749. *The Mechanism of the Decarboxylation of Substituted Malonic Acid Derivatives.*

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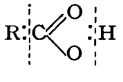
Experiments have been carried out on the decarboxylation of optically active disubstituted malonic acid derivatives. The results are consistent with the special intramolecular decarboxylation mechanism proposed by Westheimer and Jones (*J. Amer. Chem. Soc.*, 1941, **63**, 3283) and Schenkel and Schenkel-Rudin (*Helv. Chim. Acta*, 1948, **31**, 514) for the decarboxylation of β-keto-acids.

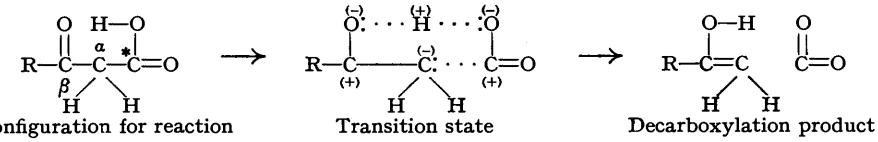
The preparation and the decarboxylation of optically active ethyl hydrogen ethylmethylmalonate, ethylmethylcyanoacetic acid, and α-benzyl-α-cyanopropionic acid, to give optically inactive decarboxylation products, are described. The preparation of the products of decarboxylation in optically active forms, and their optical stability to heat, are also described.

KINETIC measurements of the decarboxylation of malonic acid and its mono- and di-substituted derivatives, under a wide variety of experimental conditions, have been made by several workers (*inter al.*, Lindner, *Monatsh.*, 1907, **28**, 1041; Bernouilli and Wege, *Helv. Chim. Acta*, 1919, **2**, 511; Bernouilli and Jakubowicz, *ibid.*, 1921, **4**, 1081; Hinshelwood, *J.*, 1920, 156; Muus, *J. Phys. Chem.*, 1935, **39**, 343; Fairclough, *J.*, 1938, 1190; Ogata and Oda, *Bull. Inst. Phys. Chem. Res. Japan*, 1944, **23**, 217; Hall, *J. Amer. Chem. Soc.*, 1949, **71**, 2691). In almost all the experiments, the decarboxylation reactions were found to follow a first-order decomposition law.

A theory on the mechanism of decarboxylation reactions has been surveyed by Schenkel and Schenkel-Rudin (*Helv. Chim. Acta*, 1948, **31**, 514), who conclude that the decarboxylation of a carboxylic acid $R{\cdot}CO_2H$ in the liquid phase results in the retention of the binding electrons by R, which then combines with a liberated proton, the reaction being an electrophilic substitution (see inset).



The ready decarboxylation of β-keto-acids was explained by a special mechanism involving the formation of a double bond between C_α and C_β, the C_α–*C linkage dissociating unimolecularly. Thus the acid $R{\cdot}CO{\cdot}CH_2{\cdot}CO_2H$ would be decarboxylated according to the following mechanism :



Configuration for reaction — Transition state — Decarboxylation product

. . . Bonds breaking or forming; : Position of electron pairs after fission.

It was suggested by Schenkel and Schenkel-Rudin that the decarboxylation of certain substituted malonic acids probably occurred by an analogous mechanism.

It was considered of interest to attempt to ascertain what contribution for or against such a mechanism could be made by studying the decarboxylation of optically active acids in which the molecular dissymmetry resided in the carbon atom α to the carboxyl group. If during the course of the reaction, a double bond were to be formed between C_α and C_β, then the molecular dissymmetry would be lost and the decarboxylation product would inevitably be racemic.

Accordingly, (±)-ethyl hydrogen ethylmethylmalonate was prepared from ethyl malonate and resolved into its optically active forms by the use of quinine and cinchonidine. When the (+)- and the (−)-ethyl hydrogen ethylmethylmalonates were decarboxylated at 170°, the resulting ethyl ethylmethylacetate was optically inactive. Since the lowest temperature at which decarboxylation occurred at a reasonable rate was 170°, it was considered desirable to examine the thermal stability of optically active ethyl ethylmethylacetate. The results recorded in the Experimental section show that this ester can be maintained at 175° for several hours, without suffering any loss in rotatory power.

The general similarity in chemical behaviour, and the comparable ease of decarboxylation by heat, of cyanoacetic acid formed the basis of a second series of experiments in which decarboxylation experiments were carried out with optically active disubstituted cyanoacetic acids. (±)-Ethylmethylcyanoacetic acid [(±)-α-cyano-α-methylbutyric acid] was prepared from ethyl cyanoacetate, but it was not found possible to resolve it into its optically active forms by the use of its crystalline salts with brucine, quinine, cinchonidine, or quinidine. No ready explanation can be advanced for this failure, since other disubstituted cyanoacetic acids have been resolved without notable difficulty (*e.g.*, Fischer and Flatau, *Ber.*, 1909, **42**, 2981). An active ethylmethylcyanoacetic acid was obtained by the use of strychnine although recrystallisation of this alkaloidal salt proved very difficult and, as a result, the acid obtained was probably not optically pure.

(+)-Ethylmethylcyanoacetic acid underwent decarboxylation at 180—190° and the resulting ethylmethylacetonitrile (α-methylbutyronitrile) proved inactive. In this case also experiments were made to examine the thermal stability of the decarboxylation product. Ethylmethylacetonitrile was obtained in an optically active form by the interaction of phosphoric oxide with (−)-ethylmethylacetamide, itself obtained from (±)-ethylmethylacetic acid, which was resolved by the method of Schütz and Marckwald (*Ber.*, 1896, **29**, 53). It was found that (−)-ethylmethylacetonitrile could be kept at 175° for several hours without loss of rotatory power.

By converting the (−)-ethylmethylacetonitrile into (−)-ethylmethylacetic acid by hydrolysis and by comparison of the rotatory powers of the (−)-ethylmethylacetic acid obtained with that of the acid used in the preparation of the (−)-nitrile, an approximate value for the specific rotation of the nitrile could be calculated.

Decarboxylation experiments were then repeated using another disubstituted cyanoacetic acid. (±)-α-Benzyl-α-cyanopropionic acid was prepared from ethyl cyanoacetate, and resolved into its optically active forms by the use of brucine. (+)- and (−)-α-Benzyl-α-cyanopropionic acids underwent smooth decarboxylation at 165°/18 mm., to yield α-benzylpropionitrile which also was devoid of optical activity.

The decarboxylation product was obtained in an optically active form by the interaction of phosphoric oxide with (+)-α-benzylpropionamide, itself prepared from (±)-α-benzylpropionic acid, which was resolved by the method of Kipping and Hunter (*J.*, 1903, 1005). It was found that (+)-α-benzylpropionitrile could be kept at 160—170° for several hours, without loss of rotatory power. By hydrolysing (+)-α-benzylpropionitrile to (+)-α-benzylpropionic acid, an approximate value for the specific rotation of the nitrile was calculated.

The close resemblance between these decarboxylation experiments and the Marckwald asymmetric synthesis (*Ber.*, 1904, **37**, 349) led to a reinvestigation of this experiment, the results of which will be communicated shortly.

Experimental.

Ethyl methylmalonate was prepared (yield, 75%) from ethyl malonate by the method described in *Org. Synth.*, **2**, 28, and had b. p. 93—95°/19 mm., n_D^{18} 1·4138.

Ethyl Ethylmethylmalonate.—To a stirred solution of sodium (32 g.) in absolute ethanol (600 c.c.) was slowly added ethyl methylmalonate (240 g.), followed during 3 hours by ethyl iodide (300 g.). The reaction was completed by heating the mixture under reflux for 0·5 hour. After removal of the precipitated sodium iodide by filtration, and of the ethanol by distillation, the residue was dissolved in ether, and the solution washed with water in which the separated sodium iodide had been dissolved. The aqueous layer was extracted three times with ether, the combined ethereal extracts were dried (Na_2SO_4), and the solvent was evaporated. The residual ester (83%) had b. p. 98—100°/15 mm., n_D^{18} 1·4190.

(±)-*Ethyl Hydrogen Ethylmethylmalonate.*—This was prepared by a method based on the procedure of Breslow, Baumgarten, and Hauser (*J. Amer. Chem. Soc.*, 1944, **66**, 1287); a preliminary experiment on unsubstituted ethyl malonate was carried out in order to ascertain the working conditions.

To a solution of ethyl ethylmethylmalonate (200 g.) in absolute ethanol (800 c.c.) was added during one hour, a solution of potassium hydroxide (60 g.) in absolute ethanol (700 c.c.). Next morning the solution was boiled and the crystals (A; 50 g.) insoluble in hot ethanol were removed by filtration. The filtrate was concentrated to 300 c.c. and cooled in ice, whereupon crystals (B; 120 g.) were obtained. Concentration of the second filtrate yielded a further small crop of crystals, which were added to B. Crop B was washed with dry ether and dried *in vacuo* over phosphoric oxide (Found: A, K, 46·0; B, K, 19·1. $C_6H_8O_4K_2$ requires K, 35·1. $C_8H_{13}O_4K$ requires K, 18·4%). Thus, crop B (highly deliquescent needles) consisted largely of the potassium salt of the monoester. The yield was 51%, there being recovered unchanged diethyl ester (30 g.) and also the dipotassium salt (50 g.).

Concentrated hydrochloric acid (50 c.c.) was slowly added to a cold solution of the monopotassium salt (120 g.) in water (55 c.c.), and the resultant mixture extracted four times with ether. Evaporation of the dried (Na_2SO_4) ethereal solution yielded (±)-*ethyl hydrogen ethylmethylmalonate* which, after several hours *in vacuo* over sodium hydroxide, was obtained as a mobile, odourless liquid (96%) (on titration, 0·394 g. required 22·9 ml. of 0·1N-NaOH. $C_8H_{14}O_4$ requires 22·2 ml.). The S-*benzylthiuronium* salt, prepared in the usual way, was obtained as plate-like crystals (from aqueous ethanol), m. p. 117—118° (Found: N, 8·2; S, 9·3. $C_{16}H_{24}O_4N_2S$ requires N, 8·2; S, 9·4%).

Resolution. Quinine (72·5 g.) was added to a solution of (±)-ethyl hydrogen ethylmethylmalonate (38·5 g.) in aqueous ethanol (400 c.c. of 80%), and the whole warmed until dissolution was complete. After 2 days at 0°, the separated crystals were removed by filtration (43 g.; m. p. 103—110°). Two further recrystallisations from the same solvent gave a quinine salt (33 g.) as needles, m. p. 98—100°, which on decomposition with hydrochloric acid yielded (+)-*ethyl hydrogen ethylmethylmalonate* of constant rotatory power, $[\alpha]_D^{18}$ +3·38° (*l*, 2; *c*, 15·0 in chloroform).

A lævorotatory acid (22 g.) was obtained by decomposition of the more soluble fractions of the quinine salt. A portion of this acid (4 g.) was dissolved in acetone (30 c.c.), cinchonidine (6·8 g.) added, and the whole warmed until dissolution was complete. Three recrystallisations of the salt obtained from minimum quantities of acetone gave needles (5·6 g.) of m. p. 154—155°. The remainder of the acid (18 g.) was dissolved in acetone (250 c.c.), and cinchonidine (37·5 g.) was added. The solution was seeded with the recrystallised cinchonidine salt obtained earlier. Two recrystallisations from acetone gave needles (22 g.) of m. p. 155—156°, which on decomposition yielded the (−)-*ester* of $[\alpha]_D^{25}$ −3·47° (*l*, 2; *c*, 5·03 in chloroform); in one equivalent of aqueous sodium hydroxide, $[\alpha]_D^{18}$ was +3·64° (*l*, 2; *c*, 3·57).

Decarboxylation of (+)- *and* (−)-*Ethyl Hydrogen Ethylmethylmalonates.*—(i) The acid (2·0 g.) of $[\alpha]_D^{18}$ +3·38°, contained in a small distillation flask, was heated (oil-bath) at 170—175° for 2 hours. The distillate, dissolved in ether, was washed with dilute sodium hydrogen carbonate solution and dried (Na_2SO_4), and the solvent removed. The residual ethyl ethylmethylacetate (α-methylbutyrate) (1·22 g.) was devoid of optical activity in ethereal solution (*l*, 2; *c*, 3·35) and in the homogeneous state (*l*, 0·5).

(ii) The experiment was repeated with the acid (2·5 g.) of $[\alpha]_D^{25}$ −3·47°; the decarboxylation product was again optically inactive both in the homogeneous state (*l*, 0·5) and in ethereal solution (*l*, 2; *c*, 5·28).

Both distillates showed n_D^{20} 1·3965, and a mixture of the two was converted *via* the acid chloride into (±)-ethylmethylacetamide (α-methylbutyramide), which separated from ether in platelets, m. p. 108·5—109·5°, alone and when mixed with an authentic specimen.

Thermal Stability of Ethyl (−)-*Ethylmethylacetate.*—(±)-Ethylmethylacetic (α-methylbutyric) acid was prepared (yield, 93%) from ethyl ethylmethylmalonate, and resolved by Schütz and Marckwald's method (*Ber.*, 1896, **29**, 53). Three recrystallisations of the brucine salt gave the (−)-acid, b. p. 86·5—87·5°/26 mm., $[\alpha]_D^{20}$ −17·5° (homogeneous, d_D^{20} 0·934; *l*, 1). To the (−)-acid (5·5 g.) was added thionyl chloride (7 c.c.), and the mixture warmed on the steam-bath for 1 hour. The excess of thionyl chloride was removed and the (−)-acid chloride distilled (b. p. 115—120°; 5·2 g.). Treatment with absolute ethanol yielded ethyl (−)-ethylmethylacetate (5·2 g., 74%), b. p. 139—141°, $[\alpha]_D^{22}$ −17·5° (homogeneous, d_4^{22} 0·864; *l*, 0·5).

A specimen of the (−)-ester (1·0 g.), sealed in a glass tube, was heated (oil-bath) at 175° for 3 hours. The product showed b. p. 139—141°, $[\alpha]_D^{22}$ −17·5° (homogeneous, d_4^{22} 0·864; *l*, 0·5), before and after redistillation.

Ethyl (±)-*Ethylmethylcyanoacetate.*—This was prepared (56%) from ethyl cyanoacetate in an analogous manner and had b. p. 98—100°/19·5 mm., n_D^{20} 1·5725.

(±)-*Ethylmethylcyanoacetic* (α-*Cyano*-α-*methylbutyric*) *Acid.*—Hydrolysis of the ester by Henle and Haakh's method (*Ber.*, 1908, **41**, 4261) gave the acid as a pale yellow, hygroscopic oil (93%). Its *silver* salt forms needles, m. p. 155·5—156·5° (Found: Ag, 46·1. $C_6H_8O_2NAg$ requires Ag, 46·1%). The p-*bromophenacyl* ester, prepared from the acid in the usual way, separates from aqueous ethanol in platelets, m. p. 51·5—52·5° (Found: C, 51·9; H, 4·5; N, 4·1; Br, 24·5. $C_{14}H_{14}O_3NBr$ requires C, 51·9; H, 4·4; N, 4·3; Br, 24·6%).

Resolution. (i) After three recrystallisations, the brucine salt of the acid, prepared in the usual way, formed large prisms, m. p. 114—116°, from which only the (±)-acid could be obtained. (ii) A similarly recrystallised quinine salt (prisms) of m. p. 189—190° gave the (±)-acid on decomposition. (iii) The cinchonidine salt (needles) of m. p. 203—205° also afforded no resolution. (iv) No crystalline salt could be obtained with quinidine. (v) To the (±)-acid (4 g.) dissolved in aqueous ethanol (30 c.c. of 50%) was added strychnine (10·5 g.), and the whole warmed until dissolution was complete. After several weeks at room temperature, crystals (2·8 g.) of ill-defined crystalline form, m. p. 120—127°, were obtained.

To the (±)-acid (31 g.) in acetone (100 c.c.) was added strychnine (81·5 g.). The solution was concentrated to about half its volume, and seeded with the strychnine salt obtained earlier. After several weeks, when the solvent had almost completely evaporated, the needle-like crystals (15 g.) of m. p. 127—130° were removed from the viscous mother-liquor by decantation and quickly washed with small quantities of acetone. This salt was twice recrystallised from minimum quantities of acetone. Decomposition with dilute ammonia gave (+)-*ethylmethylcyanoacetic* (*α-cyano-α-methylbutyric*) *acid*, $[\alpha]_D^{20}$ +3·85° (*l*, 2; *c*, 5·99 in ethanol) (Found : equiv., 130·3. $C_6H_9O_2N$ requires equiv., 127·1).

Decarboxylation of (+)-*ethylmethylcyanoacetic acid.* The (+)-acid (2 g.) was decarboxylated under conditions similar to those used for (+)-ethyl hydrogen ethylmethylmalonate, the temperature being kept at 180—190°. The isolated ethylmethylacetonitrile (α-methylbutyronitrile), after purification (1·1 g.), was devoid of optical activity in the homogeneous state (*l*, 0·5) and in ethereal solution (*l*, 2; *c*, 5·3); it had n_D^{25} 1·3880, micro-b. p. 123°.

Thermal Stability of (−)-*Ethylmethylacetonitrile* (*α-Methylbutyronitrile*).—(−)-Ethylmethylacetyl chloride (37 g.) from partly resolved (−)-ethylmethylacetic acid was added during an hour to ammonia solution (80 c.c.; *d* 0·88) cooled in an ice-bath, and the mixture stirred continuously. The product was stirred for an additional half hour, and then evaporated to dryness *in vacuo* over concentrated sulphuric acid. The product was extracted for 3 hours in a Soxhlet apparatus with chloroform, to separate it from ammonium chloride. The chloroform solution was concentrated to 50 c.c. and ligroin added. The white, plate-like crystals obtained (19·2 g.) were recrystallised from chloroform–ligroin, (−)-ethylmethylacetamide (17·6 g., 62%), m. p. 113—114°, $[\alpha]_D^{24\cdot5}$ −4·21° (*l*, 2; *c*, 8·93 in water), being obtained.

To finely powdered (−)-ethylmethylacetamide (16·5 g.), in a 250-c.c. distillation flask, was added phosphoric oxide (28 g.), and the mixture quickly shaken to ensure thorough mixing. The mixture was heated over a flame, whereupon crude (−)-ethylmethylacetonitrile [(−)-α-methylbutyronitrile] (12 g.) distilled. The product was added to an equal volume of water, and anhydrous potassium carbonate added until the solution was saturated. The nitrile was separated and redistilled over phosphoric oxide (2 g.). The product (9·8 g., 72%), a colourless, volatile liquid, had b. p. 124·5—125·5°, n_D^{25} 1·3880, $[\alpha]_D^{25}$ −5·14° (homogeneous; d_4^{25} 0·824; *l*, 0·5).

The nitrile (2 g.), when heated (oil-bath) at 175° for 3 hours, showed $[\alpha]_D^{25}$ −5·14° (homogeneous, d_4^{25} 0·824; *l*, 0·5) and n_D^{25} 1·3880.

A portion of the (−)-nitrile (5·0 g.) was heated under reflux for 3 hours with concentrated hydrochloric acid (25 c.c.). It gave unchanged nitrile (2·4 g.) and (−)-ethylmethylacetic acid (2·6 g.), which after redistillation showed $[\alpha]_D^{20}$ −2·60° (homogeneous, d_D^{20} 0·934; *l*, 0·5). Thus the specific rotation of (−)-ethylmethylacetonitrile is between −22° and −33°. (The more probable value is −22°, since it was found, in the case of α-benzylpropionitrile, that considerable racemisation can occur during the hydrolysis of the optically active nitrile to the acid.)

Ethyl (±)-*α-Benzyl-α-cyanopropionate.*—The *ester*, prepared (37%) from ethyl cyanoacetate in the usual way, by substitution with methyl bromide and benzyl chloride, had n_D^{20} 1·498, b. p. 162—165°/14 mm. (Found : C, 71·6; H, 7·4; N, 6·4. $C_{13}H_{15}O_2N$ requires C, 71·9; H, 7·0; N, 6·4%).

(±)-*α-Benzyl-α-cyanopropionic Acid.*—The ester (60 g.), mixed with alcoholic potasium hydroxide (290 c.c.; N.), was heated under reflux for 1·5 hours, and most of the alcohol removed by evaporation. The product (about 80 c.c.) was mixed with an equal volume of water, extracted three times with ether, acidified with hydrochloric acid, and again extracted with ether. Evaporation of the dried (Na_2SO_4) ethereal extract yielded a product (48 g.) which slowly set to a solid (92%) of m. p. 73—79°. Recrystallisation from ligroin gave white leaflets of (±)-*α-benzyl-α-cyanopropionic acid*, m. p. 93—94° (Found : C, 69·8; H, 5·9; N, 7·4. $C_{11}H_{11}O_2N$ requires C, 69·8; H, 5·9; N, 7·2%).

Resolution. Brucine (3·4 g.) was added to a solution of the (±)-acid (1·5 g.) in aqueous acetone (50 c.c. of 75%). The crystals obtained overnight (1·4 g.), m. p. 125—132°, were twice recrystallised from the same solvent, to give needles (0·8 g.), m. p. 135—137°.

The racemic acid (20 g.) and brucine (45 g.) were dissolved in hot aqueous acetone (200 c.c. of 75%), and the cooled solution inoculated with a crystal of the previously prepared salt. After 2 days the crystals were removed by filtration, providing needles, m. p. 135—137° (19 g.). Decomposition gave the (+)-acid (plates; 4·0 g.) which, after recrystallisation from ligroin, had m. p. 87·5—88·5°, $[\alpha]_D^{19}$ +25·1° (*l*, 2; *c*, 2·43 in chloroform).

The mother-liquors containing the (−)-acid were concentrated to dryness *in vacuo*. The resulting solid (33 g.) was recrystallised three times from aqueous ethanol (75%), when plate-like crystals (17 g.) of m. p. 127—129° were obtained. Decomposition of the salt with dilute hydrochloric acid gave the (−)-acid (3·0 g.) as platelets, m. p. 88—89° (after recrystallisation from chloroform–ligroin), $[\alpha]_D^{18\cdot5}$ −25·7° (*l*, 2; *c*, 2·54 in chloroform).

Decarboxylation of (+)- *and* (−)-*α-Benzyl-α-cyanopropionic Acids.*—(i) The acid (2 g.) of $[\alpha]_D^{19}$ +25·1°, contained in a small distillation flask, was heated at 165°/18 mm. until distillation ceased (about 1 hour). The product was washed with dilute sodium hydrogen carbonate in the usual manner, and found to be devoid of optical activity in the homogeneous state (*l*, 0·5) and in ethereal solution (*l*, 2; *c*, 8·4).

(ii) The experiment was repeated with the (−)-acid (2 g.), and the decarboxylation product was again found to be optically inactive in the homogeneous state (*l*, 0·5) and in ethereal solution (*l*, 2; *c*, 9·2).

The two distillates were combined and redistilled, having b. p. 125—127°/15 mm., n_D^{25} 1·5091. (±)-*α-Benzylpropionitrile* was a colourless oil (Found : C, 83·1; H, 7·6; N, 9·7. $C_{10}H_{11}N$ requires C, 82·9; H, 7·6; N, 9·7%). The nitrile was converted into (±)-α-benzylpropionamide by hydrolysis. This formed needles, m. p. and mixed m. p. 104·5—105·5°.

Thermal Stability of (+)-α-*Benzylpropionitrile.*—Ethylbenzylmalonate was prepared by a modification of the normal method due to Phillips (*Ind. Chem.*, 1945, **21**, 678), whereby sodium ethoxide was added to a mixture of ethyl malonate and benzyl chloride. The product (86%) had b. p. 168·5—169·5°/12 mm., n_D^{20} 1·4880. This ester was converted into ethyl benzylmethylmalonate in the usual manner (yield 96%; b. p. 179—180°/23 mm.; $n_D^{20\cdot5}$ 1·4863). The last was hydrolysed to benzylmethylmalonic acid (yield 96%, crude), and this acid was decarboxylated to (±)-α-benzylpropionic acid (92%), which solidified after distillation (b.p. 174—176°/30 mm.) to needles, m. p. 35—36°.

(±)-Benzylmethylacetic acid was resolved by Kipping and Hunter's method (*J.*, 1903, 1005). Two recrystallisations from aqueous ethanol gave the quinine salt as needles, m. p. 109—110°, from which (+)-benzylmethylacetic acid of α_D^{19} +13·40° (*l*, 1), n_D^{25} 1·5126, b. p. 167—169°/23 mm. was obtained in 38% yield.

The (+)-acid (45 g.) was converted into (+)-benzylpropionyl chloride (86%), b. p. 120—122°/20 mm., by means of thionyl chloride. The acid chloride was converted by treatment with ammonia solution into (+)-benzylpropionamide, needles (78%) (from aqueous ethanol), m. p. 105—106°, $[\alpha]_D^{20}$ +26·4° (*l*, 2; *c*, 0·592 in ether).

The (+)-amide (26 g.) was distilled with phosphoric oxide (28 g.) under reduced pressure, crude (+)-α-benzylpropionitrile (24 g.) being obtained. Purification and redistillation gave the (+)-nitrile as a colourless oil (20 g., 86%), n_D^{25} 1·5091, α_D^{21} +21·96° (*l*, 1), b. p. 127—128°/17 mm.

A specimen of the nitrile (3 g.) was heated under reflux (oil-bath) at 160—170° for 3 hours. The product was slightly yellow and showed α_D^{21} 21·98°, n_D^{25} 1·5091, before and after distillation, b. p. 127—128°/17 mm.

The nitrile (3·0 g.) was kept at room temperature for several months in concentrated hydrochloric acid (15 c.c.). The product was diluted with an equal volume of water and extracted 3 times with ether. The ethereal extracts were extracted 3 times with sodium hydrogen carbonate solution, and the acidic component was re-extracted with ether after acidification. Evaporation of the dried (Na_2SO_4) ethereal extract yielded (+)-α-*benzylpropionic acid* (2·1 g.), α_D^{21} +13·52° (*l*, 1), n_D^{25} 1·5134 (Found: equiv., 166·1. $C_{10}H_{12}O_2$ requires equiv., 164·2). Hence an approximate value for the rotation of optically pure α-benzylpropionitrile is α_D^{21} 33° (*l*, 1), calculated on optically pure benzylmethylacetic acid.

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