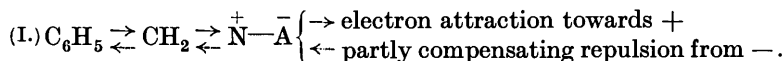


XLI.—*The Nature of the Alternating Effect in Carbon Chains. Part XI. Further Evidence on the Substitution of Benzylamine Salts.*

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It has previously been suggested (Goss, Ingold, and Wilson, J., 1926, 2440) that the formation of comparatively large quantities of *m*-isomeride in the nitration of benzylamine salts arises from the action of the dipole contained in the salt grouping, which sets up electronic strain of a similar kind to that produced by the free charge in the corresponding ion (I; A = H); and in support of this view it has, *inter alia*, been shown (Baker and Ingold, J., 1926, 2462) that phenylnitromethane, a substance analogous to a benzylamine salt but containing a stable dipole (I; A = O), nitrates in the *m*-position to approximately the same extent as benzylamine itself.



Although this result was predicted from the analogous constitution of the two types, agreement in a single case may possibly be fortuitous, and it was therefore considered desirable to extend the comparison to a series of substituted benzylamines (II) and the corresponding phenylnitromethane derivatives (III) in order to ascertain if the agreement were general.



The nitration of benzylamine itself (II; RR' = H₂), of β-nitro-β-phenylpropane (III; RR' = Me₂), and of phenylnitromethane (III; RR' = H₂) had already been carried out, and in this paper the nitration of α-phenylethylamine (II; RR' = MeH), α-phenylisopropylamine (II; RR' = Me₂), and α-nitro-α-phenylethane (III; RR' = MeH) is described. The results obtained render possible a comparison between the three pairs of analogously constituted benzylamine and phenylnitromethane derivatives.

The proportion of *m*-isomeride formed in each case is indicated in the following table :

Type.	RR' = H ₂ .	RR' = MeH.	RR' = Me ₂ .	
C ₆ H ₅ ·CRR'·NH ₂ X	49	40	26	% meta-derivative.*
C ₆ H ₅ ·CRR'·NO ₂	50	43	27	„ „ „ *

* Estimated from the weights of separated but unrecrystallised *m*-nitrobenzoic acid obtained after oxidation of the mixed isomerides (compare preceding paper).

In all three cases the anticipated agreement is found to exist.

EXPERIMENTAL.

In this section, only those details are recorded which could not be inferred from the experimental descriptions given in Parts VIII, IX, and X (J., 1926, 2440, 2462; preceding paper).

(i) *Nitration of α-Nitro-α-phenylethane.*—The nitro-compound (b. p. 126—130°/30 mm.), prepared as already described (Baker and Ingold, *loc. cit.*), was nitrated at -15° with nitric acid (*d*¹⁶ 1.49). The rate of addition of the nitro-derivative to the acid was 1.0 g. per hour, and the mixture was kept for a further 3.0 hours at -15—-10° before being warmed to 0°; ice was then added. On being worked up as in the nitration of phenylnitromethane (*loc. cit.*), the nitration product (Found: C, 48.8; H, 4.6. Calc.: C, 48.6; H, 4.2%) was obtained; it crystallised almost completely, and a portion when drained had m. p. 80°. The total yield was 91%, and a further 3% of the material was accounted for as acid by-products. The whole nitration product, on oxidation by permanganate, gave mixed nitrobenzoic acids (Found: C, 50.4; H, 3.6. Calc.: C, 50.3; H, 3.0%) in 96% yield. The separated *p*-nitrobenzoic acid (34%) had m. p. 228° (mixed m. p. 231°). The separated *m*-nitrobenzoic acid (43%) was collected in two portions, one, the major portion (precipitated), having m. p. 136° (mixed m. p. 141°), and the second (extracted with ether) having m. p. 123° (mixed m. p. 134—135°).

(ii) *Nitration of α-Phenylethylamine.*—*α*-Phenylethylamine (10 g.) was nitrated with nitric acid (60 g.; *d*¹⁶ 1.50) at -10°. The addition occupied 3.5 hours, and the product was kept at -10° for a further 1.5 hours, warmed to 0° during 1.5 hours, and mixed with ice. After the extraction of neutral and acid by-products with ether, the nitro-bases were liberated by addition of sodium hydroxide and extracted with ether, and then re-extracted from the ethereal solution with dilute hydrochloric acid. The yield of hydrochlorides was 89% (Found: Cl, 17.7. Calc.: Cl, 17.5%). Oxidation by permanganate gave nitrobenzoic acids in a yield of 89% (Found: *M*, 167; benzoic acid, by sublimation, nil).

The separated *p*-nitrobenzoic acid (56%) had m. p. 229° (mixed m. p. 233—234°), and the *m*-acid (38%) m. p. 133° (mixed m. p. 139°).

The mixed hydrochlorides were converted into picrates and these were crystallised from 50% methyl alcohol. The crystallised portion (64%, m. p. 190—205°), on oxidation with permanganate, gave nitrobenzoic acids (Found: *M*, 168; benzoic acid, nil) in 85% yield. On separation, the *p*-acid (75%) had m. p. 234—235° (mixed m. p. 234—235°) and the *m*-acid (20%) had m. p. 131—137° (mixed m. p. 138—140°). The mother-liquor from the crystallisation of the picrates was evaporated with water to remove the methyl alcohol and oxidised; nitrobenzoic acids were then isolated in 82% yield (Found: *M*, 166; benzoic acid, 1.1%). The separated *p*-acid (17%) had m. p. 230—234° (mixed m. p. 232—235°), and the *m*-acid (78%) m. p. 129—136° (mixed m. p. 137—140°). After one crystallisation from ethyl acetate-ligroin, the latter melted at 140°. Combining the results obtained with these two picrate fractions, the original nitration product is estimated to have contained: para, $0.17 \times 36 + 0.75 \times 64 = 54\%$; meta, $0.78 \times 36 + 0.20 \times 64 = 41\%$. The mean of the two determinations gives *para* 55%, *meta* 40%.

(iii) *Nitration of α -Phenylisopropylamine*.—This base was prepared according to the scheme $\text{CH}_2\text{Ph}\cdot\text{CN} \longrightarrow \text{CMeHPh}\cdot\text{CN} \longrightarrow \text{CMe}_2\text{Ph}\cdot\text{CN} \longrightarrow \text{CMe}_2\text{Ph}\cdot\text{CO}\cdot\text{NH}_2 \longrightarrow \text{CMe}_2\text{Ph}\cdot\text{NH}_2$, Haller and Bauer's procedure (*Ann. Chim. Phys.*, 1918, 9, 8) being followed in the first three stages. The last stage has been effected by Brander (*Rec. trav. chim.*, 1918, 37, 67), who, however, records no detailed directions. Bromine (27 g.) and the amide (27 g.) were successively added to a solution of potassium hydroxide (9.5 g.) in water (90 c.c.), and the yellow suspension thus formed was gradually added with cooling to a solution of potassium hydroxide (28.5 g.) in water (300 c.c.). After heating on the water-bath for 1 hour, the mixture was cooled and extracted with ether, and the base was extracted from the ether with aqueous hydrochloric acid, liberated by the addition of alkali, and then re-extracted with ether. It had b. p. 94—95°/22 mm., and the hydrochloride had m. p. 240° (decomp.) (Found: Cl, 20.7. Calc.: Cl, 20.7%). The same base was also obtained in small yield by reduction of β -nitro- β -phenylpropane, as described by Konovalov (*J. Russ. Phys. Chem. Soc.*, 1894, 26, 68); the hydrochloride obtained in this way had the same m. p., and a mixture with the other specimen showed no m. p. depression (Konovalov records m. p. 235.5°).

Nitration was effected at -10° with nitric acid (d^{16° 1.49), the speed of addition being 1.1 g. per hour. The product was kept

for a further 3 hours at about -10° and for 0.3 hour at 0° ; ice was then added and the mixed nitro-bases were isolated as hydrochlorides. The yield was 95% (Found: Cl, 16.4. Calc.: Cl, 16.4%), and a further 2% of the material used was obtained as acid by-product, evidently formed by oxidation. The mixed chlorides, on oxidation with nitric acid, gave nitrobenzoic acids in 82% yield (Found: *M*, 165.5; benzoic acid, nil). The separated *p*-acid (58%) had m. p. $233-235^{\circ}$ and the mixed m. p. was $234-235^{\circ}$. The *m*-acid was collected in two portions; one (precipitated; yield 19%) had m. p. $138-139^{\circ}$, the mixed m. p. being 140° , whilst the other (extracted; 8%) had m. p. $129-134^{\circ}$ (mixed m. p. $137-139^{\circ}$), and on crystallisation from ethyl acetate-ligroin had m. p. $139-140^{\circ}$. The total *m*-acid was therefore 27%.

The mixed hydrochlorides (2.00 g.) were converted into picrates, which crystallised from 300 c.c. of boiling water in bunches of sulphur-yellow needles, m. p. 230° (1.68 g.). These, on crystallisation from 125 c.c. of boiling water, yielded 1.51 g. (40%) of crystals, m. p. 234° , and further crystallisation did not alter this m. p. This compound appears to be α -*p*-nitrophenylisopropylammonium picrate (Found: C, 44.5; H, 3.7. $C_{15}H_{15}O_9N_5$ requires C, 44.0; H, 3.7%), since oxidation of the corresponding nitrate with nitric acid gave *p*-nitrobenzoic acid, m. p. $230-233^{\circ}$, mixed m. p. $232-235^{\circ}$, in 86% yield. The combined mother-liquors, containing 60% of the original mixed picrates, were worked up for nitro-bases and these were oxidised; an 81% yield of nitrobenzoic acids was then obtained (Found: *M*, 168; benzoic acid, nil). The separated *p*-nitrobenzoic acid (33%) had m. p. $225-232^{\circ}$, mixed m. p. $229-234^{\circ}$; the *m*-acid was isolated in two portions, one (precipitated) having m. p. $136-139^{\circ}$, mixed m. p. $139-140^{\circ}$ (32%), and the other (extracted from solution with ether) having m. p. $126-132^{\circ}$, mixed m. p. $136-140^{\circ}$ (10%). The latter portion, after a single crystallisation from ethyl acetate-ligroin, had m. p. 140° . The original mixture of picrates is therefore estimated to have contained: *para*, $40 + 0.33 \times 60 = 60\%$; *meta*, $0.42 \times 60 = 25\%$. The mean of the two determinations gives *para*, 59%; *meta*, 26%.

We desire to thank the Royal Society for defraying part of the expense of this research.