue which distilled as a colourless, viscous oil, b. p. 154—155°/1·5 mm. (Found: C, 62·3, 62·4; H, 6·6, 6·65. $C_{16}H_{20}O_6$ requires C, 62·3; H, 6·5%).

(b) *Ethyl phenylchloromalonate.* 10 G. of ethyl phenylmalonate, dissolved in 30 c.c. of carbon tetrachloride, were saturated at 0° with dry chlorine gas and left for 16 hours. After removal of the solvent, the residue was distilled under reduced pressure, giving 2 g. of a fraction, b. p. 70—140°, and 7 g. of the desired *ester* as a colourless, fluid oil, b. p. 143—144°/2—1·5 mm. [Found: Cl (Carius), 13·0. $C_{13}H_{15}O_4Cl$ requires Cl, 13·1%].

(c) *Substances already known.* The remaining compounds used had the following distillation points: benzyl chloride, 177—177·5°; benzyl bromide, 197—198°; benzal chloride, 203—203·5°; benzotrichloride, 213—213·5°; ethyl phenyldichloroacetate, 258—259°; ethyl phenylbromomalonate, 156—157°/2 mm.; ethyl phenylacetate, 226—227°; ethyl phenylchloroacetate, 108—109°/2 mm.; and ethyl phenylmalonate, 151°/8 mm., 140°/3 mm., 135°/1—1·5 mm.

Nitrations.—The conditions and actual weighings in connexion with all the nitrations included in Table I are to be found in Table II. Besides these, nitrations of benzyl bromide and benzal chloride in nitric acid (*d* 1·52) *alone* were carried out, but were found to lead to a very high degree of hydrolysis, with a large increase in *m*-nitration due to the initial formation of benzaldehyde in the latter case and, presumably, of benzyl nitrate in the former. For instance, 10·3 g. of benzyl bromide added within 2 hours to 83 g. of nitric acid (*d* 1·52) and then poured on ice, etc., yielded 12·244 g. plus 0·030 g. of bicarbonate-soluble matter. The spent acid, freed from organic material by repeated extraction with ether, gave with silver nitrate no less than 4·99 g. of silver bromide. 1 G. of the acids obtained by oxidation of the product of nitration yielded 0·007 g. of benzoic acid, 1·390 g. of tribromoaniline, and 0·610 g. of tribromoaminobenzoic acid, corresponding to a ratio $m/p + o$ of 38·6%, compared with the true ratio of 7·45% in the absence of hydrolysis (see Table I).

The standard method of determining the isomerides in the nitration product was only departed from (*a*) in the case of benzotrichloride, where, instead of oxidation, hydrolysis was effected (by Holleman's method) by running 1 part (by weight) of the nitration product into 70 parts (by volume) of boiling 20% hydrochloric acid within 1 hour and boiling for 2 hours; and (*b*) in the case of ethyl phenylmethanetricarboxylate, where, for the first time within our experience with such toluene derivatives, permanganate failed as an oxidant—though even here it had to be resorted to at a later

TABLE II.

										Reduction and bromination of acids.					
											Found (g.).				
No.	Substance nitrated.	G.	Nitrating agent.	Temp.	Duration of addition and standing.	Yield (g.).	$KHCO_3$-soluble (g.).	Oxidised (g.).	Yield of acids (g.).	Reduced (g.).	Benzoic acid.	Tri-bromo-aniline.	Tri-bromo-amino-benzoic acid.	Silver halide from spent acid (g.).	Appearance of nitration product.
1	CH_2PhCl	11·00	88 g. HNO_3	−10° to −8°	2 hrs.; then 15′ at −10°, 15′ at room t.	15·143	+0·053	4·751 2·824	1·730 p- (235—236°) +1·568 0·930 p- (234—235°) +0·849	1·000 0·500	0·003 0·004	1·503 0·740	0·546 0·270	0·401	Semi-solid, pale yellow.
2	CH_2PhCl	12·30	19·5 g. HNO_3 + 10 g. Ac_2O	20—25°	20′; then 15′ at room t.	16·20	—	3·525	1·453 p- (233—235°) +1·590	1·000	0·045	1·429	0·501	0·0188	,,
3	$CH_2Ph\cdot CO_2Et$	10·40	83 g. HNO_3	−10° to −8°	90′; then 15′ at −10°, 15′ room.	13·195	+0·056	2·450	1·549	1·000	0·011	1·699	0·265	0	,,
4	$CH_2Ph\cdot CO_2Et$	5·51	44 g. HNO_3	−10° to −8°	,,	6·930	+0·033	3·640	1·135 p- (233—236°) +1·029	1·029	0·005	1·492	0·566	0	,,
5	$CHPhCl_2$	10·14	in 10 c.c. Ac_2O; this added to 20 g. HNO_3 + 10 g. Ac_2O	15—18°	20′; then 10′ room.	12·40	—	2·859 4·522	1·921 1·050 p- (233—236°) +1·759	1·000 1·000	0·023 0·050	1·263 0·833	0·752 1·188	0·1811	Oil, pale yellow.
6	$CHPhCl\cdot CO_2Et$	8·253	8·4 g. HNO_3 + 4·2 g. Ac_2O	15—16°	25′; then 15′ room.	8·800	—	5·100 2·600	2·607 1·332	1·000 1·000	0·428 0·469	0·765 0·716	0·380 0·350	0·0168	Oil, very slightly yellow.
7	$CHPh(CO_2Et)_2$	10·88	88 g. HNO_3	−10° to −8°	1 hr.; then 30′ at −10°, 15′ room.	12·301	+0·070	1·901 4·044	0·905 1·860	0·500 1·000	0·006 0·009	0·708 1·426	0·271 0·555	0	Oil, brown.
8	$CPhCl_3$	10·63	in 10·5 c.c. Ac_2O; this added to 16 g. HNO_3 + 8 g. Ac_2O	17—19°	15′; then 12½′ room.	12·666	—	2·080 2·141	hydrolysed all ,,	 ,,	0·237 0·241	0·892 0·928	1·620 1·692	0·3160	Oil, pale yellow.
9	$CPhCl_2\cdot CO_2Et$	5·39	4·5 g. HNO_2 + 2·25 g. Ac_2O	20°	20′; then 15′ room.	5·92	—	2·724 2·865	1·280 1·299	1·000 1·000	0·384 0·361	0·456 0·450	0·815 0·796	0·1429	,,
10	$CPhCl(CO_2Et)_2$	6·95	5·2 g. HNO_3 + 2·6 g. Ac_2O	20°	10′; then 40′ room.	7·97	—	2·188 2·440	0·864 0·972	0·800 0·800	0·042 0·039	0·601 0·619	0·927 0·920	0·0904	,,
11	$CPh(CO_2Et)_3$	6·90	55 g. HNO_3	−10° to −9°	20′; then 5′ at −10°, 60′ at room.	7·812	+0·040	2·545 3·340						0	,,
12	CH_2PhBr	10·11	in 20 c.c. Ac_2O; this added to 11·2 g. HNO_3 + 5·6 g. Ac_2O	16—18°	45′; then 10′ room.	12·53	+0·023	2·23 2·77	1·394 1·760	1·000 1·000	0·034 0·039	1·745 1·760	0·148 0·150	0·0425	Sticky solid, yellow.
13	$CPhBr(CO_2Et)_2$	11·10	90 g. HNO_3	−10°	1 hr.; then 30′ at 10°, 15′ room.	12·555	+0·045	4·800 3·44	1·721 1·185	1·000 1·000	0·011 0·015	1·185 1·190	0·882 0·868	0·210	Oil, pale yellow.

stage of the oxidation process. No doubt owing to steric hindrance (compare the well-known resistance of the analogously constituted esters of triphenylacetic acid to hydrolysis), the side chain was attacked so slowly by the permanganate that in the meantime the greater part of the product was destroyed by nuclear oxidation. Attempts to hydrolyse the ester to the acid (and thereby obtain nitrophenylacetic acid) also failed; but initial boiling with dilute nitric acid of Baker and Ingold's concentration, followed by treatment with permanganate as indicated by us, achieved the desired result.

Our usual method of permanganate oxidation gave 30 mol. % of acids, or less. Hydrolysis by 10 parts (by vol.) of sulphuric acid (*d* 1·19) and 4 parts (by vol.) of alcohol per part of ester gave, even when carried out for 40 hours at 130°, on subsequent oxidation with permanganate, only 0·355 g. of acids from 2·45 g. of the ester. Hydrolysis by boiling with 5% aqueous sodium hydroxide appeared to produce nitrophenols.

Action of Dilute Nitric Acid on Nitrated Ethyl Phenylmethanetricarboxylate, followed by Treatment with Permanganate.—2·545 G. of the nitrated oil were boiled for 12 hours with 40 c.c. of nitric acid (*d* 1·125). The acids formed were then separated from the unaltered ester, and the latter was boiled for 12 hours with 30 c.c. of the above nitric acid. 0·190 G. of the ester was still unchanged. This was boiled for 27 hours with 10 c.c. of the nitric acid and yielded 0·030 g. of acids and 0·115 g. of ester. This 0·115 g. was oxidised for another 27 hours with nitric acid, then with a little permanganate, and yielded 0·024 g. of acids, m. p. 115—125°, giving on reduction, etc., 0·036 g. of tribromoaniline together with a mere trace of tribromoaminobenzoic acid. Similarly, the above 0·030 g. of acids, when boiled with permanganate (0·03 g.) for 1 hour, and reduced, etc., gave 0·033 g. of tribromoaniline and a mere trace of the amino-acid. The main fraction of the acids (1·305 g.), as indicated by its yield, was of higher molecular weight than nitrobenzoic acid, but gave the latter, by 1 hour's boiling with 1·5 g. of permanganate, in a yield of 0·821 g., from which, on reduction, etc., 0·617 g. of tribromoaniline and 1·103 g. of tribromoaminobenzoic acid were obtained. In a repetition of the oxidation 3·34 g. of the original nitrated oil were boiled with 40 c.c. of the nitric acid for 9 hours, and the acid and ester fractions were separated. The ester fraction was again boiled with nitric acid for 9 hours and separated, and so on, such boiling being altogether performed four times. The residual ester fraction then weighed 0·301 g. The united (incompletely oxidised) acid fractions were boiled with 2 g. of permanganate for ½ hour, and the nitrobenzoic acids (1·019 g.)

obtained were reduced, etc., yielding 0·745 g. of tribromoaniline and 1·400 g. of tribromoaminobenzoic acid. Since in this repetition the acids produced were exposed for a shorter time to subsequent destructive oxidation than in the first experiment, and since the relative yields of *m*- and *o*-,*p*-acids were identical in both experiments, the figures obtained may be regarded as conclusive notwithstanding the prolonged oxidation. It is seen that the final, most resistant, ester fraction contained scarcely any *m*-isomeride. It might be expected that the *o*-isomeride would be most difficult to oxidise in such a case, and the melting point of the nitrobenzoic acid (see above) obtained from the residual ester of the first experiment confirms this by indicating the absence also of the *p*-isomeride. The 0·301 g. of residual ester obtained in the repetition melted at 78—80°, and, after recrystallisation from petrol (b. p. 60—80°), 0·248 g. of colourless prisms was obtained, showing the constant m. p. 83—84° (Found: N, 4·3. $C_{16}H_{19}O_8N$ requires N, 4·0%). The compound is, therefore, *ethyl* o-*nitrophenylmethanetricarboxylate*.

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