607. *Researches on Acetylenic Compounds. Part XL.* The Synthesis of Some ω-Acetylenic Acids.*

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Syntheses, by convenient routes, of a number of straight-chain aliphatic acids possessing terminal acetylenic groups are described. Known primary acetylenic alcohols were used as starting materials.

A RANGE of acids of type (I) was required for an investigation of prototropic rearrangements in molecules containing a terminal acetylenic linkage and another functional group, not necessarily in close proximity. The synthetical methods employed were based on chain-extension from primary acetylenic alcohols. The work described in Parts XXVII (Eglinton and Whiting, *J.*, 1950, 3650) and XXXVIII (Eglinton, Jones, and Whiting, *J.*, 1952, 2873) arose from the need for intermediates in the present syntheses.

$HC{:}C{\cdot}[CH_2]_n{\cdot}CO_2H$ (I) $HC{:}C{\cdot}[CH_2]_n{\cdot}CH_2{\cdot}OH$ (II)

The first member (excluding propiolic acid) is readily available (Heilbron, Jones, and Sondheimer, *J.*, 1949, 604). The acid (I; $n = 2$) was first prepared, in very low yield, by Perkin and Simonsen (*J.*, 1907, **91**, 816); it was also obtained, again by an unsatisfactory method, by Schjånberg (*Ber.*, 1938, **71**, 569). As an attempt at improvement, prop-2-ynyl bromide was treated with sodiomalonic ester, and a mixture of the mono- and di-substituted malonic esters with unchanged malonic ester was readily obtained. Careful fractionation under reduced pressure gave a 40% yield of the monopropynyl ester; hydrolysis and decarboxylation then proceeded normally and in good yield. Alternatively, prop-2-ynyl bromide was found to react with β-dimethylamino- or β-diethylamino-crotonic ester to give an ether-insoluble quaternary salt, which was hydrolysed by warm water to the pure monosubstituted acetoacetic ester in excellent overall yield. The advantages of this method over the normal acetoacetic ester synthesis are obvious; they depend on the important fact that the proton-exchange equilibrium between (III) and (IV) is not readily established (cf. Robinson, *J.*, 1916, 1038). This selective alkylation is, unfortunately,

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* Part XXXIX, *J.*, 1952, 2873.

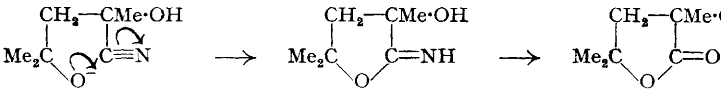
applicable only to halides of unusual reactivity, since attempts to employ 4-bromobut-1-yne or the corresponding iodide or toluene-*p*-sulphonate were unsuccessful.

$$\mathrm{R'Br} + \underset{\text{(III)}}{\mathrm{Me_2N{\cdot}CMe{:}CH{\cdot}CO_2R}} \longrightarrow \underset{\text{(IV)}}{\mathrm{Me_2\overset{+}{N}{:}CMe{\cdot}CHR'{\cdot}CO_2R}}\ \ \mathrm{Br^-}$$

The monopropynylacetoacetic ester was readily hydrolysed to (I; $n = 2$) and to hex-5-yn-2-one, though the yield of the former was low. At about this time, however, a very convenient synthesis of pent-4-yn-1-ol (II; $n = 2$) was devised (Part XXXVIII, *loc. cit.*), and direct oxidation of this alcohol with chromic acid in aqueous solution gave the best route to (I; $n = 2$), a 50% yield being obtained.

For the synthesis of pent-4-yne-1-carboxylic acid (I; $n = 3$), which at the time was unknown, three methods were investigated. The first, involving the interaction of but-3-ynyl toluene-*p*-sulphonate (Part XXVII, *loc. cit.*) with sodiomalonic ester, gave vinylacetylene as the main product. Hydrolysis of the small non-volatile fraction did, however, give a 3·5% yield of the expected monosubstituted malonic acid, which was smoothly decarboxylated to (I; $n = 3$). The use of 4-iodobut-1-yne in place of the toluene-*p*-sulphonate increased the yield of the butynylmalonic ester only to 7%. As an alternative route, pent-4-ynyl toluene-*p*-sulphonate and potassium cyanide in alcohol gave the expected nitrile in 75% yield. Controlled hydrolysis of the nitrile led to (I; $n = 3$) in excellent yield.

When acetone was used instead of alcohol as solvent for the preparation of the nitrile, the yield fell to 60%, and a by-product (V) was isolated in considerable quantity; this had been previously obtained *inter al.* from diacetone alcohol *via* the cyanohydrin by Henze, Thompson, and Speer (*J. Org. Chem.*, **1943**, **8**, 17). Although hydrolysis of the acetylenic nitrile was negligible, that of the hydroxy-cyanohydrin proceeded readily, presumably facilitated by the proximity of the reacting centres :

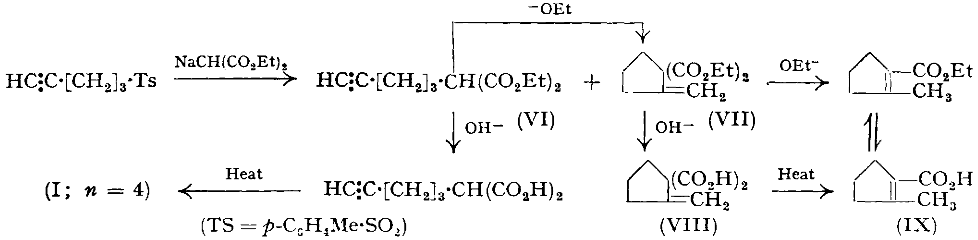


(V)

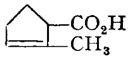
Pent-4-yne-1-carboxylic acid was also obtained by direct oxidation of hex-5-yn-1-ol (Part XXXVIII, *loc. cit.*), giving a good three-stage synthesis from tetrahydro-2-pyranylmethanol.

The obvious method for the synthesis of hex-5-yne-1-carboxylic acid (I; $n = 4$) involved the interaction of pent-4-ynyl toluene-*p*-sulphonate with sodiomalonic ester. Unexpectedly the product was a complex mixture. Provided that an appreciable excess of malonic ester over sodium ethoxide was used, this mixture could be separated into (*a*) a fraction containing two isomeric esters, $C_{12}H_{18}O_4$, discussed below, (*b*) diethyl undeca-1 : 10-diyne-6 : 6-dicarboxylate, the expected disubstitution product, and (*c*) a little unchanged starting material. The two lower boiling esters could only be partly separated by distillation, but hydrolysis of concentrates gave two isomeric acids, $C_8H_{10}O_4$. One of these, m. p. 94—95° (decomp.), obtained from the higher-boiling ester fraction, gave an acid, m. p. 22—22·5°, on decarboxylation. This was clearly (I; $n = 4$), since it showed no light absorption of high intensity above 2200 Å, absorbed two molecular proportions of hydrogen to form *n*-heptanoic acid, and was converted readily into an ester which gave a silver derivative. The other, m. p. 120—130° (decomp.), gave an acid, m. p. 131—132°, on decarboxylation to which the structure (IX) was assigned on the basis of (*a*) its absorption maximum at 2300 Å (ε 10,300), (*b*) its uptake of only one molecular proportion of hydrogen, to give a liquid acid of which the physical constants and the melting-point of the amide agreed with those recorded for 2-methyl*cyclo*pentane-1-carboxylic acid, and (*c*) the known existence of two acids, m. p.s 130° and 131°, to which structure (IX*a*) had been ascribed on evidence which did not exclude (IX) (Haworth and Perkin, *J.*, 1908, **93**, 584; Wallach and Ollichmacher, *Annalen*, 1899, **305**, 225). More recently (IX) has been prepared by Shimizu (*Chem. Abs.*, 1950, **44**, 8868) who reported m. p. 132° and rigorously proved the structure of his product.

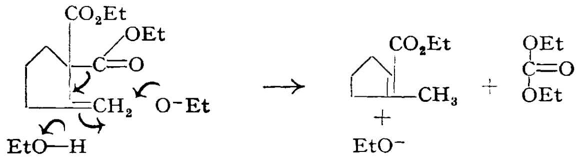
Given the structures of (VI), the necessary precursor of (I; $n = 4$), and (IX), those of the intermediates (VII and VIII) followed, and were confirmed by the transparency of (VIII) above 2200 Å, and the presence of a strong band at 900 cm.$^{-1}$ ($>C\!:\!CH_2$) in the infra-red spectrum of (VII) (personal communication from the late Dr. H. P. Koch); (VII) also gave a 22% yield of formaldehyde on ozonolysis. The refluxing of a solution of (VI) in ethanol containing a little sodium ethoxide gave (VII), suggesting that the reaction involves addition of the $-\bar{C}(CO_2Et)_2$ moiety to the acetylenic linkage; since (VII) was never obtained free from (VI), an equilibrium between the two esters is not excluded. Nucleophilic additions to acetylenic compounds, especially acetylene itself, are now known to take place much more readily than with the corresponding olefins. Addition of malonic ester residues has not been reported, and unsuccessful attempts were therefore made to carry out such reactions with hex-1-yne and diethyl malonate and methylmalonate, temperatures considerably higher than those used in the cyclisation of (VI) being without effect. Clearly an intramolecular environment here favours cyclisation.



When (VI) was treated with more than one equivalent of sodium ethoxide in refluxing ethanol, a lower-boiling product resulted which consisted essentially of the ethyl ester of (IX), also obtained (though with difficulty) from (IX) in ethanolic sulphuric acid; hydrolysis of the ester to (IX) also proved difficult. The decarbethoxylation reaction is a variant of the well-known reversed Claisen condensation :



(IX*a*)



A small quantity of the ethyl ester of (I; $n = 4$) was, however, also present, apparently as the result of a reversed Claisen condensation with (VI) preceding cyclisation; it was recognised by the detection of a substance containing an ethynyl grouping in the crude ethyl 2-methyl*cyclo*pentene-1-carboxylate.

In collaboration with Mr. G. H. Whitham it was found that the mixed malonic acids, obtained by hydrolysis of the C_{12} esters (VI) and (VII), could be decarboxylated in *N*-hydrochloric acid at 100°, and that (IX) then separated almost quantitatively at 0°. Extraction and distillation gave (I; $n = 4$) in 44% overall yield from pent-4-ynyl toluene-*p*-sulphonate.

An attempt was made to determine the structural features required for the novel cyclisation described above. Diethyl hept-6-yne-1 : 1-dicarboxylate was obtained from hex-5-ynyl toluene-*p*-sulphonate without difficulty but would not cyclise. The condensation product from pent-4-ynyl toluene-*p*-sulphonate and sodioacetoacetic ester proved to be the straight chain product, and on warming with sodium ethoxide in ethanol gave mainly low-boiling decarbethoxylated and deacetylated products from which, however, a small quantity of (IX) was obtained after hydrolysis. On the other hand, the ester of (I; $n = 4$) itself did not cyclise under the normal conditions, while very vigorous alkaline treatment would, of course, result in prototropic migration of the triple bond. Thus the conditions for this reaction apparently include a chain of three methylene groups between an acetylenic linkage and a pseudo-acidic centre comparable in strength with $-CH(CO_2Et)_2$.

Hept-6-yne-1-carboxylic acid (I; $n = 5$) was readily prepared by hydrolysis and decarboxylation of diethyl hept-6-yne-1 : 1-dicarboxylate. It had previously been obtained by Newman and Wotiz (*J. Amer. Chem. Soc.*, 1949, **71**, 1293).

Of the remaining ω-acetylenic acids, two have been prepared from the corresponding ethylenes by bromination and dehydrobromination (dec-9-yne-1-carboxylic acid, *inter al.* by Lauer and Gensler, *J. Amer. Chem. Soc.*, 1945, **67**, 1171: nonadec-18-yne-1-carboxylic acid by Stenhagen, *Arkiv Kemi*, 1949, **1**, 99). The first member (I; $n = 1$) of the series is unusually sensitive to alkalis, (I; $n = 2$) is hydrated more readily than most acetylenic compounds in acidic solution, and the two acids (I; $n = 2$ and 3) are both isomerised in boiling 20—40% sodium hydroxide solution. With these exceptions, to be discussed later, ω-acetylenic acids can be esterified and recovered from esters, etc., in the usual manner provided that exceptionally drastic conditions are avoided.

EXPERIMENTAL

Unless otherwise specified, light petroleum refers to the fraction of b. p. 40—60°. Melting-points denoted m. p. (K) were determined on the Kofler block. Light-absorption data were obtained in alcoholic solution. The ethynyl group estimations were carried out by a method developed in the laboratories of Messrs. Glaxo Ltd. (personal communication from Dr. R. M. Evans): the sample (*ca.* 0·15 g.) was dissolved in ethanol (35 c.c.) containing 6 drops of a solution of methyl red (0·1 g.) and methylene blue (0·05 g.) in ethanol (100 c.c.); aqueous silver nitrate solution (10%; 12·5 c.c.) was added, and the mixture was titrated to a blue-grey end point with sodium hydroxide solution ($\text{NaOH} \equiv \cdot\text{C}\vdots\text{CH}$).

The preparation of the primary acetylenic alcohols and their toluene-*p*-sulphonates was described in Parts XXVII and XXXVIII (*locc. cit.*).

Diethyl But-3-yne-1 : 1-dicarboxylate.—Prop-2-ynyl bromide (29·5 g.) was slowly added to an alcoholic suspension of ethyl sodiomalonate [from sodium (5·9 g.), ethyl alcohol (100 c.c.), and ethyl malonate (40 g.)], and the mixture was stirred for 16 hr. and then poured into water. After isolation with ether, the product was distilled through a 30-cm. Fenske column into three main fractions: (*a*) ethyl malonate (7 g.); (*b*) diethyl but-3-yne-1 : 1-dicarboxylate (20 g., 40%), b. p. 109·5°/13 mm., n_D^{20} 1·4384 (Found: C, 60·5; H, 7·2. Calc. for $C_{10}H_{14}O_4$: C, 60·6; H, 7·1%) (Perkin and Simonsen, *J.*, 1907, 816, 840, give b. p. 129°/22 mm.); and (*c*) diethyl hepta-1 : 6-diyne-4 : 4-dicarboxylate (7 g.), b. p. 122—126°/13 mm., m. p. 45°, n_D^{20} 1·4510 (supercooled liquid) (Brockmühl, Schwabe, and Ehrhart, *Chem. Zent.*, 1928, II, 1823; 1931, II, 742, give m. p. 45·5°).

But-3-yne-1 : 1-dicarboxylic Acid.—Diethyl but-3-yne-1 : 1-dicarboxylate (2 g.) was shaken with a solution of potassium hydroxide (1·5 g.) in water (1 c.c.), and the resultant solution set aside for 24 hr. The acid, after isolation with ether, was obtained as deliquescent needles (540 mg., 38%), m. p. 139° (decomp.) after recrystallisation from ether–light petroleum (b. p. 60—80°) [Perkin and Simonsen (*loc. cit.*) give m. p. 139° (decomp.)]. Decarboxylation at 150° of a small sample gave but-3-yne-1-carboxylic acid (I; $n = 2$), m. p. 56—57° [Perkin and Simonsen (*loc. cit.*) record m. p. 57°].

Ethyl 2-Oxohex-5-yne-3-carboxylate.—(*a*) A solution of prop-2-ynyl bromide (39 g.) in dry ether (20 c.c.) was added to a stirred and cooled suspension of ethyl sodioacetoacetate [from sodium (7·3 g.) and ethyl acetoacetate (43 g.)] in dry ethanol (100 c.c.) at such a rate that the temperature did not exceed 30°. After being stirred at 20° for 24 hr., the suspension was filtered and the solvent removed from the filtrate by evaporation. Water was added and the product isolated with ether. Fractionation at high reflux ratio through a 30-cm. Fenske column gave ethyl acetoacetate (4·6 g.), *ethyl 2-oxohex-5-yne-3-carboxylate* (26·3 g., 50%), b. p. 104—105°/16 mm., n_D^{20} 1·4480 (Found: C, 64·5; H, 6·9. $C_9H_{12}O_3$ requires C, 64·2; H, 7·2%), and a fraction (14·5 g.), b. p. 119—127°/16 mm., n_D^{20} 1·4636, which gave a silver derivative and was probably essentially the disubstituted ester.

(*b*) A mixture of ethyl β-dimethylaminocrotonate (3·1 g.; Glickman and Cope, *J. Amer. Chem. Soc.*, 1945, **67**, 1019) and prop-2-ynyl bromide (3·0 g.) was set aside at 20° for 3 days. The syrupy quaternary salt, after repeated extraction with dry ether, was hydrolysed by heating it under reflux with water (4 c.c.) for 5 min. The product was isolated with ether and distilled to give the ester (2·85 g., 86%), b. p. 48—49°/0·05 mm., n_D^{24} 1·4450.

(*c*) The use of β-diethylaminocrotonic ester in a similar reaction gave a very hygroscopic crystalline quaternary salt, m. p. *ca.* 118°, in a rather slower reaction. Hydrolysis gave the acetylenic ketone described below.

Hex-5-*yn*-2-*one*.—Ethyl 2-oxohex-5-yne-3-carboxylate (5·2 g.) was shaken for 16 hr. with a 5% aqueous solution of sodium hydroxide (40 c.c.). The resulting solution was washed with ether and then carefully acidified with dilute sulphuric acid (1 : 1), and the product was isolated with ether. Distillation gave the ketone (1·2 g., 35%), b. p. 76°/85 mm., n_D^{18} 1·4340—1·4355 (Gardner and Perkin, *J.*, 1907, 848, give b. p. 149°/749 mm.). But-3-yne-1-carboxylic acid (0·2 g.), m. p. 55—56°, was isolated from the distillation residue. The ketone semicarbazone had m. p. 135—136°, after crystallisation from methanol (Gardner and Perkin, *loc. cit.*, give m. p. 135—136°). The 2 : 4-*dinitrophenylhydrazone* formed plates, m. p. 138—139°, from carbon tetrachloride (Found: C, 52·25; H, 4·4. $C_{12}H_{12}O_4N_4$ requires C, 52·2; H, 4·35%).

But-3-*yne*-1-*carboxylic Acid* (preparative method).—Chromic acid (6N in 12N-sulphuric acid) (240 c.c.) was added during 1 hr. to a stirred and cooled (below 20°) solution of pent-4-yn-1-ol (28·4 g.) in water (200 c.c.). After 16 hr. the acidic fraction (20 g.) was isolated with ether and crystallised from light petroleum giving lustrous plates (16·4 g., 50%), m. p. (K) 57—58° after recrystallisation from the same solvent. *Pent*-4-*ynyl but*-3-*yne*-1-*carboxylate*, b. p. (bath temp.) 60°/0·1 mm., n_D^{21} 1·4591, was isolated in small yield from the neutral fraction in another experiment (Found: C, 73·15; H, 7·2. $C_{10}H_{12}O_2$ requires C, 73·15; H, 7·35%).

Yields of the acid were 34, 36, and 11% when the solvents employed were ethyl methyl ketone, acetone and glacial acetic acid, other conditions being unchanged.

Pent-4-*yne*-1 : 1-*dicarboxylic Acid*.—(*a*) Ethyl malonate (9·6 g.) was added to a solution of sodium ethoxide (from 1·0 g. of sodium) in dried ethanol (20 c.c.) at 25°. Addition of but-3-ynyl toluene-*p*-sulphonate (9·1 g.) resulted in precipitation of sodium toluene-*p*-sulphonate, which was collected after 24 hr. (7·3 g., 95%). An odour of vinylacetylene was noticed. Isolation and distillation of the neutral portion gave a fraction (0·45 g.), b. p. 69—129°/0·1 mm., which was hydrolysed with potassium hydroxide at room temperature. Crystallisation of the solid acid fraction from benzene gave the *acid* (250 mg., 3·5%), m. p. 101·5—102° after recrystallisation (Found: C, 53·75; H, 4·9. $C_7H_8O_4$ requires C, 53·85; H, 5·15%).

(*b*) 4-Iodobut-1-yne (6 g.) was added to a suspension of ethyl sodiomalonate [from sodium (0·7 g.) and diethyl malonate (5·3 g.)] in ethanol (15 c.c.), and the mixture stirred at 20° for 48 hr. The alkaline suspension was diluted with water and the neutral product isolated. Distillation gave unchanged diethyl malonate and a fraction from which substantially pure *diethyl pent*-4-*yne*-1 : 1-*dicarboxylate* (0·5 g.), b. p. 118°/14 mm., n_D^{15} 1·4428, was obtained (Found: C, 61·75; H, 7·85. $C_{11}H_{16}O_4$ requires C, 62·3; H, 7·55%). The ester gave a white silver salt. Hydrolysis of the ester (270 mg.) afforded crude pent-4-yne-1 : 1-dicarboxylic acid (140 mg.), m. p. (K) 101—102° after recrystallisation from benzene. No depression of melting-point was observed on admixture with a sample prepared as under (*a*).

5-*Cyanopent*-1-*yne*.—Pent-4-ynyl toluene-*p*-sulphonate (24 g.), potassium cyanide (12 g.), and 80% ethanol (100 c.c.) were heated under reflux for 48 hr. Water was added and the mixture was extracted with ether. Evaporation of the dried extract, followed by distillation, gave the *cyanide* (6·9 g., 75%), b. p. 65·5°/7 mm., n_D^{17} 1·4409 (Found: C, 77·2; H, 7·35. C_6H_7N requires C, 77·4; H, 7·6%).

The cyanide was obtained in only 60% yield when the solvent was aqueous acetone: ether extraction of the acidified aqueous layer gave 4-methyl-2 : 4-dihydroxypentane-2-carboxylactone (*ca.* 12 g.), b. p. 68—69°/0·4 mm., which crystallised from benzene in needles, m. p. (K) 66·5—67·5° (Found: C, 58·3; H, 8·3. Calc. for $C_7H_{12}O_3$: C, 58·3; H, 8·4%). Light absorption: $\lambda_{max.}$ 2210 Å, $\varepsilon = 72$. (Henze, Thompson, and Speer, *J. Org. Chem.*, 1943, **8**, 17, give m. p. 65°.)

Pent-4-*yne*-1-*carboxylic Acid*.—(*a*) 5-Cyanopent-1-yne (20 g.) was heated under reflux with 10% potassium hydroxide solution (200 c.c.) for 7 hr., and the solution then acidified and extracted with ether. Evaporation of the dried extract followed by distillation gave the *acid* (I, $n = 3$) (21·9 g., 90%), m. p. *ca.* −8°, b. p. 106°/9 mm., n_D^{17} 1·4500 (Found: C, 63·9; H, 7·3. $C_6H_8O_2$ requires C, 64·25; H, 7·15%). The p-*bromophenacyl* ester crystallised in iridescent plates, m. p. (K) 74·5°, from ethanol (Found: C, 54·25; H, 4·35. $C_{14}H_{13}O_3Br$ requires C, 54·35; H, 4·25%). Hydrogenation of the acid in ethyl acetate with platinic oxide catalyst (uptake: 101% of theory) gave hexanoic acid, identified as its *p*-bromophenacyl ester, m. p. (K) 71° undepressed on admixture with an authentic specimen, m. p. (K) 70·5—71°.

(*b*) Chromic acid (6N; 10 c.c.) was slowly added to a stirred and cooled (*ca.* 10°) solution of hex-5-yn-1-ol (1·4 g.) in acetone (10 c.c.). After 30 min. the acid fraction was isolated with ether; distillation gave the acid (410 mg., 27%), b. p. 135°(bath temp.)/14 mm., n_D^{19} 1·4502. The *p*-bromophenacyl ester was identical with that derived from 5-cyanopent-1-yne.

The neutral fraction was heterogeneous but, after purification *via* the silver derivative, it gave an ester (200 mg.), b. p. 120°(bath temp.)/0·3 mm., n_D^{20} 1·4631, which was evidently *hex-5-ynyl pent-4-yne-1-carboxylate* (Found: C, 74·35; H, 8·1. $C_{12}H_{16}O_2$ requires C, 74·9; H, 8·4%).

Diethyl Hex-5-yne-1 : 1-dicarboxylate.—(*a*) Diethyl malonate (70·5 g.) was slowly added to a hot, stirred solution of sodium ethoxide [from sodium (10 g.)] in dry ethanol (200 c.c.), and the solution was heated under reflux for 30 min. Pent-4-ynyl toluene-*p*-sulphonate (100 g.) was added during 1 hr., and after a further 4 hr., the cooled, neutral mixture was filtered, most of the ethanol removed, the filtrate and precipitate added to water (1 litre), and the neutral fraction isolated with ether and carefully distilled to give six fractions.

It was evident from the ethynyl determinations that the lower fractions contained some diethyl 2-methylene*cyclo*pentane-1 : 1-dicarboxylate (see below), and the higher fractions a little of the disubstituted ester. Redistillation of fraction 3 (b. p. 95—97°/0·2 mm.; n_D^{17} 1·4458) obtained in another experiment gave essentially pure *diethyl hex-5-yne-1 : 1-dicarboxylate* (Found: C, 63·95; H, 7·95; ·C⋮CH, 10·95. $C_{12}H_{18}O_4$ requires C, 63·7; H, 8·0; ·C⋮CH, 11·1%). When fraction 6 (b. p. 103—140°; n_D^{17} 1·4635) was redistilled the main portion had b. p. 130—134°/0·2 mm., and solidified on being set aside at 20°. The solid was freed from adhering liquid which contained unchanged toluene-*p*-sulphonate, and was recrystallised at −6° from light petroleum (b. p. 30—40°) giving *diethyl undeca-1 : 10-diyne-6 : 6-dicarboxylate* as prisms, m. p. 31—32° (open tube). Analyses were erratic, although an ethynyl determination showed the material to be pure (Found: ·C⋮CH, 17·3. $C_{17}H_{24}O_4$ requires ·C⋮CH, 17·3%).

(*b*) From a similar condensation between ethyl sodiomalonate [from sodium (5 g.) and ethyl malonate (35 g.)] in dry ethanol (100 c.c.) and 5-iodopent-1-yne (32 g.), the following were obtained on distillation of the neutral fraction: ethyl malonate (5 g.); a fraction (i) (20·6 g.), b. p. 83—108°/0·6 mm., n_D^{22} 1·4532; and a fraction (ii) (3 g.), b. p. 134°/0·6 mm., n_D^{22} 1·4600. Fraction (i) was mainly *2-methylene*cyclo*pentane-1 : 1-dicarboxylate*, b. p. 67—69°/0·1 mm., n_D^{19} 1·4553 (Found: C, 63·8; H, 8·05. $C_{12}H_{18}O_4$ requires C, 63·7; H, 8·0%). An ethynyl determination indicated the presence of *ca.* 10% of the isomeric acetylenic ester, which was later confirmed by an infra-red examination.

Catalytic hydrogenation required 98% of the calculated volume of hydrogen. The saturated ester was hydrolysed with aqueous potassium hydroxide to give 2-methyl*cyclo*pentane-1 : 1-dicarboxylic acid, which separated in needles, m. p. (K) 171—172°, from ether (Colman and Perkin, *J.*, 1888, **193**, give m. p. 173—175°). Decarboxylation by distillation gave 2-methyl*cyclo*pentane-1-carboxylic acid, b. p. (bath temp.) 120°/14 mm., $n_D^{19.5}$ 1·4520, identified as the amide, which after sublimation (80°/0·1 mm.) followed by crystallisation from benzene had m. p. (K) 151—153° (Ney, Crouch, Rannefeld, and Lochte, *J. Amer. Chem. Soc.*, 1943, **65**, 770, describe the acid as having b. p. 220°, n_D^{20} 1·4521, and as forming an amide, m. p. 149—150°).

Hex-5-yne-1 : 1-dicarboxylic Acid.—Diethyl hex-5-yne-1 : 1-dicarboxylate (4·5 g.) was shaken for 5 min. with a solution of potassium hydroxide (4·4 g.) in water (5 c.c.), and the resultant solution was set aside for 16 hr. at 18°. Several crystallisations of the solid acid fraction (2·8 g., 85%) from benzene gave the *acid* as needles, m. p. (K) 94—95° (decomp.) (Found: C, 56·5; H, 5·9. $C_8H_{10}O_4$ requires C, 56·45; H, 5·9%).

Hex-5-yne-1-carboxylic Acid (I; *n* = 3).—(*a*) Diethyl hex-5-yne-1 : 1-dicarboxylate (33·5 g.; fraction 3 from the experiment described above) was dissolved in a 5% aqueous ethanolic solution of potassium hydroxide (350 c.c.) and the mixture set aside at 20° for 3 days. After most of the ethanol had been removed by distillation, the solution was acidified and heated under reflux for 1 hr. On cooling, 2-methyl*cyclo*pent-1-ene-1-carboxylic acid (0·16 g.) separated in needles, which had m. p. (K) 132·5—133° after recrystallisation from nitromethane. The filtrate was thoroughly extracted with ether and the dried extract was evaporated and distilled. Hex-5-yne-1-carboxylic acid (15·6 g., 80%), b. p. 89—92°/0·05 mm., n_D^{21} 1·4520, formed a mass of needles, m. p. 20°, raised to 22—22·5°, after recrystallisation from light petroleum (b. p. 40—60°). (Taylor and Strong, *J. Amer. Chem. Soc.*, 1950, **72**, 4263, describe the acid as an oil, b. p. 93—94°/0·1 mm., n_D^{25} 1·4495.) The p-*bromophenacyl* ester crystallised from aqueous ethanol in needles, m. p. (K) 71·5—72·5° (Found: C, 55·85; H, 4·5. $C_{15}H_{15}O_3Br$ requires C, 55·75; H, 4·7%). The acid absorbed 98% of the calculated volume of hydrogen to give hexane-1-carboxylic acid [*p*-bromophenacyl ester, m. p. 71° (Huntress and Mulliken, "Identification of Pure Organic Compounds," Wiley, London, 1941, give m. p. 72°)].

When other fractions of less pure diethyl hex-5-yne-1 : 1-dicarboxylate were hydrolysed, the yields of hex-5-yne-1-carboxylic acid were in approximate agreement with those to be expected from their estimated ethynyl group content. The overall yield of hex-5-yne-1-carboxylic acid from the toluene-*p*-sulphonate was 44%.

(*b*) Hex-5-yne-1 : 1-dicarboxylic acid (1·1 g.) was slowly heated to 160° under reduced pressure (18 mm.), simultaneous decarboxylation and distillation then occurring. The acid (750 mg., 92%) had b. p. 110° (bath temp.)/0·06 mm., n_D^{21} 1·4540.

Ethyl Hex-5-yne-1-carboxylate.—A solution of hex-5-yne-1-carboxylic acid (8·0 g.) in absolute ethanol (50 c.c.) containing sulphuric acid (1·5 c.c.) was set aside at 20° for 5 days. Isolation with ether followed by distillation gave the *ester* (8·1 g., 84%), b. p. 96—97°/20 mm., n_D^{23} 1·4355 (Found : C, 69·85; H, 9·2; ·C⋮CH, 16·2. $C_9H_{14}O_2$ requires C, 70·1; H, 9·15; ·C⋮CH, 16·2%).

*2-Methylene*cyclo*pentane-1 : 1-dicarboxylic Acid.*—Diethyl 2-methylene*cyclo*pentane-1 : 1-dicarboxylate (5·5 g.; containing *ca.* 10% of the isomeric acetylenic ester) was shaken with a solution of potassium hydroxide (7·5 g.) in water (8 c.c.) for 2 hr. and the resultant solution was set aside for 4 days. The acid fraction was then isolated by continuous extraction with ether and the dried extract was evaporated to leave a solid residue. Trituration of the crystalline mass with benzene–light petroleum gave the *acid* (3·3 g., 80%) as needles, m. p. 120—130° (decomp.), unaltered after several crystallisations from nitromethane (Found : C, 56·3; H, 5·85. $C_8H_{10}O_4$ requires C, 56·45; H, 5·9%). Light absorption : rising absorption down to 2150 Å, ε = 945 and 322 at 2150 Å and 2300 Å, respectively.

*2-Methyl*cyclo*pent-1-ene-1-carboxylic Acid.*—(*a*) 2-Methylene*cyclo*pentane-1 : 1-dicarboxylic acid (3 g.) was distilled at 0·1 mm., giving the monocarboxylic acid (2·2 g., 98%), which formed needles, m. p. (K) 131—132° after crystallisation from nitromethane (Found : C, 66·35; H, 7·85. Calc. for $C_7H_{10}O_2$: C, 66·6; H, 8·0%). Light absorption : $\lambda_{max.}$ 2300 Å, ε = 10,500. Shimizu (*loc. cit.*) gives m. p. 132°.

The structure of the acid was confirmed by catalytic hydrogenation (absorption 97% of theoretical value) to 2-methyl*cyclo*pentane-1-carboxylic acid, n_D^{20} 1·4510 [amide, m. p. (K) 152—154° undepressed on admixture with the amide, m. p. (K) 151—153°, originating from diethyl 2-methyl*cyclo*pentane-1 : 1-dicarboxylate].

(*b*) Diethyl 2-methylene*cyclo*pentane-1 : 1-dicarboxylate (3 g.) was shaken for 4 hr. with a solution of potassium hydroxide (3·5 g.) in water (6 c.c.), the hydrolysis being completed under reflux for a further 3 hr. After being washed with ether, the cooled solution was neutralised and evaporated to dryness. Dilute sulphuric acid (1 : 1; 7 c.c.) was added, the solution was brought to boiling, and the monocarboxylic acid was removed by steam-distillation. The acid (1·24 g., 74%) formed prismatic needles, m. p. (K) 131—132°.

*Methyl 2-Methyl*cyclo*pent-1-ene-1-carboxylate.*—2-Methyl*cyclo*pent-1-ene-1-carboxylic acid (169 mg.) was esterified with diazomethane; distillation furnished the *ester* (174 mg., 93%), b. p. 85—90°(bath temp.)/18 mm., n_D^{19} 1·4750 (Found : C, 68·4; H, 9·05. $C_8H_{12}O_2$ requires C, 67·8; H, 8·6%; other samples underwent explosive decomposition). Light absorption : $\lambda_{max.}$ 2315 Å, ε = 10,300.

*Ethyl 2-Methyl*cyclo*pent-1-ene-1-carboxylate.*—A solution of 2-methyl*cyclo*pent-1-ene-1-carboxylic acid (600 mg.) in dry ethanol (5 c.c.) containing sulphuric acid (0·1 c.c.) was heated under reflux for 10 hr. Isolation and distillation of the neutral fraction gave the *ester* (400 mg., 50%), b. p. 190°(bath temp.)/520 mm., n_D^{21} 1·4660 (Found : C, 69·7; H, 9·05. $C_9H_{14}O_2$ requires C, 70·0; H, 9·1%). Light absorption : $\lambda_{max.}$ 2325 Å, ε = 10,300.

Much of the acid was recovered unchanged from an attempted esterification at 20° (36 hr.). The ester was also remarkably resistant to hydrolysis : a small portion had undergone little hydrolysis after contact with aqueous potassium hydroxide (30%) for several days.

Diethyl Hept-6-yne-1 : 1-dicarboxylate.—Hex-5-ynyl toluene-*p*-sulphonate (3 g.; prepared from crude hex-5-yn-1-ol containing some tetrahydro-2-pyranylmethanol) in dry ether (10 c.c) was added to a stirred suspension of ethyl sodiomalonate [from sodium (0·3 g.) and ethyl malonate (2·1 g.)] in dry ethanol (10 c.c.), the suspension heated under reflux for 15 hr., and the neutral fraction was then isolated with ether. Distillation gave unchanged ethyl malonate and two fractions : (*a*) 1·27 g., b. p. 120—125°(bath temp.)/0·01 mm., n_D^{18} 1·4470; and (*b*) 0·75 g., b. p. 190°(bath temp.)/0·01 mm., which partly solidified on cooling. Fraction (*a*) was redistilled to give substantially pure *diethyl hept-6-yne-1 : 1-dicarboxylate* (1·1 g., 40%), b. p. 110°(bath temp.)/0·005 mm., n_D^{22} 1·4455 (Found : C, 64·5; H, 8·3; ·C⋮CH, 10·8. $C_{13}H_{20}O_4$ requires C, 65·0; H, 8·3; ·C⋮CH, 10·4%). Newman and Wotiz (*J. Amer. Chem. Soc.*, 1949, **71**, 1293) did not isolate this ester although it was an intermediate in their route to hept-6-yne-1-carboxylic acid. The crystalline material from fraction (*b*), after crystallisation from light petroleum, had m. p. (K) 71—72°, undepressed on admixture with a specimen of tetrahydro-2-pyranylmethyl toluene-*p*-sulphonate, m. p. (K) 72·5° (cf. Eglinton, Jones, and Whiting, *loc. cit.*).

Hept-6-yne-1-carboxylic Acid.—Diethyl hept-6-yne-1 : 1-dicarboxylate (310 mg.) was shaken with potassium hydroxide solution (0·7 c.c.; *ca.* 50%) and the solution was set aside for 18 hr.

Isolation of the acid fraction with ether gave hept-6-yne-1 : 1-dicarboxylic acid (230 mg.), m. p. 80—86°. A small sample crystallised from benzene–light petroleum (b. p. 60—80°) in rhombs, m. p. (K) 84—85°. The acid was heated at 160° for 1 hr., yielding hept-6-yne-1-carboxylic acid (130 mg., 72%), m. p. 18—20° [Newman and Wotiz (*loc. cit.*) give m. p. 20°]. The acid was characterised by conversion, *via* the acid chloride, into the amide which separated from light petroleum (b. p. 60—80°) in needles, m. p. (K) 89·5—90° undepressed on admixture with a genuine sample, m. p. (K) 90·5—91°, kindly supplied by Professor M. S. Newman.

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