806. *Syntheses of Long-chain Acids. Part VII.*[1] *Preparation and Reduction of Some Alkadiynoic Acids*

By D. E. Ames, A. N. Covell, and T. G. Goodburn

12,20-Heneicosadiynoic acid is prepared by condensation of deca-1,9-diyne with 11-bromoundecanoic acid in the presence of lithamide, and the selective hydrogenation of this diynoic acid is examined. Similar reaction between diynes and ω-bromo-acids is used to obtain diynoic acids with two, three, four, five, or six methylene units between the two (non-terminal) acetylenic groups. Semihydrogenation of these acids gives the corresponding dienoic acids.

αω-Dihalogenoalkanes are condensed with ω-acetylenic alcohols to give diacetylenic diols in good yields. These are useful intermediates for the synthesis of saturated and unsaturated dicarboxylic acids.

The condensation of alkylacetylenes with ω-bromo-acids in liquid ammonia in the presence of lithamide has been shown to provide a direct synthesis of long-chain acetylenic acids[1,2] but the efficiency of the method falls as the chain length of the alkylacetylene is increased. The use of αω-diacetylenes in condensation with ω-bromo-acids has now been examined

---

[1] Part VI D. E. Ames, A. N. Covell, and T. G. Goodburn, *J.*, **1965**, 894.
[2] D. E. Ames and A. N. Covell, *J.*, **1963**, 775.

in the hope that the solubilities of the dilithio-derivatives might be more favourable for long-chain compounds.

Condensation of 8-bromo-octanoic acid with deca-1,9-diyne (5 mol.) in the presence of lithamide (10 mol.) in liquid ammonia gave octadeca-9,17-diynoic acid (I; $m = 6$, $n = 7$) in 66% yield. Similarly, condensation with 11-bromoundecanoic acid gave heneicosa-12,20-diynoic acid (I; $m = 6$, $n = 10$), also in 66% yield. Use of tetradeca-1,13-diyne with 11-bromoundecanoic acid, however, gave a rather lower yield (48%) of pentacosa-12,24-diynoic acid (I; $m = 10$, $n = 10$). These results show no advantage in comparison with the use of monoalkylacetylenes.[1] An attempt to prepare tetracosa-1,23-diyne by condensation of 1,20-dibromoeicosane with sodioacetylene was unsuccessful, and the use of longer diynes was therefore not investigated.

$$\mathrm{H{\cdot}C{\equiv}C{\cdot}[CH_2]_{\mathit{m}}{\cdot}C{\equiv}C{\cdot}[CH_2]_{\mathit{n}}{\cdot}CO_2H}\quad \text{(I)}$$

$$\underset{\text{(II)}}{\mathrm{R{\cdot}C{\equiv}C{\cdot}[CH_2]_{\mathit{n}}{\cdot}C{\equiv}C{\cdot}H}} \longrightarrow \underset{\text{(III)}}{\mathrm{R{\cdot}C{\equiv}C{\cdot}[CH_2]_{\mathit{n}}{\cdot}CH{=}CH_2}} \longrightarrow$$

$$\underset{\text{(IV)}}{\mathrm{R{\cdot}CH{=}CH{\cdot}[CH_2]_{\mathit{n}}{\cdot}CH{=}CH_2}} \longrightarrow \underset{\text{(V)}}{\mathrm{R{\cdot}CH{=}CH{\cdot}[CH_2]_{\mathit{n}}{\cdot}CH_2{\cdot}CH_3}}$$

The partial reduction of the alkadiynoic acid (I) was next examined. Catalytic hydrogenation of undeca-1,7-diyne (II; $R = C_3H_7$, $n = 4$) has been studied by Raphael and his co-workers,[3] who showed that the sequence (II) ⟶ (IV) was involved. Although the diene (IV) was almost entirely *cis*-isomer, the final olefin (V) contained about 50% of *trans*-isomer, unless Lindlar's catalyst was used. Thus, palladium catalysts (except Lindlar's) may interconvert *cis*- and *trans*-olefins under hydrogenation conditions. Similar results were obtained in the present work on hydrogenation of heneicosa-12,20-diynoic acid. Absorption of two mol. of hydrogen occurred readily and slightly impure *cis*-heneicosa-12,20-dienoic acid (IV; $n = 6$, $R = [CH_2]_{10}{\cdot}CO_2H$) could be obtained if hydrogenation was interrupted at this point. When Lindlar's catalyst was used, the diene acid contained very little *trans*-isomer (very weak band at 967 cm.$^{-1}$). Use of palladised barium sulphate with quinoline,[4] however, gave *cis*-acid contaminated with an appreciable amount of *trans*-isomer. In both cases, the terminal olefin group was present (bands at 911, 990 cm.$^{-1}$). Further hydrogenation of the diynoic acid until three mol. of hydrogen had been absorbed proceeded more slowly and gave impure *cis*-heneicos-12-enoic acid. This product contained a little *trans*-isomer (weak band at 967 cm.$^{-1}$) and also some terminal olefin (bands at 990, 910 cm.$^{-1}$; $\cdot CH{:}CH_2$). Treatment of this product with perbenzoic acid, and then formic acid, followed by alkaline hydrolysis and further hydrogenation, gave *threo*-12,13-dihydroxyheneicosanoic acid (VI). The structure of the dihydroxy-acid was confirmed by cleavage with periodic acid to give nonanal. The dihydroxy-acid was transformed through the dibromo-acid into *trans*-heneicos-12-enoic acid (VII).[5]

$$\mathrm{CH_3{\cdot}[CH_2]_7{\cdot}CH(OH){\cdot}CH(OH){\cdot}[CH_2]_{10}{\cdot}CO_2H}\quad \text{(VI)}$$

$$\mathrm{CH_3{\cdot}[CH_2]_7CH{:}CH{\cdot}[CH_2]_{10}{\cdot}CO_2H}\quad \text{(VII)}$$

Attempts to effect selective oxidation at the non-terminal double bond of *cis*-heneicosa-12,20-dienoic acid by treatment with perbenzoic acid, or with iodine–silver acetate in moist acetic acid,[6] gave unsatisfactory results.

Many syntheses of long-chain conjugated and " skipped " dienoic acids have been reported,[7] but little attention has been directed to dienoic acids with isolated double bonds,

---

[3] N. A. Dobson, G. Eglinton, M. Krishnamurti, R. A. Raphael, and R. G. Willis, *Tetrahedron*, 1961, **16**, 16.

[4] D. J. Cram and N. L. Allinger, *J. Amer. Chem. Soc.*, 1956, **78**, 2522.

[5] D. E. Ames and R. E. Bowman, *J.*, 1951, 1079.

[6] F. D. Gunstone and L. J. Morris, *J.*, 1957, 487.

[7] *E.g.*, G. Eglinton, *Ann. Reports*, 1961, **58**, 219; 1962, **59**, 276.

although several such acids have recently been found to occur naturally.[8] Gunstone and Sykes[9] condensed diynes (VIII; $n = 2$ and 4) with chloroalkyl iodides and then obtained the corresponding diynoic acids from the chloro-diyne through the nitrile. The condensation of ω-bromo-acid *NN*-dimethylamides with diynes and of ω-halogeno-alkynes with an ω-acetylenic alcohol have also been used[1] to prepare the necessary diyne containing a terminal group, which can subsequently be transformed into carboxyl. In each case, the resulting diynoic acids were semihydrogenated to give the corresponding *cis,cis*-dienoic acids.

The direct condensation of diynes with ω-bromo-acid to prepare diynoic acids of this type has now been effected. Thus, hexa-1,5-diyne (VIII; $R = H$, $m = 2$) was first alkylated with octyl bromide, in the presence of lithamide in liquid ammonia, to give tetradeca-1,5-diyne (VIII; $R = n\text{-}C_8H_{17}$, $m = 2$). Similar condensation of the latter with 8-bromo-octanoic acid gave docosa-9,13-diynoic acid (IX) in 62% yield. By this method, acids having three, four, five, or six methylene groups between the two acetylenic bonds were also prepared. These acids were characterised by reduction to the saturated acids and also as the benzylamides.

$$R{\cdot}C{\equiv}C{\cdot}[CH_2]_m{\cdot}C{\equiv}C{\cdot}H \qquad \text{(VIII)}$$

$$n\text{-}C_8H_{17}{\cdot}C{\equiv}C{\cdot}[CH_2]_2{\cdot}C{\equiv}C{\cdot}[CH_2]_7{\cdot}CO_2H \qquad \text{(IX)}$$

Catalytic semihydrogenation of the diynoic acids in the presence of Lindlar's catalyst and quinoline gave the corresponding dienoic acids. These consisted of *cis,cis*-isomer containing little, if any, *trans*-isomers (no infrared band at about 970 cm.$^{-1}$). The acids were converted into the benzylamides, which were also obtained by semihydrogenation of the diynoic acid benzylamides.

The condensation of alkyl halides with ω-acetylenic alcohols to give long-chain alkynols in high yields has been described previously.[10] This reaction has now been applied to αω-dihalides to provide a convenient synthesis of long-chain αω-diols, and, thence of αω-dicarboxylic acids. Thus, 1,6-dibromohexane with prop-2-yn-1-ol in the presence of lithamide in liquid ammonia gave dodeca-2,10-diyn-1,12-diol (X) (88%), which was converted into the dibromide and, by malonic ester synthesis, into hexadeca-4,12-diynedioic acid (XI). Catalytic hydrogenation gave hexadecanedioic acid and, similarly,

$$HO{\cdot}CH_2{\cdot}C{\equiv}C{\cdot}[CH_2]_6{\cdot}C{\equiv}C{\cdot}CH_2{\cdot}OH \quad \text{(X)}$$

$$HO_2C{\cdot}[CH_2]_2{\cdot}C{\equiv}C{\cdot}[CH_2]_6C{\equiv}C{\cdot}[CH_2]_2{\cdot}CO_2H \quad \text{(XI)}$$

$$HO{\cdot}[CH_2]_3{\cdot}C{\equiv}C{\cdot}[CH_2]_n{\cdot}C{\equiv}C{\cdot}[CH_2]_3{\cdot}OH \quad \text{(XII)}$$

1,5-dibromopentane gave analogous products leading to pentadecanedioic acid. This sequence can thus be used to prepare odd- or even-numbered members of the saturated diacid series, and thus has some advantage over coupling methods.

Similar condensation of 1,10-dibromodecane with pent-4-yn-1-ol gave eicosa-4,16-diyne-1,20-diol (XII; $n = 10$) (58% yield), which was reduced to eicosane-1,20-diol. In the same way, 1,5-dibromopentane and pent-4-yn-1-ol reacted to give pentadeca-4,10-diyne-1,15-diol (XII; $n = 5$), which was catalytically hydrogenated to pentadecane-1,15-diol. Conversion into the dibromide, followed by malonation synthesis, gave nonadecanedioic acid.

EXPERIMENTAL

Evaporations were carried out under reduced pressure; light petroleum refers to the fraction of b. p. 40—60°, unless otherwise stated.

---

[8] M. O. Bagby, C. R. Smith, T. K. Miwa, R. L. Lohmar, and I. A. Wolff, *J. Org. Chem.*, 1961, **26**, 1261; F. Davidoff and E. D. Korn, *J. Biol. Chem.*, 1963, **238**, 3210; J. L. Gellerman and H. Schlenk, *Experientia*, 1963, **19**, 522.

[9] F. D. Gunstone and P. J. Sykes, *J.*, 1962, 3055.

[10] D. E. Ames, A. N. Covell, and T. G. Goodburn, *J.*, 1963, 5889.

Octadeca-9,17-*diynoic Acid.*—Deca-1,9-diyne [11] (26 g.) in tetrahydrofuran (50 c.c.) was added to lithamide [from lithium (2·6 g.)] in liquid ammonia (500 c.c.). After 1 hr., 8-bromo-octanoic acid (8·5 g.) in tetrahydrofuran (200 c.c.) was added and the mixture was stirred under reflux for 8 hr. When the ammonia had evaporated, dilute hydrochloric acid was added and the mixture was extracted with ether. Fractional distillation gave deca-1,9-diyne (14 g.; b. p. 100—105°/20 mm.) and then *octadeca*-9,17-*diynoic acid* (7·0 g., 66%), b. p. 180—185°/0·5 mm., m. p. 48—49°, from light petroleum (Found: C, 78·3; H, 10·2. $C_{18}H_{28}O_2$ requires C, 78·2; H, 10·2%). Similarly condensation of deca-1,9-diyne with 11-bromoundecanoic acid gave *heneicosa*-12,20-*diynoic acid* (66%), m. p. 59—60°, from light petroleum (b. p. 60—80°) (Found: C, 79·6; H, 10·4. $C_{21}H_{34}O_2$ requires C, 79·2; H, 10·8%). Condensation of tetradeca-1,13-diyne [12] with 11-bromoundecanoic acid gave *pentacosa*-12,24-*diynoic acid* (48%), m. p. 67·5—69°, from ethanol (Found: C, 79·9; H, 11·4. $C_{25}H_{42}O_2$ requires C, 80·2; H, 11·3%).

Catalytic hydrogenation of these acids in ethanol over 10% palladised charcoal gave the corresponding saturated acids: octadecanoic, m. p. and mixed m. p. 70—71°, from ethanol; heneicosanoic acid, m. p. 73·5—74°, from ethanol (lit.,[13] 75—76°); and pentacosanoic acid, m. p. 84—85°, from ethanol (lit.,[13] 84—85°).

Partial Hydrogenation of Heneicosa-12,20-*diynoic Acid.*—(*a*) The acid (4·5 g.), Lindlar's catalyst [14] (0·45 g.), and quinoline (0·2 g.) in methanol (100 c.c.) were hydrogenated. When 2·0 mol. had been absorbed, hydrogenation was interrupted and the filtered solution was evaporated. The residue in ether was washed with dilute hydrochloric acid and water, dried (Na_2SO_4), and evaporated. Recrystallisation from light petroleum at −15° gave slightly impure cis-*heneicosa*-12,20-*dienoic acid*, m. p. 37—41° (Found: C, 78·4; H, 11·8. $C_{21}H_{38}O_2$ requires C, 78·2; H, 11·9%). Infrared spectrum: bands at 990, 911, and 1630 cm.$^{-1}$ ($CH{:}CH_2$) and 967 cm.$^{-1}$ (very weak; a little *trans*-isomer present).

(*b*) In a similar experiment, hydrogenation was continued until 3·0 mol. had been absorbed, although the rate of absorption fell sharply after 2·0 mol. had been taken up. Isolated as in (*a*), the impure cis-*heneicosa*-12-*enoic acid* had b. p. 210—212°/0·5 mm., m. p. 26—27° (Found: C, 77·7; H, 12·0. $C_{21}H_{40}O_2$ requires C, 77·7; H, 12·4%). Infrared spectrum: bands at 990, 910 ($\cdot CH{:}CH_2$ impurity), and 967 cm.$^{-1}$ (weak band, some *trans*-isomer present).

threo-12,13-*Dihydroxyheneicosanoic Acid.*—The product (*b*) was esterified with ethanol–sulphuric acid and the crude ester (0·625 g.) in chloroform (15 c.c.) was treated with 0·50M-perbenzoic acid in chloroform (4·3 c.c.) at 0° for 3 hr. After the solution had been washed (Na_2CO_3 solution) and evaporated, the residue was left at room temperature with formic acid (15 c.c.) for 16 hr. and re-evaporated. The residue was refluxed for 6 hr. with ethanol (20 c.c.) and 3N-sodium hydroxide (20 c.c.). Acidification gave crude dihydroxy-acid, which was hydrogenated in ethanol over 10% palladised charcoal to obtain threo-12,13-*dihydroxyhenicosanoic acid*, m. p. 98—99°, from ethyl acetate (Found: C, 69·5; H, 11·2. $C_{21}H_{42}O_4$ requires C, 69·3; H, 11·7%).

Potassium periodate (120 mg.) in N-sulphuric acid (6·0 c.c.) was added to the dihydroxy-acid (180 mg.) in ethanol (10 c.c.) at 40°. The mixture was kept at 40° for 20 min., poured into water, and extracted with ether. Evaporation, steam-distillation of the residue, and addition of 2,4-dinitrophenylhydrazine in 2N-hydrochloric acid to the distillate, gave nonanal 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 100—102°, from ethanol.

trans-*Heneicos*-12-*enoic Acid.*—Hydrogen bromide in acetic acid (8 c.c.; *d* 1·2) and concentrated sulphuric acid (2 c.c.) were added to the dihydroxy-acid (0·25 g.). The mixture was left overnight and then heated at 100° for 8 hr.; addition of water gave a solid, which was collected and refluxed for 6 hr. with ethanol (30 c.c.) and concentrated sulphuric acid (0·6 c.c.). After addition of ether, the solution was washed with sodium carbonate solution and evaporated. Zinc dust (0·8 g.) was refluxed with ethanol (20 c.c.) containing hydrobromic acid (1 drop) and sodium acetate (0·4 g.), and the residue was added. The solution was refluxed for 1 hr., filtered, and then boiled with 5N-sodium hydroxide (10 c.c.) for 1 hr. Addition to dilute hydrochloric acid gave trans-*heneicos*-12-*enoic acid*, m. p. 53—54°, after recrystallisation from light petroleum (Found: C, 77·4; H, 12·6. $C_{20}H_{40}O_2$ requires C, 77·7; H, 12·4%).

---

[11] W. M. Lauer and W. J. Gensler, *J. Amer. Chem. Soc.*, 1945, **67**, 1171.

[12] G. Eglinton and A. R. Galbraith, *J.*, 1959, 889.

[13] P. A. Levene and F. A. Taylor, *J. Biol. Chem.*, 1924, **59**, 905.

[14] H. Lindlar, *Helv. Chim. Acta*, 1952, **35**, 446.

Alkadiynes.—(*a*) *Pentadeca*-1,8-*diyne.* Nona-1,8-diyne [15] (21 g.) in tetrahydrofuran (100 c.c.) was added to sodamide [from sodium (4 g.)] in liquid ammonia (400 c.c.). After the mixture had been stirred for 1 hr., hexyl bromide (34·6 g.) was added and the mass was stirred under reflux for 16 hr. Ammonium chloride (11 g.) was added and the solvent was allowed to evaporate. Extraction of the residue with ether and distillation gave *pentadeca*-1,8-*diyne* (14·9 g.), b. p. 146—150°/13 mm. (Found: C, 87·3; H, 11·9. $C_{15}H_{24}$ requires C, 88·2; H, 11·8%).

Similarly prepared were: *hexadeca*-1,9-*diyne*, b. p. 156—160°/13 mm., n_D^{23} 1·4584 (Found: C, 87·3; H, 11·9. $C_{16}H_{26}$ requires C, 88·0; H, 12·0%); *tetradeca*-1,5-*diyne*, n_D^{21} 1·4571, b. p. 124—128°/13 mm. (Found: C, 87·8; H, 11·6. $C_{14}H_{22}$ requires C, 88·4; H, 11·7%); and *eicosa*-1,9-*diyne*, b. p. 140—144°/0·5 mm., m. p. 36—37°, from ethanol (Found: C, 88·0; H, 13·0. $C_{20}H_{34}$ requires C, 87·5; H, 12·5%).

(*b*) *Hexadeca*-1,7-*diyne.* Sodium (3·6 g.) in liquid ammonia (200 c.c.) was converted into sodamide by using ferric nitrate catalyst, and an excess of acetylene was passed into the solution. 1-Iodotetradec-5-yne [16] (25·6 g.) was added and the mixture was stirred under reflux for 8 hr. and then allowed to evaporate. Extraction with ether and distillation gave *hexadeca*-1,7-*diyne* (14·2 g.), b. p. 85—90°/0·5 mm., n_D^{20} 1·4592 (Found: C, 87·7; H, 11·6. $C_{16}H_{26}$ requires C, 88·0; H, 12·0%). *Dodeca*-1,6-*diyne*, prepared similarly, had b. p. 100—102°/10 mm., n_D^{21} 1·4597 (Found: C, 88·4; H, 11·2. $C_{12}H_{18}$ requires C, 88·8; H, 11·2%).

Alkadiynoic Acids.—*Docosa*-11,16-*diynoic acid.* Lithamide was prepared from lithium (1·27 g.) in liquid ammonia (400 c.c.) and treated with dodeca-1,6-diyne (19 g.). After 1 hr., 10-bromodecanoic acid (11·5 g.) in tetrahydrofuran (200 c.c.) was added and the mixture was kept in an autoclave at room temperature for 16 hr. When the ammonia had evaporated, dilute hydrochloric acid was added; isolation with ether gave *docosa*-11,16-*diynoic acid* (9·6 g., 63%), m. p. 57—58°, from light petroleum (Found: C, 79·4; H, 11·0. $C_{22}H_{36}O_2$ requires C, 79·5; H, 10·9%). Fractional distillation of the mother-liquors gave recovered dodeca-1,6-diyne (5·4 g.), b. p. 100—105°/10 mm.

The following acids were prepared similarly: *docosa*-7,15-*diynoic acid* (11%), m. p. 43—45°, from light petroleum (Found: C, 79·1; H, 10·6%); *docosa*-8,15-*diynoic acid* (68%), m. p. 36·5—37·5° (Found: C, 79·1; H, 10·9%); *docosa*-9,13-*diynoic* acid (61%), m. p. 59·5—60·5°, from light petroleum (Found: C, 79·5; H, 11·1%); and *tetracosa*-9,15-*diynoic acid* (71%), m. p. 53—55°, from light petroleum (Found: C, 79·9; H, 11·0. $C_{24}H_{40}O_2$ requires C, 79·9; H, 11·2%).

Hydrogenation of each of the docosadiynoic acids in ethanol over palladised charcoal gave docosanoic (behenic) acid, m. p. and mixed m. p. 78—80°, from ethanol. Similarly, tetracosa-9,15-diynoic acid gave tetracosanoic (lignoceric) acid, m. p. and mixed m. p. 84—86°.

Benzylamides of Alkdiynoic Acids.—The acid (1 mol.) and benzylamine (1 mol.) were heated under nitrogen at 180—190° (bath) for 10 min. The mixture was cooled and recrystallised from ethanol to give the following products: N-*benzyldocosa*-9,13-*diynamide*, m. p. 85—87° (Found: C, 83·1; H, 10·7; N, 3·6. $C_{29}H_{43}NO$ requires C, 82·6; H, 10·3; N, 3·3%); N-*benzyldocosa*-11,16-*diynamide*, m. p. 75—76° (Found: C, 82·8; H, 10·3; N, 3·3%); N-*benzyldocosa*-8,15-*diynamide*, m. p. 62—63° (Found: C, 82·6; H, 10·6; N, 3·1%); N-*benzyldocosa*-7,15-*diynamide*, m. p. 63—65° (Found: C, 82·3; H, 10·4; N, 3·1%); N-*benzyldocosa*-5,13-*diynamide*, m. p. 78—80° (from acid [1]) (Found: C, 82·8; H, 10·4; N, 3·3%); and N-*benzyltetracosa*-9,15-*diynamide*, m. p. 77—78° (Found: C, 83·3; H, 10·7; N, 3·2. $C_{31}H_{47}NO$ requires C, 82·8; H, 10·5; N, 3·1%).

Alkadienoic Acids.—The acetylenic acid (1 g.), Lindlar's catalyst (0·1 g.), and quinoline (0·04 g.) in ethanol (50 c.c.) were hydrogenated until 2·0 mol. had been taken up. Evaporation of the filtered solution gave an oil, which was taken up in ether, washed with 2N-hydrochloric acid and water, and dried (Na_2SO_4). Removal of solvent, finally at 20°/0·1 mm., gave the following diene acids: *docosa*-9,13-*dienoic acid*, m. p. 12° (thermometer in liquid), n_D^{22} 1·4689 Found: C, 78·4; H, 11·6. $C_{22}H_{40}O_2$ requires C, 78·5; H, 12·0%); *docosa*-11,16-*dienoic acid*, n_D^{21} 1·4690 (Found: C, 78·2; H, 11·9%); *docosa*-8,15-*dienoic acid*, n_D^{21} 1·4698 (Found: C, 78·0, H, 11·8%); *docosa*-7,15-*dienoic acid*, n_D^{20} 1·4695 (Found: C, 78·2; H, 12·1%); and *tetracosa*-9,15-*dienoic acid*, m. p. 10—12° (sealed capillary), n_D^{20} 1·4693 (Found: C, 79·3; H, 11·9. $C_{24}H_{44}O_2$ requires C, 79·1; H, 12·2%). In each case, the infrared spectrum showed no band at about 970 cm.$^{-1}$ indicating the presence of very little, if any, *trans*-isomers.

[15] A. L. Henne and K. W. Greenlee, *J. Amer. Chem. Soc.*, 1945, **67**, 484.
[16] G. Grimmer and J. Kracht, *Chem. Ber.*, 1963, **96**, 3370.

Benzylamides of Alkadienoic Acids.—(*a*) The alkadiynoic acid benzylamide (200 mg.), Lindlar's catalyst (50 mg.), and quinoline (20 mg.) in ethanol (20 c.c.) were hydrogenated until 2·0 mol. of hydrogen had been absorbed. Evaporation of the filtered solution and recrystallisation from ethanol gave the benzylamide.

(*b*) The dienoic acid was heated with benzylamine as for the diynoic acids.

The following benzylamides were obtained by both methods (mixed m. p. determinations on the products obtained by the two methods showed no depression): N-*benzyldocosa*-9,13-*dienamide*, m. p. 46—48° (Found: C, 81·3; H, 11·0; N, 3·4. $C_{29}H_{47}NO$ requires C, 81·8; H, 11·1; N, 3·3%); N-*benzyldocosa*-11,16-*dienamide*, m. p. 34—35° (Found: C, 82·0; H, 11·3; N, 3·3%); N-*benzyldocosa*-8,15-*dienamide*, m. p. 36—37° (Found: C 81·3; H, 11·0; N, 3·3%); N-*benzyldocosa*-5,13-*dienamide* (from acid [1]), m. p. 40—42° (Found: C, 81·7; H, 11·2; N, 3·4%); and N-*benzyltetracosa*-9,15-*dienamide*, m. p. 45—47° (Found: C, 81·9; H, 11·5; N, 3·2. $C_{31}H_{51}NO$ requires C, 82·1; H, 11·3; N, 3·1%). The benzylamide of docosa-7,15-dienoic acid could not be induced to crystallise.

Dodeca-2,10-*diyn*-1,12-*diol.*—Prop-2-yn-1-ol (56 g.) in tetrahydrofuran (100 c.c.) was added to lithamide [from lithium (14 g.)] in liquid ammonia (1 l.). After 1 hr., 1,6-dibromohexane (24·4 g.) in tetrahydrofuran (400 c.c.) was added and the mixture was refluxed for 8 hr. Addition of 4N-hydrochloric acid and isolation with ether gave the *diol* (17·0 g.), m. p. 65—66°, from ethyl acetate–light petroleum (Found: C, 73·9; H, 8·9. $C_{12}H_{18}O_2$ requires C, 74·3; H, 9·2%).

In the same way 1,5-dibromopentane gave *undeca*-2,9-*diyn*-1,11-*diol* (66%), m. p. 45—46°, from ethyl acetate–light petroleum (Found: C, 72·9; H, 9·0. $C_{11}H_{16}O_2$ requires C, 73·3; H, 9·0%). Similarly, pent-4-yn-1-ol and 1,10-dibromodecane yielded *eicosa*-4,16-*diyn*-1,20-*diol* (58%), m. p. 72—73°, from ethanol (Found: C, 78·3; H, 11·3. $C_{20}H_{34}O_2$ requires C, 78·4; H, 11·2%); and pent-4-yn-1-ol and 1,5-dibromopentane gave *pentadeca*-4,11-*diyn*-1,15-*diol* (65%), m. p. 44—45°, from ethyl acetate (Found: C, 76·3; H, 10·2. $C_{15}H_{24}O_2$ requires C, 76·2; H, 10·2%).

Catalytic hydrogenation of the last two of these diols in ethanol over 5% palladised charcoal catalyst gave the saturated diols: eicosane-1,20-diol (70%), m. p. 98—99°, from ethanol (lit.,[17] 103°), and pentadecane-1,15-diol, m. p. 86—87°, from ethyl acetate (lit.,[17] 88°).

Hexadeca-4,12-*diynedioic Acid.*—Dodeca-2,10-diyn-1,12-diol (12 g.) in ether (200 c.c.) was added to phosphorus tribromide (12·5 g.) in ether (25 c.c.) containing pyridine (1 c.c.). The mixture was refluxed for 2 hr., poured on to ice, and extracted with ether. Evaporation gave crude dibromide, which was added to sodiomalonic ester solution [from sodium (11·5 g.), ethanol (500 c.c.), and ethyl malonate (80 g.)]. The solution was refluxed for 8 hr., evaporated, and refluxed with 2N-sodium hydroxide (500 c.c.) for 2 hr. After acidification and isolation with ether, the product was heated at 180° for 30 min. The *acid* (8·8 g.; 50%) had m. p. 133—134°, from ethyl acetate (Found: C, 68·9; H, 7·9. $C_{16}H_{22}O_4$ requires C, 69·0; H, 8·0%). Hydrogenation in ethanol over 10% palladised charcoal gave hexadecanedioic acid, m. p. 123—125°, from ethyl acetate (lit.,[18] 123·6—124°).

Pentadeca-4,11-*diynedioic acid* (50%), prepared similarly from undeca-2,9-diyn-1,11-diol, had m. p. 133—134°, from ethyl acetate (Found: C, 68·1; H, 7·7. $C_{15}H_{20}O_4$ requires C, 68·2; H, 7·6%). Hydrogenation gave pentadecanedioic acid, m. p. 114°, from ethyl acetate (lit.,[19] 114°). Nonadecanedioic acid (62%) was obtained from pentadecane-1,15-diol by malonic ester synthesis in the manner described, and had m. p. 117—118°, from ethyl acetate (lit.,[20] 117—119°).

CHEMISTRY DEPARTMENT, CHELSEA COLLEGE OF SCIENCE AND TECHNOLOGY,
MANRESA ROAD, LONDON S.W.3.

[*Received, January* 18*th*, 1965.]

---

[17] P. Chuit and J. Hausser, *Helv. Chim. Acta*, 1929, **12**, 483, 850.
[18] R. Kapp and A. Knoll, *J. Amer. Chem. Soc.*, 1943, **65**, 2063.
[19] R. G. Jones, *J. Amer. Chem. Soc.*, 1947, **69**, 2350.
[20] R. Toubiana and J. Asselineau, *Compt. rend.*, 1961, **253**, 1965.