1121. *Syntheses of Long-chain Acids. Part V.*[1] *Synthesis of Some ω-Hydroxy-acetylenic Acids.*

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The dilithio-derivative of prop-2-yn-1-ol in liquid ammonia–tetrahydrofuran condenses with undecyl and tridecyl bromide to give the corresponding alk-2-yn-1-ol in high yield. Conversion into the bromide and malonation synthesis yields hexa- and octa-dec-4-ynoic acid and thence the *cis*-olefinic acids. Prop-2-yn-1-ol, but-3-yn-1-ol, and pent-4-yn-1-ol similarly condense with ω-bromo-acids to give ω-hydroxy-alkynoic acids in good yields. Reduction to the ω-hydroxy-alkanoic acids provides a route for chain-extension of ω-hydroxy-acids by three, four, or five carbon atoms.

ACETYLENIC alcohols have generally been prepared by elimination reactions [2] or by condensation of a metal derivative of an alkyne with an aldehyde, a ketone, or an epoxide.[3] Butenandt and Hecker [4] described the alkylation of hept-3-en-1-yne with the tetrahydropyranyl ether of 9-bromononan-1-ol to give, after removal of the protecting group, hexadec-12-en-10-yn-1-ol. The successful alkylation of lithio- and sodio-alkynes with ω-bromo-acids [5] led us to examine the reaction of unprotected ω-halogeno-alcohols. It was found that 3-bromopropan-1-ol with a large excess of lithio-octyne gave undec-4-yn-1-ol in 74% yield; similarly, 6-bromohexan-1-ol with lithioheptyne gave tridec-7-yn-1-ol in 70% yield.

The direct alkylation of acetylenic alcohols was next examined. Condensation of 3-methylpent-1-yn-3-ol (I; R = H) with ethyl bromide in presence of sodium in liquid ammonia was described by Shimo and Ando,[6] who obtained 3-methylhept-3-yn-3-ol (II) in good yield, but when ferric nitrate was also present 3-ethoxy-3-methylpent-1-yne (I; R = Et) was isolated. In the present work, prop-2-yn-1-ol was treated with two molecular proportions of lithamide in liquid ammonia to form the dilithio-complex (III; *n* = 1).

$\mathrm{HC{\vdots}C{\cdot}C(OR)Me{\cdot}Et}$	$\mathrm{Et{\cdot}C{\vdots}C{\cdot}C(OH)Me{\cdot}Et}$	$\mathrm{LiC{\vdots}C{\cdot}[CH_2]_n{\cdot}OLi}$	$\mathrm{RC{\vdots}C{\cdot}[CH_2]_n{\cdot}OH}$
(I)	(II)	(III)	(IV)

Subsequent addition of undecyl bromide gave the *C*-alkylation product, tetradec-2-yn-1-ol (IV; R = $n\text{-}C_{11}H_{23}$, n = 1) in 87% yield. The structure of the product was shown by the absence of the ethynyl infrared absorption band and by the reactions described below. Alk-2-yn-1-ols have usually been prepared by reaction of formaldehyde with a metallic derivative of an alkyne [3] but the present method offers an efficient alternative process.

Tetradec-2-yn-1-ol was catalytically semihydrogenated, according to the procedure of Cram and Allinger,[7] to give *cis*-tetradec-2-en-1-ol which, on treatment with performic acid followed by hydrolysis, yielded tetradecane-1,2,3-triol. The acetylenic alcohol was also converted into the bromide and, by malonation, hydrolysis, and decarboxylation, into hexadec-4-ynoic acid (V; R = $n\text{-}C_{11}H_{23}$). Catalytic hydrogenation gave palmitic acid, whilst semihydrogenation [7] afforded *cis*-hexadec-4-enoic acid, characterised by oxidation with performic acid and hydrolysis to yield the γ-lactone (VI; R = $n\text{-}C_{11}H_{23}$) of *threo*-4,5-dihydroxyhexadecanoic acid.

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[1] Part IV, Ames and Islip, *J.*, 1963, 4363.

[2] Eglinton, Jones, and Whiting, *J.*, 1952, 2873; Crombie, Harper, Newman, Thompson, and Smith, *J.*, 1956, 126.

[3] Danehy, Vogt, and Nieuwland, *J. Amer. Chem. Soc.*, 1934, **56**, 2790; Henne and Greenlee, *ibid.*, 1945, **67**, 484.

[4] Butenandt and Hecker, *Angew. Chem.*, 1961, **73**, 305.

[5] Ames and Covell, *J.*, 1963, 775.

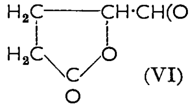
[6] Shimo and Ando, *Sci. Reports Res. Inst., Tôhoku Univ.*, 1955, Ser. A, **7**, 595 (*Chem. Abs.*, 1956, **50**, 12,807).

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

This convenient synthesis of *cis*-alk-4-enoic acids was further exemplified by condensation of tridecyl bromide with the dilithio-derivative of prop-2-yn-1-ol to give hexadec-2-yn-1-ol in 92% yield. Malonation of the corresponding bromide, followed by hydrolysis and decarboxylation, gave octadec-4-ynoic acid (V; R = n-$C_{13}H_{27}$), the overall yield from tridecyl bromide being 52%. *cis*-Octadec-4-enoic acid was obtained by catalytic semihydrogenation and likewise converted into the lactone (VI; R = n-$C_{13}H_{27}$). Treatment with hydrogen bromide in acetic–sulphuric acid gave *erythro*-4,5-dibromo-octadecanoic acid from which *trans*-octadec-4-enoic acid was obtained by debromination with zinc.[8]

$RC{:}C\cdot[CH_2]_2\cdot CO_2H$

(V)



(VI)

$HO\cdot[CH_2]_n\cdot C{:}C\cdot[CH_2]_m\cdot CO_2H$

VII)

The condensation of ω-bromo-acids with the dilithio-derivative of prop-2-yn-1-ol also proceeded smoothly to give the ω-hydroxy-alkynoic acids (VII) in good yields (see Table). An acid of this type, 12-hydroxydodec-10-enoic acid (VII; *m* = 8, *n* = 1), had been prepared [9] by condensation of an alkaline solution of undec-10-ynoic acid with formaldehyde in the presence of cuprous oxide. 14-Hydroxytetradec-12-ynoic acid, obtained in 66% yield from 11-bromoundecanoic acid by the present method, was converted into *cis*-14-hydroxytetradec-12-enoic acid by catalytic semihydrogenation; [7] this, on treatment with performic acid, followed by hydrolysis, gave *threo*-12,13,14-trihydroxytetradecanoic acid. Attempts to reduce these acetylenic hydroxy-acids to the corresponding saturated acids by catalytic hydrogenation led to extensive hydrogenolysis of the hydroxyl group, but the ω-hydroxy-alkanoic acids were obtained by addition of bromine to the *cis*-olefinic acid followed by hydrogenation in the presence of a base.

Similar condensations of the dilithio-derivatives of but-3-yn-1-ol and pent-4-yn-1-ol with ω-bromo-acids also gave good yields of the corresponding ω-hydroxy-alkynoic acids (VII; *n* = 2 and 3, respectively) (see Table). Several *cis*-hydroxyalkenoic acids were prepared by catalytic semihydrogenation of the acetylenic compounds and, in both series, hydrogenation of the acetylenes over palladised charcoal gave the ω-hydroxy-alkanoic acid. These reactions thus provide an efficient sequence for the chain-extension of ω-hydroxy-acids (through the ω-bromo-acids) by three, four, or five carbon atoms.

Hydroxy-acetylenic acids.

	(VII)		Yield		Found (%)			Required (%)	
Acid	*m*	*n*	(%)	M. p.	C	H	Formula	C	H
10-Hydroxydec-8-ynoic	6	1	59	60—61·5° [a]	65·2	8·8	$C_{10}H_{16}O_3$	65·2	8·8
11-Hydroxyundec-9-ynoic ...	7	1	76	56·5—57 [a, b]	66·9	9·1	$C_{11}H_{18}O_3$	66·6	9·2
14-Hydroxytetradec-12-ynoic	10	1	66	82—83 [a, c]	69·8	10·2	$C_{14}H_{24}O_3$	70·0	10·1
10-Hydroxydec-7-ynoic	5	2	52	45—45·5 [a, d]	65·3	9·0			
12-Hydroxydodec-9-ynoic ...	7	2	53	60—61 [e]	68·1	9·4	$C_{12}H_{20}O_3$	67·9	9·5
15-Hydroxypentadec-12-ynoic	10	2	62	74—75 [f]	70·3	10·0	$C_{15}H_{26}O_3$	70·8	10·3
13-Hydroxytridec-9-ynoic ...	7	3	51	54—55 [g]	68·9	9·9	$C_{13}H_{22}O_3$	69·0	9·8
16-Hydroxyhexadec-12-ynoic	10	3	54	63—64 [e]	71·3	10·4	$C_{16}H_{28}O_3$	71·6	10·5

[a] From ethyl acetate. [b] B. p. 158—164°/0·3 mm. [c] B. p. 158—160°/0·1 mm. [d] p-*Phenylphenacyl ester*, m. p. 70—71° (from ethyl acetate) (Found: C, 76·0; H, 6·8. $C_{24}H_{26}O_4$ requires C, 76·2; H, 6·9%). [e] From methanol. [f] From ethyl acetate–light petroleum (b. p. 60—80°). [g] From aqueous methanol.

EXPERIMENTAL

Undec-4-yn-1-ol.—Octyne (28 g.) was added to lithamide (from lithium, 1·75 g.) in liquid ammonia (*ca.* 400 c.c.) and the mixture was stirred for 1 hr. After addition of 3-bromopropan-1-ol (7·0 g.) in tetrahydrofuran (200 c.c.), the suspension was refluxed for 8 hr. and allowed to

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[8] Boughton, Bowman, and Ames, *J.*, 1952, 671.

[9] Crombie and Jacklin, *J.*, 1957, 1622.

evaporate. Addition of dilute hydrochloric acid and isolation with ether gave *undec-4-yn-1-ol* (6·25 g.), b. p. 135—140°/20 mm., n_D^{22} 1·4520 (Found: C, 78·5; H, 12·0. $C_{11}H_{20}O$ requires C, 78·5; H, 11·8%). The undecynol (1·7 g.) in methanol (50 c.c.) was hydrogenated over palladised charcoal catalyst (0·5 g.; 10%). Filtration and distillation gave undecan-1-ol (1·3 g.), b. p. 145°/40 mm. The phenylurethane had m. p. and mixed m. p. 60—61°.

Similarly, condensation of lithioheptyne with 6-bromohexan-1-ol gave *tridec-7-yn-1-ol* (70%), b. p. 110—115°/0·4 mm., n_D^{22} 1·4699 (Found: C, 79·2; H, 11·7. $C_{13}H_{24}O$ requires C, 79·5; H, 12·3%).

Tetradec-2-yn-1-ol.—Prop-2-yn-1-ol (42 g.) was added to lithamide (from lithium, 10·4 g.) in liquid ammonia (1 l.). After 1 hr., undecyl bromide (102 g.) in tetrahydrofuran (500 c.c.) was added and the mixture was refluxed for 8 hr. and allowed to evaporate. Addition of dilute hydrochloric acid and isolation with ether gave *tetradec-2-yn-1-ol* (80 g.), m. p. 40—42° (from aqueous ethanol) (Found: C, 80·2; H, 12·4. $C_{14}H_{26}O$ requires C, 79·9; H, 12·5%).

cis-*Tetradec-2-en-1-ol*.—The acetylenic alcohol (2·0 g.) in methanol (50 c.c.) was hydrogenated[7] in presence of quinoline (0·2 g.) and palladised barium sulphate (0·2 g.; 5%) until the rate of absorption fell sharply. The filtered solution was evaporated and the residue was taken up in ether, washed with 2N-hydrochloric acid, and distilled, to give cis-*tetradec-2-en-1-ol*, b. p. 115—120°/0·3 mm., n_D^{20} 1·4554 (Found: C, 79·8; H, 13·3. $C_{14}H_{28}O$ requires C, 79·2; H, 13·3%).

The alcohol (0·55 g.) was warmed at 40° for 4 hr. with formic acid (2·5 c.c.; 98%) and hydrogen peroxide (0·3 c.c.; 30%). After addition of excess of 3N-sodium hydroxide, the solution was refluxed for 2 hr. and poured into 2N-hydrochloric acid and ice. The product, threo-*tetradecan-1,2,3-triol*, had m. p. 79—81° (from aqueous ethanol) (Found: C, 68·6; H, 12·5. $C_{14}H_{30}O_3$ requires C, 68·2; H, 12·3%). The product synthesised by Ulagay[10] had m. p. 83—84° and was regarded as the *erythro*-isomer.

1-*Bromotetradec-2-yne*.—Phosphorus tribromide (2·5 c.c.) was added to tetradec-2-yn-1-ol (11·4 g.) in pyridine (0·5 c.c.) and ether (50 c.c.). The mixture was refluxed for 2 hr., poured into ice–water, and extracted with ether. Distillation gave 1-bromotetradec-2-yne (12·5 g.), b. p. 110°/0·3 mm., n_D^{22} 1·4794 (Found: C, 60·9; H, 9·0. $C_{14}H_{25}Br$ requires C, 61·5; H, 9·2%).

Hexadec-4-ynoic Acid.—The bromide (12 g.) was refluxed for 7 hr. with sodiomalonic ester solution [from sodium (1·03 g.), diethyl malonate (8·0 g.), and ethanol (60 c.c.)]. After removal of most of the ethanol by distillation, 2N-sodium hydroxide (100 c.c.) was added and the solution was refluxed for 2 hr. and poured into 4N-hydrochloric acid containing ice. The crude malonic acid was collected and heated at 150° until decarboxylation ceased. Recrystallisation from light petroleum (b. p. 60—80°) gave *hexadec-4-ynoic acid* (8·8 g.), m. p. 68—70° (Found: C, 76·1; H, 11·3. $C_{16}H_{28}O_2$ requires C, 76·1; H, 11·2%). Hydrogenation in ethanol over palladised charcoal catalyst gave palmitic acid, m. p. 61·5—63° (from methanol).

cis-*Hexadec-4-enoic Acid*.—Hexadec-4-ynoic acid (3·35 g.) in methanol (100 c.c.) was hydrogenated in the presence of quinoline (0·34 g.) and palladised barium sulphate (0·34 g.; 5%) until the rate of absorption fell, when 1·0 mol. had been taken up. The solution was evaporated and the residue dissolved in ether and washed with 2N-hydrochloric acid. Distillation gave cis-*hexadec-4-enoic acid* (2·8 g.), b. p. 138—141°/0·35 mm., m. p. 40—41° (from light petroleum) (Found: C, 75·3; H, 11·7. $C_{16}H_{30}O_2$ requires C, 75·5; H, 11·9%).

The acid (2·4 g.) was warmed with formic acid (8·0 c.c.; 98%) and hydrogen peroxide (1·2 c.c.; 30%) for 2 hr. and refluxed for 2 hr. with excess of 3N-sodium hydroxide. The solution was poured into 3N-hydrochloric acid and ice, to give the *γ-lactone* of threo-4,5-*dihydroxyhexadecanoic acid*, m. p. 61—63° (from aqueous ethanol) (Found: C, 71·0; H, 11·0. $C_{16}H_{30}O_3$ requires C, 71·1; H, 11·2%), $\nu_{max.}$ (in CCl_4) 1784 cm.$^{-1}$ (γ-lactone).[11]

Hexadec-2-yn-1-ol.—Prop-2-yn-1-ol (37 g.) in tetrahydrofuran (100 c.c.) was added to lithamide (from lithium, 9·2 g.) in liquid ammonia (1 l.), and the mixture was stirred for 1 hr. Tridecyl bromide (36 g.) was added and the suspension was refluxed for 8 hr. and left to evaporate. Addition of dilute hydrochloric acid, isolation with ether, and distillation furnished *hexadec-2-yn-1-ol* (30 g.), b. p. 128—130°/0·3 mm., m. p. 54—55° (from aqueous ethanol) (Found: C, 80·3; H, 12·8. $C_{16}H_{30}O$ requires C, 80·6; H, 12·7%).

1-*Bromohexadec-1-yne*.—Phosphorus tribromide (10 c.c.) in ether (50 c.c.) was added to a stirred solution of the alcohol (28 g.) and pyridine (2·0 c.c.) in ether (200 c.c.). After the mixture

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[10] Ulagay, *Rev. Fac. Sci. Univ. Istanbul*, Ser. C, 1957, **22**, 28 (*Chem. Abs.*, 1957, **51**, 15,403).

[11] Grove and Willis, *J.*, 1951, 881.

had been refluxed for 2 hr., it was poured into water; the separated organic layer was washed with dilute hydrochloric acid and distilled, to give the *bromide* (28 g.), b. p. 130—134°/0·5 mm. (Found: C, 63·8; H, 10·0. $C_{16}H_{29}Br$ requires C, 63·8; H, 9·7%).

Octadec-4-ynoic Acid.—A mixture of the bromide (27 g.) and sodiomalonic ester [from sodium (2·3 g.) and ethyl malonate (18 g.)] in ethanol (200 c.c.) was refluxed for 7 hr., concentrated to small volume, and boiled for 2 hr. with 2N-sodium hydroxide (250 c.c.). The solution was poured into ice–dilute hydrochloric acid and the precipitate was collected, dried *in vacuo*, and heated at 160° for ½ hr., to give *octadec-4-ynoic acid* (18 g.), m. p. 75—76° [from light petroleum (b. p. 60—80°)] (Found: C, 77·4; H, 11·4. $C_{18}H_{32}O_2$ requires C, 77·1; H, 11·5%). Hydrogenation of a portion in ethanol over palladised charcoal gave stearic acid, m. p. and mixed m. p. 70—71°.

cis-*Octadec-4-enoic Acid.*—The acetylenic acid (9 g.) in methanol (200 c.c.) was hydrogenated in the presence of palladised barium sulphate (0·9 g.; 5%) and quinoline (0·9 g.) until 1·0 mol. had been taken up. Distillation of the filtered solution gave the acid (7·0 g.), b. p. 158—162°/0·3 mm., m. p. 44·5—45·5° [from light petroleum (b. p. 40—60°)] (lit.,[8] m. p. 41°) (Found: C, 77·0; H, 12·2. Calc. for $C_{18}H_{34}O_2$: C, 76·5; H, 12·1%).

trans-*Octadec-4-enoic Acid.*—Hydroxylation of the olefinic acid, as for the lower homologue, yielded threo-*4,5-dihydroxyoctadecanoic acid γ-lactone* (6·5 g.), m. p. 58—60° (from aqueous ethanol) (Found: C, 72·0; H, 11·4. $C_{18}H_{34}O_3$ requires C, 72·4; H, 11·5%).

The lactone was treated with hydrogen bromide in acetic–sulphuric acid following the procedure used [8] for the corresponding 5-methoxy-lactone. *erythro*-4,5-Dibromo-octadecanoic acid thus obtained had m. p. 65—66° (lit.,[8] 64—64·5°). Debromination with zinc in methanol [8] furnished *trans*-octadec-4-enoic acid, m. p. 58—59° (lit.,[8] 59·5—60·5°).

ω-*Hydroxy-acetylenic Acids* (*General Procedure*).—The acetylenic alcohol (0·5 mol.) was added to lithamide (1·0 mol.) in liquid ammonia (*ca.* 800 c.c.) and the mixture was stirred under reflux for 1 hr. After addition of the ω-bromo-acid (0·05 mol.) in tetrahydrofuran (400 c.c.), the mixture was refluxed for 8 hr. and left to evaporate. 5N-Hydrochloric acid (500 c.c.) was added and the crude product was isolated with ether. Some of the hydroxy-acids could be distilled without lactonisation (see Table) but they were usually purified by recrystallisation.

cis-ω-*Hydroxy-olefinic Acids.*—The acetylenic acid (3 g.) in methanol (100 c.c.) was hydrogenated [7] in the presence of quinoline (0·3 g.) and palladised barium sulphate (0·3 g.; 5%). The rate of absorption fell sharply when 1·0—1·05 mol. had been taken up, and the solution was then filtered and evaporated. The residue was dissolved in ether and washed with dilute hydrochloric acid. Evaporation and recrystallisation gave the following hydroxy-acids: cis-10-*hydroxydec-8-enoic acid*, m. p. 40—41·5° (from ethyl acetate) (Found: C, 64·2; H, 9·7. $C_{10}H_{18}O_3$ requires C, 64·5; H, 9·7%); cis-*14-hydroxytetradec-12-enoic acid*, m. p. 43—44° [from ethyl acetate–light petroleum (b. p. 40–60°)] (Found: C, 69·6; H, 10·7. $C_{14}H_{26}O_3$ requires C, 69·4; H, 10·8%); cis-*15-hydroxypentadec-12-enoic acid*, m. p. 53—54° (from methanol) (Found: C, 70·1; H, 11·0. $C_{15}H_{28}O_3$ requires C, 70·3; H, 11·0%); cis-*16-hydroxyhexadec-12-enoic acid*, m. p. 46—47° (from aqueous methanol) (Found: C, 70·9; H, 11·2. $C_{16}H_{30}O_3$ requires C, 71·1; H, 11·2%).

threo-*12,13,14-Trihydroxytetradecanoic Acid.*—*cis*-14-Hydroxytetradec-12-enoic acid (0·5 g. was warmed at 40° for 2 hr. with formic acid (2·2 c.c.; 98%) and hydrogen peroxide (0·3 c.c.; 30%). The mixture was refluxed for 2 hr. with 3N-sodium hydroxide (50 c.c.) and poured into ice–dilute hydrochloric acid. The resulting threo-*12,13,14-trihydroxytetradecanoic acid* had m. p. 119—121° (from aqueous methanol) (Found: C, 61·3; H, 10·0. $C_{14}H_{28}O_5$ requires C, 60·8; H, 10·2%).

Saturated ω-Hydroxy-acids.—(*a*) *14-Hydroxytetradecanoic acid.* Bromine (1·6 g.) in carbon tetrachloride (25 c.c.) was added to crude *cis*-14-hydroxytetradec-12-enoic acid (from 3 g. of acetylenic acid) in carbon tetrachloride (25 c.c.). The solution was evaporated under reduced pressure and toluene (25 c.c.) was added. The oil obtained on re-evaporation was dissolved in methanol (50 c.c.) and hydrogenated in presence of triethylamine (10 g.) and Raney nickel until absorption ceased. After evaporation of the filtered solution, dilute hydrochloric acid was added and the mixture was extracted with ether. Evaporation afforded 14-hydroxytetradecanoic acid (1·4 g.), m. p. 88—89° (from methanol) (lit., 91—91·5°,[12] 93—95° [13]) (Found: C, 68·6; H, 11·2. Calc. for $C_{14}H_{28}O_3$: C, 68·8; H, 11·5%).

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[12] Chuit and Hausser, *Helv. Chim. Acta*, 1929, **12**, 463.

[13] Ruzicka and Stoll, *Helv. Chim. Acta*, 1928, **11**, 1159.

By the same procedure *cis*-10-hydroxydec-8-enoic acid was reduced to 10-hydroxydecanoic acid, m. p. 71·5—73° [from ethyl acetate–light petroleum (b. p. 60—80°)] (lit.,[14] 75·5—76·5°); also, *cis*-11-hydroxyundec-9-enoic acid was converted into 11-hydroxyundecanoic acid, m. p. 69—70·5 [from ethyl acetate–light petroleum (b. p. 60—80°)] (lit.,[12] 70—70·5°).

(*b*) The following acids were obtained by catalytic hydrogenation of the corresponding acetylenic acids in ethanol over palladised charcoal: 10-hydroxydecanoic acid (88%) (from 10-hydroxydec-7-ynoic acid), m. p. 73—74°, mixed m. p. with sample described above 72—73° (Found: C, 63·9; H, 10·9. Calc. for $C_{10}H_{20}O_3$: C, 63·8; H, 10·7%); 12-hydroxydodecanoic acid (92%) m. p. 84—85° [from ethyl acetate–light petroleum (b. p. 60—80°)] (lit.,[12] 84—85°); 15-hydroxypentadecanoic acid (86%), m. p. 84—85° (from methanol) (lit.,[12] 84·8—85·2°); 13-hydroxytridecanoic acid (78%), m. p. 78—79° [from ethyl acetate–light petroleum (b. p. 60—80°) (lit.,[12] 79·5°); 16-hydroxyhexadecanoic acid (83%), m. p. 92—93° (from ethyl acetate) (lit.,[12] 95°).

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[14] Chuit, Boelsing, Hausser, and Malet, *Helv. Chim. Acta*, 1926, **9**, 1074.