57. *Reactions of α-Cyanoprene (1-Cyanobuta-1 : 3-diene). Part I. Addition of Nitro-paraffins.**

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Nitroethane, 1- and 2-nitropropane, and nitro*cyclo*hexane react with α-cyanoprene (1-cyanobuta-1 : 3-diene) in the presence of a basic catalyst to give 5-substituted 5-nitropentenyl cyanides [$NO_2{\cdot}CRR'{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CN$]. Nitroethane and nitromethane also add respectively to two and three moles of α-cyanoprene. Some of the products are hydrogenated over palladium on calcium carbonate to saturated nitro-cyanides, and over Raney nickel to amino-cyanides and diamines, and are reduced with iron and acid to unsaturated amino-cyanides. Amino- and nitro-acids are also prepared by hydrolysis of the appropriate cyanides. Treatment of the 2-nitropropane adduct, 5-*nitro*-5-*methylhex*-2-*enyl cyanide*, with secondary amines (*e.g.*, morpholine) gives the Δ^1(?)-*isomer*, together with, *e.g.*, 5-*nitro*-2-*morpholino*-5-*methylhexyl cyanide*.

Bruson and his co-workers (*J. Amer. Chem. Soc.*, 1942, **64**, 2547, 2850; 1943, **65**, 18, 23) have shown that a wide variety of compounds containing active hydrogen atoms can be added to vinyl cyanide. The synthetic value of this " cyanoethylation " reaction prompted interest in the possibility of extending it to α-cyanoprene (1-cyanobuta-1 : 3-diene) (I). If α-cyanoprene formed 1 : 4-adducts with compounds containing active hydrogen, this would offer a synthetic method for the introduction of a straight chain of five carbon atoms into many organic substances.

α-Cyanoprene was first prepared, though in poor yield, by Coffman (*J. Amer. Chem. Soc.*, 1935, **57**, 1981), by interaction of 1-chlorobuta-2 : 3-diene with sodium cyanide in methyl alcohol. Coffman confirmed the structure of the product by hydrolysis to 2-vinylacrylic acid and by reduction to *n*-amylamine. A better method of preparation was later reported by Gudgeon, Hill, and I.C.I. Ltd. (E.P. 515,737); this involved the pyrolysis of esters of crotonaldehyde cyanohydrin at about 500°. The α-cyanoprene used in this work was prepared by pyrolysis of crotonaldehyde cyanohydrin acetate.

As by-products in his preparation of α-cyanoprene, Coffman isolated two liquids, one of which was shown to be 4-methoxybut-2-enyl cyanide (II) and the other an addition product with two moles of methyl alcohol (either III or IV).

$CH_2{:}CH{\cdot}CH{:}CH{\cdot}CN$ (I.)

$MeO{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CN$ (II.)

$MeO{\cdot}CH_2{\cdot}CH(OMe){\cdot}CH_2{\cdot}CH_2{\cdot}CN$ (III.)

$MeO{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OMe){\cdot}CH_2{\cdot}CN$ (IV.)

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* Patent protection pending.

The second product was also obtained by heating α-cyanoprene with methyl alcohol in the presence of sodium methoxide. Coffman also obtained ethyl 4-chlorobut-2-ene-1-carboxylate ($CH_2Cl{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CO_2Et$) by the interaction of α-cyanoprene with hydrogen chloride.

Similar addition reactions have now been carried out with primary and secondary nitro-paraffins, which add readily to α-cyanoprene in the presence of a basic catalyst. For most of the reactions described, methyltriethylammonium hydroxide has been used as catalyst and dioxan as solvent, but other bases (sodium hydroxide or methoxide) are effective, and alcohol can be used as a solvent as the rate of addition of alcohols to α-cyanoprene is low.

2-Nitropropane reacted with α-cyanoprene to give an adduct *A* or *B*, according to whether 1 : 4- or 1 : 2-addition had occurred.

$$NO_2{\cdot}CMe_2{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CN \quad (A.) \qquad CH_2{:}CH{\cdot}CH(CMe_2{\cdot}NO_2){\cdot}CH_2{\cdot}CN \quad (B.)$$

This adduct, after ozonisation followed by treatment with hydrogen peroxide, gave an acid, $C_4H_8(NO_2){\cdot}CO_2H$, m. p. 103—104°, thus excluding the possibility of an acid derived from *B*. The acid must therefore be β-nitro*iso*valeric acid (XX) though no m. p. has previously been recorded and attempts to repeat the literature preparations (Bredt, *Ber.*, 1881, **14**, 1782; 1882, **15**, 2319; Dessaignes, *Annalen*, 1851, **79**, 374) have been unsuccessful.

This result, taken in conjunction with the fact that 1 : 4-addition to α-cyanoprene has been established in the cases of methyl alcohol and hydrochloric acid (Coffman, *loc. cit.*), acetylacetone, and ethyl malonate (Part II, following paper), has led us to formulate all the nitro-paraffin derivatives as 1 : 4-adducts. Further confirmation followed from the reduction of the adducts: if 1 : 2-addition had occurred, the resulting 2-nitrocyanides would hydrogenate to give pyrrole derivatives (cf. Buckley and Elliot, *J.*, 1947, 1508), whereas normal reduction to open chain compounds was obtained with all the cyanoprene adducts.

The adduct from 2-nitropropane is therefore 5-*nitro*-5-*methylhex*-2-*enyl cyanide* (*A*). Similarly, 1-nitropropane and nitro*cyclo*hexane gave 5-*nitrohept*-2-*enyl cyanide* (type V) and 4-(1-*nitro*cyclo*hexyl*)*but*-2-*enyl cyanide* (type V), respectively.

$$CH_2{:}CH{\cdot}CH{:}CH{\cdot}CN + NO_2{\cdot}CHRR' \longrightarrow NO_2{\cdot}CRR'{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CN \qquad (V.)$$

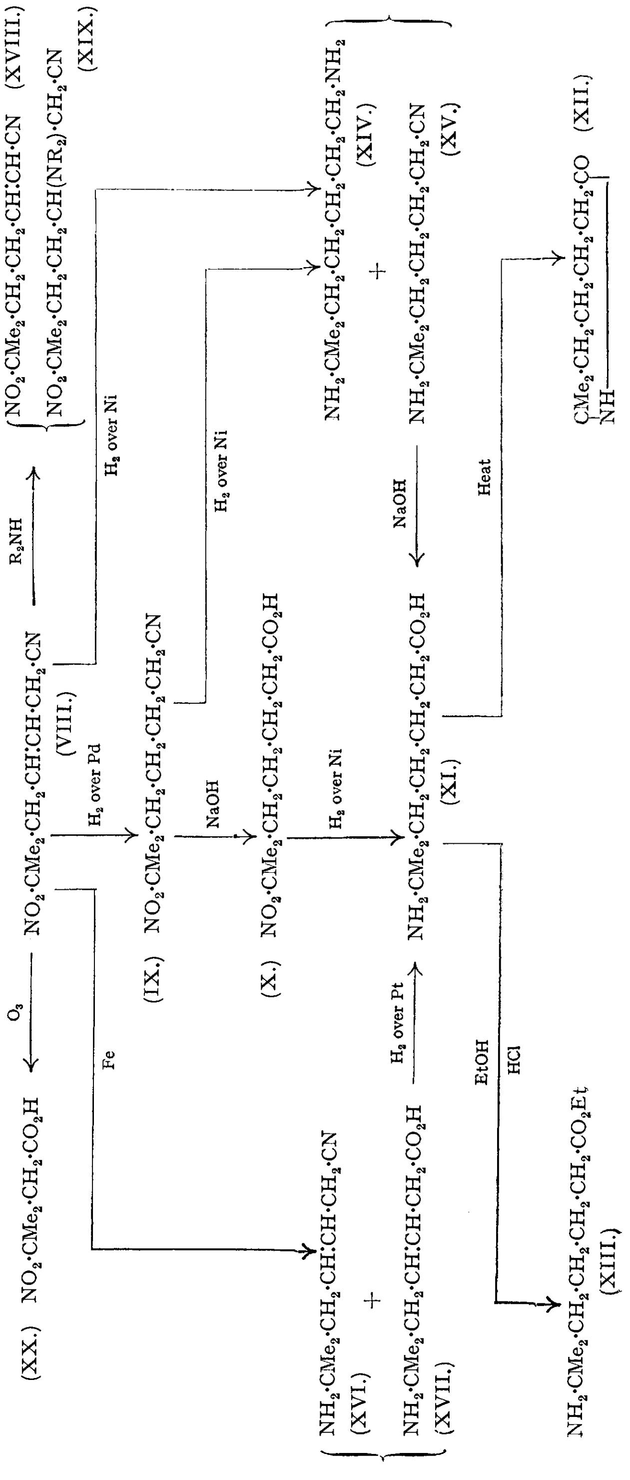
With nitroethane both the mono-adduct, 5-*nitrohex*-2-*enyl cyanide* (V; R = Me, R′ = H), and the bis-adduct, 5-*nitro*-1 : 9-*dicyano*-5-*methylnona*-2 : 7-*diene* (VI) were obtained; from nitromethane, only the tris-adduct (VII) could be isolated. (VII) was unstable and was characterised as its hexahydro-derivative.

$$NO_2{\cdot}CMe(CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CN)_2 \quad (VI.) \qquad NO_2{\cdot}C(CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CN)_3 \quad (VII.)$$

Hydrogenation of the adducts over Raney nickel generally proved unsatisfactory, reduction of the ethylene linkage being accompanied by varying amounts of reduction of the cyanide groups to amine. In all cases, however, the double bonds alone were reduced by using 5% palladium on calcium carbonate as catalyst: further reduction of the cyanide groups could then be effected over Raney nickel.

The reactions of the adducts have been studied chiefly with those derived from the two readily accessible nitro-paraffins, nitroethane and 2-nitropropane. The bis-adduct from nitroethane (VI) was hydrogenated over palladium on calcium carbonate to 5-*nitro*-1 : 9-*dicyano*-5-*methylnonane*, which was hydrolysed to the corresponding *di-acid* and hydrogenated over Raney nickel to 1 : 6 : 11-*triamino*-6-*methylundecane*. Similarly, the 2-nitropropane adduct (VIII) was hydrogenated over palladium on calcium carbonate to 5-*nitro*-5-*methylhexyl cyanide* (IX). Hydrolysis gave the *nitro-acid* (X), and this was reduced over Raney nickel to 5-*amino*-5-*methylhexane*-1-*carboxylic acid* (XI) which, on being heated at 260°, gave the *lactam* (XII), and was esterified to the *ethyl* ester (XIII). Hydrogenation of the adduct (VIII) over Raney nickel gave a mixture of 1 : 6-*diamino*-6-*methylheptane* (XIV) [which was also obtained by similar reduction of the saturated nitro-cyanide (IX)] and 5-*amino*-5-*methylhexyl cyanide* (XV) which was hydrolysed to the *amino-acid* (XI) previously obtained by reduction of the nitro-acid (X).

Reduction of 5-nitro-5-methylhex-2-enyl cyanide (VIII) with iron gave three products, (*a*) 5-*amino*-5-*methylhex*-2-*enyl cyanide* (XVI), (*b*) 5-*amino*-5-*methylhex*-2-*ene*-1-*carboxylic acid* (XVII) [identified by reduction over platinum to the saturated amino-acid (XI)], and (*c*) a base isomeric with the unsaturated amino-cyanide. The last has not been examined, but presumably either has the double bond αβ to the cyano-group or is the cyclised form of this, *i.e.*, 2-cyano-6 : 6-dimethylpiperidine.



Reactions of 5-nitro-5-methylhex-2-enyl cyanide.

Attempts to cause migration of the double bond from the βγ-position in (VIII) to the αβ-position in (XVIII) by the use of sodium in *iso*propanol were unsuccessful. When the hex-2-enyl cyanide (VIII) was treated with morpholine, two products were obtained, a base and a neutral oil. The base was shown by analysis to be an adduct of morpholine to (VIII), a reaction which probably involves first isomerisation of (VIII) to (XVIII), followed by addition to this substituted vinyl cyanide, giving 5-*nitro*-2-*morpholino*-5-*methylhexyl cyanide* (XIX). The neutral product was isomeric with the starting material (VIII), and though it is possibly the *cis–trans* isomer of (VIII), it is more likely, in view of the formation of the adduct (XIX), to be 5-*nitro*-5-*methylhex*-1-*enyl cyanide* (XVIII). With piperidine in place of morpholine, the same neutral product (XVIII) was isolated, together with the adduct 5-*nitro*-2-*piperidino*-5-*methylhexyl cyanide* (XIX).

EXPERIMENTAL.

Analyses are by Mr. E. S. Morton. All m. ps. are uncorrected.

Reactions of α-Cyanoprene with Nitro-paraffins.—The "catalyst" used in all these additions was a 38% aqueous solution of methyltriethylammonium hydroxide.

(a) *With* 2-*nitropropane.* α-Cyanoprene (158 g.) was added slowly to a stirred solution of 2-nitropropane (178 g.) and catalyst (10 c.c.) in dioxan (200 c.c.) at 40°. After 2 hours at 40°, the mixture was poured into water, neutralised with 2N-hydrochloric acid, and the oil extracted with ether, washed with water, and dried. The solvent was removed, and the oil (300 g.) dissolved in alcohol (300 c.c.), cooled to − 10°, and the precipitate collected, m. p. 37—38° (135 g.). The filtrate was cooled to − 60° and a further precipitate, m. p. 32—38° (45 g.), was obtained. Recrystallisation from alcohol gave 5-*nitro*-5-*methylhex*-2-*enyl cyanide*, m. p. 38—39° (Found: C, 56·8; H, 7·2; N, 16·4. $C_8H_{12}O_2N_2$ requires C, 57·1; H, 7·1; N, 16·6%).

The same product was obtained when alcohol was used in place of dioxan or with sodium hydroxide or sodium ethoxide in place of the quaternary base catalyst. With these modifications, however, the yield was more variable.

(b) *With* 1-*nitropropane.* α-Cyanoprene (79 g.) was added slowly to a stirred solution of 1-nitropropane (45 g.) and catalyst (5 c.c.) in dioxan (50 c.c.) at 35°. The temperature was raised to 40° and maintained thereat for 1 hour. The mixture was poured into water, neutralised with 2N-hydrochloric acid, and the oil extracted with ether, washed and dried. Distillation gave 5-*nitrohept*-2-*enyl cyanide* as a pale yellow oil, b. p. 102°/0·07 mm. (Found: C, 57·6; H, 6·9; N, 16·4. $C_8H_{12}O_2N_2$ requires C, 57·2; H, 7·1; N, 16·6%).

(c) *With nitro*cyclo*hexane.* α-Cyanoprene (20 g.) was added slowly to a stirred solution of nitro*cyclo*hexane (32 g.) and catalyst (3 c.c.) in dioxan (30 c.c.) at 40°. After 1 hour at 40°, the mixture was poured into water, neutralised with 2N-hydrochloric acid, and the oil extracted with ether, washed, and dried. Distillation gave 4-(1-*nitro*cyclo*hexyl*)*but*-2-*enyl cyanide*, a pale yellow liquid, b. p. 142°/0·08 mm. (Found: C, 63·3; H, 7·7; N, 14·0. $C_{11}H_{16}O_2N_2$ requires C, 63·5; H, 7·7; N, 13·5%). In the first experiment the oil readily solidified and, after recrystallisation from alcohol, had m. p. 30° (Found: C, 63·3; H, 7·4; N, 13·5%), but in later preparations the oil could not be induced to solidify even with seeding. Presumably these are the *cis*- and *trans*-forms.

(d) *With nitroethane.* (i) α-Cyanoprene (119 g.) was added to a stirred solution of nitroethane (56 g.) and catalyst (6 c.c.) in dioxan (100 c.c.) at 30°. The temperature was maintained at 40° for 2 hours, and the mixture poured into water and neutralised with 2N-hydrochloric acid; 5-*nitro*-1 : 9-*dicyano*-5-*methylnona*-2 : 7-*diene* then separated as white needles (114 g.; 65% theory), m. p. 77° (from alcohol) (Found: C, 62·1; H, 6·5; N, 18·1. $C_{12}H_{15}O_2N_3$ requires C, 61·8; H, 6·4; N, 18·0%). (ii) α-Cyanoprene (40 g.) was run into a stirred mixture of nitroethane (160 g.) and catalyst (6 c.c.) at 25—30°. The temperature was then maintained at 40° for 1 hour, the mixture poured into water, neutralised with 2N-hydrochloric acid, extracted with ether, and dried. Distillation gave 5-*nitrohex*-2-*enyl cyanide* as a colourless oil (45 g.), b. p. 88°/0·05 mm. (Found: C, 54·0; H, 6·7; N, 18·1. $C_7H_{10}O_2N_2$ requires C, 54·5; H, 6·9; N, 18·1%). A small amount (10 g.) of 5-nitro-1 : 9-dicyano-5-methylnona-2 : 7-diene, m. p. 77°, was also isolated.

(e) *With nitromethane.* α-Cyanoprene (24 g.) was run during ½ hour into a stirred solution of nitromethane (6 g.) and catalyst (3 c.c.) in dioxan (50 c.c.) at 25—30°. The mixture was diluted with 2N-hydrochloric acid to precipitate nitrotris-(4-cyanobut-2-enyl)methane (VII), m. p. 72° (from dioxan). This product rapidly decomposed and good analyses could not be obtained.

Reduction of α-Cyanoprene Adducts.—(a) *Over* 5% *palladium on calcium carbonate.* The adducts in methyl alcohol were shaken with hydrogen and the catalyst at ordinary temperature and pressure until absorption ceased, and the product was isolated by distillation or crystallisation. The following compounds were thus obtained. 5-*Nitro*-5-*methylhexyl cyanide* (IX), b. p. 100—102°/0·09 mm., m. p. 10°, $n_D^{19°}$ 1·4513 (Found: C, 56·9; H, 8·1; N, 16·8. $C_8H_{14}O_2N_2$ requires C, 56·5; H, 8·3; N, 16·5%). 5-*Nitroheptyl cyanide*, b. p. 100°/0·1 mm. (Found: C, 56·4; H, 7·9; N, 16·8. $C_8H_{14}O_2N_2$ requires C, 56·5; H, 8·3; N, 16·5%). 4-(1-*Nitro*cyclo*hexyl*)*butyl cyanide*, m. p. 36° (from alcohol) (Found: C, 62·7; H, 8·2; N, 13·4. $C_{11}H_{18}O_2N_2$ requires C, 62·8; H, 8·5; N, 13·3%). 5-*Nitro*-1 : 9-*dicyano*-5-*methylnonane*, m. p. 27° (from alcohol) (Found: C, 60·5; H, 7·8; N, 17·4. $C_{12}H_{19}O_2N_3$ requires C, 60·7; H, 8·0; N, 17·6%). *Nitrotris*-4-*cyanobutylmethane*, m. p. 49° (from dioxan) (Found: C, 63·1; H, 8·0; N, 18·2. $C_{16}H_{24}O_2N_4$ requires C, 63·2; H, 7·9; N, 18·4%).

(b) *With Raney nickel.* The adducts in methyl alcohol were reduced over Raney nickel at ordinary temperature and pressure and the products isolated by fractional distillation. 5-Nitro-5-methylhex-2-enyl cyanide gave: (i) 5-*Amino*-5-*methylhexyl cyanide* (XV), b. p. 53—55°/0·06 mm. (Found: C, 68·8; H, 11·6; N, 19·7; equiv., 139·1. $C_8H_{16}N_2$ requires C, 68·6; H, 11·4; N, 20·0%; equiv., 140); *picrate*,

m. p. 130—131° (from water) (Found: C, 45·4; H, 5·35. $C_8H_{16}N_2,C_6H_3O_7N_3$ requires C, 45·5; H, 5·2%); *benzoyl* derivative, m. p. 94—95° (from *cyclo*hexane) (Found: N, 11·2. $C_{15}H_{20}ON_2$ requires N, 11·5%); 2 : 4-*dinitrophenylurea* (cf. McVeigh and Rose, *J.*, 1945, 621), m. p. 163—164° (from alcohol) (Found: C, 52·0; H, 5·1; N, 19·8. $C_{15}H_{19}O_5N_5$ requires C, 51·6; H, 5·4; N, 20·0%). (ii) 1 : 6-Diamino-6-methylheptane (XIV), b. p. 36—37°/0·12 mm.; *dihydrochloride*, m. p. 195—196° (from alcohol–acetone) (Found: Cl, 32·5. $C_8H_{20}N_2$,2HCl requires Cl, 32·7%); *dibenzoyl* derivative, m. p. 162—163° (from alcohol) (Found: C, 75·2; H, 8·0; N, 8·5. $C_{22}H_{28}O_2N_2$ requires C, 75·0; H, 8·0; N, 8·0%); *dipicrate*, m. p. 212° (decomp.) (from alcohol) (Found: C, 40·05; H, 4·45. $C_8H_{20}N_2,2C_6H_3O_7N_3$ requires C, 39·9; H, 4·3%). 5-Nitrohept-2-enyl cyanide gave 1 : 6-diamino-octane, b. p. 100°/0·08 mm.; *dipicrate*, m. p. 158—160° (from water) (Found: C, 40·15; H, 4·65; N, 18·75. $C_8H_{20}N_2,2C_6H_3O_7N_3$ requires C, 39·9; H, 4·3; N, 18·6%). 4-(1-Nitro*cyclo*hexyl)but-2-enyl cyanide (both forms) gave 5-(1-amino*cyclo*hexyl)amylamine, b. p. 147°/15 mm.; *mono*-2 : 4-*dinitrophenylurea* derivative (cf. McVeigh and Rose, *loc. cit.*), m. p. 138—140° (from xylene) (Found: C, 54·9; H, 7·0; N, 17·9. $C_{18}H_{27}O_5N_5$ requires C, 54·9; H, 6·8; N, 17·8%). 5-Nitro-1 : 9-dicyano-5-methylnona-2 : 7-diene gave 1 : 6 : 11-triamino-undecane, b. p. 131°/0·1 mm.; *tripicrate*, m. p. 125° (from water) (Found: C, 39·9; H, 4·2; N, 18·5. $C_{12}H_{29}N_3,3C_6H_3O_7N_3$ requires C, 39·9; H, 4·2; N, 18·6%).

(c) *With iron.* Iron dust (30—60 mesh; 25 g.) in water (50 c.c.) was treated with 35% hydrochloric acid (10 c.c.) and stirred at 90° until no longer acid to Congo-red. 5-Nitro-5-methylhex-2-enyl cyanide (VIII) (20 g.) was added during ½ hour and the temperature maintained at 95° for a total of 4½ hours. The product was cooled, filtered, and evaporated to dryness at 60°/16 mm. Addition of acetone to the gum gave a crystalline solid which, after recrystallisation from acetone, gave a hydrochloride, m. p. 163—164°, from which the *picrate*, m. p. 121—123° (decomp.) (from water), was formed (Found: C, 45·95; H, 4·75. $C_8H_{14}N_2,C_6H_3O_7N_3$ requires C, 45·8; H, 4·6%); *benzoyl* derivative, m. p. 59—60° (from water) (Found: C, 74·35; H, 7·4. $C_{15}H_{18}ON_2$ requires C, 74·4; H, 7·4%). This base is probably 2-cyano-6 : 6-dimethylpiperidine.

The original acetone filtrate was evaporated to dryness, dissolved in excess of aqueous sodium hydroxide, and repeatedly extracted with ether. The ethereal solution was dried and distilled to give 5-amino-5-methylhex-2-enyl cyanide (1·4 g.; 9%), b. p. 49—51°/0·15 mm.; *picrate*, m. p. 175—176° (from water) (Found: C, 45·65; H, 4·4; N, 19·1. $C_8H_{14}N_2,C_6H_3O_7N_3$ requires C, 45·8; H, 4·6; N, 19·1%).

The aqueous layer after ether extraction was acidified with hydrochloric acid, evaporated to dryness, extracted with concentrated hydrochloric acid, and the sodium chloride separated. The filtrate was again evaporated to dryness, treated with excess of silver oxide in water, filtered, and the solution of silver salt saturated with hydrogen sulphide and filtered. The filtrate was evaporated to dryness, giving 5-amino-5-methylhexene-1-carboxylic acid (2·6 g.), partly purified by dissolving in water and precipitating with acetone: the decomposition point varied between 210° and 230° according to the rate of heating. Good analytical figures for the acid were not obtained, but hydrogenation in water over Adams's platinum gave 5-amino-5-methylhexane-1-carboxylic acid (XI), m. p. and mixed m. p. with authentic specimen 256—258° (decomp.).

Reactions with 5-*Nitro*-5-*methylhex*-2-*enyl Cyanide*.—(a) *Ozonisation.* The nitro-cyanide (10 g.) in alcohol (30 c.c.) was treated with excess of ozonised oxygen and run slowly into a mixture of 10% hydrogen peroxide (36 c.c.) containing sulphuric acid (0·56 c.c.). The mixture was heated to 86° during 1 hour and refluxed at that temperature for 2 hours. After cooling, water (50 c.c.) was added and the mixture thoroughly extracted with ether. The ethereal extract was washed with aqueous sodium carbonate, and the alkaline extract acidified and evaporated to dryness. The solid residue was extracted with ether; on removal of the ether a solid (1·9 g.) was obtained which was recrystallised from water (with considerable loss) and from *cyclo*hexane to give 2-nitro*iso*valeric acid (XX), m. p. 104—105° (Found: C, 40·65; H, 6·15; N, 9·3; equiv., 146·0. Calc. for $C_5H_9O_4N$: C, 40·8; H, 6·1; N, 9·5%; equiv., 147·0).

(b) *Action of morpholine.* The nitro-cyanide (10 g.) in morpholine (20 c.c.) was kept for 7 days, then warmed to 40° for 3 hours, cooled, poured into water, and acidified with hydrochloric acid to Congo-red. By ether-extraction, a neutral product, 5-*nitro*-5-*methylhex*-1-*enyl cyanide* (XVIII), b. p. 102—108°/0·1 mm., $n_D^{18^\circ}$ 1·4716, was obtained (Found: C, 57·5; H, 6·9; N, 17·1. $C_8H_{12}O_2N_2$ requires C, 57·2; H, 7·1; N, 16·7%). This did not solidify on being seeded with the starting material. The aqueous layer was basified, and a base, 5-*nitro*-2-*morpholino*-5-*methylhexyl cyanide* (XIX), isolated by ether extraction; b. p. 148—151°/0·08 mm., m. p. 36—37° (from *cyclo*hexane) (Found: C, 56·3; H, 8·1; N, 16·1. $C_{12}H_{21}O_3N_3$ requires C, 56·5; H, 8·2; N, 16·5%).

(c) *Action of piperidine.* A similar experiment using piperidine (20 c.c.) in place of morpholine gave 5-nitro-5-methylhex-1-enyl cyanide (XVIII), b. p. 96—98°/0·05 mm., $n_D^{20^\circ}$ 1·4702 (Found: C, 57·1; H, 7·2%), and 5-*nitro*-2-*piperidino*-5-*methylhexyl cyanide* (XIX), b. p. 134—136°/0·25 mm. (Found: C, 61·95; H, 8·9; N, 16·7. $C_{13}H_{23}O_2N_3$ requires C, 61·7; H, 9·1; N, 16·6%).

Miscellaneous Reactions.—(a) *Hydrolysis and hydrogenation of* 5-*nitro*-5-*methylhexyl cyanide* (IX). The cyanide (84 g.) was refluxed in alcohol (280 c.c.) with 32% aqueous sodium hydroxide (60 c.c.) for 10 hours, excess of alkali removed with 35% hydrochloric acid (15 c.c.), and the solution, after clarification with carbon, evaporated to dryness. The solid was dissolved in water (200 c.c.), clarified with carbon, and the acid precipitated with hydrochloric acid; m. p. 45—48° (91 g.). The 5-*nitro*-5-*methylhexane*-1-*carboxylic acid* (X) was purified by distillation, b. p. 116°/0·08 mm., m. p. 47—48° (Found: N, 7·45; equiv., 191. $C_8H_{15}O_4N$ requires N, 7·4%; equiv., 189); *benzylthiuronium* salt, m. p. 168—169° (from alcohol) (Found: C, 53·6; H, 7·15. $C_8H_{15}O_4N,C_8H_{10}N_2S$ requires, C, 54·1; H, 7·0%).

This nitro-acid (X) (57·5 g.) in N-sodium hydroxide (308 c.c.) was hydrogenated over Raney nickel. The product was filtered, strongly acidified with hydrochloric acid, evaporated to dryness, and the amino-acid hydrochloride extracted from sodium chloride with 35% hydrochloric acid (100 c.c.). [A sample of the *hydrochloride* was crystallised from alcohol–ether; m. p. 172—174° (decomp.) (Found: N, 6·95; Cl, 17·9. $C_8H_{17}O_2N$,HCl requires N, 7·2; Cl, 18·2%).] The hydrochloride in water was heated at 70° with excess of silver oxide, and the hot solution filtered and saturated with hydrogen sulphide. The silver sulphide was separated and the aqueous solution evaporated to dryness. The residue was dissolved in water and treated with acetone to precipitate 5-*amino*-5-*methylhexane*-1-*carboxylic acid* (XI), m. p. 259—261° (decomp.) (34 g.) (Found: C, 60·4; H, 10·8; N, 9·2. $C_8H_{17}O_2N$ requires C, 60·4; H, 10·7; N, 8·8%). The *ethyl* ester (XIII), prepared by heating the acid with hydrogen chloride in alcohol, had b. p. 120°/19 mm. (Found: C, 64·0; H, 11·2. $C_{10}H_{21}O_2N$ requires C, 64·2; H, 11·2%). The acid (XI) was heated at 280° for $\frac{1}{2}$ hour and the residue distilled to give the *lactam* (XII), b. p. 135°/13 mm., m. p. 102—103° (from ligroin) (Found: C, 67·7; H, 10·5; N, 9·85. $C_8H_{15}ON$ requires C, 68·1; H, 10·6; N, 9·9%).

(b) *Hydrolysis of* 5-*amino*-5-*methylhexyl cyanide* (XV). The cyanide (7·1 g.) was refluxed in alcohol (35 c.c.) with 32% aqueous sodium hydroxide (7·1 c.c.) for 16 hours. The mixture was acidified with hydrochloric acid, evaporated to dryness, and the 5-amino-5-methylhexane-1-carboxylic acid (XI) isolated as in (a); m. p. 256—259° (decomp.), mixed m. p. with acid prepared as in (a), 257—259° (decomp.).

(c) *Hydrolysis of* 5-*nitro*-1 : 9-*dicyano*-5-*methylnonane*. The dicyano-compound (100 g.) was refluxed for 20 hours in alcohol (400 c.c.) with 32% aqueous sodium hydroxide (120 c.c.). Excess of alkali was neutralised with hydrochloric acid. the solution clarified with carbon and filtered, and the acid precipitated by addition of excess of hydrochloric acid and crystallised from water to give 5-*nitro*-5-*methylnonane*-1 : 9-*dicarboxylic acid*, m. p. 75—76° (Found: C, 52·55; H, 7·65; N, 5·5. $C_{12}H_{21}O_6N$ requires C, 52·4; H, 7·6; N, 5·1%), *bisbenzylthiuronium* salt, m. p. 151—152° (from methyl alcohol–acetone) (Found: N, 11·6. $C_{12}H_{21}O_6N,2C_8H_{10}N_2S$ requires N, 11·5%).

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