CCXCII.—*The Nature of the Alternating Effect in Carbon Chains. Part XXXI. The Directive Influence of ψ-Acid Systems in Aromatic Substitution. Nitration of ψ-Acidic Phenylnitromethanes and their Salts.*

By John William Baker.

As a result of previous work on the genesis of orienting effects in aromatic substitution the broader features of directive action by ionic and neutral substituents are now known, but several points still require elucidation with regard to direction by ionogenic systems, that is, substituents which tend to acquire a charge by interaction with the medium under the conditions employed for further substitution of the aromatic nucleus. The simple case presented by phenols and amines in which charges may be generated on the atom adjacent to the nucleus by ion-formation under the conditions of substitution has frequently been discussed, and the major phenomena do not present theoretical difficulty. A more complex case arises when ion-formation may create a charge at a distance from the nucleus, and the side chain has a structure which admits of the transference of this charge by tautomeric change to the atom adjoining the nucleus—in which position, of course, its influence on orientation will be paramount. This phenomenon should appear in compounds in which phenyl is attached to the "pseudo-position" either of a *ψ*-acidic or of a *ψ*-basic group (Baker, J., 1928, 1281; Ingold, *Ann. Reports*, 1928, 140), and the present paper relates to the former of these examples.

According to the general theory of tautomerism advocated from these laboratories, the production of ionisation by either a positive or a negative charge in any substance containing a formal tautomeric system is followed instantly and automatically by the distribution of this charge between all the positions in the structure to which tautomeric electron displacements can give it access. Thus in the anion of *ψ*-acidic phenylnitromethane derivatives, the free access of the anionic charge to the α-carbon atom, $\mathrm{C_6H_5\cdot\overbrace{CR{\vdots}\underset{\oplus}{N}\underset{\ominus}{O}\cdot O}^{\ominus}}$, as and when the substituting agent demands available electrons in the aromatic nucleus, should lead to *op*-orientation, despite the contrary influence of the more distant dipole in the nitro-group and the possible contrary influence of R (compare *loc. cit.*).

Evidence on this matter should be obtainable from a comparative study of the substitution of *ψ*-acidic phenylnitromethanes and their salts. Flürscheim and Holmes record (J., 1928, 453) that the sodium salt of phenylcyanonitromethane yields *op*-products on nitration,* but the metal-free parent *ψ*-acid is insufficiently stable to be nitrated, and a direct comparison of results is consequently impossible. Ethyl α-nitrophenylacetate, $\mathrm{C_6H_5\cdot CH(CO_2Et)\cdot NO_2}$, was, however, nitrated smoothly, and its *lithium* salt proved to be a tractable, readily purified substance. Evidence of the expected

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* Flürscheim and Holmes state that more than 99% of *op*-nitro-products are formed, but in the author's hands (see p. 2264) the nitration was far from being the smooth reaction suggested by the data they record (*loc. cit.*). A circumstance which, however, has defeated the exact repetition of Flürscheim and Holmes's work on this substance is that in four of their five experiments the weights of the separated products, given in the experimental portion of their paper, when converted into molecular percentages and summed, indicate quantitative recovery (more than 99·5%), whilst the present author finds it difficult to maintain an average recovery of much more than 90% even for nitrations that proceed smoothly, and in the instance now considered the formation of unidentified matter impairs the yield still further.

effect was most strikingly revealed in the observations that on nitration with nitric acid ($d_{4^\circ}^{15^\circ}$ 1·497) at — 15° the free ψ-acid gave a mononitration product containing 84% of *m*-derivative, whereas the mononitro-derivatives obtained from the salt contained only 29% of the *m*-isomeride.

Interesting results were obtained on studying, side by side, the effect of changing the concentration of the nitric acid on the proportions of the isomerides formed by nitration of the ψ-acid and its salts. An increase in the strength of the acid from $d_{4^\circ}^{15^\circ}$ 1·497 to $d_{4^\circ}^{15^\circ}$ 1·529 had no perceptible effect on the proportions of the isomerides obtained from the free ψ-acid, the amount of *m*-derivative remaining at 84—85%. On the other hand, the proportions of *m*-isomeride obtained from the salt rose over the same range of acid concentrations from 29% to 78—82%, the limits arising from the circumstance that the lithium salt separates from ethyl alcohol with one molecule of solvent and that the solvated and solvent-free salts, which were both studied, behave slightly differently in acid of high concentration. The general result, the essential numerical data for which are in the following table, suggested that the speed of conversion of the liberated anion into the molecular ψ-acid is greatly increased with increasing strength of the acid medium, and that therefore the lowest *m*-proportion actually realised in the nitration of the salt (29%) is higher than that which would be observed if the anion could be " caught " by the reagent before any conversion into the ψ-acid had occurred.

Nitration of Ethyl α-Nitrophenylacetate.

				Composition of product (mols. %).			Composition of mononitration product (mols. %).	
No.	HNO_3, $d_{4^\circ}^{15^\circ}$ (10 parts).	Temp.	Time (hrs.).	Unsubstituted.	*op*-Nitro-.	*m*-Nitro-.	*op*-.	*m*-.
1	1·497	−12°	1·25	3·5	15·4	81·1	15·9	84·1
2	1·529	−12	1·50	5·2	13·8	81·0	14·6	85·4
3	1·529	−5 room	1·75 0·08	3·8	15·7	80·5	16·4	83·6
						Mean	15·6	84·4
				Nitration of Lithium Salt of Ethyl α-Nitrophenylacetate.				
4*	1·497	−12	1·25	59·3	28·7	12·0	70·5	29·5
5*	1·517	−12	1·25	18·2	24·7	57·1	30·2	69·8
6*	1·529	−12	2·00	6·9	20·7	72·4	22·2	77·8
7	1·517	−12	1·00	13·6	18·8	67·6	21·7	78·3
8	1·529	−5 room	1·50 0·08	5·3	17·1	77·6	18·0	82·0
9	1·529	0 room	2·00 0·50	4·1	16·8	79·1	17·5	82·5

* Salt with 1EtOH.

Similar results have been obtained for the nitration of phenylnitromethane and its potassium and sodium salts. The proportion of *m*-isomeride in the mononitration product of the free ψ-acid is 67% independently of the concentration of the nitric acid between $d_{4^\circ}^{15^\circ}$ 1·483 and 1·529. The proportion of *m*-isomeride formed by nitration of the salts rises from 42% in acid $d_{4^\circ}^{15^\circ}$ 1·497 to 67% in acid $d_{4^\circ}^{15^\circ}$ 1·529. This change (42%⟶67%) is less marked than the corresponding change shown by the carbethoxy-derivative (29%⟶80%) over the same range of acid concentration; and this is a result which might have been expected, because the absence of the electron-attracting carbethoxyl group will reduce the stability of the anion relatively to that of the molecular ψ-acid, so that under given conditions a smaller proportion of the anion will undergo nitration prior to its conversion into the ψ-acid.

*Nitration of Phenylnitromethane.**

No.	HNO$_3$, $d_{4^\circ}^{15^\circ}$ (10 parts).	Temp.	Time (hrs.).	Composition of product (mols. %).			Comp. of mononitration product (mols. %).	
				Unsubd.	*op*-Nitro-.	*m*-Nitro-.	*op*-.	*m*-.
10	1·483	−12°	1·75	7·0	30·0	63·0	32·2	67·8
11	1·529	−12	3·00	0·0	34·2	65·8	34·2	65·8
						Mean	33·2	66·8

Nitration of Salts of Phenylnitromethane.

12 (K)	1·483	−15	1·00	96·3	2·3	1·4	62*ca.*	38*ca.*
13 (K)	1·497	−12	1·50	64·2	20·6	15·2	57·6	42·4
†14 (Na)	1·529	−10 (room)	2·75 0·50	11·8	30·2	58·0	34·2	65·8
15 (Na)	1·529	−15	3·50	24·0	24·0	52·0	31·6	68·4
16 (Na)	1·529	−15	3·50	12·3	27·6	60·1	31·5	68·5

* Compare Baker and Ingold, this vol., p. 423, footnote.

† Prepared from unpurified phenylnitromethane.

The experimental data on which the figures in the last five columns of the above tables are based are recorded on p. 2263.

EXPERIMENTAL.

Preparation of Materials.—1. Ethyl α-nitrophenylacetate was prepared by Wislicenus and Ender's method (*Ber.*, 1902, **35**, 1707). These investigators describe it as an oil which cannot be purified by distillation. It can, however, be readily purified through its crystalline lithium compound.

Condensation of ethyl phenylacetate (33 g.) and ethyl nitrate (18·2 g.) in ether (100 c.c.) with sodium wire (4·6 g.) proceeded smoothly, a white sodium compound separating. This was filtered off and well washed with ether containing a little alcohol. The filtrate and washings were extracted with water, the aqueous solution was acidified with hydrochloric acid and extracted with ether, and the ethereal solution was repeatedly extracted with potassium hydrogen carbonate solution to remove phenylacetic acid. The residue (10 g.) from the dried ethereal solution was a yellow oil consisting of crude ethyl α-nitrophenylacetate. This was added with cooling to alcoholic lithium ethoxide prepared from lithium (0·35 g.) and absolute alcohol (20—30 c.c.). After a few minutes the mass became almost solid owing to separation of the *lithium* salt. This, after being collected and washed with a 50% alcohol–ether mixture and finally with dry ether, crystallised well from hot absolute alcohol in clusters of fine needles containing 1 mol. of alcohol, which was lost by heating to 150°; the solvent-free salt had m. p. 200° (Found : Li, 2·6; C_2H_5·OH, by loss of weight at 150°, 17·8. $C_{10}H_{10}O_4NLi,C_2H_5$·OH requires Li, 2·7; C_2H_5·OH, 17·6%).

The sodium salt which separated during the original condensation did not appear to be a salt of ethyl α-nitrophenylacetate. Acidified with ice-cold dilute sulphuric acid and extracted with ether, it yielded a yellow syrup, which immediately began to evolve nitrous fumes when the last traces of ether were removed on a steam-bath. The product, on treatment with alcoholic lithium ethoxide, yielded a relatively small amount of a solid derivative only after several days. This substance, containing lithium and nitrogen, crystallised from ether–ligroin, but was not further investigated. After some weeks, the original syrup yielded a small amount of crystalline material which consisted of a mixture of two substances readily separated by fractional crystallisation from ethyl acetate–ligroin, colourless needles, m. p. 162—163°, separating first, and the mother-liquor yielding yellow crystals, m. p. 133—134°. These have not yet been investigated.

Pure ethyl α-nitrophenylacetate (Found : C, 57·4; H, 5·2. Calc. for $C_{10}H_{11}O_4N$: C, 57·4; H, 5·3%) was obtained in the usual manner from the purified lithium salt.

2. Phenylnitromethane was prepared by Holleman's method (*Rec. trav. chim.*, 1894, **13**, 405). The sodium salt was obtained by the action of the theoretical quantity of alcoholic sodium ethoxide on pure phenylnitromethane. It could not be crystallised and was purified by precipitation with ether from its solution in alcohol (Found : Na, 13·2. Calc. : Na, 14·4%). The potassium salt, obtained similarly, could be crystallised from absolute alcohol (compare Wislicenus and Grunthner, *Ber.*, 1907, **42**, 1932).

3. The sodium salt of phenylcyanonitromethane was prepared by Wislicenus and Ender's method (*loc. cit.*) and purified by crystallisation from absolute alcohol.

Nitration. General Procedure.—The phenylnitromethane derivative was added slowly (from a dropping-funnel if a liquid) with mechanical stirring to 10 parts of the nitric acid cooled to the requisite temperature in a freezing mixture. The nitration mixture was poured on crushed ice and neutralised with precipitated calcium carbonate and the neutral portion was extracted with ether. The density of the nitric acid was determined in a 5 c.c. pyknometer in the usual manner. The particular conditions are specified in the tables on p. 2259, the composition of the product there recorded being the proportions of the total recovered material. In the table on p. 2263, the actual weights of material used and recovered are given, the percentages recorded in the previous tables being calculated from these figures. In all cases 90—98% of the material was accounted for after nitration either as un-nitrated substance or as neutral mononitrated product.

Details relating to Special Cases.—*Experiment No.* 2. The nitration product partly crystallised and an attempt was made to separate one of the isomerides by crystallisation. The product (0·6670 g.) was washed with ice-cold ether, in which the oil was more readily soluble, 0·5990 g. passing into solution. The residual solid, crystallised from absolute alcohol, yielded 0·0291 g. (4·4%) of a substance, m. p. 187°, which was probably ethyl *αp*-dinitrophenylacetate, but it was not obtained in sufficient quantity for investigation. An attempt to prepare this isomeride by condensing ethyl *p*-nitrophenylacetate and ethyl nitrate in presence of sodium was not successful.

Experiment No. 10. In this case a portion of the nitration product was oxidised directly with boiling 3% potassium permanganate solution, and the remainder by Flürscheim and Holmes's method C, in order to determine whether an appreciable amount of re-arrangement occurs by use of the former method. The proportions of *op*- and *m*-nitro-products found were, respectively, 39·4 and 60·6% by the direct method and 32·2 and 67·8% by the latter method, indicating that a slight amount of re-arrangement renders the direct method less trustworthy in the case of phenylnitromethane derivatives. In Experiment No. 6 a similar comparison was made with similar results, the proportions of *op*- and *m*-nitro-products found being, respectively, 24·5 and 75·5% and 22·3 and 77·7%.

Experiment No. 11. The partly solid nitration product (0·5459 g.) was crystallised from 6 c.c. of pure ether. The first crop of crystals (0·2135 g.) had m. p. 95—96° and consisted of pure *m*-nitrophenylnitromethane (39·1%). From the mother-liquor and washings a further 0·1005 g. (18·4%) of a less pure product, m. p. 70°, was obtained.

Composition of the Nitration Products.

						Reduction and Bromination of Acids.				
							Found (g.).			
No.	Material used (g.).	Yield (g.) of product, neutral.	Yield (g.) of product, acid.	Product oxidised (g.).	Yield of acids (g.).	Used (g.).	Benzoic.	Tribromoaniline from *op*-nitro-acid.	Tribromoamino-benzoic acid from *m*-nitro-acid.	Method of oxidation.
I. Ethyl *a*-nitrophenylacetate.										
1	1·820	2·055	—	1·858	0·860	0·707	0·016	0·189	1·109	F. & H. method C.
2	2·121	2·408	—	1·573	0·874	0·595	0·020	0·139	0·920	,,
3	1·301	1·446	—	1·204	0·624	0·560	0·014	0·153	0·896	,,
II. Lithium salt of ethyl *a*-nitrophenylacetate.										
4	2·50	2·386	—	2·213	0·792*	0·637	0·290	0·381	0·184	,,
5	2·476	2·522	—	2·170	1·322	0·874	0·094	0·351	0·918	,,
6	4·00	4·130	—	2·235	1·035	0·771	0·030	0·239	0·941	,,
				1·562	0·813	0·572	0·050(?)	0·222	0·774	Direct
7	1·012	1·250	—	1·088	0·560	0·476	0·045	0·169	0·687	F. & H. method C.
8	0·780	0·910	—	0·791	0·450	0·398	0·012	0·105	0·458	,,
9	1·500	1·795	—	1·568	0·964	0·720	0·020	0·221	1·182	,,
III. Phenylnitromethane.										
10	2·169	2·812	—	2·049	1·653	1·148	0·049	0·586	1·360	,,
				0·625	0·481	0·474	0·033	0·289	0·505	Direct
11	2·182	2·740	—	2·033	1·834	1·002	0·00	0·623	1·365	F. & H. method C.
IV. Salts of phenylnitromethane.										
12	1·500	0·813	—	0·813	0·612	0·549	0·476	0·030	0·021	,,
13	1·200	0·791	—	0·791	0·476	0·453	0·207	0·183	0·153	,,
14	3·000	2·407	0·799	2·024	1·389	0·828	0·072	0·443	0·985	Direct
15	1·552	0·990	—	0·90	0·693	0·628	0·095	0·258	0·633	,,
16	1·414	1·132	0·394	1·017	0·868	0·759	0·055	0·334	0·816	F. & H. method C.
V. Sodium salt of phenylcyanonitromethane.										
17	3·00	2·531	—	2·531	1·760	0·664	0·154	0·620	(0·219)†	Direct
18	2·00	1·938	—	1·286	0·730	0·646	0·254	0·553	(0·081)†	F. & H. method C.

A bar signifies not weighed. * Some mechanical loss before weighing. † Material which is not pure tribromoaminobenzoic acid.

Experiments Nos. 17 *and* 18. In these experiments, details of which are not recorded in the tables given in the introduction, the conditions of nitration were as follows : No. 17. Nitration was effected with nitric acid $d_{4^\circ}^{15^\circ}$ 1·529 (8 parts) at – 10° for 1·8 hours, and the nitration mixture was kept at room temperature for 0·25 hour before being worked up in the usual manner. In No. 18, Flürscheim and Holmes's conditions (*loc. cit.*) were used, nitration being effected with nitric acid $d_{4^\circ}^{15^\circ}$ 1·481 (13 parts) at 15° for 1 hour.

The author wishes to thank the Chemical Society for a grant in aid of this work.

THE UNIVERSITY, LEEDS. [*Received, July* 8*th*, 1929.]