398. *The Preparation of β-Amino-alcohols.*

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Reduction of α-benzamido-acids with lithium aluminium hydride gives β-benzylamino-alcohols which may be readily debenzylated to β-amino-alcohols. The method is particularly convenient for the preparation of optically active β-amino-alcohols. Resolution of DL-α-amino-α-*cyclo*hexyl-acetic acid is described.

THE reduction of amino-acids with lithium aluminium hydride in ether is often unsatisfactory, not only because of inherent low solubility of the acids in ether, but also owing to the formation of insoluble inorganic complexes which prevent complete reaction. To overcome this difficulty, Dornow, Messwarb, and Frey [1] used a mixture of ether and tetrahydrofuran in the reduction of tyrosine by lithium aluminium hydride, and Vogl and Pöhm [2,3] reduced several amino-acids in tetrahydrofuran alone. Karrer and his co-workers reported reductions of several amino-esters [4] and also of the benzoyl derivatives of histidine ethyl ester, in which reduction was accompanied by debenzoylation.[5] The reduction of *N*-acetyl-, *N*-formyl-, and *N*-ethoxycarbonyl-amino-acids or their ethyl esters has also been reported.[1,3,6]

We have found that many benzamido-acids are sufficiently soluble in ether to be reduced with lithium aluminium hydride, giving in most cases good yields of the corresponding benzylamino-alcohols.

With optically active amino-acids this method is particularly convenient as the *N*-benzoyl derivatives are those most frequently used for their resolution and the resolved compounds can be reduced directly without isolating the free acids. Moreover, the benzylamino-alcohols can be debenzylated by catalytic hydrogenolysis,[7] which minimises racemisation of the amino-alcohols.

[1] Dornow, Messwarb, and Frey, *Chem. Ber.*, 1950, **83**, 445.
[2] Vogl and Pöhm, *Monatsh.*, 1952, **83**, 541.
[3] *Idem*, *ibid.*, 1953, **84**, 1097.
[4] (*a*) Karrer, Portmann, and Suter, *Helv. Chim. Acta*, 1948, **31**, 1619; (*b*) Karrer and Portmann, *ibid.*, p. 2088.
[5] Karrer, Suter, and Waser, *ibid.*, 1949, **32**, 1936; Karrer and Saemann, *ibid.*, 1953, **36**, 570.
[6] Wessely and Swoboda, *Monatsh.*, 1951, **82**, 621; Berlinguet, *Canad. J. Chem.*, 1954, **32**, 31.
[7] Stoll, Peyer, and Hofmann, *Helv. Chim. Acta*, 1943, **26**, 929.

Benzylamino-alcohols have thus been obtained from hippuric acid, benzoyl-D- and -L-alanine, benzoyl-DL-valine, benzoyl-L-phenylalanine, and benzoyl-L-glutamic acid. In most cases it was convenient to use the Soxhlet extraction procedure of Nystrom and Brown ; [8] otherwise solutions or suspensions of the benzamido-acids were used.

In most of the experiments, 3 mols. (100% excess) of lithium aluminium hydride were used and reaction times were 5—20 hr., though hippuric acid was not completely extracted after 70 hr. Under these conditions, both carboxyl and amide groups were usually reduced, although small amounts of benzamido-alcohols were sometimes isolated : in one experiment with benzoyl-L-glutamic acid in tetrahydrofuran (reaction time 75 min.) the main product was L-2-benzamidopentane-1 : 5-diol. Slow reduction of monosubstituted amides by lithium aluminium hydride has been noted before.[9]

The reaction mixtures were worked up by addition of the theoretical amount of water, giving a solid which was easily filtered off and from which the benzylamino-alcohol (in most cases freely ether-soluble) was readily extracted. This is in marked contrast to those procedures which give as the main product unsubstituted amino-alcohols which are frequently of low solubility in ether and difficult to remove from the mass of inorganic material.

By this method D- and L-α-benzamido-α-phenylacetic acid gave D- and L-2-benzylamino-2-phenylethanol; the L-isomer was also obtained by resolving the DL-form with di-*p*-toluoyl-L-tartaric acid. D-2-Benzylamino-2-phenylethanol gave crystalline D-2-amino-2-phenylethanol ($[\alpha]_D^{25}$ −27·2°) of higher optical purity than that prepared as a liquid by Ovakimian, Kuna, and Levene [10] ($[\alpha]_D^{25}$ −15°).

Since completion of our work, Arpesella and La Manna [11] reported the preparation of both isomers by lithium aluminium hydride reduction of the ethyl α-amino-α-phenylacetates. Their values for the D-isomer agree with ours.

(+)-α-Amino-α-*cyclo*hexylacetic acid prepared by hydrogenation of (+)-α-amino-α-phenylacetic acid was described by Reihlen and Knöpfle [12] who indirectly related the configuration of the latter acid to L-(+)-valine. We have prepared DL-α-amino-α-*cyclo*hexylacetic acid by hydrogenating α-amino-α-phenylacetic acid and have resolved the benzoyl derivative with quinine, obtaining D- and L-α-benzamido-α-*cyclo*hexylacetic acid. Hydrolysis of the benzoyl-D-acid gave D-α-amino-α-*cyclo*hexylacetic acid, $[\alpha]_D^{25}$ −33·8° in 5N-HCl. Reihlen and Knöpfle found $[\alpha]_D$ −31° in 0·5N-HCl, and Rudman, Meister, and Greenstein,[13] using an enzymic method of resolution claimed to give a product of >99·9% purity, obtained $[\alpha]_D^{26}$ −35·0° in 5N-HCl. The benzoyl-L-acid has been reduced to L-2-benzylamino-2-*cyclo*hexylethanol and debenzylated to L-2-amino-2-*cyclo*hexylethanol.

Experimental

2-Benzylaminoethanol.—Hippuric acid (12 g.), in a Soxhlet extractor, was reduced with lithium aluminium hydride (8·4 g., 3·3 mols.) in dry ether (300 ml.) under nitrogen, by Nystrom and Brown's procedure.[8] After 70 hr. some hippuric acid (2·8 g.) remained undissolved and was rejected. Water (10 ml.) was added dropwise to the cooled mixture, and the insoluble material filtered off and washed with ether. The oil (6·3 g.) remaining after evaporation of the combined ether solutions was distilled, giving the amino-alcohol (4 g.), b. p. 106—107°/0·5 mm., $n_D^{20\cdot5}$ 1·5419 (Found : C, 71·4; H, 8·5; N, 9·05. Calc. for $C_9H_{13}ON$: C, 71·5; H, 8·7; N, 9·3%). The picrate had m. p. 134° (lit.,[14] 134—135°) (Found : C, 47·7; H, 4·3; N, 14·4. Calc. for $C_{15}H_{16}O_8N_4$: C, 47·4; H, 4·2; N, 14·7%).

D-*2-Benzylaminopropanol.*—By the same procedure benzoyl-D-alanine (7·7 g.) was reduced during 3 hr. with lithium aluminium hydride (4·5 g., 3 mols.) in ether (300 ml.). The product (4·6 g.), obtained as before, recrystallised from hot *cyclo*hexane (10 ml.) on addition of light

[8] Nystrom and Brown, *J. Amer. Chem. Soc.*, 1947, **69**, 2548.
[9] *E.g.*, Mićović and Mihailović, *J. Org. Chem.*, 1953, **18**, 1190.
[10] Ovakimian, Kuna, and Levene, *J. Biol. Chem.*, 1940, **135**, 91.
[11] Arpesella and La Manna, *Il Farmaco*, 1953, **8**, 212.
[12] Reihlen and Knöpfle, *Annalen*, 1936, **523**, 199.
[13] Rudman, Meister, and Greenstein, *J. Amer. Chem. Soc.*, 1952, **74**, 551.
[14] Gabriel and Stelzer, *Ber.*, 1896, **29**, 2385.

petroleum (b. p. 40—60°; 25 ml.), giving needles (3·35 g.), m. p. 46·5°, $[\alpha]_D^{27.5}$ −44·5° (*c* 4 in EtOH) (lit.,[7] m. p. 47—49°, $[\alpha]_D^{22}$ −44·25°) (Found: C, 72·8; H, 8·8; N, 8·25. Calc. for $C_{10}H_{15}ON$: C, 72·7; H, 9·15; N, 8·5%). The hydrogen tartrate (from ethanol) had m. p. 94° undepressed with an authentic sample.[7]

L-2-*Benzylaminopropanol.*—By the same procedure benzoyl-L-alanine (19 g.) was reduced with lithium aluminium hydride (12·5 g., 3·3 mols.) in ether (500 ml.). The product (14·0 g.) had m. p. 45°, $[\alpha]_D^{21}$ +43·5° (*c* 4 in EtOH) (lit.,[7] m. p. 47—49°) (Found: C, 72·5; H, 9·1; N, 8·35. Calc. for $C_{10}H_{15}ON$: C, 72·7; H, 9·15; N, 8·5%). The hydrogen oxalate (prisms from ethanol) had m. p. 187° (lit.,[7] 187—189°) (Found: N, 5·3. Calc. for $C_{12}H_{17}O_5N$: N, 5·5%).

DL-2-*Benzylamino*-3-*methylbutanol.*—Benzoyl-DL-valine (7·8 g.), reduced as above with lithium aluminium hydride (4·0 g., 3 mols.) in dry ether (250 ml.), gave an oil (6·1 g.) which was distilled at 155—157°/9 mm., redistilled at 93—94°/0·01 mm. (5·36 g.), then having n_D^{14} 1·5212 (Found: C, 74·8; H, 9·8; N, 7·2. Calc. for $C_{12}H_{19}ON$: C, 74·6; H, 9·9; N, 7·25%). The picrate (from ethanol) melted at 128—129° (lit.,[7] 131—133°).

L-2-*Benzylamino*-3-*phenylpropanol.*—A solution of *N*-benzoyl-L-β-phenylalanine (1·6 g.) in dry ether (50 ml.) was added during 10 min. with stirring under nitrogen to lithium aluminium hydride (0·5 g., 2·2 mols.) in dry ether (25 ml.). After the initial vigorous reaction, the mixture was refluxed for 5 hr. and kept overnight. Water (1·2 ml.) was added, the precipitate filtered off, and the residue extracted with ether (Soxhlet) for 3 hr. The extract, together with the original ethereal filtrate, was evaporated and the residue digested with hot light petroleum (b. p. 60—80°; 100 ml.). The filtered solution, on cooling, deposited L-2-benzamido-3-phenylpropanol which, recrystallised from benzene, had m. p. 169° (lit.,[15] 169°) (Found: C, 75·1; H, 6·6; N, 5·1. Calc. for $C_{16}H_{17}O_2N$: C, 75·3; H, 6·7; N, 5·5%). The petroleum solution, on concentration, deposited L-2-*benzylamino*-3-*phenylpropanol* which recrystallised from light petroleum (b. p. 40—60°) in needles, m. p. 60—61°, $[\alpha]_D^{23}$ −8·3° (*c* 5·03 in EtOH) (Found: C, 79·6; H, 8·1; N, 5·6. $C_{16}H_{19}ON$ requires C, 79·65; H, 7·9; N, 5·8%). The *oxalate* had m. p. 208° (from alcohol) (Found: C, 65·1; H, 6·3; N, 3·7. $C_{18}H_{21}O_5N$ requires C, 65·2; H, 6·4; N, 4·2%).

L-2-*Amino*-3-*phenylpropanol.*—L-2-Benzylamino-3-phenylpropanol (0·48 g.) and hydrated oxalic acid (0·25 g.) were partially dissolved in 1 : 1 aqueous alcohol (30 ml.). 10% Palladium–charcoal (1 g.) was added, and the mixture was shaken with hydrogen for 2 hr. The catalyst was filtered off and washed, the filtrate and washings were evaporated under reduced pressure, and the residue was dried azeotropically with benzene and dissolved in alcohol (10 ml.). Ether (30 ml.) was added and the solid separating recrystallised from alcohol, giving L-α-(*hydroxymethyl*)*phenethylamine hydrogen oxalate*, m. p. 177° (0·16 g.) (Found: C, 54·8; H, 6·1; N, 5·2. $C_{11}H_{15}O_5N$ requires C, 54·8; H, 6·3; N, 5·8%), $[\alpha]_D^{23}$ *ca.* +1·9° (Karrer *et al.*[4a] give m. p. 161—163°). The oxalate (0·23 g.) was treated with 10% sodium hydroxide solution (4 ml.), and the base extracted with ether. The extract was dried (K_2CO_3), concentrated to about 10 ml., and filtered. After evaporation to 5 ml. and cooling (ice–salt), L-2-amino-3-phenylpropanol separated as plates, m. p. 90—91°, $[\alpha]_D^{23}$ −24·7° (*c* 3·1 in EtOH) (Oeda [15] gives m. p. 92—94°, $[\alpha]_D^{23}$ −24·4°; Karrer *et al.*[4a] give m. p. 85—86°, $[\alpha]_D^{17}$ −4·1°) (Found: C, 71·35; H, 8·8; N, 9·0. Calc. for $C_9H_{13}ON$: C, 71·5; H, 8·7; N, 9·3%).

Reduction of N-*Benzoyl*-L-*glutamic Acid.*—(*a*) Lithium aluminium hydride [2 g., 2·5 mols. (theor., 2·25 mols.)] was covered with tetrahydrofuran (40 ml.; purified by refluxing and distillation over sodium, redistillation over $LiAlH_4$), and to the stirred sludge under nitrogen was added during 15 min. a solution of benzoyl-L-glutamic acid (5 g.) (m. p. 134°, $[\alpha]_D$ −13·8°) in tetrahydrofuran (15 ml.). The mixture was then refluxed 1 hr., cooled in ice, and treated with water (5 ml.). The inorganic material was filtered off and washed with tetrahydrofuran (2 × 10 ml.). Evaporation of the filtrate and washings gave a syrup which crystallised and was triturated with ether. The crystals were filtered off (2 g.) and dissolved in methanol (charcoal), and the solution was filtered, diluted with ether (80 ml.), and cooled. L-2-*Benzamidopentane*-1 : 5-*diol* separated as needles and, recrystallised from benzene (50 ml.)–ethyl acetate (30 ml.), had m. p. 109°, $[\alpha]_D$ −28·6° (*c* 1·9 in EtOH) (Found: C, 64·9; H, 7·6; N, 6·4. $C_{12}H_{17}O_3N$ requires C, 64·3; H, 8·1; N, 6·2%).

(*b*) Benzoyl-L-glutamic acid (3·3 g.) in a Soxhlet extractor was reduced with lithium aluminium hydride (3·5 g., 7 mols.) in ether (150 ml.) under nitrogen during 20 hr. The mixture was cooled and treated with water (6 ml.), and the inorganic material filtered off and washed

[15] Oeda, *Bull. Chem. Soc. Japan*, 1938, **13**, 465.

with ether. Evaporation of the ether gave a cloudy syrup which, on dissolution in benzene, slowly deposited crystals (0·2 g.) which after recrystallisation from ethyl acetate had m. p. 108° undepressed on admixture with the benzamido-diol above. The benzene mother-liquor was evaporated and the residual oil distilled. The fraction of b. p. 160°/0·01 mm. (0·6 g.) was dissolved in alcohol, and oxalic acid added (hydrated, 0·5 g.). Addition of ether (20 ml.) caused separation of L-2-*benzylaminopentane*-1 : 5-*diol mono*(*hydrogen oxalate*) which recrystallised from alcohol had m. p. 120°, $[\alpha]_D^{27}$ +8·1° (*c* 1·7 in H_2O) (Found : C, 55·95; H, 7·0; N, 4·3. $C_{14}H_{21}O_6N$ requires C, 56·2; H, 7·1; N, 4·7%).

α-*Amino*-α-cyclo*hexylacetic Acid.*—α-Amino-α-phenylacetic acid (7·5 g.) in 2N-hydrochloric acid (75 ml.) with Adams platinum catalyst (0·2 g.) was shaken with hydrogen. The theoretical volume (3 mols.) was taken up in 24 hr. The catalyst was filtered off, the filtrate made slightly alkaline with ammonia, and the separated acid filtered off, washed, and air-dried (6·8 g.; sublimes above 310°).

α-*Benzamido*-α-cyclo*hexylacetic Acid.*—The above acid (10·2 g.) was dissolved in water (50 ml.) by the addition of saturated sodium hydroxide solution (5·2 ml.). To the stirred mixture at 0°, benzoyl chloride (12·1 ml.) was added during 40 min., the solution being kept alkaline by the simultaneous addition of 4% sodium hydroxide solution. After a further hour's stirring the mixture was acidified with hydrochloric acid to Congo-red, and the precipitate filtered off and washed by stirring repeatedly with di*iso*propyl ether (3 × 15 ml.). Twice recrystallised from 1 : 1 aqueous alcohol (200 ml.) and dried (P_2O_5), the *acid* (14·2 g.) had m. p. 200° (Found : C, 68·9; H, 7·4; N, 5·4. $C_{15}H_{19}O_3N$ requires C, 68·95; H, 7·3; N, 5·4%).

The inactive acid (6·8 g.) and anhydrous quinine (8·45 g.) were dissolved in boiling 3 : 2-aqueous alcohol (130 ml.). The filtered solution was cooled to opalescence and seeded with a crystal of quinine salt from an initial experiment. Separation of quinine salt as small prisms commenced immediately and was completed by cooling and storage overnight. The filtered salt was washed with 3 : 2 aqueous alcohol (50 ml.) and recrystallised twice from the same solvent. After drying *in vacuo* at 100° (P_2O_5) *quinine* D-α-*benzamido*-α-cyclo*hexylacetate* (5 g.) had m. p. 149° after softening at 141°, $[\alpha]_D^{23}$ −112° (*c* 0·4 in EtOH) (Found : C, 69·5; H, 7·5; N, 6·85. $C_{35}H_{43}O_5N_3,H_2O$ requires C, 69·6; H, 7·5; N, 7·0%).

The quinine salt (8 g.), suspended in water (150 ml.), was acidified with dilute hydrochloric acid to Congo-red, and the mixture extracted with ether. The residue after evaporation of the dried ether solution, when recrystallised from benzene, gave the D-*benzamido-acid* (3 g.), m. p. 171—172°, $[\alpha]_D^{23}$ −26·1° (*c* 0·803 in 0·5N-NaOH) (Found : C, 69·2; H, 7·3; N, 5·05%).

D-α-*Amino*-α-cyclo*hexylacetic Acid.*—The D-benzamido-acid (1 g.) was refluxed with concentrated hydrochloric acid (40 ml.) and water (20 ml.) for 8 hr., then evaporated to dryness under reduced pressure and the residue freed from benzoic acid by several extractions with ether, redissolved in a little water, and made faintly alkaline with ammonia. The acid, which separated on ice-cooling, recrystallised from water as plates (sublimed above 260°), $[\alpha]_D^{25}$ −33·8° (*c* 0·4 in 5N-hydrochloric acid) (lit.,[13] $[\alpha]_D^{26}$ −35·0°) (Found : C, 61·0; H, 9·65; N, 8·95. Calc. for $C_8H_{15}O_2N$: C, 61·1; H, 9·6; N, 8·9%).

L-α-*Benzamido*-α-cyclo*hexylacetic Acid.*—The mother-liquor separated from the quinine salt of the D-acid was evaporated under reduced pressure to remove most of the alcohol. The residue was acidified with dilute hydrochloric acid and extracted with ether. Evaporation of the dried ethereal extract gave 2·48 g. of crude acid which was extracted with boiling benzene (75 ml.) and filtered from some insoluble material. The solution, on cooling, gave crystals (1·27 g.) of *acid* which on recrystallising from benzene (80 ml.) had m. p. 172—173°, $[\alpha]_D^{23}$ +25·9° (*c* 1·082 in 100 ml. of water containing 4·4 ml. of N-sodium hydroxide) (Found : C, 69·25; H, 7·4; N, 4·95. $C_{15}H_{19}O_3N$ requires C, 68·95; H, 7·3; N, 5·4%). The benzene-insoluble residue above (0·95 g.) was optically inactive and had m. p. 198° undepressed on admixture with DL-α-benzamido-α-*cyclo*hexylacetic acid.

L-2-*Benzylamino*-2-cyclo*hexylethanol.*—A slurry of L-α-benzamido-α-*cyclo*hexylacetic acid (1·88 g.) in dry ether (125 ml.) was added during 10 min. under nitrogen with stirring to lithium aluminium hydride (0·82 g., 3 mols.) in ether (30 ml.). After the initial vigorous reaction the mixture was refluxed for 5 hr., cooled, and decomposed by water (2 ml.). The insoluble material which separated was filtered off and washed with ether. The solid remaining after evaporation of the combined ether solutions was treated with boiling *cyclo*hexane, and the solution, filtered from an insoluble fraction, deposited, on cooling, a small amount of L-2-*benzamido*-2-cyclo*hexylethanol*, m. p. 166°. A mixed m. p. showed that this material was

identical with the *cyclo*hexane-insoluble residue (Found : C, 72·6; H, 8·6; N, 5·9. $C_{15}H_{21}O_2N$ requires C, 72·85; H, 8·6; N, 5·7%). The *cyclo*hexane solution was evaporated and the residue was distilled. The L-*benzylamino-alcohol* boiled at 141°/0·06 mm. (1·17 g.) and had $[\alpha]_D^{23}$ +8·1° (*c* 4·7 in EtOH) (Found : C, 77·3; H, 10·2; N, 5·3. $C_{15}H_{23}ON$ requires C, 77·2; H, 9·9; N, 6·0%) : its *maleate* (from alcohol) had m. p. 172° (Found : C, 65·15; H, 7·8; N, 3·85. $C_{19}H_{27}O_5N$ requires C, 65·3; H, 7·8; N, 4·0%).

L-2-*Amino*-2-cyclo*hexylethanol*.—The benzylamino-compound prepared as above (0·81 g.), dissolved in aqueous alcohol (25%) with hydrated oxalic acid (0·45 g.), was shaken with hydrogen in the presence of 10% palladium–charcoal (1 g.). The residue after evaporation of the filtered solution at reduced pressure was treated with absolute alcohol (20 ml.) and filtered from a small amount of insoluble material. The solution was evaporated to *ca.* 10 ml. and dry ether (100 ml.) was added. The crude oxalate which separated (0·62 g.) was dissolved in water, and the base liberated by the addition of 20% sodium hydroxide solution (10 ml.) was extracted with ether. The ether solution was dried (K_2CO_3) and evaporated, giving the L-*amino-alcohol* which recrystallised from *cyclo*hexane–light petroleum (b. p. 40—60°) had m. p. 74°, $[\alpha]_D^{25}$ +10·4° (*c* 4·4 in EtOH) (Found : C, 67·0; H, 11·9; N, 9·9. $C_8H_{17}ON$ requires C, 67·1; H, 11·9; N, 9·8%). Its *maleate* had m. p. 186—187° (Found : C, 55·9; H, 8·2; N, 5·75. $C_{12}H_{21}O_5N$ requires C, 55·6; H, 8·2; N, 5·4%).

DL-2-*Benzylamino*-2-*phenylethanol*.—α-Benzamido-α-phenylacetic acid (12·75 g.) in a Soxhlet extractor was reduced with lithium aluminium hydride (6·25 g., 3·3 mols.) in ether (250 ml.). After refluxing for 3½ hrs. under nitrogen, the mixture was cooled and decomposed by water (10 ml.), and the solid was filtered off and washed with moist ether (2 × 75 ml.). The combined ether solutions were dried ($MgSO_4$) and evaporated. The residue was recrystallised from light petroleum (b. p. 40—60°), giving the *benzylamino-alcohol*, m. p. 69—70° (8·2 g.) (Found : C 79·5; H, 7·45; N, 6·05. $C_{15}H_{17}ON$ requires C, 79·25; H, 7·5; N, 6·2%).

L-2-*Benzylamino*-2-*phenylethanol*.—(*a*) L-α-Benzamidophenylacetic acid [16] (1·88 g.) was reduced by the above method with lithium aluminium hydride (0·94 g.) in ether (150 ml.). The *amino-ethanol*, recrystallised from light petroleum (b. p. 40—60°), had m. p. 86° (0·94 g.), $[\alpha]_D^{23}$ +80·0° (*c* 2 in EtOH) (Found : C, 79·7; H, 7·6; N, 5·8%).

(*b*) DL-2-Benzylamino-2-phenylethanol (4·84 g.) and di-*p*-toluoyl-L-tartaric acid [17] were dissolved in boiling 2 : 3 aqueous ethanol (100 ml.). Crystallisation which commenced on cooling was completed in ice. The L-benzylamine di-*p*-toluoyl-L-tartrate (3·6 g.) was obtained as prisms, m. p. 171° (decomp.), by recrystallising the filtered salt from absolute ethanol. This salt (3 g.), suspended in boiling water, was treated with excess of hydrochloric acid, and the mixture cooled and filtered from the precipitated acid. The base liberated with sodium hydroxide and obtained by ether-extraction was purified by dissolving it in light petroleum (b. p. 40—60°, 150 ml.), the solution maintained at 35—40° then being seeded with a crystal of the L-isomer obtained as above. The crystalline product was filtered off at 35—40° and after recrystallising from light petroleum had m. p. 86—87° undepressed on admixture with L-2-benzylamino-2-phenylethanol obtained as in (*a*) and $[\alpha]_D^{25}$ +80° (*c* 2 in EtOH).

L-2-*Amino*-2-*phenylethanol*.—L-2-Benzylamino-2-phenylethanol (0·84 g.) and anhydrous oxalic acid (0·375 g.) in ethanol (60 ml.) and water (15 ml.) were shaken with hydrogen and palladium black (0·2 g.). The theoretical amount was taken up in 5 hr. The catalyst was filtered off, the solution evaporated almost to dryness, and absolute ethanol added. The oxalate which separated was filtered off and recrystallised from ethanol {needles, m. p. 207° (decomp.), $[\alpha]_D^{25}$ −22·9° (*c* 1·7 in H_2O)}. From an aqueous solution of the oxalate, made alkaline with 2N-sodium hydroxide solution and saturated with sodium chloride, the product was obtained by ether-extraction and was recrystallised from benzene–light petroleum (b. p. 40—60°), giving the base, m. p. 77—78°, $[\alpha]_D^{25}$ −27·2° (*c* 9·9 in MeOH) (lit.,[11] m. p. 78—79°, $[\alpha]_D^{17}$ −25·4°) (Found : C, 69·8; H, 7·7; N, 9·9. Calc. for $C_8H_{11}ON$: C, 70·0; H, 8·1; N, 10·2%).

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[16] Minorici, *Chem. Zentr.*, 1920, III, 587.
[17] Stoll and Hofmann, *Helv. Chim. Acta*, 1943, **26**, 922; Hunt, *J.*, 1957, 1926.