310. *Lipids. Part V.* Total Synthesis of Ximenynic Acid, Homoricinstearolic Acid, and Two Fatty Hydroxy-acids with Allenic Side-branches.*

By L. Crombie and A. G. Jacklin.

Ximenynic (octadec-*trans*-11-en-9-ynoic) acid (VII) is synthesised from dec-3-en-1-yne by chain extension with 1-chloro-7-iodoheptane, followed by nitrile synthesis, and is identical with the natural substance. A preparative sequence making 1-chloro-7-iodoheptane more accessible is reported.

Methyl and ethyl 11-bromoundec-9-ynoate and methyl 12-bromododec-10-ynoate are prepared by a formaldehyde coupling procedure, and their behaviour in Reformatski reactions with *n*-heptaldehyde is examined. Methyl 12-bromododec-10-ynoate gives a mixture of 11-hydroxy-10-vinylideneheptadecanoic acid (XVII) and 13-hydroxynonadec-10-ynoic (homoricinstearolic) acid (XIX) in the proportion 7 : 3 (by infrared analysis); the two are separated by clathrate formation with urea. The structure of the allenic acid (XVII) is established by degradation to formaldehyde and 11-hydroxy-10-oxoheptadecanoic acid: with lead tetra-acetate the latter gives heptaldehyde and sebacic acid. Spectroscopic results are in agreement. 10-Hydroxy-9-vinylidenehexadecanoic acid is prepared by a similar route. The method is more useful for preparing hydroxy-acids with allenic side-branches than for the synthesis of ricinstearolic acid and related substances.

Ximenynic (santalbic) acid was first recognised in Nature by Ligthelm and Schwartz [1] but it is now known to occur in a number of seed fats of the genera *Ximenia* and *Santalum*.[2,3] Its structure, octadec-11-en-9-ynoic acid (VII), emerges from the following facts.[4] It can be hydrogenated to stearic acid with absorption of three mols. of hydrogen, the ultraviolet absorption suggests an enyne chromophore (which is confirmed since addition of one mol. of hydrogen over a poisoned catalyst increases the extinction coefficient), and on ozonolysis it gives *n*-heptaldehyde and azelaic acid. Ozonolysis establishes the orientation of the enyne system in the chain. Other data support the structure.[3,4] Three facts show that it has the *trans*-configuration: it is not stereomutated when heated with selenium,[4] it has a strong absorption band [5] at 955 cm.$^{-1}$, and when hydroxylated with performic acid and then hydrogenated it gives *erythro*-11 : 12-dihydroxystearic acid.[3]

Since ximenynic acid can be obtained by dehydrating (+)-ricinstearolic acid,[6,7] and since (±)-ricinstearolic acid was synthesised in Part II, a formal total synthesis has already been achieved.[7] Nevertheless, in order to develop a bridge between methods suitable for the synthesis of ricinoleic acid and those for elaeostearic acid, we have undertaken a direct total synthesis. In the synthesis of ricinoleic acid,[7] a terminal yn-β-ol system was first

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* Part IV, *J.*, 1957, 479.

[1] Ligthelm and Schwartz, *J. Amer. Chem. Soc.*, 1950, **72**, 1868.

[2] Hatt and Szumer, *Chem. and Ind.*, 1954, 962; Ligthelm, Horn, Schwartz, and von Holdt, *J. Sci. Food Agric.*, 1954, **5**, 281; Hatt and Schoenfeld, *ibid.*, 1956, **7**, 130.

[3] Gunstone and Russell, *J.*, 1955, 3782.

[4] Ligthelm, Schwartz, and von Holdt, *J.*, 1952, 1088.

[5] Ahlers and Ligthelm, *J.*, 1952, 5039.

[6] Grigor, MacInnes, McLean, and Hogg, *J.*, 1955, 1069.

[7] Crombie and Jacklin, *Chem. and Ind.*, 1954, 1197; *J.*, 1955, 1740.

constructed, the hydroxyl function was protected, the chain extended by a $\cdot[CH_2]_6\cdot I$ unit, and elaboration continued by malonate synthesis and removal of the tetrahydropyranyl protective grouping. (±)-Ricinoleic acid was finally produced by semihydrogenation. There are objections to this sequence when thermally sensitive systems are carried in the centre of the molecule and we have, therefore, avoided the malonate procedure in the synthesis of ximenynic acid.

Reformatski reaction between heptaldehyde and propargyl bromide gave the customary mixture of dec-1-yn-4-ol (I) and deca-1 : 2-dien-4-ol [7] which was converted into the toluene-*p*-sulphonyl derivative (II). Attempted deacylation with 30% aqueous potassium hydroxide was ineffective but sodium *n*-butoxide in butanol or, better, sodamide in liquid ammonia, was satisfactory,[8] the latter giving a 79% yield of dec-3-en-1-yne (III). The infrared spectrum of dec-3-en-1-yne showed no allenic contaminant and the presence of a substantial band at 952 cm.$^{-1}$ suggests that it is largely *trans*,[9] though it is not possible to assert that *cis*-material is absent. The synthesis is thus not stereospecific.

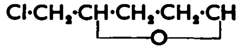
$$\text{(I)}\quad Me\cdot[CH_2]_5\cdot CH(OH)\cdot CH_2\cdot C{\equiv}CH \longrightarrow Me\cdot[CH_2]_5\cdot CH(OTs)\cdot CH_2\cdot C{\equiv}CH \quad \text{(II)} \longrightarrow$$

$$\text{(III)}\quad Me\cdot[CH_2]_5\cdot CH{=}CH\cdot C{\equiv}CH \longrightarrow Me\cdot[CH_2]_5\cdot CH{=}CH\cdot C{\equiv}C\cdot[CH_2]_7\cdot Cl \quad \text{(IV)} \longrightarrow$$

$$\text{(VI)}\quad Me\cdot[CH_2]_5\cdot CH{=}CH\cdot C{\equiv}C\cdot[CH_2]_7\cdot CN \longrightarrow Me\cdot[CH_2]_5\cdot CH\overset{t}{=}CH\cdot C{\equiv}C\cdot[CH_2]_7\cdot CO_2H \quad \text{(VII)}$$

$$Ts = p\text{-}C_6H_4Me\cdot SO_2$$

To permit insertion of the carboxylic group by nitrile or Grignard synthesis, 1-chloro-7-iodoheptane was needed as chain extender. Though Huber has made use of it on one occasion,[10] the substance has been little used in fatty acid syntheses, presumably because expensive pimelic acid is needed for preparation of heptane-1 : 7-diol by his lithium aluminium hydride route. The synthesis shown, however, makes heptane-1 : 7-diol readily accessible in batches of 100 g. or more. Pent-4-yn-1-ol (IX), prepared by treating tetrahydrofurfuryl chloride (VIII) with sodamide in liquid ammonia,[11] is converted into the tetrahydropyranyl ether (X) and the chain extended with ethylene oxide [12] to give 7-2′-tetrahydropyranyloxyhept-3-yn-1-ol (XI). Removal of the tetrahydropyranyl residue and hydrogenation with Raney nickel gives heptane-1 : 7-diol in an overall yield of 59% (74% conversion of material) from the chloride (VIII). Heptane-1 : 7-diol can be satisfactorily converted into the iodochloride *via* the dichloride.[10] When the hydrogenation was carried out over palladium–barium sulphate at atmospheric pressure, considerable amounts of *n*-heptanol and undistillable material were formed. Though partial hydrogenolysis is the rule for 2-ethylenic alcohols it has generally been thought unusual for 3-acetylenic or ethylenic alcohols. However, we have previously encountered hydrogenolysis under similar conditions with this catalyst (6-methyloct-3-en-1-ol gives 3-methyloctane),[13] so it may be met in other instances.



$$Cl\cdot CH_2\cdot CH\cdot CH_2\cdot CH_2\cdot CH_2 \;(\text{ring closed through } O)$$

(VIII)

$$\longrightarrow HC{\equiv}C\cdot[CH_2]_3\cdot OH \;\text{(IX)} \longrightarrow$$

$$HC{\equiv}C\cdot[CH_2]_3\cdot OPy \;\text{(X)} \longrightarrow HO\cdot[CH_2]_2\cdot C{\equiv}C\cdot[CH_2]_3\cdot OPy \;\text{(XI)} \longrightarrow HO\cdot[CH_2]_7\cdot OH \;\text{(XII)}$$

Py = 2-tetrahydropyranyl.

When treated with 1-chloro-7-iodoheptane, sodiodec-3-en-1-yne (cf. III) in liquid ammonia gave 17-chloroheptadec-7-en-9-yne (IV) in 65% yield. The latter was heated

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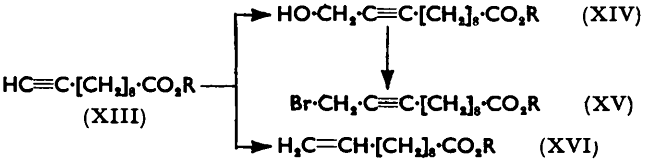
[8] Eglinton and Whiting, *J.*, 1950, 3650.
[9] Allan, Meakins, and Whiting, *J.*, 1955, 1874.
[10] Huber, *J. Amer. Chem. Soc.*, 1951, **73**, 2730.
[11] Eglinton, Jones, and Whiting, *J.*, 1952, 2873.
[12] Cf. Raphael and Roxburgh, *J.*, 1952, 3875; and ref. 24.
[13] Crombie and Harper, *J.*, 1950, 2685.

with sodium iodide and sodium cyanide in ethanol and, without isolation, the nitrile (VI) was hydrolysed to ximenynic acid (VII). This product was purified by formation of the urea clathrate compound and was obtained crystalline. It absorbed three mols. of hydrogen to give stearic acid and had the spectroscopic properties of a *trans*-enyne. Mixed m. p. and infrared comparisons showed it to be identical with the natural acid. Any *cis*-impurity in the intermediates must have been removed during purification.

Our opinion of the malonate reaction for syntheses of this type was confirmed by converting sodiodec-3-en-1-yne into 16-chlorohexadec-7-en-9-yne by reaction with 1-chloro-6-iodohexane. The unsaturated chloride was heated with sodium iodide in acetone and then used in the malonate reaction. After hydrolysis and decarboxylation there was little distillable product and the latter showed no enyne absorption.

We now deal with another approach to acids of the ricinstearolic and ximenynic type. This employs a Reformatski reaction with compounds of the type $Br\cdot CH_2\cdot C{\equiv}C\cdot[CH_2]_n\cdot CO_2R$, where $n = 7$ or 8 and R = Et or Me, and is potentially capable of reducing the number of synthetic stages. Nevertheless, we expected difficulties because many reactions of 2-acetylenic halides lead to mixtures of allenes and acetylenes.[14, 15] This is encountered in the Reformatski reaction between propargyl bromide and an aldehyde (above and Part II), as was originally pointed out by Wotiz,[15] but it is not a source of serious difficulty because the terminal acetylene is readily purified,[16] or, if the mixture is used directly in chain-extension operations, the allene is easily eliminated. Wotiz refers to the phenomenon as the propargylic rearrangement,[15] and though other explanations are possible, suggests that an intermediate ion represented as $R\cdot C{\equiv}C\cdot\overset{+}{C}H_2 \longleftrightarrow R\cdot\overset{+}{C}{=}C{=}CH_2$ may be involved. Thus replacement reactions with halide ions, reductive elimination of halogen, and carboxylation of propargylic Grignard reagents all lead to mixtures of the allene and acetylene.[14]

Undec-10-ynoic acid was prepared by a standard method [17] (though we obtained much higher yields than those cited without modifying the recommended procedure), and converted into dec-9-ynoic acid by Barbier–Wieland degradation.[18] Another specimen was made by carrying out the degradation on undec-10-enoic acid [18] and then brominating and dehydrohalogenating the product. As is well known,[19] terminally acetylenic alcohols couple with formaldehyde in the presence of cuprous oxide, giving diols, and when this procedure was extended to sodium undec-9- and -10-ynoates, and the products were esterified, methyl (and ethyl) 11-hydroxyundec-9-ynoate and methyl 12-hydroxydodec-10-ynoate (XIV; R = Me) were obtained. Conversions were far from complete in the former case. In one experiment with methyl undec-10-ynoate, a low-boiling fraction was isolated which was not unchanged methyl undec-10-ynoate, but methyl undec-10-enoate. The latter was fully characterised and must arise by hydrogen transfer. On the other hand, the low-boiling fraction from the experiment with potassium dec-9-ynoate is almost entirely methyl dec-9-ynoate. The hydroxy-esters were converted into bromides, which showed no allenic bands, with phosphorus tribromide and pyridine.



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[14] *Inter al.*, Wotiz, *J. Amer. Chem. Soc.*, 1950, **72**, 1639; Wotiz and Palchak, *ibid.*, 1951, **73**, 1971; Wotiz and Matthews, *ibid.*, 1952, **74**, 2559; see Jacobs and Brill, *ibid.*, 1953, **75**, 1314 for early references.

[15] Wotiz, *J. Amer. Chem. Soc.*, 1951, **73**, 693.

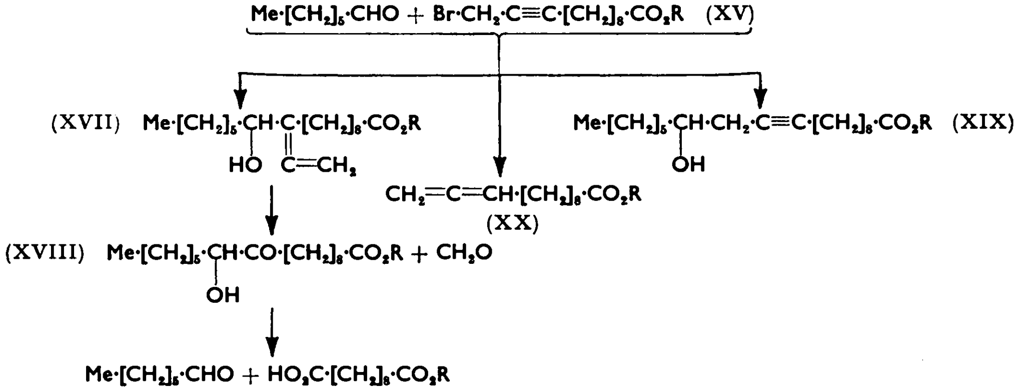
[16] Celmer and Solomons, *ibid.*, 1953, **75**, 3430.

[17] *Org. Synth.*, 1952, **32**, 104.

[18] Black and Weedon, *J.*, 1953, 1785.

[19] Heilbron, Jones, and Sondheimer, *J.*, 1947, 1586; Paul and Tchelitcheff, *Compt. rend.*, 1950, **230**, 1872; Heuberger and Owen, *J.*, 1952, 910.

When methyl 12-bromododec-10-ynoate (XV) was treated under Reformatski conditions with heptaldehyde, and then distilled and hydrolysed, a mixture, m. p. 47—55°, of two crystalline acids was isolated. They could not be separated by fractional crystallisation from light petroleum, and reversed-phase partition chromatography did not resolve the mixture fully. Formation of the urea clathrate compound gave a complete separation as only one acid gave a complex. The other, m. p. 61°, showed strong allenic infrared absorption (1957 cm.$^{-1}$, ε 55·7, in CCl_4), gave correct analyses for the acid (XVII; R = H), and absorbed 2 mols. of hydrogen over a catalyst. When it was ozonised under controlled conditions, and the formaldehyde produced determined quantitatively by a technique similar to that of Knights and Waight,[20] exactly one mol. was found to be released. A preparative ozonolysis experiment gave a good yield of a ketol acid which must be (XVIII), as degradation with lead tetra-acetate gave heptaldehyde and sebacic acid. Spectroscopic results are in complete agreement. The acid, m. p. 52—53°, which formed a urea complex, and is therefore less heavily branched than the other, was isomeric with it. It must be the expected homoricinstearolic acid (XIX) for, although absorbing two mols. of hydrogen over a catalyst, it showed no high-intensity ultraviolet absorption and showed no allenic vibration in the infrared spectrum. Hydroxyl and carboxyl functions were present, but, as has previously been observed for compounds of this type, the acetylenic stretching vibration is too weak to be detected [21] (cf. ricinstearolic acid). The amounts of (XVII) and (XIX) in the product were found, by intensity measurements at 1957 cm.$^{-1}$, to be 69·5% and 30·5% respectively.



When an excess of methyl 12-bromododec-10-ynoate was used in the Reformatski reaction, a new lower-boiling ester was isolated. This gave correct analyses for an ester (XX; R = Me) and had strong allenic infrared absorption though it may not be homogeneous. Dehalogenation of propargylic halides, generally secondary or tertiary, with a zinc–copper couple or lithium aluminium hydride has been used to prepare allenes though most of the examples are simple ones.[22] Hydrolysis of the ester gave a crystalline acid which was hydrogenated to dodecanoic acid. However, although its infrared spectrum showed allenic absorption at 1957 cm.$^{-1}$, the latter was very weak and further degradative work is needed to establish the structure with certainty since isomerisation of a terminal allene to the methylacetylene could occur under alkaline conditions.

Less success was attained in Reformatski experiments with methyl 12-bromoundec-9-ynoate and heptaldehyde. The products from two experiments were, after hydrolysis,

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[20] Knights and Waight, *J.*, 1955, 2830; Naves, *Helv. Chim. Acta*, 1949, **32**, 1151; Doeuvre, *Bull. Soc. chim. France*, 1936, **3**, 613; cf. Naves, *ibid.*, 1956, 297.

[21] Wotiz and Miller, *J. Amer. Chem. Soc.*, 1949, **71**, 3441; Sammul, Hollingsworth, and Wotiz, *ibid.*, 1953, **75**, 4856.

[22] Bertrand, *Bull. Soc. chim. France*, 1956, 461; Ginzburg, *J. Gen. Chem.* (*U.S.S.R.*), 1940, **10**, 513, 516; Hennion and Sheehan, *J. Amer. Chem. Soc.*, 1949, **71**, 1964; Jacobs, Teach, and Weiss, *ibid.*, 1955, **77**, 6254; see also refs. 14 and 15.

oils which could not be satisfactorily purified. A third experiment, with ethyl 12-bromoundec-9-ynoate, gave an oil which yielded to low-temperature crystallisation. The product failed to give a urea complex and was purified by crystallisation to m. p. 52—52·5°. The infrared spectrum was similar to that of the allene (XVII): it had a strong allene band at 1955 cm.$^{-1}$ (ε 54·8, in CCl_4) and must, by analogy, be

$$Me{\cdot}[CH_2]_5{\cdot}CH(OH){\cdot}C({=}C{=}CH_2){\cdot}[CH_2]_7{\cdot}CO_2H$$

Analytical and microhydrogenation results are in agreement. Ricinstearolic acid is undoubtedly present in the mother-liquors but was not isolated.

We conclude that in propargylic Reformatski reactions the steps involving introduction of the central functional groupings and the $\cdot[CH_2]_7\cdot CO_2H$ unit are best separated when straight-chain acids are wanted, but Reformatski reactions with $Br{\cdot}CH_2{\cdot}C{\equiv}C{\cdot}[CH_2]_n{\cdot}CO_2R$ are suited to the preparation of long-chain acids with an allenic side unit. For the synthesis of elaeostearic acid we have therefore developed further the techniques used in the synthesis of ximenynic acid.

EXPERIMENTAL

The ultraviolet absorption data were determined in pure ethanol with a Unicam S.P. 500 instrument. Infrared measurements were made by Mr. R. L. Erskine, B.Sc., A.R.C.S., using a Grubb-Parsons double-beam instrument. Extinction data were determined at a slit width of 0·11 mm. Analyses were carried out in the Microanalytical Laboratory (Miss J. Cuckney) of Imperial College.

Dec-3-*en*-1-*yne* (III).—Toluene-*p*-sulphonyl chloride (8·4 g.) was dissolved in warm pyridine (4 ml.) and rapidly cooled in ice to afford small crystals. Dec-1-yn-4-ol (6·2 g., containing allene, see Part II) was added slowly, and with shaking, and the mixture set aside (12 hr.). Water was added and the heavy oil removed with ether. The ethereal extracts were washed with 2N-sulphuric acid, sodium hydrogen carbonate solution, and water. After drying (Na_2SO_4) and evaporation, the crude toluene-*p*-sulphonate (II) was used without further purification. The toluene-*p*-sulphonate was dissolved in butan-1-ol, added to a solution of sodium *n*-butoxide prepared from sodium (1·0 g.) and butan-1-ol (45 ml.), at 60°, and set aside for 30 min. Water and light petroleum (b. p. 40—60°) were added, and the light petroleum layer was separated, washed with water, dried, and evaporated. Distillation gave *dec*-3-*en*-1-*yne* (2·69 g., 49%), b. p. 65°/10 mm., n_D^{20} 1·4500 (Found: C, 87·85; H, 11·85. $C_{10}H_{16}$ requires C, 88·15; H, 11·85%). Microhydrogenation, 2·8H_2. Light absorption: max. 222 mμ (ε 10,200).

The toluene-*p*-sulphonate prepared from dec-1-yn-4-ol (3·11 g.), as above, was treated at 100° in nitrogen with potassium hydroxide (1·5 g.) in water (4·5 ml.) containing two drops of detergent. After the usual working up, no product was obtained which distilled at a bath-temp. below 145°/10 mm.

Dec-1-yn-4-ol (28·1 g.), toluene-*p*-sulphonyl chloride (34·9 g.), and pyridine (14·4 g.) were allowed to react as above, and were set aside for 30 min. at 0° and 48 hr. at 20°. Working up gave the crude ester as a red oil (52·0 g., 93%). The latter was added in ether dropwise to a suspension of sodamide [from sodium (7·7 g.)] in liquid ammonia (500 ml.) and stirred overnight. Ammonium chloride (30 g.) was added, followed by water (100 ml.) and pentane (100 ml.). The pentane layer was separated and the aqueous layer further extracted with pentane (2 × 50 ml.): the united pentane extracts were washed with water, 2N-hydrochloric acid, and sodium hydrogen carbonate solution. After drying ($MgSO_4$), the pentane was distilled through a 12" Dufton column. Distillation of the residue gave dec-3-en-1-yne (18·0 g., 79%), b. p. 70—74°/15 mm., n_D^{25} 1·4492.

16-*Chlorohexadec*-7-*en*-9-*yne*.—Dec-3-en-1-yne (3·32 g.) was added to sodamide [from sodium (0·62 g.)] in liquid ammonia (80 ml.). After stirring (3 hr.), 1-chloro-6-iodohexane (6·5 g.) was added and the mixture stirred overnight. Working up in the usual way gave, on distillation, 1-*chlorohexadec*-9-*en*-7-*yne* (1·66 g.), b. p. 108—113°, n_D^{20} 1·4809 (Found: Cl, 14·8. $C_{16}H_{27}Cl$ requires Cl, 13·9%). Ultraviolet max.: 226 mμ (ε 10,700).

Reaction between 16-*Iodohexadec*-7-*en*-9-*yne and Malonic Ester*.—16-Chlorohexadec-7-en-9-yne (1·6 g.) was heated in nitrogen and under reflux, with excess of sodium iodide in acetone for 4 hr. Water was added and the solution thoroughly extracted with ether. The extracts were dried and evaporated and the residual iodo-compound, in ethanol (10 ml.), added to sodiomalonic ester prepared from diethyl malonate (1·2 g.), sodium (0·19 g.), and ethanol (15 ml.). The mixture was heated under reflux (nitrogen) for 21 hr., then cooled, and potassium hydroxide (1·5 g.) in 95% methanol (10 ml.) was added. After 44 hr. at 20°, the crude malonic acid was isolated in the usual way and heated to 150°/10^{-6} mm. An oil (91 mg.) distilled, but it showed no light absorption characteristic of an enyne acid.

17-*Chloroheptadec*-7-*en*-9-*yne* (IV).—Sodamide was prepared by dissolving sodium (0·848 g.) in redistilled liquid ammonia. Dec-3-en-1-yne (4·45 g.) in dry ether was added and the mixture stirred for 3½ hr. with protection from moist air. 1-Chloro-7-iodoheptane (8·7 g.) was added and stirring continued overnight. Ammonium chloride (10 g.) was added and the ammonia allowed to evaporate. The residue was extracted with ether, and the extract washed, dried, evaporated and distilled, to give 17-*chloroheptadec*-7-*en*-9-*yne* (5·7 g., 65%), b. p. 100—104°/10^{-4} mm., n_D^{25} 1·4790 (Found: C, 75·35; H, 11·0; Cl, 13·0. $C_{17}H_{29}Cl$ requires C, 75·95; H, 10·85; Cl, 13·2%). Ultraviolet max.: 227 mμ (ε 14,000). The infrared spectrum (liquid film) showed bands at 2224 w (·C≡C·) and 954 cm.$^{-1}$ (*trans*-CH=CH conjugated with an acetylenic linkage).

Octadec-trans-11-*en*-9-*ynoic* (*Ximenynic*) *Acid* (VII).—17-Chloroheptadec-7-en-9-yne (2·5 g.), sodium iodide (1·0 g.), and sodium cyanide (1·0 g.) in 80% ethanol (12 ml.) were heated under reflux (40 hr.) in nitrogen. Potassium hydroxide (5·0 g.) in water (12 ml.) was added, and refluxing continued until no more ammonia was liberated (29 hr.). The acidic product was isolated in the usual way and dissolved in hot methanol (50 ml.), containing urea (15 g.). On cooling to 0°, a clathrate compound crystallised which was washed with a little ice-cold methanol saturated with urea and then decomposed by dilute hydrochloric acid. The solid product (0·87 g.) had m. p. 35—37°. By dilution with water and ether-extraction, the methanolic filtrate from the complex gave crude acid which, after crystallisation from 80% methanol, melted over several degrees up to 30° (0·21 g.).

Crude ximenynic acid, m. p. 35—37°, was recrystallised from light petroleum (b. p. 40—60°) and the acid formed white plates, m. p. and mixed m. p. 39—40° (Found: C, 77·35; H, 10·9. Calc. for $C_{18}H_{30}O_2$: C, 77·65; H, 10·85%). Microhydrogenation: 2·95H_2. Ultraviolet max. 228 mμ (ε 16,800). Infrared bands at 2224 (C≡C), 952 (*trans*-C=C), and 1708 cm.$^{-1}$ (CO_2H). On hydrogenation and crystallisation from 80% ethanol, stearic acid, m. p. and mixed m. p. 70°, was obtained. Recorded data[4] for natural ximenynic acid are m. p. 39—40°, $\lambda_{max.}$ 229 mμ (ε 16,600). The infrared bands of the natural acid include those just listed.

4-2′-*Tetrahydropyranyloxypent*-1-*yne* (X).—Tetrahydrofurfuryl chloride, prepared[23] in 67% yield, had b. p. 46°/13 mm., n_D^{22} 1·4540—1·4544. It was converted into pent-4-yn-1-ol by the sodamide ring-fission method of Eglinton, Jones, and Whiting.[11] Pent-4-yn-1-ol (72% yield) had b. p. 59°/8 mm., n_D^{24} 1·4430—1·4437, and was converted into the tetrahydropyranyl ether, b. p. 90—94°/10 mm., n_D^{22} 1·4561—1·4565, in the usual way (95% yield).

7-2′-*Tetrahydropyranyloxyhept*-3-*yn*-1-*ol* (XI).—4-2′-Tetrahydropyranyloxypent-1-yne (117·6 g.) in ether (120 ml.) was added to sodamide prepared from sodium (16·8 g.) in liquid ammonia (3·5 l.). After 3½ hours' stirring ethylene oxide (40 ml.) in dry ether (100 ml.) was added, and the mixture stirred for 19 hr. The ammonia was allowed to evaporate, water (1 l.) added, and the product extracted three times with ether (total, 1½ l.). The extracts were dried ($MgSO_4$), evaporated, and distilled. A fraction (48 g., 41%), b. p. 90—120°/13 mm., n_D^{21} 1·4558—1·4570, was largely unchanged 4-2′-tetrahydropyranyloxypent-1-yne and was followed by 7-2′-*tetrahydropyranyloxyhept*-3-*yn*-1-*ol* which distilled as a viscous oil (73·0 g., 82% yield, 50% discounting recovered material), b. p. 143—158°/0·1 mm., n_D^{21} 1·4798—1·4805 (Found: C, 67·9; H, 9·6. $C_{12}H_{20}O_3$ requires C, 67·9; H, 9·5%).

In a second experiment, pent-4-yn-1-ol (176 g.) was mixed with dihydropyran (183 g.) and a few drops of phosphorus oxychloride in the usual way, and after 2 hr. added to a solution of sodamide (from sodium, 50·5 g.) in liquid ammonia (6 l.) as above. The amount of ethylene oxide was increased to provide a 50% excess. This resulted in a yield of 82% (271 g.) and an increased conversion (61%).

Hept-3-*yne*-1 : 7-*diol.*—7-2′-Tetrahydropyranyloxyhept-3-yn-1-ol (71·5 g.) was refluxed in methanol (620 ml.) with toluene-*p*-sulphonic acid (1·2 g.) for 1¾ hr. Sodium carbonate (0·8 g.) was added, and most of the methanol evaporated. After filtration, distillation of the filtrate gave hept-3-yne-1 : 7-diol (39·1 g., 90%), b. p. 111—124°/0·1 mm., n_D^{22} 1·4837—1·4840 (Found: C, 65·55; H, 9·55. Calc. for $C_7H_{12}O_2$: C, 65·6; H, 9·45%). Jones, Mansfield, and Whiting[24]

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[23] *Org. Synth.*, 1945, **25**, 84.

[24] Jones, Mansfield, and Whiting, *J.*, 1954, 3208.

give b. p. 102—104°/0·05 mm., n_D^{18} 1·4870, for a specimen made by a similar procedure but *via* a Grignard intermediate.

Heptane-1 : 7-*diol*.—Hept-3-yne-1 : 7-diol (30·5 g.) in methanol (250 ml.) was completely hydrogenated over Raney nickel at 20°/30—50 atm. The catalyst was filtered off, the methanol evaporated, and the residue distilled. Heptane-1 : 7-diol (28·8 g., 91%) was obtained having b. p. 117—126°/0·03 mm., n_D^{24} 1·4527—1·4540, m. p. 20° (Found : C, 63·85; H, 12·15. Calc. for $C_7H_{16}O_2$: C, 63·6; H, 12·2%). Huber[10] gives b. p. 112—115°/3 mm., n_D^{25} 1·4520, m. p. 20—22°.

On a larger scale, undistilled 7-2′-tetrahydropyranyloxyhept-3-yn-1-ol (271 g.) was refluxed in methanol (1800 ml.) containing toluene-*p*-sulphonic acid (3 g.) for 2 hr. Potassium hydroxide (1·0 g.) was then added and the solution evaporated to 500 ml. Raney nickel was added and the mixture hydrogenated at 20°/130 atm. Working up as above gave heptane-1 : 7-diol (170·7 g., 100%).

Hept-3-yne-1 : 7-diol (36·1 g.) was hydrogenated in methanol (100 ml.) over 5% palladium–barium sulphate (absorption, 12·45 l. at N.T.P. Theor., 12·63 l.). The catalyst was removed, the solvent evaporated, and the residual oil distilled, to give *n*-heptanol (4·55 g.), b. p. 40—42°/0·2 mm., n_D^{18} 1·4248. The α-naphthylurethane crystallised from light petroleum (b. p. 100—120°) in plates, m. p. 56°, undepressed when admixed with an authentic specimen m. p. 57° (Found : C, 75·45; H, 8·0. Calc. for $C_{18}H_{23}O_2N$: C, 75·75; H, 8·1%). Continued distillation gave heptane-1 : 7-diol (3·3 g.), b. p. 107—108°/0·1 mm., n_D^{22} 1·4521, m. p. 16—18°. A large white spongy residue remained in the flask.

1 : 7-*Dichloroheptane*.—Heptane-1 : 7-diol (170 g.) was mixed with pyridine (22 ml.), and thionyl chloride (660 g.) added dropwise with stirring, at 0°. The product was heated on the steam-bath for 2 hr., cooled, poured into ice, and extracted with light petroleum (b. p. 40—60°) (3 × 500 ml.). The extract was washed twice with concentrated sulphuric acid (150 ml.), twice with saturated sodium hydrogen carbonate solution, and finally with water. Drying (Na_2SO_4), evaporation, and distillation gave 1 : 7-dichloroheptane (147 g., 69%), b. p. 106—110°/15 mm., n_D^{19} 1·4591. The yield is low because of an accidental loss. Huber gives b. p. 124—125°/35 mm., n_D^{25} 1·4565.

1-*Chloro*-7-*iodoheptane*.—1 : 7-Dichloroheptane (147 g.) was heated under reflux with sodium iodide (125 g.) in acetone (1 l.) for 4 hr. Most of the acetone was distilled off and water and ether added. The ether extracts were washed with sodium thiosulphate solution, and then water, dried, evaporated, and distilled through a Dufton column. Material of b. p. 52—56°/0·5 mm., n_D^{23} 1·4609, was recovered dichloroheptane (64·5 g., 44%). Chloroiodoheptane, b. p. 82—84°/0·5 mm., n_D^{23} 1·5136, was then isolated in 40% yield (91 g.). Huber[10] gives b. p. 95°/2 mm., n_D^{25} 1·5158.

Undec-10-*ynoic Acid*.—This was prepared from undecenoic acid (157·5 g.) according to the directions given in *Org. Synth.*[17] Undec-10-ynoic acid, b. p. 134°/0·06 mm., m. p. 41—43°, was obtained. One crystallisation raised the m. p. to 42·5° (125 g., 79%) (lit.,[17] m. p. 42·5—43°; 38—49% yield). One further crystallisation from light petroleum (b. p. 40—60°) raised the m. p. to 43—43·5°. The above yield was reproduced in other runs. The methyl ester, prepared by esterification with methanolic sulphuric acid, had b. p. 78°/0·04 mm., n_D^{21} 1·4452 (92%).

Methyl 12-*Hydroxydodec*-10-*ynoate* (XIV; R = Me).—Undec-10-ynoic acid (97 g.) was neutralised with aqueous sodium hydroxide solution (∼500 ml.), and cuprous oxide [prepared from cuprous chloride (70 g.) by dissolution in 5N-hydrochloric acid and precipitation with 40% potassium hydroxide solution] added, together with 40% aqueous formaldehyde (500 ml.) and calcium carbonate (4 g.). The mixture was heated and stirred under nitrogen on a steam-bath for 40 hr., and then acidified with 2N-hydrochloric acid and extracted with ether. The extracts were washed with 3N-hydrochloric acid until the washings were no longer coloured, dried, and evaporated. Methanol (200 ml.), benzene (300 ml.), and sulphuric acid (40 ml.) were added to the residue and the mixture heated under reflux in nitrogen for 10 hr. The ester was isolated in the usual way and on distillation *methyl* 12-*hydroxydodec*-10-*ynoate* (40·0 g., 33%), b. p. 162—172°/0·3 mm., n_D^{21} 1·4656, was obtained (Found : C, 68·35; H, 9·9. $C_{13}H_{22}O_3$ requires C, 68·95; H, 9·8%). The infrared spectrum showed maxima at 3413 s (OH), 2291 mw and 2234 mw (·C≡C·) and 1734 s cm.$^{-1}$ (ester). The hydroxy-ester crystallised at 0° in long white needles, m. p. 20°, but was not recrystallised. The 1-*naphthylurethane* crystallised as plates from light petroleum (b. p. 100—120°), m. p. 63—63·5° (Found : C, 72·6; H, 7·5; N, 3·6. $C_{24}H_{29}O_4N$ requires C, 72·9; H, 7·4; N, 3·55%). A low-boiling fraction, b. p. 80°/0·1 mm.

(20·2 g.), was also isolated in the above distillation and, as it gave a precipitate with alcoholic silver nitrate, it contains at least some recovered methyl undec-10-ynoate.

In another experiment methyl undec-10-ynoate (8·1 g.) was heated and stirred for 45 hr. with 40% formaldehyde solution (20 ml.) in dioxan (35 ml.) and cuprous oxide (from 4·5 g. of cuprous chloride). After working up as before, methyl 12-hydroxydodec-10-ynoate (2·1 g.), b. p. 131—136°/0·03 mm., n_D^{24} 1·4661, was obtained, together with a fraction, b. p. 66°/0·04 mm., n_D^{23} 1·4379 (1·43 g.). The latter gave no precipitate with alcoholic silver nitrate and analysed correctly for methyl undec-10-enoate (Found: C, 72·65; H, 11·25. Calc. for $C_{12}H_{22}O_2$: C, 72·7; H, 11·2%). Microhydrogenation 1·0H_2. On hydrolysis (0·65 g. of ester), undec-10-enoic acid (0·44 g.), m. p. 22°, was obtained, which gave a *p*-bromophenacyl ester, m. p. 60°. Mixed m. p.s with authentic specimens were undepressed.

12-*Hydroxydodec*-10-*ynoic Acid* (XIV; R = H).—Hydrolysis of the methyl ester (0·50 g.) with ethanolic potassium hydroxide, and recrystallisation of the acidic product from 1 : 1 acetone–light petroleum (b. p. 60—80°), gave 12-*hydroxydodec*-10-*ynoic acid* (0·32 g.), m. p. 73° (Found: C, 67·8; H, 9·6. $C_{12}H_{20}O_3$ requires C, 67·9; H, 9·5%). The *p*-bromophenacyl ester crystallised from ethanol in plates, m. p. 63·5°.

Methyl 12-*Bromododec*-10-*ynoate* (XV; R = Me).—Methyl 12-hydroxydodec-10-ynoate (7·29 g.), dissolved in dry ether (12 ml.) and pyridine (0·5 ml.), was cooled in ice and stirred whilst phosphorus tribromide (3·22 g.) was added dropwise. The mixture was stirred for 1 hr. at 0° and for 30 min. at 20°. Ether and ice-cold 2N-hydrochloric acid were added and the ether layer was separated, washed with 2N-hydrochloric acid and water, and dried ($MgSO_4$). The ether was evaporated under reduced pressure and the *methyl* 12-*bromododec*-10-*ynoate* distilled; it had b. p. 136°/10^{-3} mm., n_D^{23} 1·4860 (Found: C, 54·25; H, 7·45; Br, 27·5. $C_{13}H_{21}O_2Br$ requires C, 54·0; H, 7·3; Br, 27·65%). The yield was 5·64 g. (61%). The infrared spectrum (liquid film) showed an acetylenic linkage (2309 w and 2239 m cm.$^{-1}$) but no allenic absorption.

Reformatski Reaction between Methyl 12-*Bromododec*-10-*ynoate and Heptaldehyde.*—Zinc (1·2 g.; washed with 2N-hydrochloric acid and then dried) was treated with some of a mixture of methyl 12-bromododec-10-ynoate (5·01 g.), heptaldehyde (2·31 g.), and dry tetrahydrofuran (20 ml.). Mercuric chloride (50 mg.) was added and, after a few minutes on the steam-bath, reaction began and the solution became pale green. The remainder of the reactants was then added dropwise and, finally, the product was heated under reflux (45 min.) and set aside overnight. A little zinc (0·17 g.) remained unused. Iced dilute acetic acid was added and the product extracted well with ether. The ether extracts were united, washed with sodium hydrogen carbonate solution and then with water, dried ($MgSO_4$), evaporated, and distilled. The distillate (2·03 g., 36%), b. p. 152—174°/3 × 10^{-4} mm., $n_D^{19·5}$ 1·4702—1·4711, was hydrolysed for 2 hr., under reflux, with potassium hydroxide (0·60 g.) in ethanol (15 ml.) and water (1 ml.). Water was added, the potassium salts were extracted with ether, and the extracts rejected. The aqueous layer was acidified and then extracted with ether, and the ether extracts were dried and evaporated. Crystallisation of the residue (twice) from light petroleum (b. p. 60—80°) gave white plates, m. p. 47—53° (0·81 g.) (Found: C, 72·9; H, 11·05. Calc. for $C_{19}H_{34}O_3$: C, 73·45; H, 11·05%). The mixture of acids showed no high-intensity maximum in the ultraviolet and in the infrared spectrum (paraffin mull) bands were present at 3300 s and 3195 s (OH), 1957 m (allene) and 1711 s cm.$^{-1}$ (CO_2H).

Methyl 12-bromododec-10-ynoate (6·59 g.), heptaldehyde (1·9 g.; for complete reaction with the bromo-compound 2·6 g. are needed), and zinc (1·45 g.) gave, on Reformatski reaction, the mixed ester (1·50 g.) mentioned above, together with an *ester*, b. p. 86—96°/0·05 mm., $n_D^{21·5}$ 1·4550. (Found: C, 74·3; H, 10·8. $C_{13}H_{22}O_2$ requires C, 74·25; H, 10·55%). The latter had a medium-strong infrared band (liquid film) at 1957 cm.$^{-1}$, indicating an allenic function (ester 1731 s cm.$^{-1}$). By alkaline hydrolysis an *acid* was obtained, having, after crystallisations, m. p. 45—46° (Found: C, 72·8; H, 10·35. $C_{12}H_{20}O_2$ requires C, 73·4; H, 10·25%). The p-*bromophenacyl ester* crystallised in plates (from ethanol), m. p. 56—57° (Found: C, 60·65; H, 6·3. $C_{20}H_{25}O_3Br$ requires C, 61·05; H, 6·4%). On hydrogenation the acid gave lauric acid (m. p. and mixed m. p. 43—44°). As the allene absorption (in CCl_4 solution) at 1957 cm.$^{-1}$ was much weaker than that of the original ester, acceptance of its structure as dodec-10 : 11-dienoic acid requires further degradative evidence.

13-*Hydroxynonadec*-10-*ynoic* (*homoricinstearolic*) (XIX) *and* 11-*Hydroxy*-10-*vinylideneheptadecanoic Acid* (XVII). The Reformatski product, m. p. 47—53° (473 mg., see above), was dissolved in methanol (10 ml.) containing urea (2 g.). Cooling in ice gave a clathrate compound which was removed. After recrystallisation from methanol (5 ml.) saturated with urea, water was added and 13-*hydroxynonadec*-10-*ynoic acid* (85 mg.) filtered off. It had m. p. 48—51°, raised by crystallisation from light petroleum (b. p. 60—80°) to m. p. 52—53° (white plates) (Found: C, 73·5; H, 11·1. $C_{19}H_{34}O_3$ requires C, 73·45; H, 11·05%). Microhydrogenation 1·96H_2. No allenic or acetylenic absorption was present in the infrared spectrum (paraffin mull). There were bands at 3330 m and 1081 m (OH) and 1712 s and 1694 s cm.$^{-1}$ (CO_2H doublet).

The methanolic filtrate from urea clathrate formation was treated further with urea (2 g.), and the crystals, which were deposited on cooling, were filtered off. On decomposition with water only a slight turbidity was formed. Water was added to the filtrate and 11-*hydroxy*-10-*vinylideneheptadecanoic acid* (301 mg.) filtered off. It had m. p. 57—59° raised by two recrystallisations from light petroleum (b. p. 60—80°) to 61° (Found: C, 73·6; H, 11·2%). Microhydrogenation 2·0H_2. The allenic band at 1957 cm.$^{-1}$ had ε 55·7 in CCl_4. The mixture, m. p. 47—53°, had ε 38·8 at 1957 cm.$^{-1}$ and thus contains 69·5% of 11-hydroxy-10-vinylideneheptadecanoic acid.

Ozonolysis of 11-*Hydroxy*-10-*vinylideneheptadecanoic Acid.*—The acid (56·0 mg.) was dissolved in purified acetic acid–ethyl acetate (5 ml.) in a 15 ml. bubbler attached to the ozoniser. A second bubbler contained further solvent (2 ml.). Ozonised oxygen was passed through the two bubblers and then into a 20 ml. portion of 2% potassium iodide which was renewed and titrated at 1 min. intervals. After 15 min., when successive titration figures had become constant, the solutions were washed into a 250 ml. graduated flask, and a standard Schiff's reagent (75 ml.) added, followed by concentrated hydrochloric acid (37·5 ml.) and water to adjust the volume. The solution was set aside for 3 hr. at 22° and the absorption at 570 mμ measured with a Unicam SP 600 instrument. The reading was compared with a calibration curve and, after correction for a small solvent blank (0·12 mg.), corresponded to 5·42 mg. (100%) of formaldehyde. Standard Schiff's reagent was prepared by dissolving rosaniline hydrochloride (1 g.) in distilled water (500 ml.), and adding a solution of sodium sulphite (25 g.) in water (460 ml.) and then concentrated hydrochloric acid (15 ml.). The solution was set aside overnight and then decolorised with charcoal. Standard formaldehyde solutions for calibration (*ca.* 0·4%) were estimated by oxidation with hydrogen peroxide in the presence of 0·1N-alkali followed by back-titration with 0·1N-hydrochloric acid to thymol-blue.

11-*Hydroxy*-10-*oxoheptadecanoic Acid* (XVIII).—11-Hydroxy-10-vinylideneheptadecanoic acid (84 mg.) was ozonised in ethyl acetate (3 ml.) and glacial acetic acid (2 ml.) at 0° for 20 min. The solvent was partly evaporated under reduced pressure and water added. 11-*Hydroxy*-10-*oxoheptadecanoic acid* (58 mg.) was filtered off; it had m. p. 67·5—68·5°, raised by recrystallisation to 68·5° (Found: C, 68·35; H, 10·55. $C_{17}H_{32}O_4$ requires C, 67·95; H, 10·75%). The infrared spectrum (paraffin mull) showed bands at 3279 s and 3185 s cm.$^{-1}$ (OH), 1711 s cm.$^{-1}$ (CO_2H), and 1682 s cm.$^{-1}$ (bonded CO). There was no allene absorption.

Action of Lead Tetra-acetate on 11-*Hydroxy*-10-*oxoheptadecanoic Acid.*—Lead tetra-acetate (57·8 mg.) and 11-hydroxy-10-oxoheptadecanoic acid (24·2 mg.) were dissolved in 90% acetic acid (1 ml.) and set aside for 1 hr.: the odour of heptaldehyde could be detected. Concentrated sulphuric acid (18 mg.) was added and the lead sulphate centrifuged off. After being made just alkaline, the solution was extracted with ether, and the ether extracts were added to methanolic 2 : 4-dinitrophenylhydrazine hydrochloride and set aside for 1 hr. The product was evaporated on a steam-bath and the residue chromatographed on alumina with benzene–ether (2 : 1) as eluant. The fast-running band was isolated and gave crude *n*-heptaldehyde 2 : 4-dinitrophenylhydrazone (9·6 mg.), m. p. 102°. When recrystallised from 90% methanol it had m. p. 104° (3·4 mg.), undepressed by an authentic specimen (m. p. 106°).

The aqueous layer after removal of heptaldehyde was acidified, washed with light petroleum (b. p. 60—80°), and evaporated to dryness. Sebacic acid (6·1 mg.), isolated from the residue by ether-extraction followed by recrystallisation from water, had m. p. 132—133°. The mixed m. p. with an authentic specimen, m. p. 133—134°, was 133°.

1 : 1-*Diphenylundec*-1-*en*-10-*yne.*—Phenylmagnesium bromide was prepared from bromobenzene (390 g.), magnesium (60 g.), and ether. Ethyl undec-10-ynoate (160·5 g., prepared[25] in 92% yield) was dissolved in ether and added during 4 hr. to the stirred Grignard reagent. Next morning, ice-cold dilute sulphuric acid and ether were added. The ether extracts were dried ($MgSO_4$) and the ether was evaporated. The yellow oily residue was dehydrated in an oil-bath at 220—230° (1 hr.) and then distilled, to give 1 : 1-diphenylundec-1-en-10-yne (211 g.,

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[25] Jeffrey and Vogel, *J.*, 1948, 674.

92%), b. p. 174—180°/0·2 mm., n_D^{24} 1·5578—1·5599, which crystallised in a few minutes (m. p. 34°; plates). Ultraviolet max: 251 mμ (ε 18,100). Black and Weedon[18] report b. p. 152°/0·02 mm., n_D^{21} 1·5620, $\lambda_{max.}$ 251 mμ (ε 18,000) (70% yield), but no m. p.

Dec-9-ynoic Acid.—(*a*) 1 : 1-Diphenylundec-1-en-10-yne (210 g.) was dissolved in glacial acetic acid (2 l.) and stirred whilst chromium trioxide (143 g.) in water (250 ml.) was added dropwise at 55—60°. Procedure according to Black and Weedon's directions[18] gave dec-9-ynoic acid (70 g., 60%), b. p. 123—126°/0·03 mm., n_D^{21} 1·4560, m. p. 22°. Lit.,[18] b. p. 88°/0·1 mm., n_D^{27} 1·4565, m. p. 22°.

(*b*) By chromic oxide oxidation,[18] 1 : 1-diphenylundeca-1 : 10-diene gave dec-9-enoic acid (63%), b. p. 124—126°/0·05 mm., n_D^{23} 1·4480. Dec-9-enoic acid (51·9 g.) in ether (300 ml.) was treated with bromine (approx. 15 ml.) until a slight excess remained. The crude dibromide was added to sodamide in liquid ammonia (1·5 l.) prepared from sodium (32·4 g.), and the mixture was stirred overnight. Ammonium chloride (50 g.) was added and the ammonia allowed to evaporate. Working up in the usual way gave dec-9-ynoic acid (40·8 g., 80%), b. p. 110—118°/10^{-4} mm., n_D^{21} 1·4592, m. p. 19—22·5° (five fractions).

1 : 1-*Diphenylundeca*-1 : 10-*diene*.—Prepared according to Black and Weedon's directions and dehydrated at 230° for 45 min. this had b. p. 186—188°/0·3 mm., n_D^{22} 1·5550 (yield 148 g., 70%). Lit.,[18] b. p. 228—230°/12—14 mm., n_D^{21} 1·5545 (yield 80%).

Methyl 11-*Hydroxyundec*-9-*ynoate.*—Dec-9-ynoic acid (57·2 g.) was neutralised with potassium hydroxide in ethanol (150 ml.); cuprous oxide (from 50 g. of cuprous chloride), 40% aqueous formaldehyde (360 ml.), and calcium carbonate (5 g.) were added. Procedure as described for methyl 12-hydroxydodec-10-ynoate gave (i) recovered methyl dec-9-ynoate (30·5 g.), b. p. 70—76°/10^{-4} mm., n_D^{23} 1·4433, infrared bands (liquid film) at 3257 m and 2126 w cm.$^{-1}$ (C≡CH) and 1736 s cm.$^{-1}$ (CO_2Me), which was hydrolysed to dec-9-ynoic acid, m. p. 18—20°, n_D^{25} 1·4563, and (ii) *methyl* 11-*hydroxyundec*-9-*ynoate* (11·0 g.), b. p. 123—124°/0·002 mm., n_D^{23} 1·4646 (Found: C, 67·65; H, 9·65. $C_{12}H_{20}O_3$ requires C, 67·9; H, 9·5%). The latter ester had infrared bands (liquid film) at 3413 s cm.$^{-1}$ (OH), 2288 w and 2230 mw cm.$^{-1}$ (C≡C) and 1734 s cm.$^{-1}$ (CO_2Me). A similar preparation from decynoic acid (60·2 g.), esterified with ethanol, yielded ethyl dec-9-ynoate (30 g.) and ethyl 11-hydroxyundec-9-ynoate (9·63 g.), b. p. 130—131°/10^{-4} mm., n_D^{21} 1·4654.

Methyl 11-*Bromoundec*-9-*ynoate.*—Methyl 11-hydroxyundec-9-ynoate (8·17 g.) was dissolved in dry ether (15 ml.) and pyridine (0·5 ml.), cooled in ice, and phosphorus tribromide (4·00 g.) was added dropwise. The mixture was stirred at 0° for 1 hr. and at 20° for 1 hr. and worked up as was methyl 12-bromododec-10-ynoate. On distillation *methyl* 11-*bromoundec*-9-*ynoate* (6·92 g., 65%), b. p. 132—133°/2 × 10^{-4} mm., n_D^{21} 1·4910, was obtained (Found: C, 52·1; H, 7·0. $C_{12}H_{19}O_2Br$ requires C, 52·35; H, 6·95%). The corresponding ethyl ester, prepared similarly, had b. p. 117—121°/0·03 mm., n_D^{18} 1·4830.

10-*Hydroxy*-9-*vinylidenehexadecanoic Acid.*—Ethyl 12-bromoundec-9-ynoate (3·63 g.) and heptaldehyde (1·70 g.) were added gradually to zinc wool (1·1 g.), activated by mercuric chloride, in tetrahydrofuran (5 ml.). Three drops of propargyl bromide had to be added to start the reaction: the solution became green and was heated on a steam-bath overnight. Water and acetic acid were added and the solution was extracted thoroughly with ether. The ethereal extracts were washed with sodium hydrogen carbonate solution and with water, dried, evaporated and distilled at 160°/10^{-6} mm. Redistillation gave an ester (1·01 g.), b. p. 150—174°/5 × 10^{-3} mm., n_D^{21} 1·4672—1·4684, which was hydrolysed by potassium hydroxide (1·0 g.) in boiling ethanol (9 ml.) and water (1 ml.) for 75 min. On working up in the usual way an acid which crystallised reluctantly at 0° was obtained: it was almost molten at 20°. The acid crystallised from acetone at −70° as plates (0·203 g.), m. p. 48—52°. [Infrared absorption at 1955 cm.$^{-1}$, ε 54·6 (in CCl_4) indicated that it was nearly pure allene.] The *acid* failed to form a clathrate compound with urea and was crystallised twice from light petroleum (b. p. 40—60°) to m. p. 52—52·5° (Found: C, 72·7; H, 10·9. $C_{18}H_{32}O_3$ requires C, 72·9; H, 10·9%). The intensity of absorption at 1955 cm.$^{-1}$ was ε 54·8. Two attempts to repeat the isolation using the methyl ester gave oily acidic products which could not be adequately purified.

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