Researches on Acetylenic Compounds. Part XLVI. Prototropic Rearrangements of Acetylenic Acids.*

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[Reprint Order No. 5304.]

Acetylenic acids may undergo prototropic rearrangements in alkaline solution to give isomeric compounds of the acetylenic, allenic, or conjugated dienoic acid types. The direction and relative rates of these changes, superficially in some cases surprising, are explained in terms of the known energy relationships between the different unsaturated groupings present in the products and in their carbanion intermediates. Hyperconjugation is shown to play a more important role than in the transformation of the related ethylenic compounds.

THE isomerisation of acetylenic hydrocarbons under alkaline conditions, a much easier process than that of the corresponding ethylenes, was discovered by Favorskii (*J. Russ. Phys. Chem. Soc.*, 1887, **19**, 414; *J. prakt. Chem.*, 1888, **37**, 382). It has recently been greatly clarified by Jacobs, Akawie, and Cooper (*J. Amer. Chem. Soc.*, 1951, **73**, 1273), who demonstrated that pent-1-yne, pent-2-yne, and penta-1 : 2-diene are each converted by contact with alcoholic potassium hydroxide at 175° into a mixture of all three, containing at equilibrium about 1·3%, 95·2%, and 3·5%, respectively. Under these conditions penta-2 : 3-diene, and penta-1 : 3-diene, presumably the most stable isomer, are not formed at an appreciable rate. If it is assumed that interconversion proceeds *via* carbanion intermediates (see below), this implies that of the three formally very similar processes (*a*, *b*, and *c*; $R = CH_3$), both (*a*) and (*b*) are considerably faster than (*c*). That the carbanion in (*a*)

$$\text{(}a\text{)}\quad CH{\equiv}C{\cdot}CH_2{\cdot}CH_2R \xrightarrow{-H^+} CH{\equiv}C{\cdot}\bar{C}H{\cdot}CH_2R \longleftrightarrow \bar{C}H{=}C{=}CH{\cdot}CH_2R$$

$$\text{(}b\text{)}\quad CH_3{\cdot}C{\equiv}C{\cdot}CH_2R \xrightarrow{-H^+} \bar{C}H_2{\cdot}C{\equiv}C{\cdot}CH_2R \longleftrightarrow CH_2{=}C{=}\bar{C}{\cdot}CH_2R$$

$$\text{(}c\text{)}\quad CH_3{\cdot}C{\equiv}C{\cdot}CH_2R \xrightarrow{-H^+} CH_3{\cdot}C{\equiv}C{\cdot}\bar{C}HR \longleftrightarrow CH_3{\cdot}\bar{C}{=}C{=}CH{\cdot}R$$

is more readily formed than that in (*c*) may be correlated with the evidence that an alkyl group partly neutralises the electron-attracting power of the acetylenic linkage in propiolic acid ($K_a = 14 \times 10^{-3}$; cf. tetrolic acid, $K_a = 2{\cdot}46 \times 10^{-3}$). The advantage of (*b*) over (*c*) is explained by the relative stability of the simple carbanions, methyl > primary > secondary > tertiary, as indicated by the reverse order of reactivity in elimination reactions on saturated ethers (see, *inter al.*, Gilman, Moore, and Baine, *J. Amer. Chem. Soc.*, 1941, **63**, 2479) and by the tendency of tertiary carbanions to add to ethylene (Bartlett, Friedman, and Stiles, *J. Amer. Chem. Soc.*, 1953, **75**, 1771). Under more drastic conditions the reaction (*c*) and obvious subsequent stages do take place (see, *inter al.*, Bourgel, *Ann. Chim.*, 1925, **3**, 325).

$$\text{(}d\text{)}\quad CH_2{=}C{=}CH{\cdot}CH_2R \xrightarrow{-H^+} \bar{C}H{=}C{=}CH{\cdot}CH_2R \longleftrightarrow CH{\equiv}C{\cdot}\bar{C}H{\cdot}CH_2R$$

$$\text{(}e\text{)}\quad CH_2{=}C{=}CH{\cdot}CH_2R \xrightarrow{-H^+} CH_2{=}C{=}C^-{\cdot}CH_2R \longleftrightarrow \bar{C}H_2{\cdot}C{\equiv}C{\cdot}CH_2R$$

$$\text{(}f\text{)}\quad CH_2{=}C{=}CH{\cdot}CH_2R \xrightarrow{-H^+} CH_2{=}C{=}CH{\cdot}\bar{C}HR \longleftrightarrow CH_2{=}\bar{C}{\cdot}CH{=}CHR$$

The behaviour of penta-1 : 2-diene implies that processes (*d*) and (*e*) are faster than (*f*). When allenes and acetylenes are treated with acidic oxides, *e.g.*, " floridin," somewhat similar transformations ensue, but conjugated dienes are then formed in quantity, indicating that the energy relationships among the various unsaturated carbonium ions are quite different.

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* Part XLV, preceding paper.

The isomerisations of acetylenic hydrocarbons are the necessary basis for understanding the observations described in the present and several subsequent papers in this Series; hence the need for the generalisations above. These reactions are also of some interest from the synthetical standpoint, especially since the products can usually be reduced specifically to the corresponding *cis-* or *trans*-olefins. Potentially more important in this second respect are similar transformations in acetylenic compounds bearing functional groups, but the only examples previously recorded are the conversion of the terminally acetylenic acids, undec-10-ynoic and tricos-22-ynoic acids, into their isomers containing $CH_3{\cdot}C{\equiv}C{\cdot}$ groups (Krafft, *Ber.*, 1896, **29**, 2232; Stenhagen, *Arkiv Kemi*, 1949, **1**, 99). The preceding paper describes an investigation of the prototropic rearrangements of the acids, $C_3H_4{\cdot}CO_2H$, and the present contribution deals with other doubly-unsaturated acids of moderate chain-length and without lateral substitution. Subsequent papers in this Series will outline the extension of these studies to a variety of acetylenic acids and other derivatives. The preparation of the ω-acetylenic acids used as starting-materials has been described by Eglinton and Whiting (*J.*, 1953, 3052).

Pent-4-ynoic acid (I) was treated with potassium hydroxide under varied conditions in preliminary experiments. Although such mild reagents as sufficed to isomerise but-3-ynoic acid had no effect, boiling 9N-potassium hydoxide converted it into penta-2 : 4-dienoic acid (III) in a maximal yield of 60% (spectroscopic, after 1 hour; 40% isolated). Presumably this must be formed by a second prototropic transformation of penta-3 : 4-dienoic acid (II):

$$\underset{\text{(I)}}{CH{\equiv}C{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H} \xrightarrow{HO^-} \underset{\text{(II)}}{CH_2{=}C{=}CH{\cdot}CH_2{\cdot}CO_2H} \xrightarrow{HO^-} \underset{\text{(III)}}{CH_2{=}CH{\cdot}CH{=}CH{\cdot}CO_2H}$$

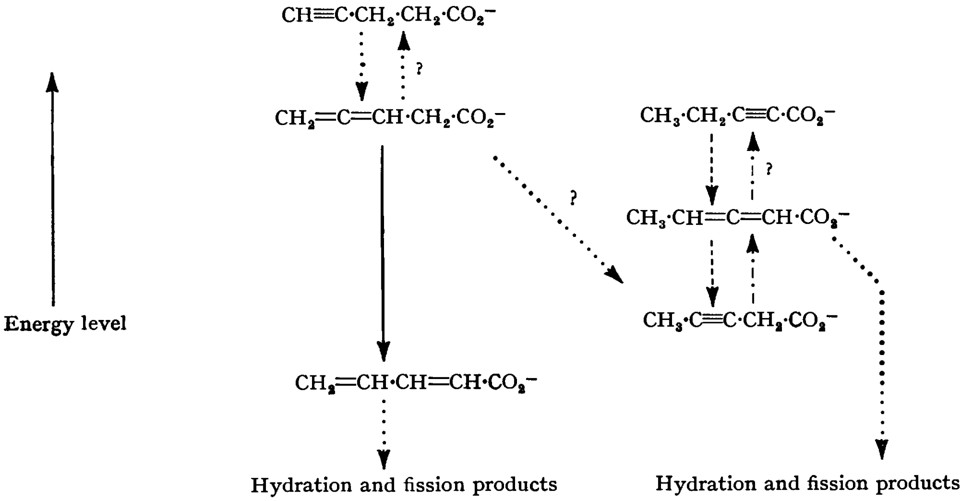
but interruption of the reaction and infra-red examination of the product did not reveal the presence of (II). Mr. P. Nayler has prepared this allenic acid by oxidation of penta-3 : 4-dien-1-ol (Bates, Jones, and Whiting, *J.*, 1954, 1854), and showed that it isomerises to penta-2 : 4-dienoic acid in higher yield (80%, spectroscopic), and under milder conditions (10% potassium carbonate solution at 60°), than pent-4-ynoic acid.

$$CH{\equiv}C{\cdot}CH{=}CH{\cdot}CH_2{\cdot}OH \xrightarrow{LiAlH_4} CH_2{=}C{=}CH{\cdot}CH_2{\cdot}CH_2{\cdot}OH \xrightarrow{CrO_3} \underset{\text{(II)}}{CH_2{=}C{=}CH{\cdot}CH_2{\cdot}CO_2H}$$

Attention was then directed to pent-3-ynoic acid (IV), the preparation of which is discussed below. This acid was apparently converted into either penta-2 : 3-dienoic or pent-2-ynoic acid under fairly drastic conditions, since the hydration product, ethyl methyl ketone, was formed in boiling aqueous 9N-potassium hydroxide, while ethylene glycol and potassium hydroxide gave the dioxalan derived from propionylacetic acid. Nevertheless these isomeric acids were not formed to any appreciable extent and could not be isolated. On the contrary, pent-2-ynoic acid was isomerised in 9N-potassium hydroxide at 60° to the Δ^3-isomer, which was isolated without difficulty since it is relatively high melting, in 64% yield, and thus clearly predominates in the equilibrium mixture. Here again an allenic acid must be assumed as an intermediate, but this time it proved possible to identify the penta-2 : 3-dienoic acid (V), by means of its intense infra-red band at 1970 cm.$^{-1}$, in the syrupy acidic fractions obtained when the reaction was interrupted. This acid was prepared by the present authors (forthcoming publication) in the course of quite independent work, and gave the same yield of pent-3-ynoic acid under similar alkaline conditions; it therefore seems probable that the hydration reaction which interferes with the prototropic shift involves the allenic, rather than the αβ-acetylenic anion, a conclusion in harmony with that drawn about the relative reactivity towards nucleophilic reagents of tetrolic and butadienoic esters in the preceding paper. Because of the formation of ethyl methyl ketone even at 60°, the proportion of pent-3-ynoic acid present in (hypothetical) equilibrium with its two isomers must presumably be more than the 60% actually isolated.

The Figure illustrates the transformations of the doubly-unsaturated C_5 straight-chain acids, all of which (except *cis*-penta-2 : 4-dienoic) have now been prepared. The speed of each reaction, as judged by the severity of the conditions required for it, is very roughly indicated by the type of line used; and the ordinate may be taken as a qualitative representation of free energy in strongly alkaline solutions, where only the derived anions need be considered. There is no means, however, of comparing directly the acids on the left with the group on the right.

FIGURE.



The symbols ——➤, -----➤, —·—·➤, and ·····➤ indicate reaction rates diminishing approximately in that order; transformations queried have not been observed but are known to be possible from the behaviour of analogous systems.

No attempt has been made to investigate every acid in the C_6 and C_7 series. Hex-5-ynoic acid, however, was converted into hex-4-ynoic acid (82%) in boiling (138°) 15N-potassium hydroxide solution, under which conditions its homologue, hept-6-ynoic acid, was quite stable. (Hex-5-ynoic acid was similarly unaffected by 9N-potassium hydroxide at 118°, which rapidly isomerised pent-4-ynoic acid.) When treated with 9N-potassium hydroxide in ethylene glycol at 160°, however, hept-6-ynoic acid was isomerised to hept-5-ynoic acid, though (perhaps because of its low melting-point) only a 33% yield could be

TABLE.

Reagent	Temp.	Reaction	Yield, %	Time, hr.
*A**	40°	$CH{\equiv}C{\cdot}CH_2{\cdot}CO_2^- \longrightarrow CH_2{=}C{=}CH{\cdot}CO_2^-$	92	3
A	60	$CH_2{=}C{=}CH{\cdot}CH_2{\cdot}CO_2^- \longrightarrow CH_2{=}CH{\cdot}CH{=}CH{\cdot}CO_2^-$	80	2
*A**	90	$CH_2{=}C{=}CH{\cdot}CO_2^- \rightleftharpoons CH_3{\cdot}C{\equiv}C{\cdot}CO_2^-$	60 ($\longrightarrow$)	8
B	60	$\left.\begin{matrix} CH_3{\cdot}CH_2{\cdot}C{\equiv}C{\cdot}CO_2^- \\ \text{or } CH_3{\cdot}CH{=}C{=}CH{\cdot}CO_2^- \end{matrix}\right\} \longrightarrow CH_3{\cdot}C{\equiv}C{\cdot}CH_2CO_2^-$	61	1
B	118	$\left.\begin{matrix} (CH_3{\cdot}C{\equiv}C{\cdot}CO_2^- \rightleftharpoons CH_2{=}C{=}CH{\cdot}CO_2^-) \\ (CH_3{\cdot}C{\equiv}C{\cdot}CH_2{\cdot}CO_2^- \longleftarrow CH_3{\cdot}CH{=}C{=}CH{\cdot}CO_2^-) \end{matrix}\right\} \longrightarrow$ hydration products		~2
B	118			
B	118	$CH{\equiv}C{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2^- \xrightarrow{\text{2 stages}} CH_2{=}CH{\cdot}CH{=}CH{\cdot}CO_2^-$	60	6
C	138	$CH{\equiv}C{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2^- \xrightarrow{\text{2 stages}} CH_3{\cdot}C{\equiv}C{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2^-$	82	1
D	160	$CH_3{\cdot}C{\equiv}C{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2^- \xrightarrow{\text{2 stages}} CH_3{\cdot}CH{=}CH{\cdot}CH{=}CH{\cdot}CO_2^-$	93	1
D	160	$CH{\equiv}C{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2^- \xrightarrow{\text{2 stages}} CH_3{\cdot}C{\equiv}C{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2^-$	33	1

Reagents: *A*, 10% K_2CO_3; *A**, 18% K_2CO_3; *B*, 9N-KOH; *C*, 15N-KOH; *D*, 9N-KOH in ethylene glycol.

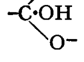
isolated. These conditions also sufficed to convert hex-4-ynoic acid almost quantitatively into sorbic acid. Hept-5-ynoic acid, on the other hand, resisted this reagent for considerable periods, and apparently underwent fission rather than isomerisation to a conjugated dienoic acid.

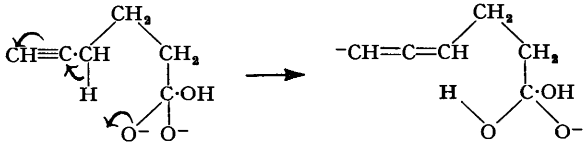
The Table summarises the isomerisations of the doubly-unsaturated acids investigated, and illustrates the extreme sensitivity of reaction rates to temperatures and—probably more important—reagent concentration. The same features are apparent in the earlier work on ethylenic acids. In these circumstances the value of ultra-violet spectroscopic methods in extensive preliminary investigations, which were used throughout the present studies, is obvious; in many reactions it has been possible accurately to select conditions for maximal yields in this way.

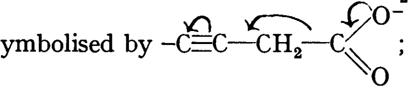
Discussion of Results.—Prototropic rearrangements of three-carbon systems in alkaline solutions were pictured by Ingold, Shoppee, and Thorpe (*J.*, 1926, 1477) as involving attack by a nucleophilic reagent on a proton to give a mesomeric carbanion, followed by addition of a second proton at the alternative site. Lowry's suggestion (*J.*, 1925, 2883) that dual proton transfers could be sychronous was further verified by Ingold, de Salas, and Wilson (*J.*, 1936, 1328), who made the important point that such " termolecular " or " concerted " reactions are typical of systems where the anion is very strongly basic. Probably the isomerisations of acetylenic hydrocarbons, and of at least most of the anions discussed in this paper, fall into this class. Nevertheless, any factor which would be expected to stabilise the formal carbanion intermediate should have a similar effect on the transition state in the termolecular process, and Ingold, Shoppee, and Thorpe's hypothesis will therefore be adopted to simplify presentation. The species suffering prototropy is obviously the anion in every case, since involvement of the free acid (which should of course be more reactive) would require a reaction-rate independent of hydroxide-ion concentration, HO^-, or some other species proportional to HO^-, being assumed to be the nucleophilic agent.

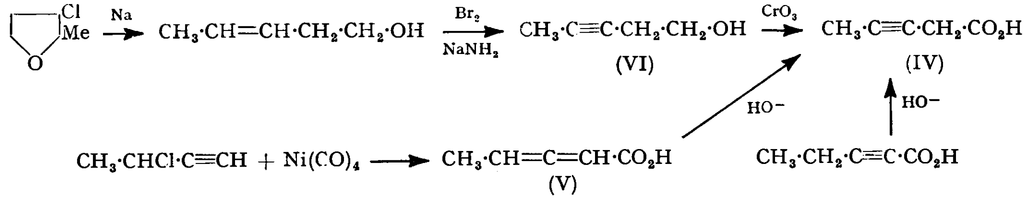
Much of the behaviour of the acetylenic acids (*e.g.*, the difference in rate of reaction between pent-4-ynoic and hex-4-ynoic acids) parallels that of the acetylenic hydrocarbons as generalised and interpreted above. The presence of a CO_2^- grouping controls the prototropy of the anion of penta-3 : 4-dienoic acid by facilitating the removal of a proton from $C_{(2)}$ [in contrast to (*d, e*) > (*f*) above, where R = Me], which results in the formation of penta-2 : 4-dienoic, rather than pent-3-ynoic, acid anion.

The rates of isomerisation of pent-4-ynoic and hex-5-ynoic acids, relative to hept-6-ynoic and higher ω-acetylenic acids and ω-acetylenic hydrocarbons, are also of interest. The proximity of $-CO_2^-$ is evidently important, and since inductive influence is implausible, especially in the case of hex-5-ynoic acid, participation of this grouping in the prototropic process is probable. The $-CO_2^-$ group, a weak base, could not of course be involved as such, since this would imply that no additional alkaline reagent was required; but reversible addition of HO^- to the carbonyl group would give the grouping (*Y*), which might well effect an internal attack:


(*Y*)



Finally, we find that pent-3-ynoic acid is appreciably more stable than either the Δ^2-acetylenic or the $\Delta^{2:3}$-allenic C_5 acids in alkaline solution. This system is difficult to investigate because of the lack of convenient analytical methods, and Mr. J. M. Thompson's observations (forthcoming publication) on the isomerisations of the corresponding di- and tri-acetylenic acids, $CH_3{\cdot}CH_2{\cdot}[C{\equiv}C]_n{\cdot}CO_2H$, are more clear-cut. Even in the present instance, however, it seems clear that if true equilibrium could be attained, at least twice as much of the Δ^3-acid anion as of the other two isomers combined would be present. Even the minimal value for the ratio (pent-3-ynoate/pent-2-ynoate), say 3, contrasts sharply with the analogous ratio, 0·61, found by Ives and Kerlogue (*J.*, 1940, 1362) for the pentenoic acid system; and the true value is probably much higher. One simple explanation involves the geometrical requirements of interaction between acetylenic and ethylenic bonds, on the one hand, and $-CO_2^-$ and $-CH_3$ or $-CH_2-$ groupings, on the other. In conjugative interaction with $-CO_2^-$, which is planar, only one of the two π-electron pairs of a triple bond can be involved, so that an acetylenic linkage will have no advantage over an ethylenic linkage. In hyperconjugative interaction with the σ electrons of the C–H bonds in a methyl group, however, the cylindrically symmetrical electron cloud of the triple bond will be more effective than that of the planar ethylenic linkage, which probably can interact efficiently with only one C–H bond (cf. Baddeley and Gordon, *J.*, 1952, 2190). Direct hyperconjugative interaction between the $-CO_2^-$ grouping and a $\beta\gamma$-acetylenic linkage (the process symbolised by  ; applying less effectively in $\beta\gamma$-ethylenic carboxylate anions) is another possible factor. Finally, one must take account of the intrinsic electron-attracting tendencies of the triple bond, which have been ascribed by Walsh (*Discuss. Faraday Soc.*, 1947, **2**, 18) to the polarity of the *sp*-bond formed by the acetylenic carbon atom, the increased *s*-component (as compared with sp^2 and sp^3 bonds) involving a tighter binding of the electron-pair involved. This implies an inductive interaction of the unsaturated linkage with adjacent groups, the effect of which is difficult to predict; it might be expected that $-CO_2^-$, electron-repelling in saturated systems as a result of large $+I$ and small $-M$ effects, should be still more so when adjacent to an acetylenic linkage. This should stabilise $-C{\equiv}C-CO_2^-$ relative to $-CH{=}CH{\cdot}CO_2^-$, *i.e.*, should act in a contrary sense to that which is observed. Work now in progress may help to disentangle the problems involved in the explanation of these equilibria; meanwhile the results obtained exemplify the fundamental differences between the chemistry of the ethylenic and acetylenic linkages.



Appendix.—The preparative work involved in this study conflicts with the literature in two instances, involving substances previously described as pent-3-ynoic and hex-3-ynoic acids. The first was reported by Schjånberg (*Ber.*, 1938, **71**, 569) as one product (5% yield) of the action of potassium hydroxide on 3 : 4-dibromopentanoic acid. Its melting-point was given as 52·5°, near to its acetylenic isomers (57° and 50·5°), its structure was not proved by degradative methods and the method of synthesis clearly does not provide sufficient evidence of constitution. In seeking a convenient method of preparation before the discovery of the prototropic rearrangements discussed above we utilised the alcohol (VI), reported by Crombie and Harper (*J.*, 1950, 877). On oxidation with chromic acid in acetone this gave an acid, $C_5H_6O_3$, m. p. 101—104°, different from pent-2-ynoic and pent-4-ynoic acids, yet optically transparent above 2000 Å ($\varepsilon \not> 400$). Its methyl ester showed infra-red absorption bands [at 2240 cm.$^{-1}$ (weak) and 1741 cm.$^{-1}$ (strong); none between 1600 and 1720 cm.$^{-1}$] which provided final confirmation that it was indeed pent-3-ynoic acid, (IV). The nature of Schjånberg's acid remains doubtful; its ethyl ester differed in refractive index by 0·005 from that of (IV), and the possibility that it was a polymorphic form of (IV) seems remote.

Marayuma and Suzuki (see *Chem. Abs.*, 1932, **26**, 1879; 1935, **29**, 1062) claimed that sorbic acid (m. p. 134°) is converted by potassium hydroxide in ethanol at 180° into " hex-3-ynoic acid," m. p. 128°. The structure of their product, *a priori* a most surprising one, was supported only by oxidation to propionic acid. We prepared hex-3-ynoic acid by oxidation of the corresponding primary alcohol (Eglinton, Jones, and Whiting, *J.*, 1952, 2873) with chromic acid, and found that its melting-point was 60—61°. Its structure was proved by hydrogenation to hexanoic acid, by permanganate oxidation to malonic acid, and by its optical transparency ($\varepsilon \ngtr 100$ above 2020 Å). We then repeated the Japanese workers' experiment, and isolated, as expected, merely unchanged sorbic acid (60% recovery), m. p. and mixed m. p. 134° when pure; thus their product was probably impure starting material.

EXPERIMENTAL

Ultra-violet spectra were determined in 95% ethanol by using a Unicam SP500 Spectrophotometer, and infra-red spectra in carbon tetrachloride (unless otherwise specified) with a Perkin Elmer Model 21 Spectrophotometer. "Light petroleum" refers to the fraction, b. p. 40—60°. Melting points were determined on the Kofler block.

*Penta-*3 : 4-*dienoic Acid* (II) (*with* P. NAYLER).—Penta-3 : 4-dien-1-ol (Bates, Jones, and Whiting, *J.*, 1954, 1854; 5 g.) in acetone (37 c.c.) was treated with chromic acid solution (37 c.c.; as below) during 40 min. at 10°. After a further 15 hr. at 20° the mixture was diluted with water, and the acidic fraction was isolated with ether. Distillation gave *penta-*3 : 4-*dienoic acid* (1·35 g.), b. p. 127°/13 mm. (slight decomp.), n_D^{18} 1·4740 (Found: C, 60·85; H, 6·9%; equiv., 98. $C_5H_6O_2$ requires C, 61·2; H, 6·1%; equiv., 98). Light absorption: no maximum above 2000 Å; $\varepsilon = 960$ at 2200 Å. The liquid absorbed intensely at 1967 cm.$^{-1}$ in the infra-red, but showed no strong bands in the $>C{=}C<$ stretching region at 1600—1650 cm.$^{-1}$. The p-*bromophenacyl* ester formed plates, m. p. 65°, from methanol (Found: C, 52·75; H, 3·85. $C_{23}H_{11}O_3Br$ requires C, 52·9; H, 3·73%). It absorbed intensely at 1970 cm.$^{-1}$.

Distillation of the neutral fraction from the oxidation mixture gave *penta-*3 : 4-*dienyl penta-*3 : 4-*dienoate* (1·3 g.), b. p. 115°/18 mm., n_D^{24} 1·4895 (Found: C, 72·9; H, 7·4. $C_{10}H_{12}O_2$ requires C, 73·2; H, 7·3%).

*Penta-*2 : 4-*dienoic Acid.*—(*a*; *with* P. NAYLER.) Penta-3 : 4-dienoic acid (230 mg.) was heated with 10% aqueous potassium hydroxide solution (20 c.c.) at 60° for 2 hr. Isolation of the acidic fraction with ether gave a solid (220 mg.) which was crystallised from pentane, giving penta-2 : 4-dienoic acid (180 mg.), m. p. 71° (Kohler, *J. Amer. Chem. Soc.*, 1926, **48**, 1041, gives m. p. 72°).

(*b*; *with* J. L. H. ALLAN.) Pent-4-ynoic acid (2·0 g.), potassium hydroxide (25 g.), and water (50 c.c.) were heated under reflux for 1·5 hr. The solution was then cooled, extracted with ether, and acidified with sulphuric acid (3N) with external cooling. Extraction of the acid solution with ether and evaporation of the dried extract at room temperature gave a partly polymeric acidic residue (1·3 g.) which was extracted with pentane, giving on cooling penta-2 : 4-dienoic acid (0·7 g.), m. p. 51—70°, the infra-red spectrum of which agreed almost exactly with that of the pure acid (0·4 g.), m. p. 71—73°, obtained after sublimation and four recrystallisations from pentane at 20°. Light absorption; maximum 2420 Å, $\varepsilon = 24{,}800$.

This experiment was based on spectroscopically-controlled runs; preparatively, the volume of solution used could be greatly reduced. When a 5 : 2 water–alcohol mixture was used as solvent, with a reaction-period of 6 hr. at 100°, the spectroscopic yield of pentadienoic acid was 60%.

*Pent-*3-*ynoic Acid* (IV).—(*a*; *preparative method, with* G. H. MANSFIELD.) Pent-2-ynoic acid (5·0 g.; Zoss and Hennion, *J. Amer. Chem. Soc.*, 1941, **63**, 1151), potassium hydroxide (5 g.), and water (to 50 c.c.) were heated to 60° for 1 hr. Cautious acidification of the cooled solution, isolation of the acidic fraction and crystallisation from benzene–light petroleum (b. p. 60—80°) gave the *acid* (3·2 g.), m. p. 103—104°. When the oil (1·0 g.) remaining in the mother-liquors was recycled a further 0·3 g. of pent-3-ynoic acid, m. p. 102—103°, was obtained (Found: C, 60·9; H, 6·4. $C_5H_6O_2$ requires C, 61·2; H, 6·15%).

(*b*) Penta-2 : 3-dienoic acid (200 mg.; Jones, Whitham, and Whiting, forthcoming publication) was treated with alkali as above, yielding pent-3-ynoic acid (106 mg.), m. p. and mixed m. p. 103—104°.

(*c*) 6N-Chromic acid in 12N-sulphuric acid (300 c.c.) was added with stirring and cooling to a solution of pent-3-yn-1-ol (29·4 g.; Crombie and Harper, *J.*, 1950, 877) in acetone (300 c.c.), the temperature being kept at 25°. Isolation of the acid fraction after 4 hr. gave the acid, which crystallised from light petroleum (b. p. 60—80°) as flat needles (16 g., 50%), m. p. 101—104° (Found: C, 60·9; H, 6·4%).

Pent-3-yn-1-ol was also obtained in small yield from prop-1-ynylmagnesium bromide and ethylene oxide (Iositch, *Bull. Soc. chim.*, 1909, **6**, 98). Unexpectedly the ring-fission of 3-chloro-

2-methyltetrahydrofuran with sodamide was also unsatisfactory, the main products being methyldihydrofurans (cf. Eglinton, Jones, and Whiting, *J.*, 1952, 2873).

2-*Ethyl*-1 : 3-*dioxalan*-2-*ylacetic Acid.*—Pent-3-ynoic acid (2 g.), ethylene glycol (20 c.c.), and potassium hydroxide (5 g.) were heated under reflux during 1 hr. After dilution and acidification of the solution, the acid fraction was isolated with ether, giving the *dioxalan* (1·4 g., 43%), b. p. 130° (bath temp.)/0·05 mm., n_D^{18} 1·4530 (Found: C, 52·7; H, 7·5. $C_7H_{12}O_4$ requires C, 52·5; H, 7·55%).

The dioxalan (0·43 g.) was heated with 20% sulphuric acid (30 c.c.), and the mixture distilled. Addition of 2 : 4-dinitrophenylhydrazine sulphate solution to the aqueous distillate gave a precipitate which crystallised from ethanol as brick-red needles (0·42 g., 62%), m. p. 115—117° undepressed on admixture with an authentic specimen of ethyl methyl ketone 2 : 4-dinitrophenylhydrazone.

Hex-3-*ynoic* Acid.—6N-Chromic acid (22 c.c.) was added to a cooled, stirred solution of hex-3-yn-1-ol (2·9 g.; Eglinton, Jones, and Whiting, *loc. cit.*) in acetone (22 c.c.) during 30 min., the temperature being maintained at 20°. The solid acid fraction, on crystallisation from light petroleum (b. p. 40—60°), gave the *acid* (0·77 g., 24%) as fine needles, m. p. 57—59°, raised to 61—63° on recrystallisation (Found: C, 64·5; H, 7·5. $C_6H_8O_2$ requires C, 64·25; H, 7·2%). The structure was proved by oxidation with potassium permanganate to malonic acid, m. p. 134·5—135°, in 18% yield.

Hex-4-*ynoic Acid.*—Hex-5-ynoic acid (1·0 g.) was heated under reflux with 15N-potassium hydroxide during 1 hr. After acidification, the acid fraction was isolated with ether and crystallised from light petroleum giving the *acid* (0·82 g., 82%), as rhombohedral needles, m. p. 100—101° (Found: C, 64·5; H, 7·5. $C_6H_8O_2$ requires C, 64·25; H, 7·2%). Its structure was proved by oxidation with potassium permanganate to succinic acid (68% yield), m. p. and mixed m. p. 186—187°. The *methyl* ester had b. p. 61·5°/10 mm., n_D^{16} 1·4440 (Found: C, 66·5; H, 7·95. $C_7H_{10}O_2$ requires C, 66·65; H, 8·0%). It gave no precipitate with ammoniacal silver nitrate.

Sorbic Acid.—Hex-4-ynoic acid (1·00 g.) and 9N-potassium hydroxide in ethylene glycol (10 c.c.) were heated to 160° for 1 hr. Dilution, acidification, and isolation with ether gave the acid (0·93 g.) as prismatic needles, m. p. and mixed m. p. 134—135°.

Hept-5-*ynoic Acid.*—Hept-6-ynoic acid (1·00 g.) and 9N-potassium hydroxide in ethylene glycol (10 c.c.) were heated to 160° for 1 hr. Distillation of the acid fraction gave an oil, b. p. 90° (bath temp.)/0·05 mm., n_D^{20} 1·4649, which solidified to a mass of needles, m. p. *ca.* 27°. After recrystallisation from light petroleum (b. p. 40—60°) the *acid* (0·33 g., 33%) was obtained as translucent plates, m. p. 36—38° (Found: C, 66·25%; H, 8·0%). Oxidation with permanganate gave glutaric acid, m. p. 95—96°, in 33% yield.

The authors are indebted to the Department of Scientific and Industrial Research for a grant to one of them (G. H. W.). They thank Miss W. Peadon and Miss J. Shallcross for spectroscopic measurements, and Messrs. E. S. Morton and H. Swift for microanalyses.

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