835. *Syntheses of Long-chain Acids. Part IV.*[1] *Synthesis of the Octadeca-*5,12-*dienoic Acids.*

By D. E. Ames and P. J. Islip.

Condensation of *cis*-dodec-6-enyl bromide with *NN*-dimethylhex-5-ynamide in presence of sodamide gives *cis-NN*-dimethyloctadec-12-en-5-ynamide, from which the four geometrical isomers of octadeca-5,12-dienoic acid have been prepared.

The use of dimethylamide as a protecting group for ω-acetylenic acids during alkylation of the acetylenic group has been described previously,[2] and linoleic acid was synthesised by this procedure.[3] The method has now been extended by synthesis of an acid with two isolated olefinic groups.

Condensation of 2-5′-chloropentyloxytetrahydropyran (I; X = Cl) with hept-1-ynylsodium gave only a 17% yield of 2-dodec-6′-ynyloxytetrahydropyran (II). The chloroether was, therefore, converted into the iodide but this could not be purified owing to persistent decomposition during distillation (cf. the instability of tetrahydro-2-7′-iodoheptyloxypyran reported by Barker, Foster, and Lamb [4]). The crude product did react

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[1] Part III, Ames and Covell, *J.*, 1963, 775.

[2] Ames and Islip, *J.*, 1961, 351.

[3] Ames and Islip, *J.*, 1961, 4409.

[4] Barker, Foster, and Lamb, *Tetrahedron*, 1962, **18**, 177.

with heptynylsodium to give compound (II) but the yields were very variable (0—56%). 5-Bromopentanol, required for the preparation of the bromide (I; X = Br), was conveniently prepared by the action of acetyl bromide on tetrahydropyran in presence of zinc bromide[5] (to give 5-bromopentyl acetate), followed by mild alkaline hydrolysis. This bromo-ether (I; X = Br) was then condensed with the heptynylsodium, and the acetylenic ether (II) was obtained in 53% yield. Hydrolysis and catalytic semihydrogenation in the presence of palladised barium sulphate and quinoline[6] afforded *cis*-dodec-6-en-1-ol (III; X = OH) and thence the bromide (III; X = Br).

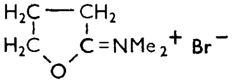
$$\text{(I) } \mathrm{Me{\cdot}[CH_2]_4{\cdot}C{\equiv}CNa + X{\cdot}[CH_2]_5{\cdot}O{\cdot}C_5H_9O} \longrightarrow \mathrm{Me{\cdot}[CH_2]_4{\cdot}C{\equiv}C{\cdot}[CH_2]_5{\cdot}O{\cdot}C_5H_9O} \text{ (II)}$$

$$\text{(III) } \mathrm{Me{\cdot}[CH_2]_4{\cdot}CH\overset{cis}{=\!=}CH{\cdot}[CH_2]_5{\cdot}X}$$

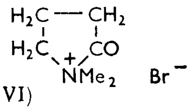
The synthesis of *NN*-dimethylhex-5-ynamide from γ-bromobutyric acid[7] was examined. γ-Bromobutyryl chloride with two mol. of dimethylamine gave a crystalline but extremely deliquescent product, $C_6H_{12}BrNO$, corresponding to the expected amide (IV). This failed to react with acetylenylsodium in liquid ammonia. It gave an acidic solution containing ionic bromide and potentiometric titration with alkali showed pK_a 10·5. Rearrangements of *N*-monosubstituted γ-bromobutyramides have been observed by Stirling.[8] The compound is tentatively assigned structure (V) (rather than VI) since the strongest band in the infrared spectrum is at 1699 cm.$^{-1}$ corresponding to the $-{}^{+}N{=}C\!<$ system studied by Leonard and Gash.[9]

$$\mathrm{Br{\cdot}[CH_2]_3{\cdot}CO{\cdot}NMe_2}$$

(IV)



(V)



(VI)

Hex-5-ynoic acid was therefore prepared by the method of Eglinton and Whiting[10] and converted into the dimethylamide (VII) which condensed with *cis*-dodec-6-enyl bromide in the presence of sodamide or lithamide to give *cis*-*NN*-dimethyloctadec-12-en-5-ynamide (VIII; R = NMe_2) in 46% yield. Alkaline hydrolysis gave the acid (VIII; R = OH), whose ultraviolet absorption spectrum showed that no rearrangement to conjugated materials had occurred (cf. the stability of *cis*,*cis*-docosa-5,13-dienoic acid to alkali[11]). Semihydrogenation then gave *cis*,*cis*-octadeca-5,12-dienoic acid (IX) containing about 5% of *trans*-isomers (estimate based on the *trans*-HC=CH band at 965 cm.$^{-1}$).

$$\text{(VII) } \mathrm{HC{\equiv}C{\cdot}[CH_2]_3{\cdot}CO{\cdot}NMe_2} \qquad \mathrm{Me{\cdot}[CH_2]_4{\cdot}CH\underset{cis}{=}CH{\cdot}[CH_2]_5{\cdot}C{\equiv}C{\cdot}[CH_2]_3{\cdot}COR} \text{ (VIII)}$$

$$\text{(IX) } \mathrm{Me{\cdot}[CH_2]_4{\cdot}CH{=}CH{\cdot}[CH_2]_5{\cdot}CH{=}CH{\cdot}[CH_2]_3{\cdot}CO_2H}$$

erythro-12,13-Dihydroxyoctadec-5-ynoic acid was prepared from this acid (VIII; R = OH) by reaction with iodine and silver acetate in wet acetic acid[12] and was semihydrogenated to *erythro*-12,13-dihydroxy-*cis*-octadec-5-enoic acid (Xa). Addition of bromine to the double bond gave an oily mixture of isomers which was converted into the tetrabromo-acid with hydrogen bromide in acetic–sulphuric acid, esterified, and debrominated[13] to give ethyl *cis*,*cis*-octadeca-5,12-dienoate. The presence of about 5—10%

$$\text{(X) } \mathrm{Me{\cdot}[CH_2]_4{\cdot}CH(OH){\cdot}CH(OH){\cdot}[CH_2]_5{\cdot}CH{=}CH{\cdot}[CH_2]_3{\cdot}CO_2H} \text{ (a) } \textit{erythro}, \text{ (b) } \textit{threo}.$$

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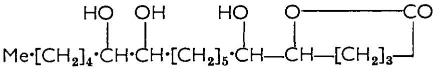
[5] Parcell, U.S.P. 2,922,788.
[6] Cram and Allinger, *J. Amer. Chem. Soc.*, 1956, **78**, 2522.
[7] Avison and Morrison, *J.*, 1950, 1471.
[8] Stirling, *J.*, 1960, 255.
[9] Leonard and Gash, *J. Amer. Chem. Soc.*, 1954, **76**, 2781.
[10] Eglinton and Whiting, *J.*, 1950, 3650; 1953, 3052.
[11] Bagby, Smith, Miwar, Lohmar, and Wolff, *J. Org. Chem.*, 1961, **26**, 1261.
[12] Gunstone and Morris, *J.*, 1957, 487.
[13] Ames and Bowman, *J.*, 1951, 1079.

of *trans*-isomers was shown by the adsorption band at 971 cm.$^{-1}$; this result is similar to that obtained in the preparation of mono-olefinic esters by debromination.[2]

threo-12,13-Dihydroxyoctadec-5-ynoic acid was prepared by hydroxylation of enynoic acid (VIII; R = OH) with performic acid, followed by hydrolysis.[14] An attempt to reduce this acid to the *trans*-olefinic acid with sodium in liquid ammonia was unsuccessful. It was therefore semihydrogenated to give *threo*-12,13-dihydroxy-*cis*-octadec-5-enoic acid (Xb). Further hydroxylation with performic acid gave a mixture of isomers of the γ-lactone (XI) of *threo-threo*-5,6,12,13-tetrahydroxyoctadecanoic acid [$\nu_{\max.}$ 1734 cm.$^{-1}$ (C=O)]. Conversion into the tetrabromo-acid and ester followed by debromination and hydrolysis gave *trans,trans*-octadeca-5,12-dienoic acid.

(XI) 

$$\mathrm{Me{\cdot}[CH_2]_4{\cdot}\overset{HO}{CH}{\cdot}\overset{OH}{CH}{\cdot}[CH_2]_5{\cdot}\overset{HO}{CH}—\overset{O—————CO}{CH—[CH_2]_3—}}$$

Similarly, *erythro-cis*-12,13-dihydroxyoctadec-5-enoic acid (Xa) was hydroxylated with peracid and converted into the tetrabromo-acid and thence into 5-*trans*-12-*cis*-octadeca-5,12-dienoic acid. The isomeric 5-*cis*-12-*trans*-dienoic acid was obtained from *threo-cis*-12,13-dihydroxyoctadec-5-enoic acid (Xb) by addition of bromine and then conversion through the tetrabromo-acid into the dienoic acid.

EXPERIMENTAL

5-*Chloropentan*-1-*ol*.—5-Chloropentyl acetate [15] (418 g.) was shaken with ethanol (1 l.) and 2N-sodium hydroxide (1275 c.c.) until the mixture became homogeneous and left at room temperature for 2 days.[16] Ethanol was removed by distillation under reduced pressure and the chloropentanol (266 g., 86%) was isolated with benzene and distilled through a Vigreux column. It had b. p. 57°/0·7 mm., n_D^{20} 1·4520. McElvain and Carney [17] report b. p. 103°/8 mm., n_D^{20} 1·4518.

Similarly 5-bromopentyl acetate [5] gave 5-bromopentan-1-ol (72%), b. p. 75—76% 0·5 mm.; n_D^{21} 1·4839.

2-5′-*Chloropentyloxytetrahydropyran*.—Dihydropyran (187 g.) was added to 5-chloropentan-1-ol (266 g.) containing concentrated hydrochloric acid [18] (0·5 c.c.) at <20°. After 3 hr. the mixture was washed with 2N-sodium hydroxide and water, dried (K_2CO_3), and distilled, to give the *ether* (351 g.), b. p. 86—87°/0·7 mm., n_D^{20} 1·4607 (Found: C, 58·4; H, 9·4; Cl, 17·3. $C_{10}H_{19}ClO_2$ requires C, 58·1; H, 9·2; Cl, 17·2%). 2-5′-*Bromopentyloxytetrahydropyran*, prepared similarly in 68% yield, had b. p. 84°/0·4 mm., n_D^{20} 1·4770 (Found: C, 48·2; H, 7·6; Br, 31·5. $C_{10}H_{19}BrO_2$ requires C, 47·8; H, 7·6; Br, 31·9%).

Tetrahydro-2-5′-*iodopentyloxypyran*.—The chloro-ether (206 g.) and sodium iodide (225 g.) in acetone (500 c.c.) were refluxed for 5 hr. The filtered solution was poured into water, the product being isolated with light petroleum (b. p. 40—60°). This material was used for condensations but a small portion was distilled to give slightly impure ether as a red oil, b. p. 90—96°/1 mm. (Found: C, 39·3; H, 6·3; I, 41·3. Calc. for $C_{10}H_{19}IO_2$: C, 40·3; H, 6·4; I, 42·6%).

2-*Dodec*-6′-*ynyloxytetrahydropyran*.—Hept-1-yne (23·2 g.) in tetrahydrofuran (150 c.c.) was added to sodamide (9·5 g.), stirred in liquid ammonia (*ca.* 300 c.c.). After 1 hr., the bromo-ether (72·8 g.) in tetrahydrofuran (50 c.c.) was added; the mixture was stirred under reflux for 5 hr. and left to evaporate. Addition of water, isolation with ether, and distillation gave the *ether* (34·3 g.), b. p. 146—148°/0·9 mm., n_D^{20} 1·4649 (Found: C, 76·2; H, 11·5. $C_{17}H_{30}O_2$ requires C, 76·6; H, 11·4%).

Dodec-6-*yn*-1-*ol*.—Ethanol was added to a mixture of the preceding ether (34·3 g.) and 2N-hydrochloric acid (200 c.c.) until it became homogeneous. The solution was left at room

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[14] Swern, Billen, Findlay, and Scanlan, *J. Amer. Chem. Soc.*, 1945, **67**, 1786.

[15] Synerholm, *J. Amer. Chem. Soc.*, 1947, **69**, 2581.

[16] Grey, Ph.D. Thesis, London, 1957.

[17] McElvain and Carney, *J. Amer. Chem. Soc.*, 1946, **68**, 2592.

[18] Cf. Parham and Anderson, *J. Amer. Chem. Soc.*, 1948, **70**, 4187.

temperature overnight, then poured into water; *dodec*-6-*yn*-1-*ol* (19·3 g.), isolated with ethyl acetate, had b. p. 100—101°/0·5 mm., n_{D}^{21} 1·4600 (Found: C, 78·6; H, 12·1. $C_{12}H_{22}O$ requires C, 79·1; H, 12·2%). The 1-*naphthylurethane* formed needles, m. p. 71—72°, from light petroleum (b. p. 80—100°) (Found: C, 77·9; H, 8·2; N, 4·1. $C_{23}H_{29}NO_2$ requires C, 78·6; H, 8·3; N, 4·0%).

cis-*Dodec*-6-*en*-1-*ol*.—The preceding acetylenic alcohol (36 g.) in methanol (250 c.c.) was hydrogenated over 5% palladised barium sulphate (1·0 g.) with quinoline (1·0 g.),[6] a large decrease in the rate occurring when 1 mol. of hydrogen had been taken up. Distillation of the filtered solution gave the olefinic *alcohol* (33 g.), b. p. 90—92°/0·4 mm., n_{D}^{20} 1·4570 (Found: C, 78·1; H, 13·0. $C_{12}H_{24}O$ requires C, 78·2; H, 13·1%).

cis-*Dodec*-6-*enyl Bromide*.—Phosphorus tribromide (14·1 c.c.) in ether (30 c.c.) was added to an ice-cooled solution of the alcohol (34·9 g.) in ether (200 c.c.) and pyridine (0·2 c.c.). The solution was stirred for 1 hr., left overnight, and poured into water. The bromide (19·2 g.), isolated with ether, had b. p. 82—83°/0·4 mm., n_{D}^{20} 1·4711 (Found: C, 58·7; H, 9·4; Br, 31·9. $C_{12}H_{23}Br$ requires C, 58·3; H, 9·3; Br, 32·4%). cis-*Dodec*-6-*enylisothiouronium picrate* formed yellow plates, m. p. 101—102°, from aqueous ethanol (Found: C, 48·5; H, 6·5; N, 15·0. $C_{19}H_{29}N_5O_7S$ requires C, 48·4; H, 6·2; N, 14·9%).

Reaction of γ-Bromobutyryl Chloride with Dimethylamine.—A solution of the acid chloride [17] (74 g.) in ether (400 c.c.) was stirred at −5° while dimethylamine (59 c.c.) was passed in. The mixture was stirred at −5° for 1 hr., water (80 c.c.) was added, and the separated organic layer was washed with saturated sodium hydrogen carbonate solution (80 c.c.) and water (80 c.c.), each aqueous layer being extracted with ether. The dried (Na_2SO_4) solution was distilled, to give (?) *tetrahydro*-2-*methyliminofuran methobromide* (V), b. p. 92—94°/0·7 mm., very deliquescent cubes, m. p. 55—60° (sealed capillary) (Found: C, 37·2; H, 6·3; Br, 40·7; Br^-, 40·1. $C_6H_{12}BrNO$ requires C, 37·1; H, 6·2; Br, 41·2%). Attempts to recrystallise the compound failed.

NN-*Dimethylhex*-5-*ynamide*.—Hex-5-ynoic acid [10] (25 g.) was treated with thionyl chloride (53 c.c.) at 30° for 1 hr., and then at 100° for 2 hr. After removal of the excess of thionyl chloride, the residue was stirred at −5° to 0° with ether (200 c.c.) while dimethylamine (22 g.) was passed in. Isolated as in the preceding case, the *amide* (22 g.) had b. p. 75°/0·5 mm., n_{D}^{21} 1·4739 (Found: C, 69·3; H, 9·3; N, 10·1. $C_8H_{13}NO$ requires C, 69·0; H, 9·4; N, 10·1%).

cis-NN-*Dimethyloctadec*-12-*en*-5-*ynamide*.—*NN*-Dimethylhex-5-ynamide (9·0 g.) in tetrahydrofuran (25 c.c.) was added to a stirred suspension of sodamide (2·5 g.) in liquid ammonia (*ca*. 150 c.c.). After 1 hr., *cis*-dodec-6-enyl bromide (19·2 g.) in tetrahydrofuran (25 c.c.) was added and the mixture was stirred under reflux for 7 hr. When the solvent had evaporated, water was added and the *product* was isolated with ether. It (8·8 g.) had b. p. 178—180°/0·5 mm., n_{D}^{21} 1·4789 (Found: C, 79·0; H, 11·4; N, 4·4. $C_{20}H_{35}NO$ requires C, 78·6; H, 11·6; N, 4·6%).

cis-*Octadec*-12-*en*-5-*ynoic Acid*.—Solutions of the amide (2·0 g.) in 2-methoxyethanol (24 c.c.) and of potassium hydroxide (2·4 g.) in water (2·4 c.c.) were mixed, refluxed (bath 170°) for 6 hr., and poured into ice and sulphuric acid. The *acid* (1·4 g.), isolated with light petroleum (b. p. 40—60°), had b. p. 170—172°/0·3 mm., f. p. 12—13°, n_{D}^{21} 1·4719 (Found: C, 77·5; H, 11·1. $C_{18}H_{30}O_2$ requires C, 77·7; H, 10·9%). Hydrogenation of a portion over palladised charcoal gave stearic acid, m. p. and mixed m. p. 68—69°.

cis,cis-*Octadeca*-5,12-*dienoic Acid*.—The last-mentioned acid (1·04 g.) in methanol (75 c.c.) was hydrogenated over 5% palladised barium sulphate (0·1 g.) in the presence of quinoline (0·1 g.).[6] The rate of absorption fell sharply when 1·01 mol. of hydrogen had been taken up, and hydrogenation was then interrupted. After evaporation of the filtered solution, the residue was taken up in ether, washed with 2N-hydrochloric acid and water, dried (Na_2SO_4), and distilled. The *dienoic acid* (0·70 g.) had b. p. 172—174°/0·4 mm., n_{D}^{21} 1·4668, m. p. −30° to −28° (sealed capillary) (Found: C, 77·4; H, 11·8%; I value, 176·7. $C_{18}H_{32}O_2$ requires C, 77·1; H, 11·5%; I value, 180·9).

erythro-12,13-*Dihydroxyoctadec*-5-*ynoic Acid*.—*cis*-Octadec-12-en-5-ynoic acid (2·96 g.) in acetic acid (69 c.c.) was shaken with iodine (2·7 g.) and silver acetate (3·9 g.) until the iodine had dissolved.[12] Acetic acid (10·7 c.c.) containing water (0·21 g.) was added and the mixture was refluxed for 1 hr. Solid was collected and washed with acetic acid and the combined filtrates were evaporated; the residue in ether was washed with 2N-hydrochloric acid and evaporated, and this residue was refluxed for 2 hr. with ethanol (48 c.c.) and 2N-sodium hydroxide (16 c.c.) and then poured into 2N-hydrochloric acid. The *dihydroxy-acid* (0·90 g.), isolated with ethyl acetate, separated from methanol as prisms, m. p. 97—99° (Found: C, 69·6; H, 10·2. $C_{18}H_{32}O_4$ requires C, 69·2; H, 10·3%).

erythro-cis-12,13-*Dihydroxyoctadec-5-enoic Acid.*—The acetylenic acid (0·82 g.) was semihydrogenated, as in the previous example, to give the *acid*, prisms, m. p. 80—82° (from methanol) (Found: C, 69·1; H, 10·6. $C_{18}H_{34}O_4$ requires C, 68·9; H, 10·9%).

Ethyl cis,cis-*Octadeca-5,12-dienoate.*—0·094M-Solution of bromine in chloroform (10·2 c.c.) was added to the olefinic acid (0·3 g.) in chloroform (95 c.c.) at 0°. The solution was stirred at 0° for 30 min., washed with water, dried (Na_2SO_4), and evaporated. A solution (5·0 c.c.; *d* 1·3) of hydrogen bromide in acetic acid, and concentrated sulphuric acid (1·25 c.c.), were added. Next day, the solution was heated to 100° during 1 hr. and kept at 100° for 7 hr., more hydrogen bromide solution (2·5 c.c.) being added after 3 hr. After addition of water, the bromo-acid was isolated with ether and azeotropically esterified, and the ester was debrominated [13] with activated zinc (15 g.) in ethanol (75 c.c.). Filtration, addition of 2N-sulphuric acid, and isolation with light petroleum (b. p. 40—60°) gave *ethyl* cis,cis-*octadeca-5,12-dienoate* (50 mg.), b. p. 200°(bath)/0·2 mm., n_D^{20} 1·4593 (Found: C, 77·6; H, 11·4. $C_{20}H_{36}O_2$ requires C, 77·9; H, 11·8%).

threo-12,13-*Dihydroxyoctadec-5-ynoic Acid.*—*cis*-Octadec-12-en-5-ynoic acid (2·78 g.) was warmed at 40° with 98% formic acid (8·5 c.c.) and 30% hydrogen peroxide (1·2 c.c.) for 1 hr. Next day, the excess of formic acid was removed under reduced pressure and the residue was refluxed for 1 hr. with ethanol (15 c.c.) and 5N-sodium hydroxide (20 c.c.). Ethanol was removed by distillation and the solution poured into ice and 2N-hydrochloric acid. threo-12,13-*Dihydroxyoctadec-5-ynoic acid* (1·8 g.), isolated with ethyl acetate, formed needles, m. p. 71—73°, from ethyl acetate (Found: C, 68·8; H, 10·7. $C_{18}H_{32}O_4$ requires C, 69·2; H, 10·3%).

A portion, hydrogenated in ethanol with 5% palladised charcoal, gave *threo*-12,13-dihydroxyoctadecanoic acid, m. p. 95—96° (Found: C, 68·1; H, 11·4. Calc. for $C_{18}H_{36}O_4$: C, 68·3; H, 11·5%). Huber [19] gives m. p. 97—98·5°.

threo-cis-12,13-*Dihydroxyoctadec-5-enoic Acid.*—The preceding acetylenic acid (1·4 g.) was semihydrogenated in the same manner as its isomer, to give the olefinic *acid* (1·1 g.), prisms, m. p. 41—43° [from ether–light petroleum (b. p. 40—60°)] (Found: C, 69·0; H, 10·9%).

trans,trans-*Octadeca-5,12-dienoic Acid.*—The last-mentioned olefinic acid (1·07 g.) was treated with 98% formic acid (5·8 c.c.) and 30% hydrogen peroxide (0·6 c.c.) and kept at 40° for 1 hr. Next day, the solution was evaporated and the residue refluxed for 2 hr. with ethanol (15 c.c.) and 5N-sodium hydroxide (20 c.c.) and poured into 2N-hydrochloric acid. The product was collected but could not be purified by recrystallisation; it appeared to be a mixture of isomers of the γ-lactone (XI) ($\nu_{max.}$ 1734 cm.$^{-1}$ in CCl_4, C=O). This product was treated with hydrogen bromide in acetic and sulphuric acid, and the resulting tetrabromo-acid was esterified and debrominated in the manner described. *Ethyl* trans,trans-*octadeca-5,12-dienoate* (0·42 g.) had b. p. 153—154°/0·4 mm., n_D^{21} 1·4568 (Found: C, 77·9; H, 11·6%). Hydrolysis of the ester (0·38 g.) by refluxing it for 1 hr. with 2N-sodium hydroxide (5 c.c.) and ethanol (10 c.c.) and pouring the mixture into dilute acid gave the *dienoic acid* (0·18 g.), b. p. 175—176°/0·4 mm., n_D^{20} 1·4671, m. p. 16—19° (Found: C, 77·0; H, 11·4%).

Ethyl 5-trans-12-cis-*Octadeca-5,12-dienoate.*—*erythro-cis*-12,13-Dihydroxyoctadec-5-enoic acid (0·43 g.) was hydroxylated by treatment with formic acid and hydrogen peroxide in the manner described. The crude tetrahydroxy-acid was converted into the tetrabromo-acid, esterified, and debrominated similarly. The *ester* had b. p. 150—152°/0·2 mm., n_D^{20} 1·4590 (Found: C, 77·9; H, 11·6%).

5-trans-12-cis-*Octadeca-5,12-dienoic Acid.*—Alkaline hydrolysis of the ester, as in the case of the *trans,trans*-isomer, gave the *acid*, b. p. 168—170°/0·3 mm., n_D^{20} 1·4684, m. p. -9° to -12° (Found: C, 76·9; H, 11·3%).

Ethyl 5-cis-12-trans-*octadeca-5,12-dienoate.*—*threo-cis*-12,13-Dihydroxyoctadec-5-enoic acid (1·4 g.) in chloroform (50 c.c.) was treated with a 0·184M-chloroformic solution (25 c.c.) of bromine at 0°. The solution was stirred at 0° for 10 min., washed with water, dried (Na_2SO_4), and evaporated. The crude dibromodihydroxy-acid (1·73 g.) was treated with a solution (10 c.c.; *d* 1·3) of hydrogen bromide in acetic acid and with concentrated sulphuric acid (2·5 c.c.), and the product was esterified and debrominated by the standard procedure, to give the unsaturated *ester* (0·30 g.), b. p. 148—151°/0·2 mm., n_D^{20} 1·4577 (Found: C, 77·6; H, 11·4%).

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[19] Huber, *J. Amer. Chem. Soc.*, 1951, **73**, 2730.

5-cis-12-trans-*Octadeca*-5,12-*dienoic Acid.*—Alkaline hydrolysis of the ester as in the previous examples gave the *acid*, b. p. 170°/0·3 mm., n_D^{20} 1·4677, m. p. $-4°$ to $-2°$ (Found: C, 77·3; H, 11·5%).

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