ACTA CHEMICA SCANDINAVICA 8 (1954) 1211—1217

# Studies on Antimetabolites

## II. Synthesis of "*Neo*tyramine" and "*Neo*hordenine", the $\beta,\beta$-Dimethyl Analogues of Tyramine and Hordenine *

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The synthesis of the $\beta,\beta$-dimethyl analogues of tyramine and hordenine, *viz.* $\beta$-(*p*-hydroxyphenyl)*iso*butylamine and N,N-dimethyl-$\beta$-(*p*-hydroxyphenyl)*iso*butylamine, and some related compounds by the reactions shown on p. 1214 is described.

In connection with the investigation of the $\beta,\beta$-dimethyl analogues of phenylalanine and tyrosine, discussed in part I of this series [1], it was of interest to test the pharmacological activity of their decarboxylation products *viz.* $\beta$-phenyl- and $\beta$-(*p*-hydroxyphenyl)*iso*butylamine (I and II resp.). These compounds were prepared, and as the intermediates were considered to be valuable for the synthesis of the above mentioned amino acids *via* the corresponding acyl cyanides and $\alpha$-ketocaids, a route which was abandoned when these acids became available by a different method [1], the syntheses were studied in some detail. In addition to the amines $\alpha$-(*p*-aminophenyl)*iso*butyric acid (III) was prepared because of its interest as a potential *p*-aminobenzoic acid antagonist, as well as the ethyl (IV) and $\beta$-N,N-dimethylaminoethyl (V) esters of the former acid, which were of some interest because of their relation to the local anesthetics of the *p*-aminobenzoic acid ester type, and to the antispasmodics of $\alpha,\alpha$-dialkylphenylacetic acid aminoalkyl ester type studied by Domenjoz *et al.* and Jensen *et al.* [2].

It is the purpose of the present paper to describe the synthetical work, whereas the results of the physiological studies will be published elsewhere.

The principle steps involved in the syntheses are shown in Fig. 1.

The starting material, $\alpha$-phenyl*iso*butyronitrile (VI), was obtained by methylation of benzyl cyanide according to Darzens and Lévy [3]. Nitration afforded a mixture of much *p*- and a little *o*-nitrophenyl*iso*butyronitrile, from which the pure *para*isomer was obtained by crystallisation and converted to $\alpha$-(*p*-methoxyphenyl)*iso*butyronitrile as shown. The latter compound

* Part I. Acta Chem. Scand. 8 (1954) 1203.

was, however, more conveniently prepared from anisic alcohol or anisole *via* the benzyl chloride and the benzyl cyanide, methylation of which by the above method afforded the *iso*butyronitrile derivative. Reduction with lithium-aluminium hydride followed by demethylation with hydrobromic acid yielded β-(*p*-hydroxyphenyl)*iso*butylamine "*neo*tyramine", (II). The N,N-dimethylderivative, "*neo*hordenine" (VII) was obtained by the same route from the N,N-dimethylamide of α-(*p*-methoxyphenyl)*iso*butyric acid, available as a by-product from a different line of investigation. It was also obtained by methylation of *neo*tyramine by the Eschweiler-Clarke procedure [4].

Attempts to obtain *neo*tyramine by catalytic hydrogenation of α-(*p*-hydroxyphenyl)*iso*butyronitrile with palladium or platinum oxide catalyst in ethanol, ethanolic ammonia or ethanolic hydrogen chloride were unsuccessful.

The α-(*p*-aminophenyl)*iso*butyric acid esters were prepared by reduction of the corresponding nitro ester hydrochlorides with powdered iron.

## EXPERIMENTAL *

*α-Phenylisobutyronitrile* was prepared in 60—70 % yield by the method of Darzens and Lévy [3] in runs using up to 580 g (5 moles) of commercial grade benzyl cyanide. The crude reaction product was freed from *iso*nitrile by washing with 20 % sulphuric acid followed by water, before distillation.

*β-Phenylisobutylamine, "neophylamine".* The above nitrile was reduced with lithium-aluminium hydride following the general directions given by Amundsen and Nelson [5]. The yield of product, b.p. 109—112°/20 mm Hg, was 65 %. It was converted to the *hydrochloride* m.p. 200—202°. (Lit. [6] 200—201.5°). (Found: Cl 19.1. Calc. for $C_{10}H_{16}ClN$: Cl 19.0.)

*α-(p-Nitrophenyl)isobutyronitrile.* α-Phenyl*iso*butyronitrile (300 g) was added drop by drop with stirring to fuming nitric acid (sp.g. 1.48 ; 1100 ml) below 0°. After the addition the cooling bath was removed, and the solution was set aside for 2 hours, poured onto ice, and the precipitated crystals collected, thoroughly washed with water and air dried. The crude product (90 % yield) was crystallised from ethanol (500 ml) and from a benzene-petrol, giving 200 to 225 g of faintly yellow needles, m.p. 67—68°. (Found: C 62.5; H 5.10. $C_{10}H_{10}N_2O_2$ requires: C 63.1; H 5.30.)

A sample (3 g) was refluxed for one hour with a solution of potassium dichromate (15 g) and conc. sulphuric acid (30 ml) in water (40 ml). *p*-Nitrobenzoic acid (0.8 g) m.p. and mixed m.p. 232—233° was obtained.

*α-(p-Nitrophenyl)isobutyric acid.* α-*p*-Nitrophenyl*iso*butyronitrile (35 g), conc. sulphuric acid (50 ml) and water (60 ml) were mixed, refluxed in an oil bath for about 20 hours, and poured into icewater. The precipitated acid crystallised from benzene-petrol (3 : 1) in coarse needles, m.p. 128—129°. Yield 31 g (80 %). (Found: N 6.73; equiv. weight 208. $C_{10}H_{11}NO_4$ requires: N 6.70; equiv. weight 209.2.)

*α-(p-Nitrophenyl)isobutyryl chloride* was prepared by refluxing the acid (one part) with thionyl chloride (two parts) for one hour on a water bath, and removing the excess thionyl chloride *in vacuo*. The product crystallised from petrol in faintly yellow prisms, m.p. 55—56° (Found: Cl 15.3 $C_{10}H_{10}ClNO_3$ requires: Cl 15.6).

*α-(p-Nitrophenyl)isobutyramide* formed coarse needles, m.p. 110—111° (from benzene). (Found: N 13.5 · $C_{10}H_{12}N_2O_3$ requires: N 13.5).

*N,N-Dimethyl-(α-p-nitrophenyl)isobutyramide* had m.p. 109—110°. (Found: N 11.8. $C_{12}H_{16}N_2O_3$ requires: N 11.9.)

*α-(o-Nitrophenyl)isobutyric acid* was isolated from the mother liquors from the crystallisation of the *p*-isomer when a hydrolysis was run with crude nitronitrile. Needles,

* All melting and boiling points uncorrected. Petrol refers to the fraction b.p. 40—60°.

m.p. 93—94°. (Found: N 6.75; equiv. weight 207. $C_{10}H_{11}NO_4$ requires: N 6.70 equiv. weight 209.2.) — Oxidation of a sample as described for the *p*-nitrophenyl*iso*butyronitrile yielded *o*-nitrobenzoic acid, m.p. and mixed m.p. 144—146°.

*Ethyl α-(p-nitrophenyl)isobutyrate.* α-*p*-Nitrophenyl*iso*butyronitrile (38 g) was refluxed for about 70 hours with 95 % ethanol (50 ml) and conc. sulphuric acid (20 ml). The solution was poured into water, the oil that separated was taken up in ether, washed with water and sodium bicarbonate solution and dried. Distillation afforded the ester, b.p. 174—176° C/10 mm, in 90 % yield. (Found: $C_2H_5O$ 18.8. $C_{12}H_{15}NO_4$ requires: $C_2H_5O$ 19.0.)

This ester was not aminolysed when heated in an autoclave for 24 hours with alcoholic ammonia, mono- or dimethylamine at 100°.

*α-(p-Aminophenyl)isobutyronitrile.* α-*p*-Nitrophenyl*iso*butyronitrile (38 g) was dissolved in ethanol (250 ml). A solution of anhydrous sodium dithionite (225 g) in hot water (200 ml) was carefully added, and the mixture was refluxed for 3 1/2 hours. The alcohol was removed, and the residual solution acidified by careful addition of conc. hydrochloric acid (200 ml) in water (200 ml). (Sulphur dioxide was generated!) The solution was refluxed for 3/4 hour, treated with decolourising carbon, cooled and made alkaline with 30 % sodium hydroxide. The amine was extracted with ether, washed with water, dried ($K_2CO_3$) and fractionated. The yield of colourless oil boiling at 173—174°/10 mm was 21 g (66 %). (Found: N 17.6 $C_{10}H_{12}N_2$ requires: N 17.5.)

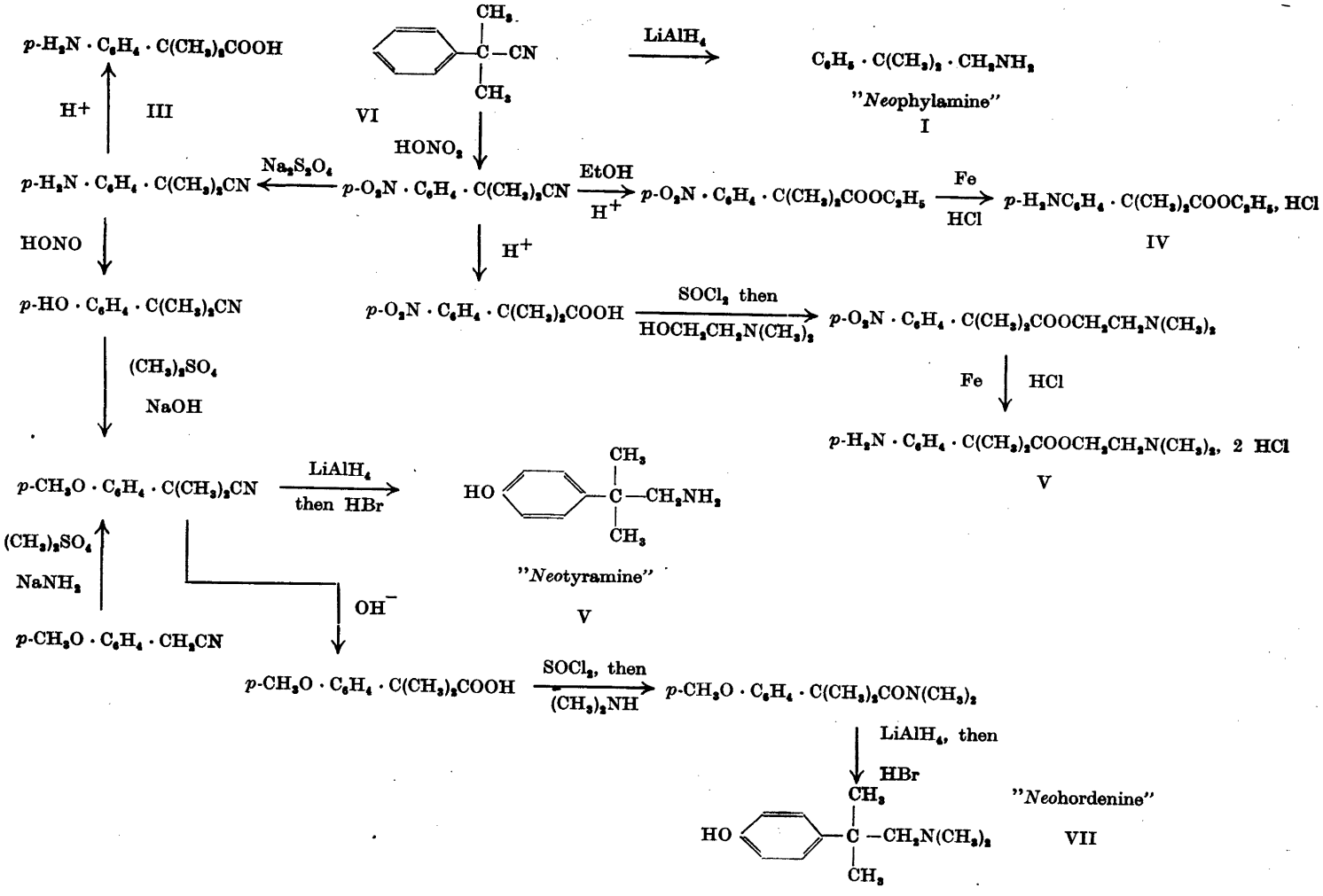
*Picrate,* yellow needles, m.p. 179—180° (decomp.). (Found: C 49.1; H 3.90. $C_{16}H_{15}N_5O_7$ requires: C 49.4; H 3.88.)

*α-(p-Aminophenyl)isobutyric acid.* α-*p*-Aminophenyl*iso*butyronitrile (7 g) was heated with conc. hydrochloric acid (20 ml) in a sealed tube at 100° for 8 hours, poured into water (75 ml) and treated with decolourising carbon. Ammonia was added to pH 6, and the amino acid isolated by filtration after cooling overnight in a refrigerator, and washed free from ammonium chloride. Needles, m.p. 217—218° (decomp.). Yield 7 g. (Found: N 7.8; equiv weight 178. $C_{10}H_{13}NO_2$ requires: N 7.8, equiv. weight 179.2.) — The *hydrochloride* was obtained by dissolving the acid in absolute ethanol saturated with hydrogen chloride and precipitating the chloride by careful addition of ether. It crystallised from ethanol-ether in needles, which decomposed at 210—215°. (Found: Cl 6.44. $C_{10}H_{14}ClNO_2$: requires Cl 6.49.)

The *N-acetylderivative,* m.p. 166—167° was prepared from the amino acid and acetic anhydride in pyridine, and crystallised from water. (Found: N 6.38; equiv. weight 223. $C_{12}H_{15}NO_3$ requires: N 6.33; equiv. weight 221.2.)

*Ethyl α-(p-aminophenyl)isobutyrate hydrochloride.* Ethyl α-*p*-nitrophenyl*iso*butyrate (15 g) was diluted with ethanol (50 ml) and conc. hydrochloric acid (15 ml). Powdered iron (20 g) was added in small portions with occasional shaking and cooling in water so that the temperature did not exceed 50°. When the reduction was complete (disapperance of the yellow colour) the reaction mixture was made slightly alkaline by careful addition of aqueous ammonia. The ferrous hydroxide sludge was filtered off and washed with ethanol. The filtrate and washings were concentrated to a small volume at reduced pressure. Absolute ethanol (100 ml) was added and the solution again concentrated to about 25 ml. The solution was saturated with dry hydrogen chloride, and the aminoester hydrochloride precipitated by careful addition of much ether. Yield 8 g. The compound crystallised from an ethyl acetate-petrol in colourless needles, m.p. 131—133° (decomp.) (Found: Cl 14.5; N 5.83. $C_{12}H_{16}ClNO_2$ requires: Cl 14.6; N 5.75.)

*β-(N,N-Dimethylamino)ethyl α-(p-nitrophenyl)isobutyrate hydrochloride.* α-*p*-Nitrophenyl*iso*butyryl chloride was prepared by refluxing the acid (20.9 g) with thionyl chloride (25 ml) for one hour on a water bath and removing the excess reagent *in vacuo.* The crude chloride was dissolved in dry benzene (50 ml) and refluxed for two hours with a solution of dimethylaminoethanol (12 g) in dry benzene (50 ml). After cooling the ester hydrochloride was extracted from the benzene solution with 2 *N* hydrochloric acid. The combined extracts were washed twice with ether, made alkaline with potassium carbonate, and the free aminoester was extracted with ether and dried ($Na_2SO_4$). The ether was removed leaving a light yellow oil (22 g), that did not crystallise. It was dissolved in a little boiling anhydrous ethanolic hydrogen chloride, from which the ester hydrochloride separated on storing. For analysis it was crystallised from dry ethanol. M.p. 148—149°. (Found: Cl 11.1. $C_{14}H_{21}ClN_2O_4$ requires: Cl 11.2.)


p-H2N · C6H4 · C(CH3)2COOH
H+
III
p-H2N · C6H4 · C(CH3)2CN
HONO
p-HO · C6H4 · C(CH3)2CN
(CH3)2SO4
NaOH
p-CH3O · C6H4 · C(CH3)2CN
LiAlH4
then HBr
(CH3)2SO4
NaNH2
p-CH3O · C6H4 · CH2CN
OH−
VI
HONO2
Na2S2O4
p-O2N · C6H4 · C(CH3)2CN
EtOH
H+
H+
p-O2N · C6H4 · C(CH3)2COOH
SOCl2 then
HOCH2CH2N(CH3)2
p-O2N · C6H4 · C(CH3)2COOCH2CH2N(CH3)2
Fe
HCl
p-H2N · C6H4 · C(CH3)2COOCH2CH2N(CH3)2, 2 HCl
V
p-CH3O · C6H4 · C(CH3)2COOH
SOCl2, then
(CH3)2NH
p-CH3O · C6H4 · C(CH3)2CON(CH3)2
LiAlH4, then
HBr
HO
CH2NH2
"Neotyramine"
V
LiAlH4
p-O2N · C6H4 · C(CH3)2CN
C6H5 · C(CH3)2 · CH2NH2
"Neophylamine"
I
Fe
HCl
p-H2NC6H4 · C(CH3)2COOC2H5, HCl
IV
HO
CH2N(CH3)2
"Neohordenine"
VII

*β-(N,N-Dimethylamino)ethyl α-(p-aminophenyl)isobutyrate dihydrochloride.* Crude β-dimethylaminoethyl α-*p*-nitrophenyl*iso*butyrate hydrochloride (14.2 g) was stirred with water (10 ml). Powdered iron (20 g) was added in small portions. The reaction started almost immediately and the mixture was cooled in water so that the temperature did not exceed 50°. When the reaction was complete, the mixture was repeatedly extracted with ether. The extracts were combined, dried ($Na_2SO_4$) and evaporated to a small volume. Dry hydrogen chloride was introduced, and the precipitated ester hydrochloride collected. It crystallised from ethanol in needles, m.p. 209—211° (decomp.). (Found: Cl 21.6; N 8.61. $C_{14}H_{24}Cl_2N_2O_2$ requires: Cl 21.9; N 8.67.)

*α-(p-Hydroxyphenyl)isobutyronitrile.* α-*p*-Aminophenyl*iso*butyronitrile (16.0 g) was dissolved in conc. hydrochloric acid (25 ml) and diazotised at 0 to 5° with an aqueous solution of sodium nitrite (6.9 g). The reaction mixture was immediately poured into a violently boiling mixture of conc. sulphuric acid (50 ml) and water (500 ml). As soon as the evolution of nitrogen ceased, the flask was cooled in ice water. The solution was extracted with ether, the combined ethereal extracts repeatedly shaken with 2 *N* sodium hydroxide and the combined alkaline extracts acidified with dilute sulphuric acid. The hydroxynitrile set free was taken up in ether and dried ($Na_2SO_4$). The ether was removed and the residual oil distilled *in vacuo*. The colourless oil boiled at 177°/11 mm and crystallised on storing, m.p. 45—48°. Yield 60—70 %. To obtain a good yield, the sulphuric acid must be boiling *violently* during the addition of the diazonium salt solution. (Found: N 8.67. $C_{10}H_{11}NO$ requires: N 8.69.)

The *benzoic acid ester* was prepared in almost quantitative yield from the hydroxynitrile and an equivalent amount of benzoyl chloride in pyridine. Crystallised from a benzene-petrol (1 : 1) it formed colourless needles m.p. 103—104°. (Found: N 5.27. $C_{17}H_{15}NO_2$ requires: N 5.28.)

*α-(p-Hydroxyphenyl)isobutyric acid.* A sample (5 g) of α-*p*-hydroxyphenyl*iso*butyronitrile was refluxed with 48 % hydrobromic acid (25 ml) for 8 hours, poured into water (75 ml) and cooled. The colourless needles that separated were collected and repeatedly crystallised from small amounts of water. M.p. 152—153°. (Found: C 66.9; H 6.70; equiv. weight 178. $C_{10}H_{12}O_3$ requires: C 66.6; H 6.71; equiv. weight 180.2).

*α-(p-Methoxyphenyl)isobutyronitrile:* a) *From α-p-hydroxyphenylisobutyronitrile.* α-*p*-Hydroxyphenylisobutyronitrile (8.2 g) and sodium hydroxide (2 g) were dissolved in methanol (50 ml) and with occasional shaking methylated by the simultaneous dropwise addition of dimethyl sulphate (10 ml) and 40 % sodium hydroxide (10 ml). After one hour the mixture was diluted with water (200 ml) and repeatedly extracted with ether. The product distilled as a colourless oil (8.0 g) b.p. 278—280° at atmospheric pressure. (Found: $CH_3O$ 17.6. $C_{11}H_{13}NO$ requires: $CH_3O$ 17.7.)

b) *From p-methoxyphenylbenzyl cyanide.* *p*-Methoxybenzyl chloride was obtained in 40—50 % yield by chloromethylation of anisole by the method of Sommelet and Marszak [7] and in 65—70 % overall yield by reduction of anisaldehyde by the crossed Cannizzaro reaction with formaldehyde by the method of Livshits *et al.*[8] followed by chlorination by shaking for 2 hours with ice cold concentrated hydrochloric acid (5 parts per 1 part anisalcohol).

The chloride was converted to the cyanide in 85 % yield by the method of Lee *et al.*[9].

*p*-Methoxybenzyl cyanide (76.5 g) was diluted with dry benzene (250 ml) and added to a stirred mixture of sodium amide (70 g, commercial, May & Baker product) and dry benzene (500 ml). Evolution of ammonia started immediately and was completed by heating the mixture for two hours on a water bath. Without cooling dimethylsulphate (198 g) diluted with an equal volume of dry benzene was added drop by drop, with continuous stirring, at such a rate that the mixture refluxed gently. After the addition the mixture was heated for one hour on the water bath, and cooled. Aqueous ethanol (100 ml; 50 %) was carefully added with stirring to destroy any residual amide, followed by conc. aqueous ammonia (100 ml) and water (500 ml). After stirring for half an hour, the benzene layer was separated, the aqueous layer extracted with benzene, and the combined benzene solutions thoroughly washed with water, dilute sulphuric acid, water and dried ($K_2CO_3$). The solvent was removed using a short column, and the residual oil fractionated *in vacuo*. A colourless liquid (157 g, 63 %) boiling at 140—142°/10 mm, 276—278° at atmospheric pressure, was obtained. (Found: $CH_3O$ 17.6.)

*α-(p-Methoxyphenyl)isobutyric acid.* α-*p*-Methoxyphenyl*iso*butyronitrile (10 g) potassium hydroxide (10 g) dissolved in water (10 ml) and ethanol (25 ml) were mixed and heated in a stainless steel autoclave at 140° for 20 hours. The liquid was poured into water (150 ml) and acidified. After some hours the crystalline product (10.1 g) was collected. Colourless plates, m.p. 84–86°, raised by crystallisation from water to 89–90°. (Found: $CH_3O$ 16.1; equiv. weight 195. $C_{11}H_{14}O_3$ requires: $CH_3O$ 16.0; equiv. weight 194.2.)

The *amide* was prepared *via* the acid chloride (thionylchloride). It crystallised from water in needles, m.p. 133°. (Found: N 7.22; $CH_3O$ 15.8. $C_{11}H_{15}NO_2$ requires: N 7.25; $CH_3O$ 16.1.) The *N,N-dimethylamide* was obtained as a colourless oil, which distilled at 170–172°/10 mm Hg and did not crystallise. (Found: N 6.23; $CH_3O$ 13.7. $C_{13}H_{19}NO_2$ requires: N 6.33; $CH_3O$ 14.0.)

*β-(p-Methoxyphenyl)isobutylamine.* α-*p*-Methoxyphenyl*iso*butyronitrile (57 g) dissolved in absolute ether (100 ml) was slowly added to a stirred suspension of lithium- aluminium hydride (15 g) in absolute ether (400 ml) at such a rate that the liquid refluxed rapidly. The mixture was stirred for further 15 minutes, and excess hydride was destroyed by careful addition of moist ether, followed by water. The precipitated aluminium hydroxide was dissolved by addition of 40 % sodium hydroxide solution, the ether layer was separated and the aqueous layer extracted with ether. The combined ethereal solutions were washed with water, and extracted with 2 *N* hydrochloric acid. The amine was liberated with sodium hydroxide solution and taken up in ether. After drying ($K_2CO_3$) the ether was removed and the residual oil fractionated *in vacuo*. Yield 43 g (74 %) of a colourless oil b.p. 124–126°/10 mm. (Found: $CH_3O$ 16.8. $C_{11}H_{17}NO$ requires: $CH_3O$ 17.3.)

The *hydrochloride* was prepared by dissolving the amine in a little anhydrous ethanolic hydrogen chloride and precipitation of the amine hydrochloride by the addition of much ether. It crystallised from ethanol-ether in needles, m.p. 155–156°. (Found: Cl 16.5; $CH_3O$ 14.2. $C_{12}H_{18}ClNO$ requires: Cl 16.4; $CH_3O$ 14.4.)

The *picrate* was prepared in aqueous methanol, m.p. 215–216°. (Found: $CH_3O$ 7.66. $C_{17}H_{20}N_4O_8$ requires: $CH_3O$ 7.60.)

*β-(p-Hydroxyphenyl)isobutylamine, "neotyramine".* β-*p*-Methoxyphenyl*iso*butylamine (5 g) and 48 % hydrobromic acid (30 ml) were refluxed for 3 hours. The excess acid was removed on the water bath at reduced pressure, the salt cake dissolved in water (30 ml) and treated with decolourising carbon. The *neo*tyramine was precipitated by adjusting the pH to 9–10 by careful addition of ammonia. The needles, that slowly separated, were collected and washed free from inorganic material. The yield was almost quantitative. M.p. 152–153° (decomp.). (Found: C 72.4; H 9.21; N 8.43. $C_{10}H_{15}NO$ requires: C 72.7; H 9.15; N 8.48.)

The *hydrochloride* was prepared in the usual way and crystallised from an ethanol-ether. Needles, which decomposed at 219–220°. (Found: Cl 17.4; N 6.91. $C_{10}H_{16}ClNO$ requires: Cl 17.6; N 6.94.)

*N,N-Dimethyl-β-(p-methoxyphenyl)isobutylamine.* N,N-Dimethyl-α-(*p*-methoxyphenyl)*iso*butyramide (30 g) was reduced with lithium aluminium hydride as described for the preparation of β-*p*-methoxyphenyl*iso*butylamine. The yield of amine, b.p. 128–130°/10 mm was 18 g (65 %). (Found: N 6.83; $CH_3O$ 14.8. $C_{13}H_{21}NO$ requires: N 6.95; $CH_3O$ 15.0.)

The *hydrochloride* crystallised from ethanol-ether, m.p. 195–96°. (Found: Cl 14.5; N 5.73. $C_{13}H_{22}ClNO$ requires: Cl 14.6; N 5.75.)

*N,N-Dimethyl-α-(p-hydroxyphenyl)isobutylamine, "neohordenine"*, was prepared in almost quantitative yield by the method described for *neo*tyramine. Needles, m.p. 116–117° (decomp.). (Found: N 7.19. $C_{12}H_{19}NO$ requires: N 7.25.)

The *hydrochloride* crystallised from ethanol-ether in colourless needles, m.p. 200–202° (decomp.). (Found: Cl 15.3; N 6.06. $C_{12}H_{20}ClNO$ requires: Cl 15.4; N 6.10.)

A product identical with the above amine (mixed m.p.) was obtained, when a sample of *neo*tyramine was methylated by the Eschweiler-Clarke procedure [4]. The reaction was carried out as described by Decker and Becker for β-phenethylamine [10].

The author wishes to acknowledge his indebtedness to *Statens Tekniska Forskningsråd* for a Fellowship, to *Cancernämnden* for financial support and to Miss E. Duintjer for skilful assistance.

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Received April 29, 1954.