CXX.—*The Nature of the Alternating Effect in Carbon Chains. Part XV. The Directive Action of Some Groups of the Form* –CR′R″·COR *in Aromatic Substitution.*

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WHEN two atoms having corresponding electronic systems in the combined state, but different nuclear charges, are directly united, it is to be expected that the electrons concerned in the union will be more strongly attracted by the more powerful positive nucleus. Thus, carbon and oxygen in the combined state both possess

10 electrons, and their nuclear charges are in the ratio 6 : 8;[*] hence the electrons of the bond C—O will be more under the influence of the oxygen than of the carbon nucleus. In other words, the oxygen atom will have more than a half-share in these shared electrons, and so on the whole it will be feebly negatively charged. Similarly, the carbon atom, possessing less than a half-share in the same pair of electrons, will on the whole be feebly positively charged: $\overset{\delta+}{\mathrm{C}}\text{—}\overset{\delta-}{\mathrm{O}}$. The electric moment of this fractional dipole will, of course, be very small, but in a double bond, where the electrons are assumed to be more loosely held, the separation of ± charges consequent on an unequal nuclear attraction should be greater and the effects traceable to dipolar character correspondingly enhanced.[†] Thus it follows that so-called non-polar (4-electron) double bonds, such as the carbonyl bond, in which there is reason to suspect an unequal sharing of the electrons, should display to a small, but possibly detectable, extent those properties which are so strikingly characteristic of the semi-polar (2-electron) double bond and depend on the creation of an electrical field.

$$\text{(I.)}\quad -\overset{+}{\mathrm{N}}\rightleftarrows\overset{-}{\mathrm{O}} \qquad\qquad -\overset{\delta+}{\mathrm{C}}=\overset{\delta-}{\mathrm{O}}\quad\text{(II.)}$$

The capacity of the semi-polar double linking (I) for producing *m*-substitution, when its positive end is separated from the benzene nucleus by a saturated carbon atom, is well illustrated by the large degree of *m*-substitution observed in the nitration of phenylnitromethane derivatives (Baker and Ingold, J., 1926, 2462; this vol., p. 261); it has been confirmed by the study of benzylsulphonyl compounds (see Part XIV).

Probably the *m*-orientation effects observed in benzoyl compounds (*e.g.*, benzaldehyde, acetophenone, benzoic acid and its esters) are to be attributed, in part at least, to the occurrence of the fractional dipole (II) in the resting state of the carbonyl group, but in these cases other mechanisms are possible, depending on the alternation of single with double linkings. In phenylacetyl compounds, however, such mechanisms are excluded, and any *m*-nitration, beyond the 3% observed in the case of toluene,[‡] must arise

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[*] The screening effect of the inner pairs of electrons will tend to increase the effective disparity, which will also be somewhat influenced by more distant electronic and nuclear charges.

[†] The permanent fractional dipole moments should be in the order $\mathrm{C}=\mathrm{O} > \mathrm{C}=\mathrm{N}$ and $\mathrm{C—F} > \mathrm{C—O} > \mathrm{C—N}$ in the absence of poles and other powerful disturbances.

[‡] For reasons given previously (J., 1926, 2462), toluene is taken as the standard of reference in the comparisons represented by:

$$\underset{(\text{meta}<3\%)}{C_6H_5{\cdot}CH_2\leftarrow X} \qquad \underset{(\text{meta}=3\%)}{C_6H_5{\cdot}CH_2—H} \qquad \underset{(\text{meta}>3\%)}{C_6H_5{\cdot}CH_2\rightarrow Y}$$

from the permanent dipole. We have therefore studied the nitration of ethyl phenylacetate and are able to show that it forms approximately 9% of *m*-nitro-derivative (IV). To confirm the matter, we have also examined the nitration of ethyl phenylmalonate,* in which the electron-attraction in the side-chain would be expected to be about twice as great, and in this case we find 20% of *m*-derivative (V).

The value for ethyl phenylacetate (IV) may be contrasted with that previously recorded for phenylnitromethane (III) :

$C_6H_5{\cdot}CH_2{\cdot}NO_2$	$C_6H_5{\cdot}CH_2{\cdot}CO_2Et$	$C_6H_5{\cdot}CH(CO_2Et)_2$
(meta, 50%)	(meta, 9%)	(meta, 20%)
(III.)	(IV.)	(V.)

EXPERIMENTAL.

Nitration of Ethyl Phenylacetate.—Radziszewski (*Ber.*, 1869, **2**, 209; 1870, **3**, 648) nitrated this substance and established the formation of the *o*- and *p*-nitro-derivatives.

The ester was run slowly into 6 vols. of nitric acid (*d* 1·50) at 0° and the product was kept at 0° for a further 4 hours, then mixed with ice, and basified with potassium hydroxide. The precipitated nitro-products were collected, washed with cold water, and dried in ethereal solution, to which the ethereal extract of the mother-liquor was added. After analysis, the mixed nitro-compounds were oxidised to nitrobenzoic acids, in which the proportion of *m*-isomeride was determined either by titration (Baker, this vol., p. 565) or by separation (Baker and Ingold, *loc. cit.*).

(Expt. 12.) From 5·350 g. of the ester, 6·174 g. (92%) of nitro-derivatives (Found : C, 57·3; H, 5·4. Calc. : C, 57·4; H, 5·3%) were obtained; a further 6% of the material was accounted for as acid by-products formed by oxidation or hydrolysis. The yield of nitrobenzoic acids was 95% (Found : *M*, 165·6. Calc., 167). On titration, 1·2374 g. required 73·68 c.c. of 0·01029*N*-baryta for the neutralisation of the *m*-acid, corresponding with 0·1266 g. of *m*-nitrobenzoic acid, which when corrected becomes 0·110 g., or 9·3%.

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* The choice of these compounds for study requires some explanation. Benzyl alkyl ketones were ruled out owing to probable disturbances arising from the presence of enols of the type $C_6H_5{\cdot}CH{:}C(OH){\cdot}R$; phenylacetic and phenylmalonic acids should give higher proportions of *m*-derivative than their respective esters *if substitution were to occur exclusively in the undissociated forms*, but, since only a small effect was being sought for, there was no guarantee that the contrary influence of ionisation (preceding paper) would be negligible; the same is true of the influence of alkyl groups in ketones such as $C_6H_5{\cdot}CMe_2{\cdot}COR$; consequently the esters examined belong to one of the few classes of compounds suitable to our purpose.

(Expt. 13.) The yield from 10·00 g. was 12·038 g. (96%) (**Found** : C, 57·3; H, 5·6%), and partial separation prior to oxidation of the unseparated part was effected as follows. An average sample (5·044 g.) was crystallised from ethyl alcohol, yielding 1·038 g. of ethyl *p*-nitrophenylacetate, m. p. 62°, and the residues from the mother-liquor were again crystallised from a small quantity of the same solvent, giving 0·382 g. of the same isomeride, m. p. 60—62° (total, 1·42 g. = 28·2%). From these fractions, by oxidation, *p*-nitrobenzoic acid, m. p. 234° (unpurified; either alone or mixed with a genuine specimen), was obtained in 87% yield. 3·390 G. of the unseparated residues were similarly oxidised in 87·4% yield to nitrobenzoic acids, and on acidification of the alkaline solution 0·667 g. of *p*-nitrobenzoic acid, m. p. 234°, mixed m. p. 234°, crystallised and was collected. Extraction with ether gave 1·680 g. of mixed acids (benzoic acid, 1·1%), 1·500 g. of which, on separation, gave a further 0·262 g. of *p*-nitrobenzoic acid (solubility correction, 0·025 g.) and two fractions of *m*-acid, one of which (0·178 g.) had m. p. 128° and the other (0·139 g.) m. p. 123°, with previous softening in each case (barium salt solubility correction, 0·045 g.). Since these m. p.'s are lower than are usually observed for *m*-acid isolated in similar separations of artificial mixtures, the two fractions were crystallised from ethyl acetate–ligroin, giving 0·152 g. of pure *m*-acid, to which the barium salt solubility correction must be added together with half the weight of the impure residues. Hence the original nitration product contained : para, 28 + 20 + 10 = 58%; meta, 9·5 ± 2·5%; ortho (by difference), 32·5 ± 2·5%.

The figure for the *p*-isomeride was confirmed by an independent nitration (yield 91%, analysis correct, yield on oxidation 93%), which gave para, 59%.

Nitration of Ethyl Phenylmalonate.—The ester (Found : C, 65·4; H, 6·5. Calc. : C, 66·0; H, 6·8%) was prepared by thermal decomposition of ethyl phenyloxaloacetate, which was obtained by condensing ethyl phenylacetate with ethyl oxalate (Wislicenus, *Annalen*, 1888, **246**, 315).

(Expt. 23.) The ester was run slowly into 6 vols. of nitric acid (*d* 1·49) at − 15° to − 10° at the rate of 1 g. per hour, and after being kept for a further hour at the same temperature the mixture was poured on to ice, nearly neutralised with potassium hydroxide, and then completely neutralised with sodium carbonate. The nitration product, a yellow oil, was extracted with ether (Found : C, 54·2; H, 5·1. Calc. : C, 55·5; H, 5·4%) and oxidised with permanganate, and the nitrobenzoic acids were isolated in the usual manner (yield, 90%; *M*, 165·3). 0·4633 G. required 60·96 c.c. of 0·01029*N*-barium hydroxide to neutralise the *m*-acid, corresponding with 0·1065 g., which when corrected becomes 0·0935 g., of this isomeride, that is, 20·2%.

Another portion of the mixed acids after removal of the benzoic acid (1·8%) by sublimation was treated as in Expt. 13, and gave 47% of *p*-acid and 21 ± 5% of *m*-acid; *o*-acid (by difference), 32 ± 5%.

(Expt. 25.) The yield of nitro-compounds from 3·623 g. was 4·161 g. (90%) (Found : C, 54·5; H, 5·4%), which on oxidation gave 0·333 g. of *p*-nitrobenzoic acid (crystallised from the aqueous solution) and 1·151 g. of mixed acids (extracted with ether) (*M*, 168). The extracted portion (0·979 g.) gave 0·142 g. (crystallised) of *m*-nitrobenzoic acid, m. p. 135°, mixed m. p. 140°, and 0·049 g. (extracted with ether), m. p. 115°, mixed m. p. 128—130°. The *p*-acid was accidentally lost before weighing. For the original nitration product, meta = 18%.

Summary.—The above results are collected together in tabular form :

Nitration of Ethyl Phenylacetate and Ethyl Phenylmalonate in Nitric Acid (d 1·5).

		Proportions by separation (%) (corrected for solubilities).			
Side-chain.	Temp. (mean).	*Para-*.	*Meta-*.	% *Meta-* (by estimation).	Mean % *meta-*.
$-CH_2\cdot CO_2Et$	± 0°	58, 59	9·5	9·3	9
$-CH(CO_2Et)_2$	−12·5	47	18, 21	20·2	20

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