CCXC.—*The Laws of Aromatic Substitution. Part IX.*

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IN Part VIII (this vol., p. 1607), the *o*-, *p*-, and *m*-percentages produced by nitration of the complete series $C_6H_5\cdot C(R_1)(R_2)(R_3)$ (R_1 and R_2 = Cl,CO_2Et,H; R_3 = Cl,CO_2Et) have been accurately determined. The results have shown that a polar effect, which had long been recognised by one of us where *o*-substitution is concerned and had been postulated by Robinson also for the *m*- and *p*-positions, actually exists, and may be very pronounced, in *all* positions. At the same time, an alternating effect (quantitative factor " *q* "), as postulated by one of us (*e.g.*, $C_6H_5\cdots\underset{\diagdown}{\overset{\diagup}{C}}\text{—}Cl$ and $C_6H_5\text{—}\underset{\diagdown}{\overset{\diagup}{C}}\cdots CO_2Et$), has been found to be superposed on the polar effect, tending in the above series to reverse the relative order in which the substituents would cause *m*-substitution if their polar effects were the only factor.

The present investigation has been extended to compounds wherein R_1 or R_1 and R_2 = CN and covers the following series :

$C_6H_5\cdot CH_2\cdot CN$;
$C_6H_5\cdot CHCl\cdot CN$, $C_6H_5\cdot CH(CO_2Et)\cdot CN$, $C_6H_5\cdot CH(CN)_2$, $C_6H_5\cdot CH(OH)\cdot CN$;
$C_6H_5\cdot C(CO_2Et)_2\cdot CN$, $C_6H_5\cdot C(CO_2Et)(CN)_2$;
also $C_6H_5\cdot CN$ and *m*-$NO_2\cdot C_6H_4\cdot N{:}CH\cdot C_6H_5$.

The new data are to be found in Table I. For comparison, the ratios of *m*- to *o*- + *p*-substitution determined in Part VIII are recapitulated in Table II.

TABLE I.

No.	Substance.	Medium.	Nitration products, mol. %. *o* + *p*.	*m*.	Mean mol. %, *m*.	$\frac{m}{o+p}$ (%).
1	PhCN	HNO_3 *d* 1·52	12·0 11·5	88·00 88·50	88·25*	751*
2	$Ph·CH_2·CN$	,,	86·85 87·75	13·15 12·25	12·70†	14†
3	$Ph·CH(CO_2Et)·CN$	,,	62·55 63·05	37·45 36·95	37·20	59·2
4	$Ph·CH(CN)_2$	,,	31·0	69·0	67·90	211·8
5	,,	,,	32·70	67·30		
6	,,	,,	32·55	67·45		
7	$Ph·C(CO_2Et)_2·CN$	,,	29·85 31·00	70·15 69·00	69·55	228·6
8	$Ph·C(CO_2Et)(CN)_2$	,,	12·10 12·95	87·90 87·05	87·5	698·4
9	Ph·CHCl·CN	,,	46·20	53·80	50·05‡	100·20‡
10	,,	,,	49·95	50·05		
11	Ph·CH(OH)·CN	,,	56·15 56·70	43·85 43·30	43·55	77·25
12	$Ph·CH{:}N·C_6H_4·NO_2$(*m*)	HNO_3 + H_2SO_4 (4% SO_3)	12·55 13·35	87·45 86·65	87·05	672·2
13	,,	HNO_3 + H_2SO_4 (5% SO_3)	12·25 12·65	87·75 87·35	87·55	703·2
14	,,	Same + $(NH_4)_2SO_4$	14·85 13·95	85·15 86·05	85·60	594·4
15	Ph·CHO	HNO_3 + H_2SO_4 (5% SO_3)	21·60 21·15	78·40 78·85	78·65	368·4

* Compare 80·53% and 413·6% respectively (Baker, Cooper, and Ingold, this vol., p. 426).

† Compare 14·25% and 16·6% respectively (*idem*, *ibid.*).

‡ See p. 2240.

TABLE II.

	$\frac{m}{o+p}$ (%).		$\frac{m}{o+p}$ (%).
$C_6H_5·CH_2Cl$	13·35	$C_6H_5·CCl_3$	160·1
$C_6H_5·CH_2·CO_2Et$	13·6	$C_6H_5·CCl_2·CO_2Et$	156·8
$C_6H_5·CHCl_2$	52·25	$C_6H_5·CCl(CO_2Et)_2$	132·6
$C_6H_5·CHCl·CO_2Et$ ...	43·35	$C_6H_5·C(CO_2Et)_3$	130·1
$C_6H_5·CH(CO_2Et)_2$	34·05	$C_6H_5·CH_2Br$	7·45
		$C_6H_5·CBr(CO_2Et)_2$......	65·05

Discussion of Results.

Application of the Theory of Varying Affinity Demand.—(1) *Relative polar effects of* Cl, CO_2Et, *and* CN. These can be ascertained (compare J., 1909, **95**, 726) from the influence on the dissociation constants of benzoic acid and aniline exercised by these substituents when they occupy the *m*- or *p*-positions. The steric effect from these positions is negligible, and the alternating effect can be eliminated by averaging the changes in the dissociation constant which a substituent produces when it occupies the *m*-position on the one hand and the *p*-position on the other. It is at present uncertain whether the average change should be calculated by the arithmetical function, polar effect $= (K_m + K_p)/2K_u$, or by the geometrical function, polar effect $= \sqrt{K_m K_p}/K_u$, where K_m, K_p, and K_u are the constants for the *m*- and *p*-derivatives and for the unsubstituted acid (or base) respectively, but the choice of function does not affect the relative order of the polar effects of the above substituents. In connexion with these, the following constants are available :

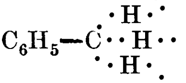
	K.
m-Chlorobenzoic acid	$1{\cdot}59 \times 10^{-4}$
p- ,, ,,	$7{\cdot}8 \times 10^{-5}$
Methyl hydrogen *iso*phthalate	$1{\cdot}28 \times 10^{-4}$
m-Cyanobenzoic acid	$1{\cdot}99 \times 10^{-4}$
Benzoic acid	$6{\cdot}0 \times 10^{-5}$

	K.
Ethyl *p*-aminobenzoate	$2{\cdot}4 \times 10^{-12}$
Methyl *p*-aminobenzoate	$2{\cdot}9 \times 10^{-12}$
,, *m*-aminobenzoate	$4{\cdot}4 \times 10^{-11}$
m-Chloroaniline	$3{\cdot}45 \times 10^{-11}$
p- ,,	$9{\cdot}9 \times 10^{-11}$
Aniline	$4{\cdot}6 \times 10^{-10}$

The constants for ethyl and methyl *p*-aminobenzoate show that ethyl has a slightly greater effect than methyl; and a comparison of methyl *p*- and *m*-aminobenzoates, also of *p*- and *m*-nitrobenzoic acids and of *p*- and *m*-nitroanilines, proves that the effect of *m*-directive substituents is greater in the *p*- than in the *m*-position. Taking this into account, the following polar effects are obtained :

	On benzoic acid.		On aniline.	
	Arithmetical mean.	Geometrical mean.	Arithmetical mean.	Geometrical mean.
m- and *p*-Cl	1·975	1·87	0·145	0·13
m- and *p*-CO_2Me	>2·13	>2·13	0·05	0·025
m- and *p*-CO_2Et	>2·13	>2·13	<0·05	<0·025
m- and *p*-CN	>3·32	>3·32	—	—

The sequence of "negative" polarity is therefore, quite conclusively, $CN > CO_2Et > Cl$, in so far as the effect on the benzene ring is concerned.

(2) *Relative alternating* ("*quantitative*") *effects of* Cl, CO_2Et, *and* CN. The affinity demand of methyl-carbon is approximately equal to that of hydrogen, but when it is linked to an atom with higher affinity demand (*e.g.*, in toluene), then an equilibrium is established resulting in an affinity content of the bond between the two which is somewhat greater than in a bond between hydrogen and either of the two atoms; for instance,  $C_6H_5{-}\overset{\cdot H \cdot\cdot}{\underset{\cdot\cdot H \cdot}{C}}{\cdot\cdot}H{\cdot\cdot}$ (compare *Chem. and Ind.*, 1925, **44**, 249, and previous papers). Chlorine has a moderate affinity demand, intermediate between those of hydrogen and hydroxyl; when it is attached to an α-methyl carbon atom, it

therefore reduces the affinity content of the bond between the latter and the nuclear carbon atom, but only very *moderately* (see below). Conversely, CO_2Et has an affinity demand only slightly inferior to that of hydrogen (see below); when CO_2Et is attached to α-methyl carbon, the affinity content of the bond between the latter and nuclear carbon is therefore *slightly* raised. Since affinity demand is at its maximum in tervalent nitrogen, the bond between CN and α-methyl carbon has a lower affinity content than the corresponding bonds in either of the other cases, and the affinity content of the bond between methyl and nuclear carbon is correspondingly higher.

(3) *Resulting directive effects of* Cl, CO_2Et, *and* CN. It follows that the polar factor should cause *m*-substitution in the order $C_6H_5{\cdot}CH_2{\cdot}CN > C_6H_5{\cdot}CH_2{\cdot}CO_2Et > C_6H_5{\cdot}CH_2Cl$, and the quantitative factor in the reverse order. In accordance with this, the degree of *m*-substitution has been found to be practically identical in all three cases. On the other hand, when the above substituents are directly attached to the nucleus, *both* factors cause *m*-substitution in the order $C_6H_5{\cdot}CN > C_6H_5{\cdot}CO_2Et > C_6H_5Cl$. For the last two compounds this sequence is, of course, a commonplace, but it has now been definitely proved to hold equally for benzonitrile, for which the value obtained by Baker, Cooper, and Ingold (*loc. cit.*) was found to be too low.

(4) *The effects of lateral subsidiary bonds.* A suggestion due to Brühl (*Ber.*, 1907, **40**, 897; compare also Smedley, J., 1909, **95**, 232), according to which there is an exchange of residual affinity (subsidiary bond) between the oxygen atoms of a carboxyl group, appears to have found general acceptance. It explains why the two oxygen atoms in ethyl benzoate—although bivalent and therefore possessed of a marked affinity demand—are barely able to reduce the affinity content of the bond between α- and nuclear carbon to a level below the content of the hydrogen bond in benzene, as shown by the fact that ethyl benzoate still yields about 30% of *o*-, *p*-nitro-derivatives, notwithstanding that its *m*-substitution is also favoured by the polar effect. Brühl's conception, already extended by Smedley (*loc. cit.*) to a subsidiary N–O bond in amides, must logically apply to all cases where two (or more) atoms possess appreciable amounts of residual affinity,* provided, of course, that the partial mutual saturation is not prevented by the spatial factor (distance). The idea explains, for instance, why tellurium hexafluoride is so much less stable than sulphur hexafluoride, since the

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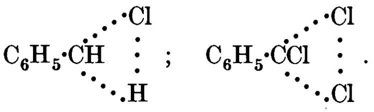
* The effect of such residual bonds on aromatic substitution was first recognised in connexion with the lowering of the affinity demand of NH_2 and OH brought about by acetylation (Flürscheim, J., 1909, **95**, 726, footnote).

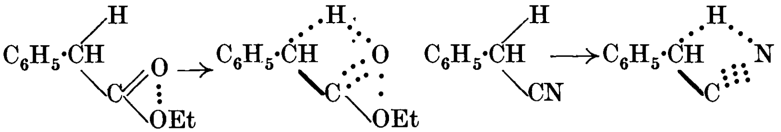
greater distance between the fluorine atoms in the former, due to the greater size of the central atom, involves a lower affinity content in the residual bonds between them. When residual bonds between atoms forming part of α-substituents in toluene are considered in relation to their effects on affinity distribution (and thereby on substitution), it becomes necessary to distinguish between three distinct cases :

(*a*) Cases where residual bonds *lower* the total affinity demand on the α-carbon atom, *e.g.*,



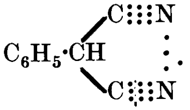
The formulæ show immediately why the alternating effect of the α-chlorine atom is substantially less marked than in the case of nuclear chlorine. Even three α-chlorine atoms can only produce preponderating, but nothing like exclusive, *m*-substitution.

(*b*) Cases where residual bonds *do not affect* the total affinity demand on the α-carbon atom, *e.g.*,



It is seen that in the measure in which the content of the bond between the α-carbon atom and another atom is reduced (broken lines) the affinity content of the bond between the α-carbon and a third atom is increased (thick lines) by the formation of a residual bond.

(*c*) Cases where residual bonds *enhance* the total affinity demand on the α-carbon atom; *e.g.*,



The observation that, whereas nitration of $C_6H_5{\cdot}CH_2{\cdot}CN$ and $C_6H_5{\cdot}CH_2{\cdot}CO_2Et$ yields practically the same $m/(o+p)$-ratio, $C_6H_5{\cdot}CH(CN)_2$ and $C_6H_5{\cdot}CH(CO_2Et)_2$ yield, respectively, ratios of 211·8% and 34·05%, is at first sight puzzling, but is now seen to be a necessary consequence of the theory. The residual bond is here N . . . N and not N . . . H, since the tervalent nitrogen has a much greater residual affinity than the hydrogen atom. Bivalent oxygen has, *ceteris paribus*, always less residual affinity than tervalent nitrogen, and when the carboxyl is compared with the cyano-group, this difference is accentuated by the residual neutralisation of affinity *within* the former group. In $C_6H_5{\cdot}CH(CO_2Et)_2$ a residual bond between the two carboxyl groups can therefore not have a marked effect; but in $C_6H_5{\cdot}CH(CN)(CO_2Et)$, where a nitrogen atom tends to saturate its residual affinity, the equilibrium principle postulates a more pronounced effect than in the dicarbethoxy-compound, although to a smaller degree than in the dinitrile, and the observed ratio (59·2) is in accordance with this.

It might be thought that the high *m*-ratio from the dinitrile could be due to a primary replacement of the mobile α-hydrogen atom by NO_2, with subsequent migration of the latter into the *m*-position. This possibility has been excluded by nitration of $C_6H_5{\cdot}C(CN)_2(CO_2Et)$, resulting in a *m*-ratio of 698·4. This compound and $C_6H_5{\cdot}C(CN)(CO_2Et)_2$, both new compounds, constitute two further cases of the examination of directive effects in toluene derivatives in which *all* the α-hydrogen atoms are replaced by substituents which, in direct linking with the nucleus, would be *m*-directive, the first such case investigated having been the nitration of $C_6H_5{\cdot}C(CO_2Et)_3$, described in Part VIII.

(5) *Directive effect of* $R{\cdot}N{=}$. It appeared desirable to examine the directive effect of an α-substituent which, in contrast to those already discussed, would combine *weak polarity* with a *high affinity demand.* Such a substituent is to be found in benzylidene-*m*-nitroaniline, which, unlike benzylamine, would even in concentrated acid preserve its nitrogen chiefly in the tervalent state and would not, in contrast to acetylbenzylamine, have the residual affinity of its nitrogen largely neutralised by a subsidiary bond. The group $R{\cdot}N{=}$ would obviously exercise a smaller polar effect than $O{=}$; if, notwithstanding this, the *m*-ratio were found to be higher for benzylidene-*m*-nitroaniline than for benzaldehyde, the expected effect of the postulated higher affinity demand of tervalent nitrogen would be established. Benzaldehyde, according to Brady and Harris (J., 1923, **123**, 484), in mixed acid yields 81% of *m*-nitro-derivative [$m/(o + p) = 426{\cdot}3\%$], a value with which our own determinations [78·65% *m*-nitration; $m/(o + p) = 368{\cdot}4\%$] are in good agreement, allowing for the difference of method. Schwalbe (*Z. Farb. Textilchem.*, 1902, **1**, 628) obtained essentially *m*-nitrobenzaldehyde from benzylidene-*m*-nitroaniline in mixed acid, but he neither determined the proportions of the isomerides formed, nor showed whether or not hydrolysis to the aldehyde *preceded* nitration.

Our own experiments prove that in the absence of hydrolysis, in a still stronger acid than Schwalbe's, the *m*-percentage 87·5 [$m/(o + p) = 703\%$] is obtained (nitration No. 13); that the compound during nitration is largely present as the *free* anhydro-base, as shown by the intensely yellow colour of its solution in concentrated sulphuric acid, compared with its colourless *hydrochloride* obtained by precipitating the base with dry hydrogen chloride; and that the high *m*-ratio is not attributable to nitration of the *m*-directive cation (compare Part V) of the sulphate of the anhydro-base. This last fact was established by testing the effect of added ammonium sulphate on the *m*-ratio, since *m*-nitration of the cation would thereby be appreciably reduced by what Pollard and Robinson (J., 1927, 2770) have named the "Flürscheim effect." A comparison of nitrations Nos. 13 and 14 with Nos. 7 and 8 of Part V (J., 1926, 1569) shows that in the present case, notwithstanding a slightly higher concentration of ammonium sulphate, this effect is very much less marked than with diethylbenzylamine. This is what would be expected since, on the basis of *any* theory, even that relatively small portion of the very weak base benzylidene-*m*-nitroaniline which may be present as salt will be less *m*-directive (according to us, less electrolytically dissociated) than the diethylbenzylammonium salt, and since even the latter, at similar concentration, is chiefly *o*-, *p*-directive. Obviously, the presence of any benzylidene-*m*-nitroaniline as sulphate would therefore *lower* the *m*-ratio, and the value for the latter found in nitration No. 14 must be regarded as a lower limit for the free anhydro-base. *The greater affinity demand of nitrogen in this compound thus clearly outweighs the higher polarity of oxygen in benzaldehyde.*

Conclusion.

The theory of varying affinity demand, relying on one single mechanism, provides a consistent interpretation of our observations. When we examine the results recorded in this paper in the light of the electronic theory of valency, we find that our remarks in Part VIII (this vol., p. 1609, last sentence of section 3) appear to apply with even greater force. It is, however, by considering the effect of substituents on *equilibria* (electrolytic and thermal dissociation) that we hope to obtain a clear-cut decision between these ideas, since the effect of a passing phase (conjugation) on a permanent equilibrium must be negligible, so that one of the two alternative electronic mechanisms can be eliminated.

EXPERIMENTAL.

Preparation of Materials.—(*a*) *Ethyl phenylcyanomalonate.* 15 G. of ethyl phenylacetate and 1·5 g. of sodium wire in 50 c.c. of dry ether were left over-night, and 10 c.c. of ethyl chloroformate were then added. On shaking, the white crystalline sodium salt gradually changed to a jelly-like mass. After the suspension had been shaken for 7 hours and kept over-night, water was added, and the ethereal layer dried and distilled; 15 g. of a thick oil were obtained which, on redistillation, boiled at 140—141°/1 mm. (Found: C, 64·4; H, 5·8; N, 5·3. $C_{14}H_{15}O_4N$ requires C, 64·4; H, 5·8; N, 5·4%).

(*b*) *Ethyl phenyldicyanoacetate.* 4 G. of phenylmalonitrile and 0·8 g. of sodium in 75 c.c. of dry absolute ether were left for 20 hours. Evolution of hydrogen was slow. After filtration, the white sodium salt was separated mechanically from unchanged sodium, introduced into 40 c.c. of sodium-dried benzene, and 5 c.c. of ethyl chloroformate were added. After 7 hours' shaking and standing over-night, a gelatinous mass had formed. The whole was then shaken with water, the benzene layer separated, and the benzene removed at reduced pressure. On recrystallising the residue from alcohol, 4·9 g., m. p. 58—59°, were obtained, showing after further recrystallisation the constant m. p. 60° (mixed m. p. depression with phenylmalononitrile) (Found: C, 67·2; H, 4·9; N, 13·3. $C_{12}H_{10}O_2N_2$ requires C, 67·3; H, 4·7; N, 13·1%).

(*c*) Phenylmalononitrile was prepared according to Hessler (*Amer. Chem. J.*, 1904, **32**, 119), who obtained it from dilute alcohol with m. p. 68—69°. By using absolute alcohol, we found m. p. 70—71° Benzylidene-*m*-nitroaniline had m. p. 72·5—73°; benzyl cyanide, b. p. 229—230°; benzonitrile, b. p. 190—191°; mandelonitrile solidified at 5°, m. p. 13° (clear); ethyl phenylcyanoacetate, b. p. 125—126°/1 mm.; α-chlorobenzyl cyanide, b. p. 135—136°/40 mm.

Methods.—(*a*) *Nitration.* The experimental conditions and yields for each nitration are given in Table III. Apart from the nitrations of benzylidene-*m*-nitroaniline (see below), where hydrolysis on subsequent dilution withdrew most of the aniline portion of the anhydro-base from the weighings, the yields were excellent in all cases.

(*b*) *Determination of the isomerides.* Oxidation of the products of nitration to the acids was carried out as described in Part VIII. Ethyl phenylcyanomalonate, however, like ethyl phenylmethanetricarboxylate, had to be treated differently (see below). Our remark (this vol., p. 449) that our modification of the permanganate method had not failed in a single instance must therefore, in the light of our subsequent experience, be qualified in the sense that compounds which—owing to steric inhibition—are exceptionally resistant to lateral oxidation are prone to nuclear destruction by permanganate. It appears that, in such cases, Baker and Ingold's modification of the nitric acid method, *followed* by the application of our modification of the permanganate method, gives trustworthy results. The composition of the acids obtained was in all cases determined by our method described in Part VI.

TABLE III.

									Reduction and bromination of acids.				
										Found (g.).			
No.	G.	Medium.	Temp.	Time.	Yield, g.	$KHCO_3$-soluble, g.	Oxidised, g.	Yield of acids, g.	Used, g.	Benzoic acid.	Tri-bromo-aniline.	Tribromo-amino-benzoic acid.	Appearance of nitration product.
1	9·370	75 g. HNO_3	−10 to −8°	1 hr. for adding; 30′ at −10°, 15′ room.	8·440 +4·70	+0·146	1·732 1·732	1·722 1·754	1·722 1·754	0·011 0·008	1·127 1·117	2·521 2·673	The 8·440 g.=pure *m*-nitro-deriv., m. p. 117·5°.
2	11·20	90 g. HNO_3	−10 to −8°	1½ hrs. for adding; 15′ at −10°, 15′ room.	14·658	+0·129	3·664 3·664	1·953 *p*- (m. p. 233—235°) +1·030 1·958 *p*- (m. p. 234—236°) +1·388	1·030 0·500	0·004 0·003	1·254 0·707	0·878 0·334	Yellow solid.
3	7·020	56 g. HNO_3	−10 to −8°	40′ for adding; 40′ at −10°, 15′ room.	8·50	—	3·525 2·660	1·742 1·385	1·000 1·000	0·004 0·007	1·216 1·212	0·825 0·805	Pale yellow oil.
4	3·400	27·2 g. HNO_3	−10°	30′ for adding; 45′ at −10°, 15′ room.	4·495	—	2·000	1·525	1·000	0·006	0·600	1·512	Brownish-yellow solid.
5	2·900	46 g. HNO_3	−5 to 0°	15′ for adding; no standing.	1·452 + 2·331	—	1·000 1·500	0·520 0·794	0·500 0·500	0·018 0·002	0·359 0·294	0·675 0·778	Brownish oil. Oil, solid on standing.
6	3·000	24 g. HNO_3	18—20°	15′ for adding; 5′ at 20°.	1·123 + 2·565	—	1·123 1·560	0·510 0·769	0·500 0·500	0·009 0·003	0·341 0·301	0·670 0·766	Brownish oil. Oil, solid on standing.
7	7·930	63·5 g. HNO_3	−10 to −8°	30′ for adding; 45′ at −10°, 15′ room.	9·200	+0·127	3·775 2·543	1·348 0·776	1·000 0·500	0·009 0·005	0·582 0·301	1·552 0·759	Thick, pale yellow oil.
8	4·500	36 g. HNO_3	−10°	10′ for adding; 25′ at −10°, 60′ room.	5·280	+0·094	1·942 1·990	0·724 0·711	0·500 0·500	0·026 0·019	0·109 0·118	0·899 0·889	Pale yellow solid (on standing).
9	7·750	62 g. HNO_3	−10 to −8°	60′ for adding; 30′ at −10°, 15′ room.	9·590	+0·141	3·111	2·117	1·000	0·004	0·904	1·193	Slightly yellow solid.
10	3·510	28 g. HNO_3	−10 to −8°	20′ for adding; 5′ at −10°.	4·390	+0·051	2·857	1·765	1·765	0·042	1·565	1·778	
11	8·140	65 g. HNO_3	−10 to −8°	60′ for adding; 30′ at −10°, 15′ room.	8·070	+2·288	2·940 2·720	2·172 1·976	1·000 1·000	0·005 0·004	1·097 1·110	0·971 0·960	Pale yellow. Nearly solid.
12	13·200	72 g. H_2SO_4 (4% SO_3) +4·1 g. HNO_3	10°	24 hrs. at room temp.	10·056	—	2·020 2·017	1·621 1·629	1·000 1·000	0·005 0·004	0·245 0·260	1·932 1·910	Dark brown solid.
13	8·000	44 g. H_2SO_4 (5% SO_3) +1·2 g. HNO_3	10°	24 hrs. at room temp.	3·677	—	2·025 1·601	1·606 1·220	1·000 1·000	0·510 0·501	0·117 0·121	0·952 0·947	Dark brown oil.
14	7·400	41 g. H_2SO_4 (5% SO_3) +1·1 g. HNO_3 +11 g. $(NH_4)_2SO_4$	10°	24 hrs. at room temp.	3·772	—	1·972 1·700	1·587 1·405	1·000 1·000	0·485 0·470	0·146 0·138	0·950 0·966	
15	6·36	72 g. H_2SO_4 (5% SO_3) +2·1 g. HNO_3	10°	24 hrs. at room temp.	7·449	+0·228	2·700 2·260	2·639 2·220	1·000 1·000	0·484 0·478	0·219 0·214	0·898 0·902	Pale yellow oil.

Details of Nitrations.—The conditions and actual weighings in connexion with the nitrations are to be found in Table III, in which the numbers in column 1 correspond with those in column 1 of Table I. The following additional information appears desirable.

Benzonitrile (No. 1). By pouring the nitration product on ice, 11·521 g. of precipitate, m. p. 108—111°, were obtained, and by extracting the filtrate with ether a further 1·621 g. were recovered which solidified on standing. By recrystallising the 11·521 g. twice from water, 8·440 g. of pure *m*-nitrobenzonitrile (m. p. 117·5°) were obtained. The mother-liquors together with the above 1·621 g. were in this case not oxidised, but hydrolysed to the acids by boiling 1 part for 8 hours with 9 parts of 15% hydrochloric acid, and completing the hydrolysis by boiling with 0·15 part of permanganate and a little potassium hydroxide in 15 parts of water for 1½ hours.

Ethyl phenylcyanoacetate (No. 3). Nitration in acetic anhydride reduced the *m*-percentage in this case as in phenylmalononitrile, but not nearly to the same extent, no doubt on account of the less pronounced reactivity of the side-chain. Two nitrations in acetic anhydride (one shown in parentheses) gave, from 1·000 (0·700) g. of oxidation acids, 1·000 (0·865) g. of tribromoaniline and 0·640 (0·514) g. of tribromoaminobenzoic acid.

Phenylmalonitrile (Nos. 4—6). That nuclear nitration was practically complete, followed from the results of the reduction and bromination of the acids. To eliminate the possibility that the high *m*-percentage might in part have been due to another nitro-group having become attached to the α-carbon atom prior to nuclear nitration, experiment No. 4 was repeated and the freshly prepared nitration *product* brought to constant weight in a vacuum over caustic potash (Found: C, 56·5; H, 2·6. $C_9H_5O_2N_3$ requires C, 57·7; H, 2·7%). The product therefore contained only *one* nitro-group. In nitrations Nos. 5 and 6, the product of nitration was extracted with benzene before being extracted with ether as usual. The upper figures in the column headed "Yield" in Table III are the weights of the benzene extracts, the lower figures being those of the ether extracts for these two nitrations. Nitration of phenylmalononitrile in the presence of acetic anhydride appeared to be preceded by some side-chain reaction, since the preponderating *m*-nitration observed in its absence was completely reversed. Thus 7·9 g. of phenylmalononitrile in 7·9 c.c. of acetic anhydride, to which a mixture of 8 g. of acetic anhydride and 8 g. of nitric acid (*d* 1·52) was added at 15—20° during 20 minutes, with subsequent standing for 30 minutes, yielded 10·35 g. of a whitish, solid mass. This gave the following results on oxidation (those of a second oxidation are added in parentheses): 2·14 (2·45) g. of nitration product gave 1·123

(1·325) g. of acids; 1·000 (1·000) g. of these gave 0·203 (0·193) g. of benzoic acid, 1·392 (1·412) g. of tribromoaniline, and 0·102 (0·110) g. of tribromo-*m*-aminobenzoic acid, thus indicating almost exclusive *o*-, *p*-substitution.

Ethyl phenylcyanomalonate (No. 7). On adding this substance to the nitrating acid, a pale red colour was produced, which gradually changed to green. Oxidation by permanganate yielded only 0·2 g. of acids from 2·3 g. of nitration product, but when 3·775 g. of the latter were boiled for 4 hours with 40 c.c. of nitric acid (*d* 1·125) and then successively with 2 g. and 1 g. of permanganate, a yield of 1·348 g. of acids (nearly 70% of the theoretical) was obtained.

Ethyl phenyldicyanoacetate (No. 8). A cyano-group being smaller than a carbethoxyl group, oxidation by permanganate succeeded in this case, but the yields were still not quite as good as usual. The nitration product, *ethyl* m-*nitrophenyldicyanoacetate,* a pale yellow solid, gave a deep red colour in alcohol, and in dilute acetone. It crystallised from alcohol in white crystals, m. p. 130—133·5°, from chloroform with m. p. 133—134·5°, and from benzene with m. p. 132—134°. In all three cases the fused specimens were *red*, and lost this colour on solidification; they were soluble in cold alcohol or acetone with a strong reddish-orange colour, which deepened on adding water, but the solution in benzene or chloroform was colourless (Found : N, 16·68. $C_{12}H_9O_4N_3$ requires N, 16·22%).

α-Chlorobenzyl cyanide (Nos. 9 and 10). Nitration in acetic anhydride at 15° only took place to the extent of about 1·5%. Since, moreover, other α-cyano-compounds behaved abnormally in this medium, it became necessary to operate in nitric acid (*d* 1·52) alone, although appreciable hydrolysis could not be avoided. In No. 9 the spent acid gave 1·2401 g. AgCl, corresponding to 16·9% of hydrolysis, and in No. 10, where exposure to the acid was shorter, 0·3306 g. AgCl (hydrolysis = 10·0%). The calculated *m*-figures (marked ‡) in Table I have therefore been based on No. 10 alone. Since No. 9, with greater hydrolysis, gave a higher *m*-percentage than No. 10, whereas mandelonitrile yielded a lower *m*-percentage than No. 10, it is obvious that a product other than mandelonitrile is initially formed by hydrolysis, and nitrated. This can only be mandelonitrile nitrate. This result is entirely in agreement with the high *m*-percentage observed in the nitration of benzyl bromide in nitric acid alone (see Part VIII); in this case benzyl nitrate must have been the initial product of hydrolysis, since benzyl alcohol would obviously lead to even less *m*-derivative than mandelonitrile. On adding α-chlorobenzyl cyanide to nitric acid, a red colour was observed, which disappeared on shaking.

Benzylidene-m-*nitroaniline* (Nos. 12, 13, and 14). The yields given in Table III were obtained by pouring the acid, without cooling, into water in order to hydrolyse most of the anhydro-base and leave the aniline portion in solution. The aldehyde portion was extracted with benzene. The fact that no appreciable hydrolysis occurred during nitration, even in No. 12 where only 4% SO_3 was present as against 5% in Nos. 13 and 14, was proved by pouring exactly one-half of the acid from No. 12 on a mixture of ice and excess of bicarbonate, whereupon 7·044 g., m. p. 142—143°, were precipitated. From 1 g. of this ochre-coloured product, recrystallised from petrol (b. p. 100—120°), 0·710 g. of almost pure *m*-nitrobenzylidene-*m*-nitroaniline, m. p. 148—154°, mixed m. p. higher, was obtained. A synthetic sample prepared by us had m. p. 160° (literature 153°). The yield given in No. 12 is double the amount recovered from the remaining half of the acid by pouring it into water. The proportion of nitric acid used in Nos. 13 and 14 was only one-half of that in No. 12. That no appreciable portion of the anhydro-base would be sulphonated in our conditions appeared probable from the stringent conditions which Schwalbe (*loc. cit.*) had to resort to for its sulphonation. We have confirmed this by leaving the base (5·5 g.) in 5% oleum (30 g.) for 2 hours at room temperature, then pouring it into 50 c.c. of water, whereby 2·313 g. of benzaldehyde were recovered.

In order to prove that the tendency to salt formation in benzylidene-*m*-nitroaniline is even less than in *m*-nitroaniline (which in turn is already millions of times weaker than diethylbenzylamine, the salt solution of which is still chiefly *o*-, *p*-directive under similar conditions), a comparison was made of the relative thermal stabilities of the *hydrochloride* of benzylidene-*m*-nitroaniline with that of *m*-nitroaniline. The former salt was obtained by passing dry hydrogen chloride through a solution of 1 g. of the base in 30 c.c. of dry benzene, and keeping the filtered salt for 48 hours in a desiccator over potassium hydroxide [Found : Cl (Carius), 13·5. $C_{13}H_{11}O_2N_2Cl$ requires Cl, 13·5%]; this salt is colourless. Carbon dioxide (purified by passage successively through water, silver nitrate solution, and concentrated sulphuric acid) was passed through flasks containing the two hydrochlorides, which were immersed side by side in an oil-bath. Until the temperature of the bath reached 110° no silver chloride was deposited in 2 hours in silver nitrate solutions through which the carbon dioxide passed on leaving the flasks. At 120° the benzylidene-*m*-nitroaniline salt began to give off hydrogen chloride, whereas the *m*-nitroaniline hydrochloride was still stable at 145°, and only began to yield a deposit at 150°. The anhydro-base could be recovered mostly unchanged by shaking 0·200 g. of the salt with benzene and potassium bicarbonate solution until everything was dissolved. The dried benzene solution left 0·174 g. of the base (m. p. 55—57·5°, mixed m. p. 57—59·5°).

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