62. *A New Synthesis of Long-chain Acetylenic Acids and Some Attempts to Prepare Pure* cis-*Olefinic Acids.*

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The *NN*-dimethylamide of a long-chain acetylenic acid is prepared by condensation of an ω-acetylenic dimethylamide and alkyl halide (or ω-bromo-dimethylamide and alkylacetylene) in presence of sodamide in liquid ammonia.

Conversion of dihydroxy-acids into dibromo-esters, followed by debromination, gives *cis*-olefinic acids containing *ca.* 2% of the *trans*-isomers. Attempts to avoid the formation of the latter failed.

Although many syntheses of long-chain acetylenic acids have been described,[1] the accessible ω-bromo- and ω-acetylenic acids have rarely been used as starting materials. Bhattacharya, Saletore, and Simonsen [2] condensed sodiodec-1-yne with ethyl 12-bromododecanoate in xylene at 160° and after hydrolysis obtained docos-13-ynoic acid in unspecified yield. A very similar procedure was employed recently by Bhattacharyya, Chakravarty, and Kumar [3] to condense ethyl undec-10-ynoate with alkyl halides (yields about 15% after hydrogenation and hydrolysis). Alkylation of methyl undec-10-ynoate by treatment of the silver derivative with methyl and ethyl iodide was achieved by Isabelle and Leitch,[4] but we have been unable to alkylate the silver derivative of ethyl undec-10-ynoate with octyl bromide.

$$\underset{\text{(I)}}{\mathrm{H{\cdot}C{\equiv}C{\cdot}[CH_2]_8{\cdot}CO{\cdot}NMe_2}} \qquad \underset{\text{(II)}}{\mathrm{C_8H_{17}{\cdot}C{\equiv}C{\cdot}[CH_2]_8{\cdot}COR}} \qquad \underset{\text{(III)}}{\mathrm{C_8H_{17}{\cdot}CH\overset{\mathit{cis}}{=}CH{\cdot}[CH_2]_8{\cdot}CO{\cdot}NMe_2}}$$

$\mathrm{C_8H_{17}{\cdot}CH(OH){\cdot}CH(OH){\cdot}[CH_2]_8{\cdot}COR}$ (IVa) *threo*; (IVb) *erythro*

$\mathrm{C_8H_{17}{\cdot}CHBr{\cdot}CHBr{\cdot}[CH_2]_8{\cdot}CO_2Et}$ (Va) *erythro*; (Vb) *threo*

$\mathrm{C_8H_{17}{\cdot}CH{=}CH{\cdot}[CH_2]_8{\cdot}COR}$ (VIa) *trans*; (VIb) *cis*

In the present work, advantage was taken of the resistance shown by the *NN*-dimethylamide group to many organometallic reagents. Thus *NN*-dimethylundec-10-ynamide (I), on treatment with sodamide in liquid ammonia, gave the sodio-derivative from which the amide could be recovered in good yield. Octyl bromide reacted with this sodio-derivative, to give *NN*-dimethylnonadec-10-ynamide (II; $R = NMe_2$) in 62% yield. Alkaline hydrolysis afforded nonadec-10-ynoic acid (II; $R = OH$).

Selective hydrogenation of the acetylenic amide by Cram and Allinger's procedure [5] gave *cis*-*NN*-dimethylnonadec-10-enamide (III) containing ~2% of the *trans*-isomer (estimate based on the intensity of *trans*-HC=CH band at 966 cm.$^{-1}$). Epoxidation with perbenzoic acid, cleavage of the oxide ring with formic acid, and mild alkaline hydrolysis afforded *threo*-10,11-dihydroxy-*NN*-dimethylnonadecanamide (IVa; $R = NMe_2$). More vigorous alkaline hydrolysis gave the acid (IVa; $R = OH$) which was converted into the dibromo-ester (Va) and thence into *trans*-nonadec-10-enoic acid (VIa). As an alternative route to the *trans*-acid, reduction of amide (II; $R = NMe_2$) with sodium in liquid ammonia was examined (cf. the preparation of the octadecenes by Elsner and Paul [6]). The only product isolated was *trans*-nonadec-10-enamide (VIa; $R = NH_2$); that is, ammonolysis occurred during the reduction though not during the original synthesis of dimethylamide (II).

In an attempt to obtain *cis*-nonadec-10-enoic acid free from the *trans*-isomer, its

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[1] *Inter al.*, Bumpus, Taylor, and Strong, *J. Amer. Chem. Soc.*, 1950, **72**, 4263; Huber, *ibid.*, 1951, **73**, 2730.

[2] R. Bhattacharya, Saletore, and Simonsen, *J.*, 1928, 2678.

[3] S. C. Bhattacharyya, Chakravarty, and Kumar, *Chem. and Ind.*, 1959, 1352.

[4] Isabelle and Leitch, *Canad. J. Chem.*, 1958, **36**, 440.

[5] Cram and Allinger, *J. Amer. Chem. Soc.*, 1956, **78**, 2522.

[6] Elsner and Paul, *J.*, 1953, 3156.

purification through the crystalline *erythro*-10,11-dihydroxynonadecanoic acid (IVb; R = OH) was examined.[7] *cis*-Hydroxylation of the semihydrogenation product (III) with iodine and silver acetate in moist acetic acid,[8] followed by mild hydrolysis, gave the amide (VIb; R = NMe_2), and vigorous hydrolysis then furnished the *erythro*-dihydroxy-acid (VIb; R = OH). This was converted by standard procedures [7] through dibromo-ester (Vb) into ethyl *cis*-nonadec-10-enoate which again contained ~2% of *trans*-isomer, even when the intermediate dihydroxy-acid was most carefully purified. Re-examination of samples of ethyl oleate and *cis*-heptadec-9-enoate prepared previously by this procedure [7] and believed to be pure showed that these also contained ~2% of the *trans*-isomers. The absorption band at *ca.* 966 cm.$^{-1}$ provides a sensitive method for detecting *trans*-isomer in *cis*-esters and -dimethylamides, whereas in the acids this band is partially masked by a broad carboxyl band.

The presence of some *trans*-isomer in these products indicates that conversion of diol into dibromide or debromination (or both steps) is not completely stereospecific. To determine at which step the isomeric product was formed, the use of a crystalline dibromide was considered. Since the 9,10-dibromo-octadecanoic acids are very low-melting, the tetrabromide obtained by addition of bromine to linoleic acid was used. Esterification, followed by debromination with zinc, gave ethyl linoleate containing about 5% of *trans*-isomers (McCutcheon's debromination procedure [9] gave similar results). The presence of *trans*-isomers in methyl linoleate obtained from the tetrabromo-acid has been reported by Hosking.[10] Thus the debromination step is not completely stereospecific (present evidence does not show whether the conversion of diol into dibromide is completely stereospecific).

$MeO{\cdot}[CH_2]_5{\cdot}COMe$ (VII) $MeO{\cdot}[CH_2]_5{\cdot}CMe{=}C(CN){\cdot}CO_2Et$ (VIII) $MeO{\cdot}[CH_2]_5{\cdot}CMe_2{\cdot}CH_2{\cdot}CN$ (IX)

$Br{\cdot}[CH_2]_5{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2H$ (X) $C_8H_{17}{\cdot}C{\equiv}C{\cdot}[CH_2]_5{\cdot}CMe_2{\cdot}CH_2{\cdot}CO{\cdot}NMe_2$ (XI)

$C_8H_{17}{\cdot}CH\overset{cis}{=}CH{\cdot}[CH_2]_5{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2H$ (XII)

Dr. J. W. Cornforth, who recently developed a stereospecific synthesis of olefins,[11] kindly discussed this problem and suggested that debromination in the presence of base might prevent the formation of *trans*-isomer, if this side-reaction were due to zinc ions' acting as Lewis acids. Debromination of ethyl di- and tetra-bromo-octadecanoate was therefore carried out in the presence of sodium acetate, pyridine, and ethylenediamine-tetra-acetic acid severally, but in each case the *trans*-isomer was formed in about the same proportion as in the previous experiments.

A pure sample of *cis*-nonadec-10-enoic acid was ultimately obtained from the semi-hydrogenation product by treatment with urea.[12]

cis-3,3-Dimethyloctadec-9-enoic acid (XII) was also synthesised by a route similar to that described above, but in this case an ω-bromo-dimethylamide was condensed with the sodio-derivative of an alkylacetylene. 7-Methoxyheptan-2-one (VII), from 4-methoxy-butyl bromide and ethyl acetoacetate, was condensed with ethyl cyanoacetate.[13] Addition of methylmagnesium iodide to the unsaturated cyano-ester (VIII), followed by hydrolysis and decarboxylation, gave methoxy-nitrile (IX), and thence 8-methoxy-3,3-dimethyl-octanoic acid. Treatment with hydrobromic and sulphuric acid gave the 8-bromo-acid (X); the dimethylamide of this was condensed with sodiodec-1-yne, and the resulting amide

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[7] Ames and Bowman, *J.*, 1951, 1079; Bounds, Linstead, and Weedon, *J.*, 1953, 2393.
[8] Gunstone and Morris, *J.*, 1957, 487.
[9] McCutcheon, *Org. Synth.*, Coll. Vol. III, p. 526.
[10] Hosking, quoted by Ackman, Dytham, Wakefield, and Weedon, *Tetrahedron*, 1960, **8**, 244.
[11] Cornforth, Cornforth, and Mathew, *J.*, 1959, 112.
[12] Cf. Crombie and Griffin, *J.*, 1958, 4443.
[13] Cope, Hofmann, Wyckoff, and Hardenbergh, *J. Amer. Chem. Soc.*, 1941, **63**, 3452.

(XI) was semihydrogenated and hydrolysed to *cis*-3,3-dimethyloctadec-9-enoic acid (containing small amounts of *trans*- and saturated acids).

EXPERIMENTAL

NN-*Dimethylundec*-10-*ynamide*.—Undec-10-ynoic acid [14] (170 g.) was warmed with thionyl chloride (230 c.c.) for 3 hr. at 70°. After the excess of thionyl chloride had been removed under reduced pressure, ether (1 l.) was added and dimethylamine was passed into the solution until the latter was alkaline. Water (1 l.) was added and the separated organic layer was washed with sodium carbonate solution and water, dried (Na_2SO_4), and distilled. The *amide* (177 g.), b. p. 125—130°/1 mm., formed prisms, m. p. 30—31°, from light petroleum (b. p. 40—60°) (Found: C, 74·9; H, 11·4; N, 6·6. $C_{13}H_{23}NO$ requires C, 74·6; H, 11·1; N, 6·7%).

NN-*Dimethylnonadec*-10-*ynamide*.—Sodamide (27 g.; commercial, crystalline material, supplied by Messrs. May and Baker, gave about the same yield as sodamide prepared *in situ*) was stirred with liquid ammonia (1 l.) for 5 min. and the acetylenic amide (140 g.) in ether (150 c.c.) was added gradually. After the mixture had been stirred for 1 hr., octyl bromide (180 g.) in ether (150 c.c.) was added slowly; the mixture was stirred under reflux for 5 hr. and then allowed to evaporate. Dilute hydrochloric acid (1 l.) was added and the product isolated with ether. Fractional distillation gave the *amide* (133 g.), b. p. 172—175°/0·1 mm., n_D^{20} 1·4725 (Found: C, 78·5; H, 12·5; N, 4·4. $C_{21}H_{39}NO$ requires C, 78·4; H, 12·2; N, 4·4%), $\nu_{max.}$ 1644 cm.$^{-1}$ (CO·NMe_2).

Nonadec-10-*ynoic Acid*.—The dimethylamide (10 g.) was refluxed in ethanol (150 c.c.) and 5N-sodium hydroxide (150 c.c.) for 8 hr. Water (150 c.c.) was added and the ethanol removed by distillation; the solution was poured into ice and dilute sulphuric acid and extracted with ether. Distillation gave the *acid*, b. p. 174—176°/0·2 mm., plates (from methanol), m. p. 43—44° (Found: C, 78·0; H, 11·3. $C_{19}H_{34}O_2$ requires C, 77·5; H, 11·6%).

Semihydrogenation of NN-*Dimethylnonadec*-10-*ynamide*.—The acetylene (31·5 g.) in methanol (200 c.c.) was hydrogenated in presence of 5% palladised barium sulphate (0·5 g.) and quinoline [5] (0·5 g.). When 1·05 mol. had been taken up, the rate of absorption fell rapidly and hydrogenation was interrupted. Distillation of the filtered solution afforded cis-NN-*dimethylnonadec*-10-*enamide* (29 g.), b. p. 164—167°/0·1 mm., n_D^{20} 1·4682 (Found: C, 78·2; H, 13·2; N, 4·2. $C_{21}H_{41}ON$ requires C, 78·0; H, 12·8; N, 4·3%), $\nu_{max.}$ 966 cm.$^{-1}$ (vw, corresponding to *ca.* 2% of *trans*-isomer).

threo-10,11-*Dihydroxy*-NN-*dimethylnonadecanamide*.—The olefin (14·1 g.) in chloroform (50 c.c.) was added gradually to 0·56M-perbenzoic acid (100 c.c.) in chloroform at 0°. After 1 hr., 96% of the peracid had reacted and the solution was washed with sodium carbonate solution and water and evaporated *in vacuo*. 98% Formic acid (50 c.c.) was added to the residue which was left overnight and then re-evaporated. The residue was refluxed with ethanol (100 c.c.) and 2N-sodium hydroxide (50 c.c.) for 1 hr.; acidification, followed by isolation with ethyl acetate, furnished the dihydroxy-amide (10·0 g.), prisms, m. p. 65—66° (from ethyl acetate) (Found: C, 70·2; H, 12·5; N, 3·9. $C_{21}H_{43}NO_3$ requires C, 70·5; H, 12·1; N, 3·9%).

threo-10,11-*Dihydroxynonadecanoic Acid*.—The amide (4·8 g.) in 2-methoxyethanol (50 c.c.) with potassium hydroxide (5 g.) in water (5 c.c.) was heated at 170° for 6 hr. under nitrogen. After the hot solution had been poured into ice and 2N-hydrochloric acid, the precipitated *acid* was recrystallised from ethyl acetate, forming plates, m. p. 93·5—94·5° (4·3 g.) (Found: C, 68·8; H, 11·6. $C_{19}H_{38}O_4$ requires C, 69·0; H, 11·6%).

Ethyl trans-*Nonadec*-10-*enoate*.—Treatment of the dihydroxy-acid (11·6 g.) with hydrogen bromide in acetic and sulphuric acid, esterification, and debromination of the dibromo-ester (which was not distilled) were carried out by general procedures.[7] The unsaturated *ester* (7·7 g.) had b. p. 144—146°/0·1 mm., n_D^{20} 1·4526 (Found: C, 77·7; H, 12·5%; I val., 77·3, 78·0. $C_{21}H_{40}O_2$ requires C, 77·7; H, 12·4%; I val., 78·2).

trans-*Nonadec*-10-*enoic Acid*.—A solution of the ester (7·3 g.) in ethanol (70 c.c.) was refluxed with potassium hydroxide (5 g.) in water (20 c.c.) under nitrogen for 1·5 hr. After addition of water (80 c.c.), ethanol was removed by distillation; acidification and isolation with ether yielded the *acid* (6·6 g.), plates, m. p. 49—50° [from light petroleum (b. p. 40—60°)] (Found: C, 77·5; H, 12·5%; I val., 85·1, 84·7. $C_{19}H_{36}O_2$ requires C, 77·0; H, 12·2%; I val., 85·6).

trans-*Nonadec*-10-*enamide*.—*NN*-Dimethylundec-10-ynamide (10 g.) in ether (100 c.c.) was

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[14] Kraft and Popova, *Zhur. obshchei Khim.*, 1957, **27**, 906.

added during 5 min. to a stirred solution of sodium (4·4 g.) in liquid ammonia (400 c.c.). The solution was stirred under reflux for 4 hr., then allowed to evaporate. Ether–methanol and then dilute acetic acid were added cautiously, and the mixture was extracted with ether. The extracts were washed with dilute sulphuric acid, sodium carbonate solution, and water, dried (Na_2SO_4), and evaporated. Recrystallisation from methanol gave the *amide* (3·8 g.), prisms, m. p. 79—81° (Found: C, 77·5; H, 12·4; N, 5·1. $C_{19}H_{37}NO$ requires C, 77·2; H, 12·6; N, 4·7%).

Hydrolysis of the amide (0·5 g.) by refluxing with 2-methoxyethanol (25 c.c.) and potassium hydroxide (5 g.) in water (5 c.c.) for 2 hr. and pouring the product into ice and dilute acid, gave *trans*-nonadec-10-enoic acid, m. p. 48—49°, identical with the sample prepared above.

erythro-10,11-*Dihydroxy*-NN-*dimethylnonadecanamide.*—*cis*-NN-Dimethylnonadec-10-enamide (5·0 g.; semihydrogenation product) was shaken for 30 min. with iodine (4·1 g.), silver acetate (5·8 g.), and acetic acid (150 c.c.). After addition of water (0·3 g.), the mixture was refluxed for 1 hr., cooled, and filtered, the solid being washed with acetic acid. The combined filtrates were evaporated under reduced pressure and the residue was taken up in ether, washed with 2N-sodium hydroxide and water, dried (Na_2SO_4), and evaporated. The residual gum was refluxed for 2 hr. with 5N-sodium hydroxide (25 c.c.) and ethanol (50 c.c.), and the solution was then poured into ice and sulphuric acid. Isolation with chloroform, followed by recrystallisation from ethyl acetate, gave the *dihydroxy-amide* (2·0 g.), prisms, m. p. 95—97° (Found: C, 70·6; H, 12·2; N, 3·7%).

erythro-10,11-*Dihydroxynonadecanoic Acid.*—The acetylenic amide (17·7 g.) was semihydrogenated and hydroxylated as in the preceding experiment. The crude product was refluxed for 10 hr. with ethanol (50 c.c.) and 5N-sodium hydroxide (50 c.c.); the precipitate formed on acidification was recrystallised from ethyl acetate and methanol to give the *dihydroxy-acid* (8·6 g.), prisms, m. p. 118·5—119·5° (Found: C, 68·8; H, 11·7%).

cis-*Nonadec*-10-*enoic Acid.*—The *erythro*-dihydroxy-acid (7·8 g.) was converted into the dibromo-ester (which was not distilled) and thence into *ethyl* cis-*nonadec*-10-*enoate* by the general procedures.[7] The ester (6·1 g.) had b. p. 156—158°/0·4 mm., n_D^{20} 1·4518 (Found: C, 77·4; H, 12·2%; I val., 78·3). It contained about 2% of *trans*-isomer (band at 969 cm.$^{-1}$).

A solution of the ester (5·7 g.) in ethanol (60 c.c.) and potassium hydroxide (5 g.) in water (5 c.c.) was refluxed under nitrogen for 1·5 hr. After addition of water (120 c.c.), ethanol was removed by distillation and the product was isolated from the acidified solution with ether. Distillation in nitrogen gave the *acid* (5·4 g.), b. p. 184—186°/0·5 mm., n_D^{20} 1·4609, f. p. (thermometer in liquid) 20·5—21·5° (Found: C, 77·1; H, 12·6%; I val., 86·1).

Purification of cis-*Nonadec*-10-*enoic Acid with Urea.*—The acetylenic acid (6·5 g.) in methanol (75 c.c.) was hydrogenated in presence of 5% palladised barium sulphate (0·2 g.) and quinoline (0·2 g.). Absorption became very slow when 1·06 mol. of hydrogen had been taken up; hydrogenation was interrupted and the filtered solution was diluted to 500 c.c. with ethanol. Urea (60 g.) was dissolved in the hot solution and the mixture allowed to crystallise by cooling. After filtration, more urea (20 g.) was added, and the solution allowed to crystallise again. The filtrate was poured into 0·3N-sulphuric acid (1·2 l.) and extracted with ether–light petroleum (b. p. 40—60°) (1 : 1; 3 × 300 c.c.). The washed, dried (Na_2SO_4) extracts were distilled, to give the acid (1·4 g.), m. p. 22—23° (sealed capillary), b. p. 170—175°/0·2 mm. (Found: I val., 84·6). This sample had no shoulder corresponding to *trans*-HC=CH absorption, whereas the previous sample had a slight shoulder at *ca.* 970 cm.$^{-1}$.

Debromination Experiments (with P. J. ISLIP).—These were carried out essentially as described by Ames and Bowman.[7] In a typical experiment, zinc (7·5 g.) was activated by heating it with ethanol to the b. p., adding 0·1 c.c. of 48% hydrobromic acid, and refluxing under nitrogen for 5 min. Anhydrous sodium acetate (4·7 g., 6 mol.) and then ethyl *threo*-9,10-dibromo-octadecanoate (4·5 g., 1 mol.) in ethanol (10 c.c.) were added, and the mixture was refluxed for 1 hr. The zinc was collected and washed with light petroleum (b. p. 40—60°); after the combined filtrates had been poured into dilute sulphuric acid, the organic layer was washed with sodium hydrogen carbonate solution and water, dried (Na_2SO_4), and distilled in nitrogen. The ethyl oleate (1·4 g.) obtained contained about 2% of *trans*-isomer.

Similar experiments with ethylenediaminetetra-acetic acid and pyridine (even 1 : 1 pyridine–ethanol as solvent) did not affect the proportion of *trans*-isomer significantly. Debromination of ethyl 9,10,12,13-tetrabromoctadecanoate gave ethyl linoleate containing about 5% of *trans*-isomers (band at 967 cm.$^{-1}$).

7-*Methoxyheptan*-2-*one*.—4-Methoxybutyl bromide [15] (450 g.) was added during 20 min. to ethyl sodioacetoacetate solution (from sodium 78 g., ethyl acetoacetate 480 g., and ethanol 1250 c.c.). The solution was stirred under reflux (bath 110°) for 6 hr. and ethanol (1 l.) was removed by distillation. 1·3N-Sodium hydroxide (3 l.) was added to the residue, and the mixture stirred at room temperature for 18 hr. After addition of 20N-sulphuric acid (300 c.c.) during 2·5 hr., the mixture was heated slowly to the b. p. and then refluxed for 1 hr. The product was isolated with ether and fractionally distilled through a short Fenske column; the slightly impure ketone (260 g.) had b. p. 95—100°/20 mm. (Found: C, 67·5; H, 11·3. Calc. for $C_8H_{16}O_2$: C, 66·6; H, 11·2%).

Ethyl 2-*Cyano*-8-*methoxy*-3-*methyloct*-2-*enoate*.—A mixture of methoxy-ketone (260 g.), ethyl cyanoacetate (210 g.), benzene (170 c.c.), acetic acid (21 g.), and ammonium acetate (13 g.) was refluxed through a phase-separator until no more water was collected.[13] The cooled solution was washed with sodium carbonate solution and water, dried (Na_2SO_4), and evaporated. Fractional distillation gave the cyano-ester (362 g.), b. p. 140—145°/2 mm., n_D^{20} 1·4706 (Found: C, 65·5; H, 8·9; N, 6·1. $C_{13}H_{21}NO_3$ requires C, 65·2; H, 8·9; N, 5·9%). A fore-run, b. p. 70—140°/2 mm., was re-treated with ethyl cyanoacetate to afford more product (31 g.).

Ethyl 2-*Cyano*-8-*methoxy*-3,3-*dimethyloctanoate*.—The Grignard reagent (from magnesium 53 g., and methyl iodide 320 g., in ether 1 l.) was stirred and cooled in ice-water while the cyano-ester (362 g.) in ether (750 c.c.) was added.[16] Next day, ammonium chloride solution and acetic acid were added and the crude product was isolated with ether. The residue was left for 2 days with sodium cyanide (75 g.) in water (250 c.c.) and ethanol (750 c.c.). After addition of water (2 l.), the mixture was extracted thrice with ethyl acetate; the combined extracts were washed with sodium carbonate solution and water, evaporated, and distilled. The *cyano-ester* (273 g.) had b. p. 125—130°/0·8 mm., n_D^{20} 1·4488 (Found: C, 66·4; H, 9·9; N, 5·5. $C_{14}H_{25}NO_3$ requires C, 65·9; H, 9·9; N, 5·5%).

8-*Methoxy*-3,3-*dimethyloctanonitrile*.—Potassium hydroxide (120 g.) in water (120 c.c.) was added to the cyano-ester (273 g.) in ethanol (1 l.), and the solution was refluxed for 1 hr. After addition of water (500 c.c.), the solution was concentrated to 1 l. under reduced pressure. Acidification and isolation with ethyl acetate gave crude cyano-acid which was heated (bath 210—240°) with glass powder (1 g.) until decarboxylation ceased (1·5 hr.). Distillation gave the *nitrile* (180 g.), b. p. 75—80°/0·15 mm., n_D^{20} 1·4398 (Found: C, 72·5; H, 11·4; N, 7·1. $C_{11}H_{21}NO$ requires C, 72·1; H, 11·6; N, 7·6%).

8-*Methoxy*-3,3-*dimethyloctanoic Acid*.—When the nitrile (180 g.) in ethylene glycol (1 l.) was refluxed (bath 190°) with potassium hydroxide (180 g.) in water (180 c.c.); evolution of ammonia was slow. Water was removed by distillation, and the residue refluxed (bath 230°) for 30 hr. and then poured into 2N-hydrochloric acid (3·6 l.). Isolated with ether, the *acid* (187 g.) had b. p. 114—116°/0·2 mm., n_D^{20} 1·4460 (Found: C, 65·6; H, 11·2. $C_{11}H_{22}O_3$ requires C, 65·3; H, 11·0%).

8-*Bromo*-3,3-*dimethyloctanoic Acid*.—Concentrated sulphuric acid (100 c.c.) was added gradually to a mixture of methoxy-acid (187 g.) and 48% hydrobromic acid (450 c.c.). The solution was refluxed for 7 hr. (bath 170°), more hydrobromic acid (100 c.c.) being added after 5 hr. After the mixture had been poured into water (2 l.) and extracted repeatedly with ethyl acetate, the combined extracts were washed with water and evaporated. Distillation furnished the *bromo-acid* (145 g.), b. p. 130—133°/0·4 mm., n_D^{20} 1·4790 (Found: C, 47·4; H, 7·6; Br, 32·4. $C_{10}H_{19}BrO_2$ requires C, 47·8; H, 7·6; Br, 31·8%).

A substantial residue from the distillation (presumably polymeric esters of the hydroxy-acid) was re-treated with hydrobromic acid (200 c.c.) and sulphuric acid (50 c.c.) and gave a further 42 g. of bromo-acid.

8-*Bromo*-3,3,N,N-*tetramethyloctanamide*.—The acid (20 g.) was refluxed with thionyl chloride (25 c.c.) for 2 hr. and excess of thionyl chloride was removed under reduced pressure. Ether (200 c.c.) was added and the solution was stirred and cooled (ice-water) while dimethylamine was passed in until the exothermic reaction ceased. Water (50 c.c.) was added and the separated aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with sodium carbonate solution (50 c.c.), dried (Na_2SO_4), and distilled. The *bromo-amide* (14 g.) had b. p. 110—114°/0·3 mm., n_D^{20} 1·4888 (Found: C, 52·3; H, 9·0; N, 4·7; Br, 28·0. $C_{12}H_{24}BrNO$ requires C, 51·8; H, 8·7; N, 5·0; Br, 28·7%).

[15] Schmidt, *Helv. Chim. Acta*, 1944, **27**, 127.

[16] Cf. Prout, *J. Amer. Chem. Soc.*, 1952, **74**, 5916; Parker and Raphael, *J.*, 1955, 1724.

3,3,N,N-*Tetramethyloctadec*-9-*ynamide*.—Dec-1-yne (28 g.) in tetrahydrofuran (50 c.c.; dried over lithium aluminium hydride) was added gradually to a suspension of sodamide (7·8 g.) in liquid ammonia (250 c.c.). After the mixture had been stirred under reflux for 1 hr., the bromo-amide (49 g.) in tetrahydrofuran (50 c.c.) was added, and the whole was refluxed for 4 hr. and then allowed to evaporate. Water (800 c.c.) was added and the product isolated with ethyl acetate. Fractional distillation gave crude acetylenic *amide*, b. p. 175—190°/0·5 mm., containing a small amount of crystalline solid, apparently dimethylamine hydrobromide. This was removed by washing with water and the oil was redistilled to afford an almost colourless oil (25·8 g.), b. p. 164—166°/0·1 mm., n_D^{20} 1·4739 (Found: C, 78·2; H, 12·3; N, 4·5. $C_{22}H_{41}NO$ requires C, 78·7; H, 12·3; N, 4·2%).

cis-3,3-*Dimethyloctadec*-9-*enoic Acid*.—A mixture of the foregoing acetylenic amide (10·2 g.), ethanol (80 c.c.), 5% palladised barium sulphate (0·2 g.), and quinoline (0·2 g.) was hydrogenated. The rate of absorption fell sharply at *ca.* 1·0 mol. and hydrogenation was interrupted when 1·05 mol. had been taken up. Distillation of the filtered solution gave cis-3,3,N,N-*tetramethyloctadec*-9-*enamide* (9·3 g.), b. p. 155—158°/0·1 mm., n_D^{20} 1·4702 (Found: C, 77·9; H, 12·8; N, 3·8. $C_{22}H_{43}ON$ requires C, 78·3; H, 12·8; N, 4·2%).

This amide (7·8 g.), potassium hydroxide (10 g.) in water (10 c.c.), and ethylene glycol (100 c.c.) were distilled until the water had been removed. The solution was refluxed under nitrogen (bath 220°) for 24 hr. and then poured into 2N-hydrochloric acid (650 c.c.). The *acid* (6·5 g.), isolated with ethyl acetate, had b. p. 166—170°/0·2 mm., n_D^{20} 1·4619 (Found: C, 77·5; H, 12·3%; I val., 77·8, 78·0. $C_{20}H_{38}O_2$ requires C, 77·4; H, 12·3%; I val., 81·2).

3,3-*Dimethyloctadecanoic Acid*.—The acetylenic amide (6·0 g.) in ethanol (50 c.c.) was hydrogenated with 5% palladised charcoal (1 g.) until absorption ceased. Evaporation of the filtered solution gave a gum which was hydrolysed as in the preceding experiment. The acid (5·2 g.), b. p. 173—176°/0·4 mm., m. p. 42—43°, recrystallised from light petroleum (b. p. 40—60°) and then had m. p. 43—44°. Cason, Sumrell, and Mitchell [17] report m. p. 44·0—44·8°.

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[17] Cason, Sumrell, and Mitchell, *J. Org. Chem.*, 1950, **15**, 850.