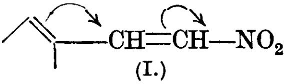
CXXII.—*The Nature of the Alternating Effect in Carbon Chains. Part XVII. The Directive Action of the Groups* $\cdot CH_2\cdot CH_2\cdot NO_2$, $\cdot CH{:}CH\cdot NO_2$ *and* $\cdot C(NO_2){:}CHR$ *in Aromatic Substitution.*

By JOHN WILLIAM BAKER and IAN STUART WILSON.

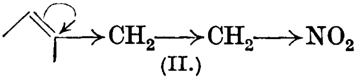
IN preceding parts of this series (Goss, Ingold, and Wilson, J., 1926, 2440; Baker and Ingold, *ibid.*, p. 2462; this vol., p. 261) it is shown that positive poles and the positive ends of dipoles constitute strongly *m*-orienting influences, the effectiveness of which decreases with the intercalation of successive saturated carbon atoms between the charged atom and the nucleus (Goss, Hanhart, and Ingold, this vol., p. 250).

It has been generally assumed that the propagation of electronic disturbances originating in a polar group takes place much more readily in unsaturated carbon chains with conjugated double linkings than in fully saturated carbon chains of similar length, and there is little doubt that this is so in reactions which involve a complete co-valency change such as occurs in triad tautomerism and in the Michael and aldol reactions (Ingold, Shoppee, and Thorpe, J., 1926, 1482; Cooper, Ingold, and Ingold, *ibid.*, p. 1868).

On the other hand, the same view would also be implicit in mechanisms of *m*-substitution in which the conjugation between the nuclear and the side-chain double linking played a fundamental rôle (compare Part XVI), and on the basis of such mechanisms it is to be expected that the transmission of a *m*-orienting influence would be facilitated by the presence of an unbroken conjugated system extending from the polar group throughout the nucleus; thus, on this view, the ω-nitrovinyl group (I) should be more strongly *m*-orienting than the ω-nitroethyl group (II), and so on:



(I.)



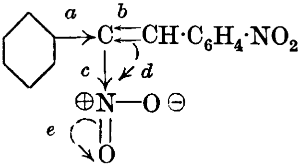
(II.)

Nevertheless, it may be thought doubtful whether such radical electronic disturbances occur even momentarily in the reactions considered, and whether the conjugation referred to is essential to the process of orientation; a preferable view seems to be (Baker and Ingold, Part XV, this vol., p. 833) that a strain or small shift of average position of the electrons is propagated from the polar group, and that it is the degree of inequality in which the electrons are shared at the junction with the aromatic nucleus which determines the *m*-orienting action of the group. If this be so, then, although the arrangement and mobility of the electrons in a non-polar double linking are still matters of speculation, the ethylenic bond undoubtedly represents a high degree of unsaturation which must arise from an adjustable electric field at this point, and therefore it is conceivable that the effect due to a positive charge, such as that of the nitro-group in ω-nitrostyrene, will be neutralised during passage through this field, and never reach the nucleus; the true orienting group will then be the α-carbon atom, and the behaviour of the compound to substituting agents should resemble that of toluene (compare Priebs, *Annalen*, 1886, **235**, 347). Toluene, on nitration in nitric acid, gives 3% of *m*-derivative. On the other hand, the hypothesis (Baker and Ingold, Part XI, this vol., p. 261) of the equivalence between the dipoles of a nitro-group and a primary ammonium salt group (Moore's constitution) requires that β-phenylnitroethane should yield the same proportion of *m*-nitro-derivative as does β-phenylethylamine. β-Phenylethylamine, on nitration, gives 12% of *m*-derivative (Goss, Hanhart, and Ingold, Part X, *loc. cit.*). Hence β-phenylnitroethane should, on this theory, yield definitely more than the unsaturated analogue. Experimental evidence, therefore, should enable a decision to be made between the two suggested mechanisms.

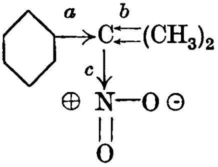
We find that ω-nitrostyrene, on nitration, yields 2% of the *m*-nitro-derivative, whilst β-phenylnitroethane under similar conditions gives 13%.

There is another possible explanation of this result, namely, that the vinyl double bond itself acts as a powerful electron source towards the nucleus, and thus dominates the electron-attraction of the nitro-group. To test this possibility, we have investigated the nitration of an α-nitrovinylbenzene, *viz.*, *p*-nitrobenzylidene-phenylnitromethane (III), in which the double bond is similarly situated with respect to the nucleus but is not in the path of transmission from the nitro-group. In this case, we find more than 20% of *m*-substitution, from which it is clear that the vinyl group, as such, has not a powerful *op*-orienting influence. Indeed, it seems remarkable that the double bond does not compete more effectively with the phenyl group in satisfying the electron-demand of the

(III.)



(meta, 21%)



(IV.)

(meta, 29%)

nitro-group, until it is remembered that each change (*d*) will be accompanied by a change (*e*) on which it is dependent, and that the two together do not alter the charge on the nitrogen atom. All that competes with the *m*-orienting shift (*a*) in satisfying the electron demand (*c*) of the positive pole is the strain represented by (*b*) (inequality of sharing) and it is therefore not surprising that the effect of a group :CHR in modifying the directive action of a nitromethyl side-chain is not much greater than that of the *gem*-dimethyl group (IV) (Baker and Ingold, Parts IX and XI, *loc. cit.*).

EXPERIMENTAL.

A. *Preparation of Materials.*—ω-*Nitrostyrene* was prepared by Thiele and Haeckel's method (*Annalen*, 1902, **325**, 7).

α-*Nitro*-β-*phenylethane* was prepared in accordance with the scheme: $CH_2Ph{\cdot}CH_2{\cdot}OH \xrightarrow{PBr_5} CH_2Ph{\cdot}CH_2Br \xrightarrow{AgNO_2} CH_2Ph{\cdot}CH_2{\cdot}NO_2$. Phosphorus pentabromide in slight excess was added in small, successive portions to β-phenylethyl alcohol, cooled in a freezing mixture. The reaction mixture was finally heated for 0·25 hour on the steam-bath. The product, after cooling, was poured on ice and water, the bromide extracted with ether, and the ethereal solution washed with water and with sodium carbonate solution. The residue from the dried ethereal extract had b. p. 99—103°/14 mm. (compare Grignard, *Compt. rend.*, 1904, **138**, 1049).

A mixture of the bromide and freshly prepared, dry silver nitrite in equal molecular quantities was left in the dark, with frequent shaking, for 1 week. It was then heated at 50—60° for 2 hours, the nitro-compound extracted with ether, the residue from the ether dissolved in dilute sodium hydroxide solution, and the insoluble, unchanged bromide extracted with ether. The nitro-compound was precipitated from the alkaline solution with carbon dioxide, extracted with ether, and the residue from the dried, ethereal extract distilled. α-*Nitro*-β-*phenylethane* has b. p. 125—135°/1 mm. (Found: * C, 61·4; H, 5·8; N, 10·1. $C_8H_9O_2N$ requires C, 63·5; H, 6·0; N, 9·3%). The yield was very small.

p-*Nitrobenzylidenephenylnitromethane.* To phenylnitromethane (5·6 g.) and *p*-nitrobenzaldehyde (6·0 g.), 1 c.c. of 33% aqueous methylamine was added, and the mixture was warmed on the steam-bath (with addition of a few drops of alcohol if necessary) until solution was complete. After remaining for 24 hours at the ordinary temperature, the now almost solid product was filtered off, washed

---

* Methane produced during the combustion accounts for the low result for carbon. The gas obtained in the nitrogen determination (Dumas) contained nitrogen 84·1%, combustible gas (chiefly methane) 15·9%.

with a little alcohol, and recrystallised from ethyl acetate containing a little ligroin (b. p. 80—100°), being thus obtained in fine, yellow needles, m. p. 155° (Found: C, 62·0; H, 3·9. $C_{14}H_{10}O_4N_2$ requires C, 62·2; H, 3·7%).

B. *Nitration Conditions and General Procedure.*—Nitration was carried out in every case at —15° to −10°, the compound being added slowly to 8—10 volumes of nitric acid (*d* 1·49), mechanically stirred. The product was isolated in the usual manner, the details varying slightly in individual cases. The proportions of the isomerides present were determined by oxidation with 2% potassium permanganate, either before or after separation of most of the *p*-isomeride in the pure state, and determination of the mixed nitrobenzoic acids produced, by Baker and Ingold's method (*loc. cit.*) or the titration method (Baker, this vol., p. 565).

C. *Details relating to Individual Cases.*—ω-*Nitrostyrene* was nitrated by Priebs (*loc. cit.*), who isolated the *o*- and *p*-derivatives, but could find no *m*-isomeride.

(*Expt.* 11.) The nitrostyrene (10 g.) was added in small successive portions to 75 c.c. of nitric acid (*d* 1·49) at −15° during 2 hours, and after a further 3 hours the partly crystalline product was poured on crushed ice and the precipitated nitro-compounds were filtered off, washed, and dried over phosphorus pentoxide in a vacuum (91·5%). A further 3·8% of nitro-compounds was obtained from the dried ethereal extract of the mother-liquor, from which any acid fraction had been removed (total yield, 95·3%) (Found: C, 49·4; H, 3·4. Calc.: C, 49·5; H, 3·1%).

A portion (3·00 g.) of the total nitration product on oxidation gave nitrobenzoic acids in 91% yield (*M*, by titration, 166·7). These, on separation by the chloroform–barium salt method, yielded 1·96 g. of *p*-nitrobenzoic acid, m. p. 228—230°, mixed m. p. 234—235°, which, with the solubility correction (0·05 g.), corresponds to 67% of this isomeride in the mixture. On conversion of the dissolved acids into their barium salts and concentration of the solution to 30 c.c., no crystallisation ensued. Hence the meta-content must be less than 0·06 g., *i.e.*, less than 2% of the whole mixture. On acidification and extraction with ether, the solution of the barium salts yielded 0·89 g. of *o*-nitrobenzoic acid, m. p. 115—130° (corresponding to 30% of the whole), which, after two crystallisations from chloroform, melted alone at 137°, at 145° when mixed with *o*-nitrobenzoic acid, and at 108—120° when mixed with *m*-nitrobenzoic acid. The composition of the nitration product is therefore *p*- 67%, *m*- $<2\%$, *o*- (by difference) 31% (30% being actually isolated). The proportion of meta-isomeride in the mixture of nitrobenzoic acids obtained by an independent oxidation (yield

81·9%) of this nitration product, determined by the titration method, was 1·9%.

(*Expt.* 12.) The main portion of the *p*-isomeride was isolated from the nitration product (yield 99%) (Found : C, 49·5; H, 3·4%) before oxidation. The nitration product (5·105 g.) on extraction with 100 c.c. of boiling, absolute alcohol left a residue (α) (2·274 g.); the extract deposited 1·449 g. of crystals (β). The mother-liquor was evaporated to dryness (γ) on the steam-bath. The fraction α had m. p. 200° (softening at 190°) and was pure ω*p*-dinitrostyrene. On oxidation, the fraction β gave nitrobenzoic acids in 94% yield (*M*, 167·5), which on separation gave *p*-, m. p. 228°, 0·501 g. (65%); no *m*-; and *o*- (by difference) 35%, of which 31% was actually isolated, m. p. (after crystallisation from chloroform) 144—145°, mixed m. p. 147°. Fraction γ, on oxidation, gave nitrobenzoic acids in 82% yield (*M*, 170), which on separation gave *p*-, m. p. 210—220°, 17·9%; *m*-, m. p. 110—114°, mixed m. p. with *m*- 128—131°, mixed m. p. with *o*- 98—120°, 10·1%; *o*- (by difference) 72%, of which 63% was isolated, m. p. 141°, mixed m. p. 142—145°. The composition of the nitration product is therefore : *p*- = 44·3% (α) + 18·4% (β) + 4·8% (γ) = 67·5%; *m*- = 2·7% (γ); *o*- (by difference) = 29·8%.

α-Nitro-β-phenylethane. Since only a very small quantity of this substance was available, owing to the difficulty of preparation, the result obtained can only be regarded as approximate. The quantity of *m*-isomeride found is, however, in agreement with that obtained on nitration of the corresponding ammonium salt $CH_2Ph{\cdot}CH_2{\cdot}\overset{+}{N}H_3{\cdot}\overset{-}{X}$ (compare p. 843).

(*Expt.* 21.) The nitro-compound (1·069 g.) was added to 15 c.c. of nitric acid (*d* 1·49) at —15° to —10° during 50 minutes, and after ½ hour the temperature was allowed to rise to —5°, a slight evolution of brown fumes then being observed. The product was poured on crushed ice, and the solution obtained was neutralised partly with 10% aqueous sodium hydroxide and finally with precipitated chalk, and extracted with ether. The yield of neutral nitration product was 78·5% (Found : C, 49·8; H, 4·0. $C_8H_8O_4N_2$ requires C, 49·0; H, 4·2%); acid products amounted to 10·8%. The neutral portion, on oxidation, gave nitrobenzoic acids in 70% yield (*M*, 164) (benzoic acid, by sublimation, 10·5%, which was deducted in calculating the percentages of isomerides present), of which 29·4% consisted of *p*-nitrobenzoic acid, m. p. 224—228°, which crystallised, the remainder being extracted with ether. Separation of a representative sample of the extracted portion in the usual manner showed it to consist of *p*-, m. p. 210—215°, mixed m. p. 220—224°, 32·5%; and *m*-, m. p. 123—125°, mixed m. p. 135—137°, 18·9%, whence the composition of the nitration mixture was *p*-, 29·4% + (32·5% of 70·5%) = 52·3%; *m*-, (18·9% of 70·5%) = 13·3%; *o*- (by difference), 34·4%.

p-*Nitrobenzylidenephenylnitromethane.* (*Expt.* 31.) In this, a preliminary experiment, the nitromethane (0·832 g.) was added to 10 c.c. of nitric acid (*d* 1·49) at —20° to —15° during 0·75 hour, the product was left in the freezing mixture for 1·3 hours and then poured on crushed ice, and the precipitated solid (yield 82%) was filtered off, washed, and dried in a vacuum over phosphorus pentoxide (Found: C, 52·9; H, 3·3. $C_{14}H_9O_6N_3$ requires C, 53·3; H, 2·9%). On oxidation, the nitro-compound gave nitrobenzoic acids in 90% yield, a large proportion of the *p*-isomeride being allowed to crystallise before extraction of the mother-liquor with ether. Separation by the chloroform–barium salt method gave, after deduction of the *p*-nitrobenzoic acid produced by oxidation of the *p*-nitrobenzylidene portion of the molecule, *p*-, m. p. 235°, 49%; *m*-, m. p. 125°, mixed m. p. 137—138°, 19·5%; *o*- (by difference), 31·5%.

(*Expt.* 33.) The nitromethane (2·02 g.) gave, under the same conditions as before, 2·306 g. of precipitated nitro-compound (Found: C, 52·6; H, 3·1%) and 0·032 g. extracted with ether (total yield 96%), of which 1·861 g. on oxidation gave 1·081 g. of *p*-isomeride, m. p. 228—232°, mixed m. p. 235°, and 0·540 g. of extracted acids (*M*, by titration, 170) (total yield 83%). On separation, 0·473 g. of the extracted acids gave 0·079 g. of *m*-acid (crystallised), m. p. 131—133°, mixed m. p. 140—141°, and 0·074 g. (extracted), m. p. 124°, mixed m. p. 138° (solubility correction, 0·0054 g.), and 0·077 g. of *p*-nitrobenzoic acid, m. p. 230—232° (solubility correction, 0·007 g.). Hence the composition of the whole of the nitrobenzoic acids obtained (1·620 g.) was *p*-, 1·080 + 0·540/0·473 of (0·077 + 0·007) = 1·175 g.; *m*-, 0·540/0·473 × 0·153 = 0·175 g. Of this 50%, the total yield, 0·810 g. is *p*-nitrobenzoic acid obtained from the oxidation of the *p*-nitrobenzylidene group, so that the 0·810 g. of mixed nitrobenzoic acids obtained by oxidation of the nitrated benzene ring contained *p*-, 0·365 g., and *m*-, 0·175 g., whence the composition is *p*-, 45·1%; *m*-, 21·6%; *o*- (by difference), 33·3%.

(*Expt.* 34.) Under the same conditions as before and by analogous methods of separation, 2·20 g. of the nitromethane yielded 2·542 g. (96%) of neutral nitration product (Found: C, 53·4; H, 2·7%), which, on oxidation, gave nitrobenzoic acids (95% yield) (*M*, 166·8; benzoic acid, by sublimation, 1·6%). Separation as before showed that the composition of the nitrobenzoic acids representing the proportions of isomerides formed by nitration was *p*-, m. p. 233°

either alone or mixed with a pure specimen, 49·7%; *m*-, m. p. 135°, mixed m. p. 141°, 20·9%; *o*- (by difference), 29·4%.

The results obtained are summarised below.

	Percentage of isomerides.					
	By separation.			By titration.	Mean %.	
Substance nitrated.	*o*.	*m*.	*p*.	*m*.	*m*.	*p*.
$CHPh{:}CH{\cdot}NO_2$	31	<2	67	1·9	2	67
	29·8	2·7	67·5	—		
$CH_2Ph{\cdot}CH_2{\cdot}NO_2$	34·4	13·3	52·3	—	13	52
$CPh(NO_2){:}CH{\cdot}C_6H_4{\cdot}NO_2$	31·5	19·5	49·0	—	21	48
	33·3	21·6	45·1			
	29·4	20·9	47·9			

We desire to thank Professor C. K. Ingold, F.R.S., for his kindly and helpful interest in this investigation, and the Royal Society for defraying part of the expense incurred.

THE UNIVERSITY, LEEDS.

[*Received, January* 15*th,* 1927.]