

Syntheses of Long-chain Acids. Part IX.¹ Docosa-3,9,15- and -5,11,17-triynoic Acids and Eicosa-5,11,14-triynoic Acid

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The acids named in the title, and also hexadeca-3,9-diyynoic and eicosa-7,13-diyynoic acids, which all contain acetylenic groups separated by a tetramethylene chain, have been synthesised. The methods employed involved alkylation of the *NN*-dimethylamide of a terminal acetylenic acid, or of an acetylenic alcohol, with final hydrolysis or oxidation, respectively. Eicosa-5,11,14-triynoic acid was prepared by alkylation of the Grignard complex of dodeca-5,11-diyynoic acid with oct-2-ynyl bromide by Osbond's method. Catalytic semihydrogenation of these acetylenic acids has been examined.

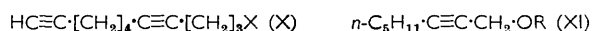
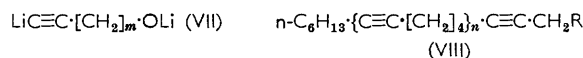
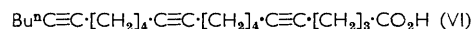
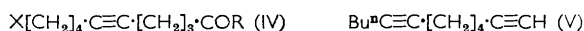
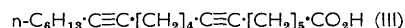
SEVERAL long-chain di- and tri-enoic acids having double bonds separated by a tetramethylene chain have been shown to occur in the fats from various plants. These acids usually contain one of the double bonds in the 3- or the 5-position.² We describe here the synthesis and partial reduction of some di- and tri-acetylenic acids of this type.

1-Iodododec-5-yne (I; $m = 1$, $X = I$) was condensed with *NN*-dimethyloct-7-ynamide (II; $n = 5$) in the presence of lithium amide;³ hydrolysis gave eicosa-7,13-diyynoic acid (III), which has been synthesised previously by a different route.⁴

Alkylation of an acetylenic *NN*-dimethylamide is applicable to the synthesis of alk-5-yynoic acids;^{3,5} docosa-5,11,17-triynoic acid was prepared by this method. Condensation of *NN*-dimethylhex-5-ynamide (II; $n = 3$) with 4-chlorobutyl iodide in presence of lithium amide in liquid ammonia gave 10-chloro-*NN*-dimethyldec-5-ynamide (IV; $R = NMe_2$, $X = Cl$) containing a small amount of the unsubstituted amide (IV; $R = NH_2$, $X = Cl$), evidently formed by ammonolysis of the *NN*-dimethylamide group.⁶ The crude chloride was therefore converted into the iodide and condensed with the sodio-derivative of dodeca-1,7-diyne (V), and the resulting amide was hydrolysed to give docosa-5,11,17-triynoic acid (VI) in low overall yield. Semihydrogenation over Lindlar catalyst⁷ gave *cis,cis,cis*-docosa-5,11,17-triynoic acid, the structure of which was confirmed by ozonolysis. Reduction of dodeca-1,7-diyne with sodium and liquid ammonia⁸ gave *trans*-dodec-7-en-1-yne, but attempts to condense this with the iodo-amide (IV; $R = NMe_2$, $X = I$), as an intermediate for the synthesis of a *trans,cis,cis*-triynoic acid, were unsuccessful.

C-Alkylation of the dilithio-derivative (VII; $m = 2$) of but-3-yn-1-ol and oxidation of the resulting alk-3-yn-1-ol yields the alk-3-yynoic acid.³ We therefore examined the extension of this process to the synthesis of di- and tri-yynoic acids with the acetylenic groups separated by a

tetramethylene chain. Attempts to condense 4-chlorobutyl iodide with the dilithio-derivative of but-3-yn-1-ol (or of prop-2-yn-1-ol) were unsuccessful. Alkylation of the lithium derivative (VII; $m = 2$) with 1-iodododec-5-yne (I; $m = 1$, $X = I$), however, gave hexadeca-3,9-diy-1-ol (VIII; $n = 1$, $R = CH_2 \cdot OH$) which was oxidised with chromic acid⁹ to hexadeca-3,9-diyynoic acid (VIII; $n = 1$, $R = CO_2H$). Catalytic semihydrogenation then gave *cis,cis*-hexadeca-3,9-dienoic acid.



Tetradeca-1,7-diyne was prepared by the reaction of octa-1,7-diyne with hexyl bromide in presence of sodamide (1 mol. equiv.), but attempts to condense the product with 4-chlorobutyl iodide to give the chloride (I; $m = 2$, $X = Cl$) were unsuccessful. As an alternative route to this chloride, the sodio-derivative of 6-chlorohex-1-yne was alkylated with 1-iodododec-5-yne (I; $m = 1$, $X = I$). The product (I; $m = 2$, $X = Cl$) could not be purified, but conversion into the iodide and condensation with the dilithio-derivative (VII; $m = 2$) yielded docosa-3,9,15-triyn-1-ol (VIII; $n = 2$, $R = CH_2 \cdot OH$), which gave docosa-3,9,15-triynoic acid (IX; $n = 2$, $R = CO_2H$) on oxidation with chromic acid. *cis,cis,cis*-Docosa-3,9,15-triynoic acid was then obtained by catalytic semihydrogenation over Lindlar catalyst.

Osbond and his collaborators¹⁰ have developed an efficient synthesis of di- and poly-acetylenic acids, with 'skipped' conjugation, by condensation of the Grignard complex of a terminal acetylenic acid with a propargylic

⁴ F. D. Gunstone and P. J. Sykes, *J. Chem. Soc.*, 1962, 3055.

⁵ D. E. Ames and P. J. Islip, *J. Chem. Soc.*, 1963, 4363.

⁶ Cf. D. E. Ames and B. T. Warren, *J. Chem. Soc.*, 1964, 5518.

⁷ H. Lindlar, *Helv. Chim. Acta*, 1952, **35**, 446.

⁸ Cf. N. A. Dobson and R. A. Raphael, *J. Chem. Soc.*, 1955, 3558.

⁹ E. R. H. Jones, G. H. Whitham, and M. C. Whiting, *J. Chem. Soc.*, 1954, 3201; J. C. Craig and M. Moyle, *ibid.*, 1963, 4402.

¹⁰ J. M. Osbond, P. G. Philpott, and J. C. Wickens, *J. Chem. Soc.*, 1961, 2779; J. M. Osbond, *Prog. Chem. Fats and Other Lipids*, 1966, **9**, 119.

¹ Part VIII, D. E. Ames and T. G. Goodburn, *J. Chem. Soc. (C)*, 1967, 1556.

² T. Takagi, *J. Amer. Oil Chemists Soc.*, 1964, **41**, 516; J. L. Gellermann and H. Schlenk, *Experientia*, 1963, **19**, 522; F. R. Earle, C. A. Glass, G. C. Geisinger, I. A. Wolff, and Q. Jones, *J. Amer. Oil Chemists Soc.*, 1960, **37**, 440; L. J. Morris, M. O. Marshall, and E. W. Hammond, *Lipids*, 1968, **3**, 91; R. P. Hansen, and S. M. Meiklen, *New Zealand J. Sci. Technol.*, 1969, **12**, 865.

³ Cf. D. E. Ames, A. N. Covell, and T. G. Goodburn, *J. Chem. Soc.*, 1965, 894.

halide. To apply this method to the synthesis of eicosa-5,11,14-triynoic acid (IX), octa-1,7-diyne was condensed with 3-chloropropyl iodide to give the chloride (X; X = Cl), which was converted through the iodide and nitrile into the acid (X; X = CO₂H). Alkylation of the dilithio-derivative (1 mol. equiv.) (VII; *m* = 1) of prop-2-yn-1-ol with pentyl bromide (1 mol. equiv.) gave oct-2-yn-1-ol (XI; R = H) in 60% yield; this product contained a small amount (6.7%) of *CO*-dialkylation product (XI; R = *n*-C₅H₁₁) which was isolated by preparative g.l.c. Dialkylation has not been encountered when only 0.5 mol. equiv. of halide is used.³ Treatment of the condensation product with phosphorus tribromide gave pure 1-bromo-oct-2-yne in good yield. The diacetylenic acid (X; X = CO₂H) was treated with ethylmagnesium bromide and the complex condensed with 1-bromo-oct-2-yne in the presence of copper(I) cyanide¹⁰ to give eicosa-5,11,14-triynoic acid (IX), which was purified by use of a fractionating molecular still. Attempted semihydrogenation of this acid did not give satisfactory results.

EXPERIMENTAL

N.m.r. spectra were determined at 60 MHz with a Perkin-Elmer R10 spectrometer, with tetramethylsilane as internal standard. Analytical g.l.c. was carried out with a Pye series 104 model 24 chromatograph (flame ionisation detector; nitrogen as carrier gas; 3% E30 column on Diatomite CQ). For preparative work, a Wilkens Aerograph Autoprep 700 was used (thermal conductivity detector; helium as carrier gas; 30% SE30 on a 20 ft Celite column). Formation of lithium and sodium amides from the metal in liquid ammonia was catalysed by iron(III) nitrate. Evaporations were carried out under reduced pressure.

1-Iodododec-5-yne.—1-Chlorododec-5-yne (42.3 g)¹¹ and sodium iodide (100 g) in acetone (1 l) were heated under reflux for 25 h. After most of the acetone had been removed by distillation, water was added; isolation with ether gave 1-iodododec-5-yne (52.9), b.p. 108–109° at 0.07 mmHg, *n*_D²⁵ 1.5029 (Found: C, 49.3; H, 7.2; I, 43.4. C₁₂H₂₁I requires C, 49.7; H, 7.2; I, 43.1%).

NN-Dimethyloct-7-ynamide.—6-Bromohexanoic acid (92 g), and thionyl chloride (200 ml) were warmed at 35° for 1 h and excess of thionyl chloride was removed by distillation under reduced pressure. The residue was dissolved in ether (300 ml), cooled at 0–10°, and treated with dimethylamine vapour until the mixture was neutral. After addition of water, the organic layer was washed with sodium carbonate solution, 2*N*-hydrochloric acid, and water. The crude bromo-amide had b.p. 104–108° at 0.5 mmHg but could not be purified owing to persistent decomposition during distillation. Lithium amide [from lithium (4.9 g)] in liquid ammonia (1 l) was treated with acetylene for 3.5 h and the bromo-amide in tetrahydrofuran (25 ml) was then added during 30 min. After the ammonia had evaporated, water was added; isolation with ether gave *NN*-dimethyloct-7-ynamide (25 g), b.p. 97–98° at 0.65 mmHg, *n*_D²⁵ 1.4736 (Found: C, 70.9; H, 10.5; N, 8.2. C₁₀H₁₇NO requires C, 71.8; H, 10.3; N, 8.4%).

Eicosa-7,13-diynoic Acid.—The acetylenic amide (28.5 g)

¹¹ W. R. Taylor and F. M. Strong, *J. Amer. Chem. Soc.*, 1950, **72**, 4263.

in tetrahydrofuran (100 ml) was added during 20 min to lithium amide [from lithium (1.1 g)] in liquid ammonia (600 ml). The mixture was stirred for 1 h, treated with 1-iodododec-5-yne (37 g) in tetrahydrofuran (100 ml), and stirred overnight. After the ammonia had evaporated, water was added; isolation with ether yielded the crude *NN*-dimethylamide (13.3 g), b.p. 180–196° at 0.2 mmHg. This was heated under reflux for 7 h with 5*N*-sodium hydroxide in ethanol (200 ml) and poured into dilute hydrochloric acid. Isolation with light petroleum (b.p. 40–60°) gave eicosa-7,13-diynoic acid (5.36 g), m.p. 44.5–45.5° (from methanol) [Found: C, 79.4; H, 11.0. Calc. for C₂₀H₃₂O₂: C, 78.9; H, 10.6%] (lit.,⁴ m.p. 45.5–46°).

erythro,erythro-7,8,13,14-Tetrahydroxyeicosanoic Acid.—The diynoic acid was reduced to *cis,cis*-eicosa-7,13-dienoic acid.⁴ This (5 g) was dissolved in a solution of sodium hydroxide (5 g) in water (6 l), and stirred at 0–2° while potassium permanganate (8 g) in water (800 ml) was added rapidly. After 5 min, sodium hydrogen sulphite and concentrated hydrochloric acid (150 ml) were added, and the precipitate was collected and washed with water. The solid was dissolved in 2-methoxyethanol (50 ml) containing acetic acid (10 ml) and poured into 2*N*-hydrochloric acid. The resulting erythro,erythro-7,8,13,14-tetrahydroxyeicosanoic acid (2.8 g) probably contained two isomers but the m.p. (167–169°) was unchanged by recrystallisation from ethanol (Found: C, 63.3; H, 10.9. C₂₀H₄₀O₆ requires C, 63.8; H, 10.7%).

Dodeca-1,7-diyne.—Octa-1,7-diyne (106 g) in tetrahydrofuran (100 ml) was added during 1 h to lithium amide [from lithium (7 g)] in liquid ammonia (1 l). The suspension was stirred for 1 h, butyl bromide (137 g) was added, and the mixture was stirred overnight. Addition of water and distillation of the organic layer through a Fenske column (150 cm) gave dodeca-1,7-diyne (80 g), b.p. 94–96° at 0.7 mmHg, *n*_D²⁵ 1.4553 (Found: C, 88.9; H, 11.0. C₁₂H₁₈ requires C, 88.8; H, 11.2%).

Docos-5,11,17-triynoic Acid.—*NN*-Dimethylhex-5-ynamide⁵ (19.5 g) in tetrahydrofuran (75 ml) was added to lithium amide [from lithium (1.2 g)] in liquid ammonia (500 ml) and tetrahydrofuran (75 ml), and the mixture was stirred for 1 h. After addition of 4-chlorobutyl iodide (30.6 g) in tetrahydrofuran (50 ml), stirring was continued overnight. Addition of water, isolation with ether, and fractional distillation gave material, b.p. 162–171° at 1–1.5 mmHg. Some crystalline product slowly separated; this was collected and recrystallised from ethyl acetate–light petroleum (b.p. 60–80°) to give 10-chlorododec-5-ynamide, m.p. 93–94° (Found: C, 59.2; H, 7.9; Cl, 17.5; N, 7.2. C₁₀H₁₆ClNO requires C, 59.6; H, 8.0; Cl, 17.6; N, 6.9%), *v*_{max}. 3340 and 3180 cm⁻¹, *τ* 3.9br (2H) (CO·NH₂). The oily chloro-amide (26 g) and sodium iodide (35 g) in acetone (300 ml) were heated under reflux for 10 h. Filtration, evaporation, and addition of water gave an oil which was taken up in ether and washed with sodium thio-sulphate solution and water. Evaporation yielded crude iodo-amide. Dodeca-1,7-diyne (9.5 g) in tetrahydrofuran (100 ml) was added to sodamide [from sodium (1.29 g)] in liquid ammonia (500 ml) and the solution was stirred while the iodo-amide in tetrahydrofuran (100 ml) was added and for a further 36 h. Addition of water and isolation with ether gave an oil which was heated under reflux (nitrogen) with potassium hydroxide (11.5 g) in ethanol (450 ml) for 21 h. After removal of the ethanol (300 ml) by distillation, 2*N*-hydrochloric acid was added; isolation with ether

yielded an oil which was added to lithium methoxide solution [from lithium (1.8 g) and methanol (50 ml)]. The salt, which separated on cooling at 0°, was collected and stirred with ether and 2*N*-hydrochloric acid. Evaporation of the ether layer and crystallisation from light petroleum (b.p. 40–60°) gave product (4.05 g), m.p. 41–42°. Repeated recrystallisation yielded *docosa-5,11,17-trienoic acid*, m.p. 43–44° (Found: C, 80.2; H, 9.8. $C_{22}H_{32}O_2$ requires C, 80.4; H, 9.8%). The acid (107 mg) in ethanol (50 ml) was hydrogenated over palladium-charcoal (5%; 100 mg) until absorption ceased. Evaporation of the filtered solution and crystallisation from light petroleum (b.p. 60–80°) gave docosanoic acid, m.p. and mixed m.p. 78.5–79.5°.

cis,cis,cis-Docosa-5,11,17-trienoic Acid.—The acetylenic acid (431 mg) in ethanol (50 ml) was hydrogenated over Lindlar catalyst⁷ (394 mg) in the presence of quinoline (100 mg) (uptake 1.0 mol. equiv.). The filtered solution was evaporated and the residue, in ether, was washed with 2*N*-hydrochloric acid and water. Evaporation yielded the *trienoic acid* (419 mg) as an oil (Found: C, 79.1; H, 11.4. $C_{22}H_{38}O_2$ requires C, 79.0; H, 11.4%). This (68 mg) in ethyl acetate (5 ml) at –70° was treated with ozonised oxygen until the blue colour persisted. After addition of hydrogen peroxide (30%; 100 mg) in acetic acid (10 ml), the solution was evaporated and the residual acid was esterified with ethereal diazomethane. G.l.c. of the esters gave peaks corresponding to methyl pentanoate, dimethyl adipate, and dimethyl glutarate.

trans-Dodec-7-en-1-yne.—Dodeca-1,7-diyne (24 g) in ether (25 ml) was added dropwise to sodamide [from sodium (5.3 g)] in liquid ammonia (500 ml). The solution was stirred for 1.5 h, sodium (10.5 g) was added in small pieces during 30 min, and stirring was continued for 2 h. Ammonium chloride (9 g) was added and the solvent was allowed to evaporate. Addition of water, isolation with ether, and distillation gave *trans-dodec-7-en-1-yne* (16.9 g), b.p. 55° at 1 mmHg, n_D^{25} 1.4463 (Found: C, 87.4; H, 11.8. $C_{12}H_{20}$ requires C, 87.7; H, 12.3%), ν_{max} 970 (*trans*-CH:CH), and 2120 and 3315 cm^{-1} (C=CH). G.l.c. showed that the product was essentially one compound (95%).

Hexadeca-3,9-diyne-1-ol.—Tetrahydrofuran (100 ml) and but-3-yn-1-ol (20 g) were added successively to lithium amide [from lithium (2 g)] in liquid ammonia (300 ml). After 75 min, 1-iodododec-5-yne (18 g) in tetrahydrofuran (25 ml) was added dropwise to the stirred solution. When the ammonia had evaporated, water was added; isolation with ether and fractional distillation gave *hexadeca-3,9-diyne-1-ol* (7.5 g), b.p. 140–144° at 0.1 mmHg, f.p. 16° (thermometer in liquid) (Found: C, 81.2; H, 11.1. $C_{16}H_{26}O$ requires C, 82.0; H, 11.1%).

Hexadeca-3,9-diyneic Acid.—8*N*-Chromic acid¹² (1.2 ml) in sulphuric acid was added dropwise to a stirred solution of the diynol (1.07 g) in acetone (30 ml) and the mixture was stirred for 30 min and evaporated to small volume. After addition of water and extraction with ether, the organic layers were extracted with sodium hydrogen carbonate solution. Acidification and isolation with ether yielded *hexadeca-3,9-diyneic acid* (0.53 g), which crystallised from light petroleum (b.p. 40–60°) as the *hemihydrate*, m.p. 51.5–52.5° (Found: C, 74.9; H, 9.3. $C_{16}H_{24}O_2 \cdot 0.5H_2O$ requires C, 74.6; H, 9.8%).

cis,cis-Hexadeca-3,9-dienoic Acid.—The diynoic acid (375

mg) in methanol (30 ml) was hydrogenated over Lindlar catalyst (200 mg) (uptake 1.0 mol. equiv.). Filtration and distillation gave *cis,cis-hexadeca-3,9-dienoic acid*, b.p. 140° at 0.1 mmHg, also obtained as the *hemihydrate*, m.p. 20–22° [from light petroleum (b.p. 40–60°) at –20°] (Found: C, 73.4; H, 11.2. $C_{16}H_{28}O_2 \cdot 0.5H_2O$ requires C, 73.5; H, 11.2%). The product contained little, if any, conjugated material (ϵ 316 at 213 nm) but it did contain traces of *trans*-isomers (very weak band at 970 cm^{-1}).

Docosa-3,9,15-triyn-1-ol.—6-Chlorohex-1-yne (70 g) in tetrahydrofuran (250 ml) was added to a stirred solution of lithium amide [from lithium (4.2 g)] in liquid ammonia (1.5 l). After 1 h 1-iodododec-5-yne (117 g) in tetrahydrofuran (250 ml) was added gradually during 1 h and the mixture was left to evaporate overnight. Addition of water and isolation with ether gave crude chloro-diyne (70 g), b.p. 150–160° at 0.1 mmHg, which was heated under reflux with sodium iodide (112 g) in acetone (1 l) for 48 h. Filtration, evaporation, addition of water, and isolation with ether gave crude iodo-diyne. This (71 g) was added to the dilithio-derivative prepared from lithium (10.6 g) and but-3-yn-1-ol (53 g) in liquid ammonia (2 l) and tetrahydrofuran (250 ml). The mixture was stirred for 20 h and allowed to evaporate, and the residue was treated with water (500 ml). Isolation with ether gave a low-melting solid which was dissolved in light petroleum (b.p. 40–60°) and applied to a column of alumina. Elution and recrystallisation (same solvent) yielded *docosa-3,9,15-triyn-1-ol* (14.2 g), m.p. 35–36° (Found: C, 83.1; H, 10.6. $C_{22}H_{34}O$ requires C, 84.0; H, 10.9%). The acetylenic alcohol in ethanol was hydrogenated over palladised charcoal to give docosan-1-ol, m.p. 70–70.5° (from methanol) (lit.,¹³ 70.5–71.5°).

Docosa-3,9,15-triynoic Acid.—Docosa-3,9,15-triyn-1-ol (2.05 g) in AnalaR acetone (30 ml) was stirred and cooled at 0–5° while 8*N*-chromic acid¹² (1.73 ml) was added during 15 min. The mixture was stirred at 0° for 15 min and at room temperature for 1 h. Evaporation and addition of water gave an oil, which was dissolved in ether and extracted with sodium hydrogen carbonate solution. Acidification and isolation with ether yielded *docosa-3,9,15-triynoic acid* (0.49 g), m.p. 61.5–62° [from light petroleum (b.p. 40–60°)] (Found: C, 80.5; H, 9.9. $C_{22}H_{32}O_2$ requires C, 80.4; H, 9.8%).

cis,cis,cis-Docosa-3,9,15-trienoic Acid.—The triynoic acid (547 mg) in methanol (50 ml) was semihydrogenated over Lindlar catalyst (293 mg) in the presence of quinoline (538 mg). The filtered solution was evaporated and the residue in ether was washed with 2*N*-sulphuric acid and water. Distillation in a ten-stage fractionating molecular still gave *cis,cis,cis-docosa-3,9,15-trienoic acid* as an oil, b.p. 180° at 0.01 mmHg (Found: C, 78.7; H, 12.0. $C_{22}H_{38}O_2$ requires C, 79.0; H, 11.5%), ν_{max} 936 (*cis*-CH:CH) and 970 cm^{-1} (slight inflection; trace of *trans*-isomers). Little, if any conjugated material was present (ϵ 505 at 216 nm).

11-*Chloroundeca-1,7-diyne*.—Octa-1,7-diyne (121 g) was added to a stirred solution of lithium amide [from lithium (8 g)] in liquid ammonia (1 l), and after 45 min 3-chloropropyl iodide (178 g) was added gradually. After 48 h, water was added and isolation with ether and distillation gave 11-*chloroundeca-1,7-diyne* (69 g), 78–90° at 0.4–0.5 mmHg, n_D^{25} 1.4790 (Found: C, 72.6; H, 8.0; Cl, 19.3. $C_{11}H_{15}Cl$ requires C, 72.3; H, 8.3; Cl, 19.4%).

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

¹² A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemlin, *J. Chem. Soc.*, 1953, 2548.

Dodeca-5,11-diynonitrile.—The chloride (69 g) was added slowly to a refluxing solution of sodium iodide (113 g) in acetone (1 l) and the mixture was heated under reflux for 20 h. Addition of water and isolation with ether gave the crude iodide (92 g), which was heated under reflux with potassium cyanide (65 g) and methanol (1 l) for 7 h. The solution was evaporated and the residue treated with water; isolation with ether furnished *dodeca-5,11-diynonitrile* (49 g), b.p. 135–144° at 4 mmHg, n_D^{25} 1.4739 (Found: C, 83.1; H, 8.6; N, 8.1. $C_{12}H_{15}N$ requires C, 83.2; H, 8.7; N, 8.1%).

Dodeca-5,11-diynoic Acid.—The nitrile (47 g), potassium hydroxide (50 g), and water (500 ml) were heated under reflux for 15 h, and the cooled solution was washed with ether and acidified with concentrated hydrochloric acid. Isolation with ether yielded *dodeca-5,11-diynoic acid* (39 g), b.p. 118° at 0.1 mmHg, n_D^{25} 1.4805 (Found: C, 75.0; H, 8.5. $C_{12}H_{16}O_2$ requires C, 74.9; H, 8.4%).

Alkylation of Dilithio-derivative of Prop-2-yn-1-ol.—Prop-2-yn-1-ol (56 g) was added to a stirred solution of lithium amide [from lithium (14 g)] in liquid ammonia (1.1 l), and after 10 min pentyl bromide (151 g) was added and the solvent was then allowed to evaporate. After addition of water and concentrated hydrochloric acid, isolation with ether and distillation gave crude oct-2-yn-1-ol (76 g), b.p. 102–120° at 21 mmHg. Preparative g.l.c. yielded oct-2-yn-1-ol (93.3%), n_D^{25} 1.4527, and oct-2-ynyl pentyl ether (6.7%), n_D^{25} 1.4413 (Found: C, 79.6; H, 12.2. $C_{13}H_{24}O$ requires C, 79.5; H, 12.3%). Taylor and Strong¹¹ report

b.p. 76–78° at 2 mmHg, n_D^{25} 1.4550, for oct-2-yn-1-ol; treatment of the crude octynol with phosphorus tri-bromide¹¹ gave 1-bromo-oct-2-yne (57%).

Eicosa-5,11,14-triynoic Acid.—A Grignard reagent was prepared from ethyl bromide (48 g) and magnesium (9.72 g) in tetrahydrofuran (140 ml) under nitrogen, and the solution was stirred at 0–5° while dodeca-5,11-diynoic acid (38.2 g) in tetrahydrofuran (100 ml) was added during 1 h. After a further 2 h, copper(I) cyanide (1 g) and then 1-bromo-oct-2-yne (18.9 g) in tetrahydrofuran (50 ml) were added, and the mixture was stirred and heated under reflux for 20 h and then poured on ice. Concentrated hydrochloric acid (100 ml) was added and the mixture was extracted thrice with ether. The extracts were washed with water, ethylenediaminetetra-acetic acid solution, and water, dried, and evaporated. Dodecadiynoic acid was removed by distillation at 0.2 mmHg (bath at 200°) and the residue was distilled in a fractionating molecular still. *Eicosa-5,11,14-triynoic acid* had m.p. 45–46° (from methanol at –20°) (Found: C, 79.6; H, 9.5. $C_{20}H_{28}O_2$ requires C, 80.0; H, 9.4%). Attempted semihydrogenation over Lindlar catalyst did not proceed satisfactorily, either with or without quinoline.

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