291. *Aliphatic Nitro-compounds. Part XII. Preparation and Reduction of 2-Nitroalkyl Cyanides.**

By G. D. Buckley, R. L. Heath, and J. D. Rose.

Interaction of alkali-metal cyanides (or mixtures of these with hydrogen cyanide) and α-nitro-olefins yields 2-nitroalkyl cyanides. 2-*Nitro*-1-*methyl*iso*propyl cyanide*, formed in 90% yield from 1-nitro-2-methylprop-1-ene and hydrogen cyanide–potassium cyanide, yields on catalytic reduction only minor quantities of the expected 2-*amino*-1-*methyl*iso*propyl cyanide* and 1 : 3-diamino-2 : 2-dimethylpropane, the major products being 2-*amino*-1-*methyl*iso*butyramide* and 5 : 5-*dimethyl*-2-(1-*carbamyl*iso*propyl*)*hexahydropyrimidine* (III). 2-*Nitropropyl cyanide*, 2-*nitro*iso*propyl cyanide*, and 2-*nitro*-1-*methylpropyl cyanide* on reduction yield, in addition to the amino-cyanides, some of the corresponding amino-amides.

In connection with a general programme of work on the addition reactions of the α-nitro-olefins, a study of the formation of 2-nitroalkyl cyanides by interaction of metallic cyanides (or mixtures of these with hydrogen cyanide) with α-nitro-olefins was undertaken. The reduction of the nitroalkyl cyanides was investigated as a potential technical route to certain 1 : 3-diamines and β-amino-acids required for synthetic work in another connection.

The literature contains only one reference to the interaction of a metal cyanide with an α-nitro-olefin. Hollemann (*Rec. Trav. chim.*, 1904, **23**, 283) showed that by interaction of β-nitrostyrene and potassium cyanide, two stereoisomerides of 1 : 4-dinitro-2-cyano-2 : 3-diphenylbutane (II) were formed.

$$\mathrm{Ph{\cdot}CH{:}CH{\cdot}NO_2} + \mathrm{HCN} \longrightarrow \underset{\text{(I.)}}{\mathrm{Ph{\cdot}CH(CN){\cdot}CH_2{\cdot}NO_2}} \xrightarrow{\mathrm{Ph{\cdot}CH{:}CH{\cdot}NO_2}} \underset{\mathrm{CH_2{\cdot}NO_2}\quad\text{(II.)}}{\mathrm{Ph{\cdot}C(CN){\cdot}CHPh{\cdot}CH_2{\cdot}NO_2}}$$

The primary reaction in the formation of (II) must be the addition of hydrogen cyanide to the nitro-olefin, giving 2-nitro-1-phenylethyl cyanide (I), which by further reaction with nitrostyrene affords (II).

Interaction of 1- and 2-nitroprop-1-ene with aqueous potassium cyanide gave 2-*nitro*iso*propyl cyanide* and 2-*nitro*-n-*propyl cyanide*, respectively, but the yields were poor (10—15%), much of the olefin being lost by polymerisation in the alkaline reaction medium. 2-Nitrobut-2-ene, which polymerises much less readily than its lower homologues, gave a 50% yield of 2-*nitro*-1-*methyl*-n-*propyl cyanide*, and 75—90% yields of *nitro*-tert.-*butyl cyanide* were obtained from 1-nitro-2-methylprop-1-ene and potassium cyanide, or mixtures of potassium cyanide with hydrogen cyanide. It was shown that hydrogen cyanide alone will not add to the ethylenic linkage of this nitro-olefin, but in the presence of small quantities of potassium cyanide (5—20% of the total of CN ion) excellent yields are obtained.

Surprising results were obtained in the reduction of the 2-nitroalkyl cyanides. Catalytic

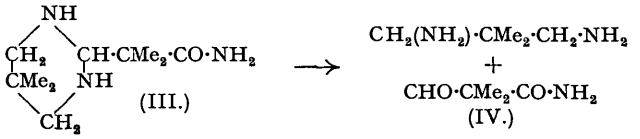
* Patent application pending.

reduction of 2-nitro*iso*propyl cyanide in methyl alcohol at ordinary temperature and pressure in presence of Raney nickel catalyst gave a low yield of β-*amino*iso*butyramide*. Similar reduction of 2-nitro-1-methyl-*n*-propyl cyanide afforded a mixture of the expected aminoalkyl *cyanide* and β-*amino*-α-*methylbutyramide*, whilst reduction in the presence of anhydrous ammonia under pressure gave the amino-amide and some 1 : 3-diamino-2-methylpropane. In none of the above cases was the yield of reduction products good, and attention was turned for closer study to the more readily available nitro-*tert.*-butyl cyanide. Chemical reduction of this with iron and hydrochloric acid gave a 65% yield of *amino*-tert.-*butyl cyanide* and 5% of β-*amino*-αα-*dimethylpropionamide*. Catalytic reduction at ordinary temperature and pressure of the nitroalkyl cyanide in methyl alcohol with a 5% palladium on calcium carbonate catalyst gave the amino-amide in 90% yield and in methyl alcoholic ammonia at 100°/100 atms. with Raney nickel, 20% of the amino-amide and 15% of 1 : 3-diamino-2 : 2-dimethylpropane were obtained. On reduction in methyl alcohol with hydrogen at ordinary temperature and pressure in the presence of Raney nickel, four products were obtained : (*a*) the aminoalkyl cyanide (1·5%), (*b*) the diamine (1·5%), (*c*) the amino-amide (50%), and (*d*) a solid, $C_{10}H_{21}ON_3$ (20%), which separated as pearly plates, m. p. 150°, when the filtered reduction solution was concentrated.

In attempting to prepare derivatives of the solid (*d*), it was observed that by the action of reagents for amines, the derivatives (*hydrochloride*, *picrate*, *benzoyl* derivative) which were obtained were identical with those formed directly from 1 : 3-diamino-2 : 2-dimethylpropane. It was, therefore, clear that the solid was a derivative of this diamine which was easily hydrolysed by acid and alkaline reagents, thus :

$$C_{10}H_{21}ON_3 + H_2O \longrightarrow CH_2(NH_2)\cdot CMe_2\cdot CH_2\cdot NH_2 + C_5H_9O_2N$$

By addition of a 2N-hydrochloric acid solution of 2 : 4-dinitrophenylhydrazine to the base, $C_{10}H_{21}ON_3$, in dilute hydrochloric acid, a 2 : 4-*dinitrophenylhydrazone*, $C_{11}H_{13}O_5N_5$, was obtained (*i.e.*, the derivative of a ketone or aldehyde, $C_5H_9O_2N$). This is formulated as α-carbamyl*iso*butaldehyde (IV), and the substance, $C_{10}H_{21}ON_3$, as 5 : 5-*dimethyl*-2-(1-*carbamyl*iso*propyl*)-*hexahydropyrimidine* (III); the ease of fission of substituted hexahydropyrimidines is well recognised (cf. Veer, *Rec. Trav. chim.*, 1938, **57**, 989).



The mechanism of formation of the hexahydropyrimidine is obscure; Veer (*loc. cit.*) showed that derivatives of 1 : 3-diaminopropane condense with aldehydes merely on warming in alcoholic solution, but it is difficult to visualise conditions during a catalytic reduction which would convert the primary nitro-group, $-CH_2\cdot NO_2$, into the aldehyde group, –CHO. It is considered more probable that the intermediate in this case is β-carbamyl*iso*butaldoxime (V), which condenses with the diaminopropane with loss of hydroxylamine, thus :

$$\begin{matrix} CH_2\cdot NH_2 \\ CMe_2\cdot CN \end{matrix} \longrightarrow \underset{\text{(V.)}}{\begin{matrix} CH{:}N\cdot OH \\ CMe_2\cdot CO\cdot NH_2 \end{matrix}} \xrightarrow{CH_2(NH_2)\cdot CMe_2\cdot CH_2\cdot NH_2} \text{(III)} + NH_2\cdot OH$$

The formation of amino-amides by mild catalytic reduction of the 2-nitroalkyl cyanides is surprising. It is thought that this is not simple addition of water to the aminoalkyl cyanide; an experiment was carried out in which nitro-*tert.*-butyl cyanide was shaken at room temperature in methyl alcohol with water (2 mols.) and Raney nickel (*i.e.*, the conditions of the hydrogenation). The aminoalkyl cyanide was recovered unchanged. It is possible that amide formation proceeds through an *iso*oxazole as intermediate product (*iso*oxazoles are known to undergo fission on hydrogenation), but no experimental proof for this can be given.

Experimental.

Analyses are by Mr. E. S. Morton. M. ps. are uncorrected.

2-Nitroisopropyl Cyanide.—1-Nitroprop-1-ene (50 g.; this series, Part I) in alcohol (240 c.c.) was added dropwise to a well-stirred solution of potassium cyanide (40 g.) in water (300 c.c.) at − 5° to 0°. The solution was stirred at 0° for a further 4 hours, acidified at 0—5° with 5N-hydrochloric acid (130 c.c.), concentrated under reduced pressure at 40° to 300 c.c., and after isolation with ether the *cyanide* (16·4 g.; 25%), b. p. 68—70°/0·5 mm., was obtained (Found : C, 42·6; H, 5·2; N, 23·9. $C_4H_6O_2N_2$ requires C, 42·1; H, 5·3; N, 24·5%).

β-Aminoisobutyramide.—The cyanide (3·25 g.) in methyl alcohol (50 c.c.) was shaken in hydrogen

at 25°/760 mm. in the presence of Raney nickel. Absorption (1916 c.c. of hydrogen) was complete in 3½ hours. The catalyst was separated, the alcohol removed, and the product distilled, giving the amide (0·44 g.; 15%), b. p. 75—82°/0·3 mm., which was identified as the *picrate*, m. p. 232° (Found: N, 20·6. $C_4H_{10}ON_2,C_6H_3O_7N_3$ requires N, 21·1%).

2-*Nitro*-n-*propyl Cyanide*.—This *compound* was prepared from 2-nitroprop-1-ene (50 g.; this series, Part I) and sodium cyanide (28·2 g.) as described for the *iso*-derivative above; it was obtained as a straw-coloured liquid (10 g.; 15%), b. p. 81—82°/0·5 mm. (Found: C, 42·7; H, 5·0. $C_4H_6O_2N_2$ requires C, 42·1; H, 5·3%).

2-*Nitro*-1-*methyl*-n-*propyl Cyanide*.—This *compound* was prepared from 2-nitrobut-2-ene (58 g.; this series, Part III) in alcohol (500 c.c.) and potassium cyanide (38 g.) in water (300 c.c.) at 10—20°. Isolation in the usual way yielded the cyanide (32 g.; 50%) as a pale yellow, mobile oil, b. p. 61—65°/0·2 mm. (Found: C, 47·0; H, 6·4. $C_5H_8O_2N_2$ requires C, 46·9; H, 6·2%).

Reduction of 2-*Nitro*-1-*methyl*-n-*propyl Cyanide*.—(a) *With Raney nickel at ordinary pressure.* The cyanide (10·4 g.) in methyl alcohol (80 c.c.) was shaken in hydrogen at 20°/750 mm. in the presence of Raney nickel. Absorption was 4930 c.c. of hydrogen at 0°/760 mm. [Calc. (3 mols.), 5460 c.c.]. The catalyst was separated and the product distilled, giving: (i) 2-Amino-1-methyl-*n*-propyl cyanide, b. p. 30°/0·05 mm. (0·5 g.), characterised as its *hydrochloride*, white crystals from alcohol–ether, m. p. 156° (Found: C, 44·6; H, 8·3; N, 20·8. $C_5H_{10}N_2$,HCl requires C, 44·6; H, 8·3; N, 20·8%). (ii) β-Amino-α-methylbutyramide, b. p. 145—155°/15 mm., 95—100°/0·05 mm. (1·7 g.), which solidified on keeping and after crystallisation from dry benzene had m. p. 62—63°. The amide was extremely deliquescent and satisfactory analyses could not be obtained. Neither the hydrochloride nor the picrate could be obtained in a crystalline condition, and the amide was characterised as the *picrolonate*, m. p. 214° (Found: N, 22·1. $C_5H_{12}ON_2,C_{10}H_8O_5N_4$ requires N, 22·1%).

(b) *With Raney nickel and anhydrous ammonia under pressure.* The cyanide (23 g.) in methyl alcohol (250 c.c.) and anhydrous ammonia (70 g.) was heated at 100° with hydrogen (initial pressure, 100 atms.) in an internally agitated stainless steel autoclave for 1 hour. The filtered solution was made acid to Congo-red with hydrochloric acid and evaporated to dryness at 40° under reduced pressure. The residue was treated with excess of aqueous potassium hydroxide and the product isolated with ether, giving: (i) 1 : 3-diamino-2-methylpropane, b. p. 60—70°/15 mm. (2 g.) (Found: equiv., 50. Calc.: 51); and (ii) β-amino-α-methylbutyramide, b. p. 145—155°/15 mm., m. p. 62—63°.

Nitro-tert.-*butyl Cyanide*.—(a) *From* 1-*nitro*-2-*methylprop*-1-*ene and potassium cyanide.* 1-Nitro-2-methylprop-1-ene (101 g.; Levy and Scaife, in the press) in alcohol (500 c.c.) was added slowly to a stirred aqueous solution of potassium cyanide (65 g. in 500 c.c.) at 20—25°. Stirring was continued for 6 hours and the mixture then acidified with 5N-hydrochloric acid (240 c.c.) at 5—10°. The white, crystalline precipitate was collected, washed with cold water and recrystallised from ether, giving *nitro*-tert.-*butyl cyanide* (96 g.; 75%), m. p. 42°, b. p. 66—67°/0·2 mm. (Found: C, 47·1; H, 6·1; N, 21·3. $C_5H_8O_2N_2$ requires C, 46·9; H, 6·2; N, 21·9%).

(b) *From* 1-*nitro*-2-*methylprop*-1-*ene, hydrogen cyanide, and potassium cyanide.* A mixture of the nitro-olefin (10·1 g.), hydrogen cyanide (6 g.), and potassium cyanide (0·325 g.; 5%) in 50% aqueous alcohol (50 c.c.) was stirred at room temperature for 24 hours. Water (50 c.c.) was then added and the solution at 0—5° made acid to Congo-red with hydrochloric acid. The precipitated cyanide was isolated with ether and recrystallised from ether, m. p. 42°. Yield, 10·3 g. (83%). In this preparation, the use of 1% of potassium cyanide reduced the yield to 10%; with 20% of potassium cyanide the yield was 87%; in the absence of potassium cyanide (hydrogen cyanide alone) no nitroalkyl cyanide was obtained.

(c) *From nitro*-tert.-*butyl acetate and potassium cyanide.* Nitro-*tert.*-butyl acetate (8 g.; this series, Part XVIII) was added dropwise to a vigorously stirred aqueous solution of potassium cyanide (4 g. in 25 c.c.) at 25—30°. Stirring was continued for 16 hours at 30°, the solution acidified at 0—5° with 5N-hydrochloric acid, and the precipitated cyanide crystallised from ether, m. p. 42°. Yield, 2·5 g. (40%).

Reduction of Nitro-tert.-*butyl Cyanide*.—(a) *With iron and hydrochloric acid.* A mixture of iron filings (35 g.), concentrated hydrochloric acid (10 c.c.), and water (75 c.c.) was allowed to react at 60—70° until evolution of hydrogen ceased. The cyanide (21 g.) in alcohol (50 c.c.) was then added at a rate sufficient to maintain the temperature of the vigorously stirred mixture at 60—70°, and stirring was continued at the same temperature for a further 8 hours. The mixture was filtered, acidified with concentrated hydrochloric acid, and evaporated to dryness, and the free bases, liberated by addition of an excess of 50% aqueous potassium hydroxide, were isolated with ether. Distillation gave: (i) *Amino*-tert.-*butyl cyanide* (10·2 g.; 65%), b. p. 63°/15 mm., m. p. 10° (Found: C, 61·5; H, 9·7. $C_5H_{10}N_2$ requires C, 61·2; H, 10·2%); *hydrochloride*, from alcohol, m. p. 260° (Found: C, 44·5; H, 8·2; N, 20·6. $C_5H_{10}N_2$,HCl requires C, 44·6; H, 8·2; N, 20·8%); *picrate*, from water, m. p. 183° (Found: C, 40·3; H, 3·8; N, 21·4. $C_5H_{10}N_2,C_6H_3O_7N_3$ requires C, 40·4; H, 3·9; N, 21·4%); *benzoyl* derivative, from alcohol, m. p. 122° (Found: C, 71·3; H, 6·6; N, 13·9. $C_{12}H_{14}ON_2$ requires C, 71·3; H, 6·9; N, 13·9%). Reduction of this aminoalkyl cyanide by shaking in methyl-alcoholic solution with hydrogen and Raney nickel at ordinary temperature and pressure afforded 1 : 3-*diamino*-2 : 2-*dimethylpropane*, b. p. 65°/15 mm., 153°/760 mm. (Found: C, 58·4; H, 13·6; N, 27·0. $C_5H_{14}N_2$ requires C, 58·8; H, 13·7; N, 27·4%); dihydrochloride, m. p. 259° [Komppa and Seron (*Ann. Acad. Sci. Fennicæ*, 1933, **37***A*, No. 7, 8; cf. *Chem. Abs.*, 1933, 3964) give m. p. 280—281°] (Found: C, 34·5; H, 8·6; N, 15·7; Cl, 40·1. Calc. for $C_5H_{14}N_2$,2HCl: C, 34·3; H, 9·1; N, 16·0; Cl, 40·6%); dipicrate, m. p. 234° (Komppa and Seron, *loc. cit.*, give m. p. 240°) (Found: C, 36·6; H, 3·6; N, 19·8. Calc. for $C_5H_{14}N_2,2C_6H_3O_7N_3$: C, 36·4; H, 3·6; N, 20·0%); *dibenzoyl* derivative, long needles from aqueous alcohol, m. p. 152° (Found: C, 73·7; H, 7·3; N, 9·0. $C_{19}H_{22}O_2N_2$ requires C, 73·5; H, 7·1; N, 9·0%). (ii) β-Amino-αα-dimethylpropionamide (1 g.; 5%), b. p. 145°/15 mm., which solidified and after crystallisation from dry benzene had m. p. 74—75° (Found: equiv. by titration, 115. Calc.: 116). This compound was highly deliquescent and satisfactory analyses could not be obtained; it was characterised as the following derivatives: *hydrochloride*, fine needles from absolute alcohol, m. p. 172° (Found: C, 39·6; H, 8·7;

N, 17·8; Cl, 23·3. $C_5H_{12}ON_2$,HCl requires C, 39·5; H, 8·5; N, 18·3; Cl, 23·3%); *hydrobromide*, plates from absolute alcohol, m. p. 202° (Found: C, 30·5; H, 6·2; N, 14·1; Br, 40·8. $C_5H_{12}ON_2$,HBr requires C, 30·5; H, 6·6; N, 14·2; Br, 40·6%); *picrate*, flat prisms from alcohol, m. p. 190° (Found: C, 38·4; H, 4·2; N, 20·4. $C_5H_{12}ON_2,C_6H_3O_7N_3$ requires C, 38·3; H, 4·3; N, 20·3%); *phenylurea*, prisms from alcohol, m. p. 199—200° (Found: C, 61·2; H, 7·0; N, 17·2. $C_{12}H_{17}O_2N_3$ requires C, 61·2; H, 7·2; N, 17·8%). The *benzoyl* derivative, prisms from alcohol–ether, m. p. 151° (Found: C, 65·5; H, 7·2; N, 12·5. $C_{12}H_{16}O_2N_2$ requires C, 65·4; H, 7·3; N, 12·7%), on being heated with excess of thionyl chloride, gave 2-benzamido-1 : 1-dimethyl-*tert.*-butyl cyanide, m. p. 122°, identical with that described above.

(b) *Reduction with hydrogen and Raney nickel at ordinary pressure.* The nitroalkyl cyanide (42 g.) in methyl alcohol (450 c.c.) was shaken in hydrogen in presence of Raney nickel at ordinary pressure and temperature. Absorption was 22·7 l. of hydrogen at N.T.P. [Calc. (3 mols.), 22·4 l.]. The catalyst was separated and the filtrate concentrated, giving a solid (*A*) and a liquid, separated by filtration. The liquid was distilled, giving the following: (i) Amino-*tert.*-butyl cyanide (0·5 g.; 1·5%), m. p. 10°. (ii) 1 : 3-Diamino-2 : 2-dimethylpropane (0·5 g.; 1·5%); dihydrochloride, m. p. 259°; dipicrate, m. p. 234°. (iii) β-Amino-αα-dimethylpropionamide (19 g.; 50%), m. p. 74—75°. The solid (*A*), above, recrystallised from absolute alcohol, gave 5 : 5-*dimethyl*-2-(1-*carbamyl*iso*propyl*)*hexahydropyrimidine* (6·5 g.; 20%) in pearly plates, m. p. 150° (Found: C, 60·2; H, 10·1; N, 20·6. $C_{10}H_{21}ON_3$ requires C, 60·3; H, 10·5; N, 21·0%). On addition of a dry, ethereal solution of hydrogen chloride to the base in alcohol at 0—10°, 1 : 3-diamino-2 : 2-dimethylpropane dihydrochloride, m. p. and mixed m. p. with an authentic specimen 259°, separated in 42% yield. Similarly, addition of hot, aqueous picric acid to an alcoholic solution of the hydropyrimidine gave 1 : 3-diamino-2 : 2-dimethylpropane dipicrate, m. p. and mixed m. p. 234°, and benzoylation by the Schotten–Baumann procedure gave 1 : 3-dibenzamido-2 : 2-dimethylpropane, m. p. and mixed m. p. 152°. Addition of 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid to a solution of the pyrimidine in hydrochloric acid gave a pale yellow, crystalline precipitate, which, crystallised from methyl alcohol, yielded β-*carbamyl*iso*butaldehyde* 2 : 4-*dinitrophenylhydrazone*, m. p. 196° (Found: C, 44·7; H, 4·4; N, 23·6. $C_{11}H_{13}O_5N_5$ requires C, 44·7; H, 4·4; N, 23·7%).

(c) *Reduction with hydrogen and palladium.* The nitro-cyanide (10 g.) in methyl alcohol (50 c.c.) was shaken in hydrogen with a 5% palladium on calcium carbonate catalyst at ordinary pressure. Absorption was 5·2 l. of hydrogen at N.T.P. [Calc. (3 mols.), 5·25 l.]. The catalyst was removed and the solution distilled, yielding β-amino-αα-dimethylpropionamide, m. p. 74—75° (8·0 g.; 89%).

(d) *Reduction with hydrogen and Raney nickel in presence of anhydrous ammonia.* The nitro-cyanide (45 g.) in methyl alcohol (250 c.c.) and anhydrous ammonia (140 g.) was heated at 100° in an internally agitated, stainless steel autoclave with hydrogen at 100 atms. initial pressure and Raney nickel (10 g.). Hydrogenation was complete in 1 hour. After evaporation of the ammonia, the catalyst was removed and the product distilled, giving: (i) 1 : 3-Diamino-2 : 2-dimethylpropane, b. p. 65°/15 mm. (5·5 g.; 15%). (ii) β-Amino-αα-dimethylpropionamide, m. p. 74—76° (8·2 g.; 20%).

β-Amino-αα-dimethylpropionic Acid.—β-Amino-αα-dimethylpropionamide (9·2 g.) was refluxed for 4 hours with 40% sulphuric acid (90 c.c.). The solution was diluted with water (300 c.c.) and barium carbonate (slight excess calculated on the sulphuric acid) was added slowly to the boiling solution through which a current of steam was passed to remove the ammonia. The excess of barium carbonate was decomposed by neutralisation (to Congo-red) with 2N-sulphuric acid, and the barium sulphate removed by filtration. The filtrate was concentrated to 75 c.c., and traces of sulphuric acid were precipitated with lead carbonate, the lead sulphate was filtered off, and the filtrate saturated with hydrogen sulphide. After removal of lead sulphide, the filtrate was concentrated and yielded β-amino-αα-dimethylpropionic acid, which separated from aqueous alcohol as large hexagonal prisms, m. p. 246° (decomp.) in 82% yield (Kohn and Schmidt, *Monatsh.*, 1907, **28**, 1055, give decomp. *ca.* 220°) (Found: C, 51·1; H, 9·4; N, 12·3. Calc. for $C_5H_{11}O_2N$: C, 51·3; H, 9·4; N, 12·0%).

Methyl β-Amino-αα-dimethylpropionate.—The acid was esterified in methyl alcohol with dry hydrogen chloride in the usual way; evaporation of the methyl alcohol yielded the *methyl ester hydrochloride*, m. p. 164° (80% yield) (Found: C, 43·0; H, 8·2; N, 8·2. $C_6H_{13}O_2N$,HCl requires C, 43·0; H, 8·4; N, 8·4%). Addition of 10N-sodium hydroxide to an aqueous solution of the hydrochloride, followed by isolation with ether and distillation, afforded the *methyl* ester, b. p. 57°/11 mm., which separated from dry ether as highly deliquescent prisms, m. p. 64° (Found: C, 54·8; H, 9·9; N, 10·5. $C_6H_{13}O_2N$ requires C, 55·0; H, 9·9; N, 10·7%). The ester was completely unchanged after standing for 2 days at 0° with methyl alcoholic ammonia; with concentrated aqueous ammonia, at 60° for 3 days, hydrolysis to the acid occurred. The *ethyl ester hydrochloride*, similarly formed, had m. p. 91° (Found: C, 45·6; H, 8·4; N, 7·8; Cl, 19·7. $C_7H_{15}O_2N$,HCl requires C, 46·2; H, 8·8; N, 7·7; Cl, 19·7%).

β-Benzamido-αα-dimethylpropionic acid, m. p. 151° (Kohn and Schmidt, *loc. cit.*, give m. p. 149—151°) (3 g.) was treated with freshly distilled thionyl chloride (6·5 c.c.; 6 mols.) and the reaction completed by 1 hours' boiling under reflux. The excess of thionyl chloride was removed under reduced pressure at 70—80°, and to the residual, pale yellow oil, saturated methyl-alcoholic ammonia (25 c.c.) was added at 0°. The solution was evaporated, the residual solid triturated with water to remove ammonium chloride, and the residue, crystallised from aqueous alcohol, gave a small yield of benzamido-*tert.*-butyl cyanide identical with that described above, m. p. and mixed m. p. 122°. Repetition of this experiment with only one mol. of thionyl chloride in benzene, and treatment of the crude acid chloride with aqueous (*d* 0·88) ammonia, gave 90% of β-benzamido-αα-dimethylpropionamide, m. p. 151°, identical with the benzoyl derivative of the amino-amide (see above).

The authors wish to acknowledge the interest and advice of Dr. H. A. Piggott in this work.

IMPERIAL CHEMICAL INDUSTRIES LIMITED, RESEARCH LABORATORIES,
HEXAGON HOUSE, BLACKLEY, MANCHESTER, 9. [*Received, January 23rd*, 1947.]