SECTION C
Organic Chemistry

The Intramolecular Acylation of Some Hex-, Hept-, and Oct-enoic Acids

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Treatment of any of the seven isomeric hexenoic acids with polyphosphoric acid at 100° yields essentially the same mixture of cyclohex-2-enone, 2-methylcyclopent-2-enone and hexan-4- and 5-olide. Comparable results are obtained with heptenoic and octenoic acids. Intramolecular acylation of these acids in the presence of trifluoroacetic anhydride is shown to be dependent on the structure and stereochemistry of the acids. The formation of cyclohept-2-enone from hept-6-enoic acid is reported. Concentrated sulphuric acid in acetic anhydride is shown to convert hex- and hept-5-enoic acid into phenyl and *o*-tolyl acetate, respectively. Some improved syntheses of alkenoic acids are reported.

INTRAMOLECULAR acylation of alkenoic acids in strong acid media has been shown to yield mixtures of 2-substituted cyclopent-2-enones, and 2-substituted cyclohex-2-enones, irrespective of the positions of the double bond and the carboxy-group.[1] Concomitant with the formation of cyclic ketones, the alkenoic acids yield the isomeric lactones, which can also yield cyclic ketones under the reaction conditions. The analysis of such mixtures of isomeric ketones and isomeric lactones is readily achieved by gas–liquid chromatography (g.l.c.). We now report an investigation of the reactions of the hexenoic acids, some heptenoic acids and the *trans*-octenoic acids in polyphosphoric acid; the reactions of *cis*-, and *trans*-hex-, hept-, and oct-4-enoic acid, hex-5-enoic acid, *cis*- and *trans*-hept- and oct-5-enoic acid, and oct-7-enoic acid with trifluoroacetic anhydride, a reagent which effects the intramolecular acylation of certain alkenoic acids;[2] and the reactions of some alkenoic acids in the presence of Lewis acids or sulphuric acid in acetic anhydride solution.

TABLE 1

Yields (%) * of products from hexenoic acids and related lactones in polyphosphoric acid at 100° for 60 min.

	Acid							Lactone	
	Δ^2		Δ^3		Δ^4				
Product	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	Δ^5	γ	δ
2-Methylcyclopent-2-enone	7	9	5	4	9	9	7	3	6
Cyclohex-2-enone	3	7	4	2	5	3	6	1	2
Hexan-4-olide...	29	43	47	52	55	46	29	44	40
Hexan-5-olide...	1	2	1	1	1	1	1	4	2
Recovered acids	16	29	20	30	14	7	21		

* Based on acid consumed.

The yields and nature of the products obtained when each of the hexenoic acids is heated with polyphosphoric acid for 1 hr. at 100° are shown in Table 1. Each yields a mixture of 2-methylcyclopent-2-enone, cyclohex-2-enone and hexan-4-olide. These results confirm the observations of Ansell and Brown[1] and of Riobé[3] on hex-4- and hex-5-enoic acid. The failure of Dominguez *et al.*[4] to obtain ketonic material from hex-2-enoic acid by the action of polyphosphoric acid was presumably due to their use of very mild (50—60°; 1½ hr.) reaction conditions. Table 1 shows that hexan-4- and 5-olides yield similar products to those obtained from the hexenoic acids; hexan-5-olide is not stable under the reaction conditions but is converted into hexan-4-olide (cf. reference 5). The results recorded in Table 3 for the reactions of three heptenoic acids and in Table 4 for the reaction of all the *trans*-octenoic acids and the related γ- and δ-lactones with polyphosphoric acid at 100° confirm the earlier work[1,3] on the cyclisation of hept-5- and 6-enoic acid and oct-5- and 6-enoic acid and parallel those obtained for the hexenoic acids except that the yields of ketonic products are higher. Collectively these results support the view[1] that the products obtained by the action of polyphosphoric acid at 100° on normal alkenoic acids are independent of the relative positions of the double bond and the carboxy-group. Such reactions are, however, temperature-dependent, and in contrast to the results obtained at 100°, at 75° (Table 4) not only are the yields of cyclic products

TABLE 2

Yields (%) * of products from hex-5-enoic acid in polyphosphoric acid at various temperatures for 30 min.

	Temperature				
Product	90°	100°	110°	120°	140°
2-Methylcyclopent-2-enone ...	2	6	11	22	29
Cyclohex-2-enone	5	8	9	13	3
Hexan-4-olide.....................	47	53	46	34	3
Hexan-5-olide.....................	4	2	1	1	0
Recovered acids..................	30	20	8	5	0

* Based on acid consumed.

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[1] M. F. Ansell and S. S. Brown, *J. Chem. Soc.*, 1958, 2955, and references cited therein.

[2] R. J. Ferrier and J. M. Tedder, *J. Chem. Soc.*, 1957, 1435.

[3] O. Riobe, *Compt. rend.*, 1958, **247**, 1016.

[4] J. A. Dominguez, G. L. Diaz, and J. Slim, *Ciencia*, 1956, **16**, 151.

[5] M. F. Ansell and M. E. Palmer, *J. Chem. Soc.*, 1963, 2640.

dependent on the position of the double bond, but the yields of ketones with exocyclic double bonds become significant and the formation of octan-5-olide, which is unstable at 100°, is observed. Similar trends are seen in Table 3, which also records the effect of temperatures higher than 100° in the case of hex-5-enoic acid; ketone formation is favoured at the expense of γ-lactone.

TABLE 3

Yields (%) * of products from heptenoic acids in polyphosphoric acid for 60 min.

Product	Acid at 100°			Δ^6-Acid at various temperatures				
	trans-Δ^2	*trans*-Δ^5	Δ^6	50°	80°	90°	110°	120°
2-Ethylcyclopent-2-enone	29	27	28	6	20	29	29	32
2-Methylcyclohex-2-enone	23	24	24	9	19	23	26	15
2-Ethylidenecyclopentanone	0	0	0	8	1	0	0	0
Heptan-4-olide	6	4	10	4	13	12	2	0
Heptan-5-olide	0	0	0	10	2	0	0	0
Recovered acids	20	10	10	30	10	10	7	5

* Based on acid consumed.

TABLE 4

Yields (%) of reaction products from the *trans*-octenoic acids and octan-4- and 5-olide in polyphosphoric acid for 30 min.

Product	Lactones at 100°		Octenoic acid at 100°						Octenoic acid at 75°					
	γ	δ	Δ^2	Δ^3	Δ^4	Δ^5	Δ^6	Δ^7	Δ^2	Δ^3	Δ^4	Δ^5	Δ^6	Δ^7
2-n-Propylcyclopent-2-enone	23	19	26	31	31	21	23	21	0	7	17	19	10	19
2-n-Propylidenecyclopentanone	Trace	Trace	2	3	0	0	0	Trace	Trace	Trace	2	1	2	2
2-Ethylcyclohex-2-ene	26	19	25	27	38	23	26	18	Trace	3	12	15	7	13
2-Ethylidenecyclohexanone	3	Trace	3	4	3	2	4	1	2	6	18	15	17	15
Octan-4-olide	9	Trace	17	3	7	3	8	4	10	32	38	14	22	13
Octan-5-olide	0	0	0	0	0	0	0	0	0	0	5	5	8	8

TABLE 5

Cyclisations with trifluoroacetic anhydride (yields in parentheses)

Acid	Product			
Hex-5-enoic	Cyclohex-2-enone	(50%)		
trans-Hept-5-enoic	2-Methylcyclohex-2-enone	(39%)	+ 2-Ethylidenecyclopentanone	(28%)
cis-Hept-5-enoic	,, ,,	(13%)	+ ,, ,,	(13%)
Hept-6-enoic	Cyclohept-2-enone	(10%)		
trans-Oct-5-enoic	2-Ethylcyclohex-2-enone	(31%)	+ 2-Propylidenecyclopentanone	(24%)
cis-Oct-5-enoic	,, ,,	(9%)	+ ,, ,,	(20%)
trans-Oct-6-enoic	2-Ethylidenecyclohexanone	(23%)		
cis-Oct-6-enoic	,, ,,	(9%)		

The use of trifluoroacetic anhydride for the conversion of alkenoic acids into ketones was first investigated by Ferrier and Tedder,[2] who showed that with this reagent pent-4-enoic acid yielded a 'linear dimer' and hex-5-enoic acid only cyclohex-2-enone (cf. reaction with polyphosphoric acid). We have confirmed these results but consider that the linear dimer is pent-4-enoic anhydride; its infrared spectrum exhibits a doublet (5·51 and 5·75 μ) and strong absorption at 9·5 and 9·7 μ, typical[6] of an anhydride. We have extended the use of this reagent to other alkenoic acids. With trifluoroacetic anhydride, hex-2-enoic acid gave hex-2-enoic anhydride (20%) and unchanged hex-2-enoic acid; likewise hex-3- and 4-enoic acids gave neutral products with spectra typical of acid anhydrides. Hex-5-enoic anhydride is converted into cyclohex-2-enone by trifluoroacetic anhydride. Oct-7-enoic acid yielded polymeric material. Trifluoroacetic anhydride yields ketones with Δ^5- and Δ^6-alkenoic acids (Table 5). In contrast to the results obtained with polyphosphoric acid, cyclic ketones with exocyclic double bonds are formed in high yield. These results can be rationalised (Scheme 1) on the assumption that trifluoroacetic anhydride does not promote double bond migration (cf. lactonisation of alkenoic acids with trifluoroacetic acid[5]).

In the cyclisations of hex-5-enoic (Scheme 1; $R = H$, $x = 1$), and hept-6-enoic (Scheme 1; $R = H$, $x = 2$) acids, the observed products might be expected to be accompanied by 2-methylenecyclopentanone and 2-methylenecyclohexanone. These are not observed, as they are extremely unstable[7] even at room temperature. Hept-6-enoic acid has been reported[2] not to cyclise under these conditions, but in our hands a low yield of cyclohept-2-enone was obtained. The formation of a seven-membered ring by the intramolecular acylation of an alkenoic acid has not previously been reported. Conditions for this reaction are electronically favourable in this case as compared with oct-6-enoic acid. Cyclis-

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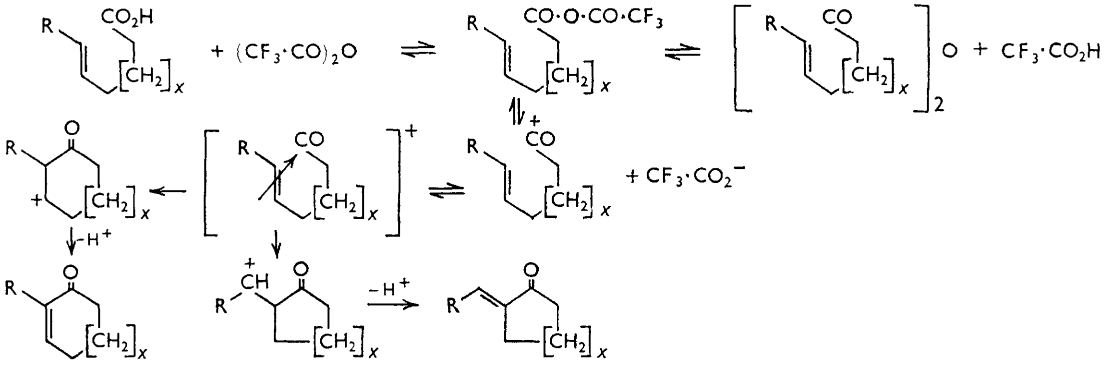
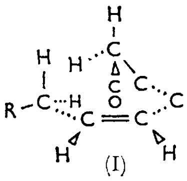
[6] L. J. Bellamy, 'Infra-red Spectra of Complex Molecules,' Methuen, 1954.

[7] R. L. Erskine and E. S. Waight, *J. Chem. Soc.*, 1960, 3425.

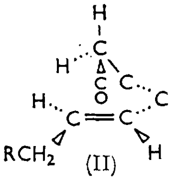
ations with trifluoroacetic anhydride are subject to steric effects, as shown by the different results obtained from *cis*- and *trans*-alk-5-enoic acids. Inspection of models shows that approach of the acylium ion to the double bond is hindered in the *cis*-isomer (I) by non-bonded interaction between the hydrogens at C-2 and the substituents (H, or H and Me) at C-7. These interactions do not occur in the *trans*-isomer (II). Such interactions explain both the overall lower yields obtained from the *cis*-5-enoic acids, and the preferential formation of the cyclopentanone derivative, especially in the case of *cis*-oct-5-enoic acids.



Scheme I



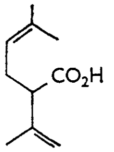
(I)



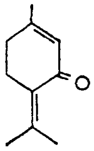
(II)

The use of zinc chloride, stannic chloride, or boron trifluoride etherate in acetic acid–acetic anhydride (cf. references 8 and 9) as cyclising agents was investigated. Like Miescher,[9] we found stannic chloride to be the most efficient reagent. The results obtained with this reagent parallel those obtained with trifluoroacetic anhydride, but the latter is preferred for convenience. Thus no ketonic product was obtained from hex- or hept-2-enoic acid, pent- or hex-4-enoic acid, or hept-6-enoic acid. Hex-5-enoic acid gave cyclohex-2-enone (40%) and *trans*-hept-5-enoic acid gave 2-methylcyclohex-2-enone (20%), 2-ethylcyclopent-2-enone (4%), and 2-ethylidenecyclopentanone (1%).

Sulphuric acid in acetic anhydride has been used[10] for the conversion of unsaturated acids into cyclic ketones [*e.g.*, (III) ⟶ (IV)]. In our hands this reagent with hex-5-enoic acid gave a mixture of phenyl acetate (23%) and phenol (2%), with a trace of cyclohex-2-enone, and hept-5- and 6-enoic acid gave (respective yields in parentheses) *o*-tolyl acetate (30 and 10%), *o*-cresol (5 and 1%), and 2-methylcyclohex-2-enone (7 and 1%). We consider that these aromatic products arise through dehydrogenation (oxidation) of the intermediate cyclohex-2-enone, since cyclohex-2-enone is converted into phenyl acetate under these conditions.



(III)



(IV)

Preparation of Alkenoic Acids.—*cis*- and *trans*-Hex-4-enoic acid have been prevously prepared[11,12] by way of the corresponding pent-3-en-1-ols. We have obtained them by selective reduction of hex-4-ynoic acid, prepared by the following improved route. The formation of pent-3-yn-1-ol, from ethylene oxide and sodiopropyne has been reported[13] to proceed in *ca.* 33% yield. We have been unable to achieve this yield, but the use of lithiopropyne gave a yield of 42%. We converted this alcohol into the corresponding chloride, bromide, or iodide by way of the toluene-*p*-sulphonate but could not carboxylate the derived Grignard reagent. However, the toluene-*p*-sulphonate reacted readily with sodium cyanide in dimethyl sulphoxide solution to yield hex-4-ynonitrile, (71%) which on hydrolysis gave hex-4-ynoic acid.

cis- and *trans*-Hex-3-enoic acid were obtained by hydrogenation of hex-3-ynoic acid, formed by the oxidation[14] of hex-3-yn-1-ol. The latter was obtained (68%) from lithiobut-1-yne; a 47% yield was obtained[15] from sodiobut-1-yne. Only *trans*-hex-3-enoic acid, obtained from the tri-(2-hydroxyethyl)amine-catalysed condensation of n-butyraldehyde and malonic ester, has been previously reported.[16]

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[8] W. S. Johnson, H. C. E. Johnson, and J. W. Peterson, *J. Amer. Chem. Soc.*, 1945, **67**, 1360; W. S. Johnson and J. W. Peterson, *ibid.*, p. 1366.

[9] J. R. Billeter and K. Miescher, *Helv. Chim. Acta*, 1951, **34**, 2053.

[10] W. Kuhn and H. Schinz, *Helv. Chim. Acta*, 1953, **36**, 161; L. Re and H. Schinz, *ibid.*, 1958, **41**, 1695.

[11] L. Crombie and S. H. Harper, *J. Chem. Soc.*, 1950, 1152.

[12] M. F. Ansell and S. S. Brown, *J. Chem. Soc.*, 1957, 1788.

[13] K. E. Shulte and K. P. Reizz, *Chem. Ber.*, 1954, **87**, 964.

[14] E. R. H. Jones, G. H. Whitham, and M. C. Whiting, *J. Chem. Soc.*, 1954, 3201.

[15] F. Sondheimer, *J. Chem. Soc.*, 1950, 877.

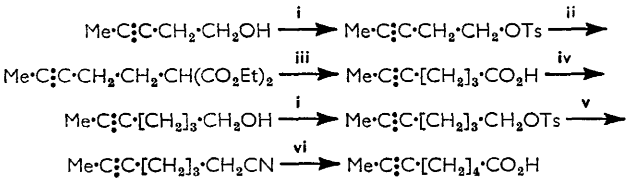
[16] D. R. Howton and R. H. Davies, *J. Org. Chem.*, 1951, **16**, 1405.

trans-Hex-2-enoic acid, prepared [17] from malonic acid and n-butyraldehyde in the presence of pyridine, contained 4% (by g.l.c.) of an isomeric impurity. The previously unreported *cis*-acid was obtained by partial hydrogenation of hex-2-ynoic acid formed (68%) by carboxylation (under pressure) of pent-1-ynyl magnesium bromide (cf. 42% yield [18] for the carboxylation of sodiopent-1-yne).

Hept-6-enoic [19] and *trans*-hept-5-enoic [12] acids were prepared by the published methods. The latter was also obtained by reduction of hept-5-ynoic acid with sodium in liquid ammonia. The previously unknown *cis*-hept-5-enoic acid was obtained by catalytic reduction of hept-5-ynoic acid (see below). *cis*- [20] and *trans*- [21] Hept-4-enoic acids have not previously been obtained by reduction of hept-4-ynoic acid, which was prepared by hydrolysis of the nitrile prepared from hex-3-ynyl toluene-*p*-sulphonate (see below). *trans*-Hept-2-enoic acid was conveniently obtained from malonic acid and valeraldehyde; this is a previously unrecorded route to this acid.

Oct-7-enoic acid, previously obtained by reduction of oct-7-ynoic acid [22] or from 6-bromohex-1-ene,[23] was obtained by carboxylation of the Grignard reagent from 7-chlorohept-1-ene.[24] *trans*-Oct-6-enoic acid was obtained by the published method; [12] the *cis*-isomer [25] was obtained from oct-6-ynoic acid prepared by the route shown in Scheme 2. This route is an improved modification of that previously reported.[26]

Scheme 2



$$Me{\cdot}C{:}C{\cdot}CH_2{\cdot}CH_2OH \xrightarrow{i} Me{\cdot}C{:}C{\cdot}CH_2{\cdot}CH_2{\cdot}OTs \xrightarrow{ii}$$

$$Me{\cdot}C{:}C{\cdot}CH_2{\cdot}CH_2{\cdot}CH(CO_2Et)_2 \xrightarrow{iii} Me{\cdot}C{:}C{\cdot}[CH_2]_3{\cdot}CO_2H \xrightarrow{iv}$$

$$Me{\cdot}C{:}C{\cdot}[CH_2]_3{\cdot}CH_2OH \xrightarrow{i} Me{\cdot}C{:}C{\cdot}[CH_2]_3{\cdot}CH_2OTs \xrightarrow{v}$$

$$Me{\cdot}C{:}C{\cdot}[CH_2]_3{\cdot}CH_2CN \xrightarrow{vi} Me{\cdot}C{:}C{\cdot}[CH_2]_4{\cdot}CO_2H$$

Reagents: i, TsCl–C_5H_5N; ii, NaOEt–$CH_2(CO_2Et)_2$; iii, KOH–H_2O; iv, $LiAlH_4$; v, KCN–Me_2SO; vi, KOH–H_2O–EtOH.

Ts = toluene *p*-sulphonyl.

Hex-3-yn-1-ol, prepared from lithiobut-1-yne and ethylene oxide, was readily converted, by way of a malonic ester synthesis on the derived toluene-*p*-sulphonate, into the previously reported [16,26] oct-5-ynoic acid. Reduction of this acid gave the required oct-5-enoic acids. In an analogous manner hept-3-yn-1-ol was converted by way of the toluene-*p*-sulphonate into oct-4-ynonitrile. Hydrolysis of this nitrile (previously prepared by dehydration of the amide) failed, as reported,[27] under mild conditions, but under more vigorous conditions (see Experimental section) was readily hydrolysed to oct-4-ynoic acid. Appropriate reduction of the latter gave either *cis* or *trans*-oct-4-enoic acid. *trans*-Oct-4-enoic acid has been obtained [25] by chain extension from pent-3-enoic acid. *trans*-Oct-3-enoic acid, obtained from n-hexanal and malonic acid in the presence of tri(2-hydroxyethyl)amine, contained *ca.* 8% of the Δ^2-isomer. Similarly, *trans*-oct-2-enoic acid, obtained from n-hexanaldehyde and malonic acid in the presence of pyridine, contained *ca.* 4% of the Δ^3-isomer. In each case g.l.c. indicated the presence of 6—8% of unidentified impurities.

Authentic Ketones and Lactones.—γ- and δ-Lactones were conveniently prepared by potassium borohydride reduction of the corresponding 4- and 5-oxo-acids. The latter were obtained by hydrolysis of the corresponding ethyl ester, formed by the reaction [28] of the appropriate dialkylcadmium with the half ester acid chloride of succinic or glutaric acid, with the exception of 5-oxohexanoic acid which was obtained by the hydrolysis of 4-ethoxycarbonyl-5-oxohexanoate.[29]

Cyclohex-2-enone and its 2-alkyl derivatives were prepared by the method of Born *et al.*,[30] and 2-alkylcyclopent-2-enones by the method of Ansell and Ducker.[31] The latter compounds, when freshly prepared, contained small amounts of the isomeric 2-alkylidenecyclopentanones, although these impurities were lost in time, presumably owing to isomerisation to the 2-alkylcyclopent-2-enones. Cyclohept-2-enone was obtained by oxidation of cyclohept-2-enol with manganese dioxide; an Oppenauer oxidation was previously used.[32] 2-Ethylidenecyclopentanone, prepared as described,[33] contained a major product (90%) which yielded acetaldehyde on ozonolysis and was identical (g.l.c.) with the minor product from the preparation of 2-ethylcyclopent-2-enone. Similarly 2-n-propylidenecyclopentanone [34] was 90% pure, yielded propionaldehyde on ozonolysis, and contained 5% of 2-n-propylcyclopent-2-enone. 2-Ethylidenecyclohexanone,[35] obtained from 2-hydroxymethylenecyclohexanone and methylmagnesium iodide, was

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[17] R. P. Linstead, E. J. Noble, and E. J. Boorman, *J. Chem. Soc.*, 1933, 557; S. E. Boxer and R. P. Linstead, *ibid.*, 1931, 740.

[18] A. O. Zoss and G. F. Henion, *J. Amer. Chem. Soc.*, 1941, **63**, 1151.

[19] P. Gaubert, R. P. Linstead, and H. N. Rydon, *J. Chem. Soc.*, 1937, 1971.

[20] L. Crombie and S. H. Harper, R. E. Stedman, and D. Thompson, *J. Chem. Soc.*, 1951, 2445.

[21] H. D. Zook and J. A. Knight, *J. Amer. Chem. Soc.*, 1954, **76**, 2302.

[22] W. R. Taylor and F. M. Strong, *J. Amer. Chem. Soc.*, 1950, **72**, 4263.

[23] J. Colonge and P. Lasfargues, *Bull. Soc. chim. France*, 1962, 177.

[24] T. D. Perrine, *J. Org. Chem.*, 1953, **18**, 1356.

[25] J. A. Knight and J. H. Diamond, *J. Org. Chem.*, 1959, **24**, 400.

[26] M. S. Newman and J. H. Wotiz, *J. Amer. Chem. Soc.*, 1949, **71**, 1292.

[27] G. B. Bachman, *J. Amer. Chem. Soc.*, 1933, **55**, 4279.

[28] R. F. Naylor, *J. Chem. Soc.*, 1947, 1106; J. Cason, *J. Amer. Chem. Soc.*, 1946, **68**, 2078.

[29] I. N. Nazarov and S. I. Zav'yalor, *Izvest. Akad. Nauk, S.S.S.R. otdel. khim. Nauk*, 1952, 300.

[30] H. Born, R. Pappo, and J. Szmuszkovicz, *J. Chem. Soc.*, 1953, 1779.

[31] M. F. Ansell and J. W. Ducker, *J. Chem. Soc.*, 1959, 329.

[32] J. E. Hodgkins and R. J. Flores, *J. Org. Chem.*, 1963, **28**, 3356.

[33] J. English and V. Lamberti, *J. Amer. Chem. Soc.*, 1952, **74**, 1909.

[34] G. Vavon and J. Flurer, *Bull. Soc. chim. France*, 1929, **45**, 754.

[35] A. S. Dreiding and S. N. Nickel, *J. Amer. Chem. Soc.*, 1954, **76**, 3965.

91% pure, yielded acetaldehyde on ozonolysis, and contained 6% of 2-ethylcyclohex-2-enone and 3% of an unidentified component.

EXPERIMENTAL

Refractive indices are for the sodium D-line at 20° unless otherwise stated.

Hex-5-enoic Anhydride.—A mixture of hex-5-enoic acid [12] (8 g.) and acetic anhydride (50 ml.) was refluxed for 2 hr., and then fractionally distilled to yield *hex-5-enoic anhydride* (5·1 g., 70%), b. p. 107—108°/0·25 mm., *n* 1·4485 (Found: C, 68·6; H, 9·0. $C_{12}H_{18}O_3$ requires C, 68·6; H, 8·6%).

Pent-3-yn-1-ol.—Sodium (46 g.) was added in small pieces to a stirred, cooled (acetone–solid carbon dioxide) solution of acetylene in liquid ammonia (1·5 l.) through which acetylene was continuously passed. The rate of addition was such that the blue colour of the solution of sodium did not spread throughout the solution. The flow of acetylene was stopped as soon as the blue colour due to the last piece of sodium had been discharged. Methyl bromide (210 g.) was condensed into the reaction mixture during 2 hr., and stirring continued for a further 3 hr. A suspension of lithamide (46 g.) in liquid ammonia (500 ml.) was added in portions, followed, after 2 hr. stirring, by ethylene oxide (176 g.) added in one portion. The temperature of the reaction mixture was maintained at *ca.* −65° for 12 hr., and then at *ca.* −35° (reflux temperature) for 12 hr., after which time ammonium chloride (160 g.) was added. The reaction mixture was left at room temperature for 24 hr., and finally heated on a steam-bath to complete the removal of ammonia. Water (1 l.) and ether (1 l.) were added, the two phases were separated and the aqueous phase was extracted with ether (3 × 250 ml.). Distillation of the dried ($MgSO_4$) combined ether extracts through a Dufton column gave pent-3-yn-1-ol (70·5 g., 42%), b. p. 63—64°/20 mm., *n* 1·4550 (lit., b. p. 99—102°/120 mm.; [13] b. p. 154—157°, *n* 1·4554 [36]). The use of sodamide in place of lithamide reduced the yield of pent-3-yn-1-ol to 15—20%.

Pent-3-ynyl Toluene-p-*sulphonate*.—Pent-3-yn-1-ol (84 g.) was added during 45 min. to a stirred slurry of toluene-*p*-sulphonyl chloride (216 g.) in pyridine (100 ml.) maintained at 20° ± 2°. After a further 2 hr. at room temperature, the mixture was poured on to ice (200 g.) and extracted with ether (3 × 100 ml.). The extract was washed successively with 6N-sulphuric acid (2 × 200 ml.), saturated sodium hydrogen carbonate solution (100 ml.), and water (50 ml.). The dried (K_2CO_3) extract was evaporated and the residue dried *in vacuo* to yield a crystalline mass of *pent-3-ynyl toluene*-p-*sulphonate* (214 g., 90%), m. p. 40—42° (from ethanol) (Found: C, 60·5; H, 5·9; S, 13·7. $C_{12}H_{14}O_3S$ requires C, 60·5; H, 5·9; S, 13·4%).

5-*Chloropent-2-yne*.—A solution of pent-3-ynyl toluene-*p*-sulphonate (104 g.) and lithium chloride (22 g.), in 2-(2-ethoxyethoxy)ethanol (500 ml.) was heated at 100° for 4 hr., and then distilled under reduced pressure 100°(bath)/15 mm. The distillate (*ca.* 40 ml.) was dissolved in an equal volume of ether, washed with water, dried ($CaCl_2$), and distilled to yield 5-*chloropent-2-yne* (30 g., 68%), b. p. 118—120°, *n* 1·4550 (Found: Cl, 35·0. C_5H_7Cl requires Cl, 34·6%).

5-*Bromopent-2-yne*.—This bromide, b. p. 44—46°/1 mm., *n* 1·4888, was prepared (54%) as for the corresponding chloride, by use of calcium bromide instead of lithium chloride, but a satisfactory analysis could not be obtained.

5-*Iodopent-2-yne*.—A solution of pent-3-ynyl toluene-*p*-sulphonate (49·5 g.) and sodium iodide (38 g.) in acetone (350 ml.) was boiled under reflux for 2 hr. The precipitated sodium toluene-*p*-sulphonate was filtered off from the cold (0°) reaction mixture and washed with ether. The combined filtrates were evaporated and the residue was washed with 10% aqueous sodium thiosulphate solution and water, dried ($MgSO_4$), and distilled, to yield 5-*iodopent-2-yne* (29·7 g., 73%), b. p. 62—63°/17 mm., *n* 1·5495 (Found: C, 31·3; H, 3·8; I, 65·3. C_5H_7I requires C, 30·9; H, 3·6; I, 65·4%).

Hex-4-ynonitrile.—A solution of pent-3-ynyl toluene-*p*-sulphonate (24·6 g.) in dimethyl sulphoxide (100 ml.) was added to a suspension of potassium cyanide in the same solvent (200 ml.). The mixture, which rapidly became homogeneous, was stirred at 100° for 4 hr., cooled, poured into water (300 ml.), and the resulting solution was continuously extracted with ether for 12 hr. The ethereal extract was washed with water (2 × 100 ml.), dried ($MgSO_4$), and distilled, to yield hex-4-ynonitrile (6·7 g., 73%), b. p. 75—76°/13 mm., *n* 1·4500 (Found: C, 77·3; H, 7·6; N, 15·2. C_6H_7N requires C, 77·4; H, 7·5; N, 15·0%). When methanol or aqueous methanol was used as solvent the cyanide was obtained in 30—40% yield after 24 hr. at reflux temperature.

Hex-4-ynoic Acid.—(a) *From* 5-*iodopent-2-yne*. A solution of the Grignard reagent prepared from 5-iodopent-2-yne (38·8 g.) and magnesium (4·8 g.) in ether (100 ml.) was added during 1 hr., to a stirred suspension of powdered solid carbon dioxide (400 g.) in ether (100 ml.). The mixture was then left for 12 hr., and the excess of carbon dioxide and most of the ether were then evaporated off. Water (150 ml.) and light petroleum (b. p. 40—60°) were added, followed by sufficient concentrated hydrochloric acid (*ca.* 40 ml.) to yield two clear phases, which were separated. The aqueous phase was extracted with light petroleum (b. p. 40—60°) (3 × 50 ml.). The combined petroleum solutions were extracted with saturated aqueous sodium hydrogen carbonate solution, dried ($MgSO_4$), and distilled, to yield *deca-2,8-diyne* (6·6 g., 50%), b. p. 81—82°/11 mm., *n* 1·4686 (Found: C, 89·6; H, 10·4. $C_{10}H_{14}$ requires C, 89·5; H, 10·4%). The above alkali extract was stirred at 0° under an equal volume of light petroleum (b. p. 40—60°) and made acid (Congo Red) with 5N-hydrochloric acid. The petroleum layer was separated, washed (water), dried ($MgSO_4$), and evaporated, to yield a solid residue of hex-4-ynoic acid (2·0 g., 14%), m. p. 98—99·5° [from light petroleum (b. p. 60—80°)].

(b) *From hex-4-ynonitrile*. A solution of hex-4-ynonitrile (7·5 g.) and potassium hydroxide (9 g.) in water (80 ml.) and ethanol (20 ml.) was refluxed for 24 hr., and then concentrated to two thirds of its bulk by distillation under reduced pressure. The cool solution was extracted with ether and the aqueous layer cooled to 0° and extracted as in (a). Evaporation of the extracts gave a crystalline residue of hex-4-ynoic acid (7·3 g., 81%), m. p. 98—99° (from petroleum (lit.,[13] 99°). The *p*-bromophenacyl ester had m. p. 99° (lit.,[13] 98°).

trans-*Hex-4-enoic Acid*.—Hex-4-ynoic acid (5·8 g.) was added in portions to a cold (−75°) stirred solution of sodium (6·9 g.) in liquid ammonia (300 ml.). The solution was allowed to warm to reflux temperature and stirred for a further 1 hr. An excess of ammonium chloride was then

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[36] L. Crombie and S. H. Harper, *J. Chem. Soc.*, 1950, 873.

added and the mixture was left overnight at room temperature. Water (100 ml.) and ether (100 ml.) were then added, and the mixture was acidified (Congo Red) with concentrated hydrochloric acid. The ether layer was removed and the aqueous layer extracted with ether (3 × 50 ml.). Distillation of the dried ($MgSO_4$) combined ethereal solutions gave *trans*-hex-4-enoic acid (5·3 g., 90%), b. p. 106—107°/16 mm., *n* 1·4390 (lit.,[12] b. p. 110—111°/17 mm., *n* 1·4385). The *p*-bromophenacyl ester had m. p. 83—83·5° (lit.,[12] 81—82°).

cis-*Hex*-4-*enoic Acid*.—A mixture of hex-4-ynoic acid (5·8 g.), ethyl acetate (100 ml.), Lindlar catalyst (0·6 g.), and quinoline (0·2 g.) was shaken with hydrogen at room temperature and pressure. The calculated uptake of hydrogen took place during 45 min., and the reaction mixture was worked up. Distillation gave *cis*-hex-3-enoic acid (5·0 g., 87%), b. p. 110—111°/19 mm., *n* 1·4408 (lit.,[12] b. p. 112—113°/17 mm., *n* 1·4406). The *p*-bromophenacyl ester had m. p. 51—53° (lit.,[12] 51—52°).

Hex-3-*yn*-1-*ol*.—This alkynol, b. p. 73—75°/25 mm., *n* 1·4562, was obtained (68%) from ethyl bromide, acetylene, and ethylene oxide, as described for pent-3-yn-1-ol. Sondheimer [15] prepared the alkynol (47%), b. p. 73·5—74·5°/23 mm., *n* 1·4562, by use of sodamide in place of lithamide.

Hex-3-*ynoic Acid*.—This acid, m. p. 58·5—60·5°, was prepared from hex-3-yn-1-ol as described.[14] The p-*bromophenacyl ester* had m. p. 123—125° (Found: C, 54·9; H, 4·4. $C_{14}H_{13}BrO_3$ requires C, 54·5; H, 4·25%). *Hex*-3-*ynyl hex*-3-*ynoate*, b. p. 93—95°/0·1 mm. (Found: C, 74·5; H, 8·5. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·3%), was obtained as a by-product.

trans-*Hex*-3-*enoic Acid*.—This acid, b. p. 98—99°/11 mm., *n* 1·4396 (lit.,[16] b. p. 106·5—108°/18 mm.), was obtained (80%) from hex-3-ynoic acid as described for *trans*-hex-4-enoic acid. The p-*bromophenacyl ester* had m. p. 78·5—79·5° (from alcohol) (Found: C, 53·8; H, 5·0. $C_{14}H_{15}BrO_3$ requires C, 54·1; H, 4·8%). This acid was also obtained [16] from butyraldehyde and malonic acid in the presence of triethanolamine.

cis-*Hex*-3-*enoic Acid*.—This acid, b. p. 102—103°/11 mm., *n* 1·4422, was obtained (80%) from hex-3-ynoic acid as described for *cis*-hex-4-enoic acid. The p-*bromophenacyl ester* had m. p. 82—83° (from alcohol) (Found: C, 53·9; H, 4·8. $C_{14}H_{15}BrO_3$ requires C, 54·1; H, 4·8%).

Hex-2-*ynoic Acid*.—A solution of pent-1-yne [37] (19 g.) in ether (25 ml.) was added to a stirred solution of ethyl magnesium bromide [from magnesium (6 g.)] in ether (100 ml.), at such a rate that a steady reflux was maintained, and the solution was then boiled for 4 hr. The cold (0°) solution of the Grignard reagent was added to powdered solid carbon dioxide (200 g.) in an autoclave, which was then sealed and left for 48 hr. at room temperature (maximum pressure 30 atmos.). The pressure was released, and the reaction mixture worked up as described for hex-4-ynoic acid, to yield hex-2-ynoic acid (19·1 g., 68%), b. p. 124—125°/21 mm. (lit.,[18] 111°/10 mm.). The p-*bromophenacyl ester* had m. p. 80—81° (from alcohol) (Found: C, 54·0; H, 4·4. $C_{14}H_{13}BrO_3$ requires C, 54·4; H, 4·2%). Carboxylation of the sodio-derivative of pent-1-yne (cf. reference 18) gave hex-2-ynoic acid (10%).

cis-*Hex*-2-*enoic Acid*.—This acid, b. p. 95—96°/11 mm., *n* 1·4493, was obtained (90%) from hex-2-ynoic acid as described for *cis*-hex-4-enoic acid. The p-*bromophenacyl ester* had m. p. 42—43·5° (from ethanol) (Found: C, 54·0; H, 4·6. $C_{14}H_{15}BrO_3$ requires C, 54·1; H, 4·8%). Bourguel [38] reports, b. p. 102·5—103·7°/17 mm., n^{21} 1·4495 for a hex-2-enoic acid (presumably *cis*).

trans-*Hex*-2-*enoic Acid*.—This acid was prepared as described.[39] The p-*bromophenacyl ester* had m. p. 73—74° (from ethanol) (Found: C, 54·0; H, 4·8. $C_{14}H_{15}BrO_3$ requires C, 54·1; H, 4·8%), and the *anhydride* (formed by the action of acetic anhydride) had b. p. 113—115°/0·1 mm., *n* 1·4720 (Found: C, 69·0; H, 8·8. $C_{12}H_{18}O_3$ requires C, 68·6; H, 8·6%).

Methyl Esters of the Hexenoic Acids.—These were prepared with diazomethane; properties in Table 6.

Table 6

Ester	B. p.	*n*	G.l.c. retention time (min.) [a]	Found (%) [b] C	H
Δ^2-*trans*	64—65°/20 mm.[c]	1·4348	46·4	65·3	9·5
Δ^2-*cis* ...	51—52/18 mm.	1·4315	41·5	65·8	9·7
Δ^3-*trans*	59—60/21 mm.	1·4259	41·6	66·0	9·4
Δ^3-*cis* ...	62—63/22 mm.	1·4266	42·3	65·6	9·7
Δ^4-*trans*	58—59/22 mm.	1·4251	42·5	65·5	9·6
Δ^4-*cis* ...	56—57/19 mm.	1·4274	41·5	65·7	9·4
Δ^5	58—59/24 mm.[d]	1·4209	35·5	65·2	9·1

[a] On Apiezon L 25% at 50°. [b] $C_7H_{12}O_2$ requires C, 65·6; H, 9·4%. [c] Lit.,[40] 56—58°/13 mm. [d] Lit.,[41] 48°/12 mm., n^{23} 1·4199.

Hept-6-*enoic Acid*.—This acid [19] gave a p-*bromophenacyl ester*, m. p. 64—65° (from ethanol) (Found: C, 54·9; H, 5·2. $C_{15}H_{17}BrO_3$ requires C, 55·4; H, 5·2%). The *anhydride* (formed by the action of acetic anhydride) had b. p. 110—111°/0·1 mm., *n* 1·4519 (Found: C, 70·7; H, 9·3. $C_{14}H_{22}O_3$ requires C, 70·6; H, 9·2%).

cis- *and* trans-*Hept*-5-*enoic Acid*.—These acids were prepared from hept-5-ynoic acid (see below) as described for *cis*- and *trans*-hex-4-enoic acid, except that for the former acid aged Raney nickel was used. cis-*Hept*-5-*enoic acid* (49% on 0·18 mole scale) had b. p. 116—117°/13 mm., *n* 1·4435 (Found: C, 65·8; H, 9·5. $C_7H_{10}O_2$ requires C, 65·9; H, 9·4%); its p-*bromophenacyl ester* had m. p. 49—50° (from methanol) (Found: C, 55·3; H, 5·2. $C_{15}H_{17}BrO_3$ requires C, 55·4; H, 5·2%). *trans*-Hept-5-enoic acid (74% on 0·16 mole scale) had b. p. 120—121°/16 mm., *n* 1·4430 (lit.,[12] b. p. 121—122°/17 mm., *n* 1·4424); its *p*-bromophenacyl ester had m. p. 60—61° (lit.,[12] 62—63°).

Hept-4-*ynonitrile*.—This *nitrile*, b. p. 82—83°/16 mm., *n* 1·4492, was obtained (78% yield on 0·2 mole scale) from hex-3-yn-1-ol (see above) by way of toluene-*p*-sulphonate as described for hex-4-ynonitrile (Found: C, 78·3; H, 8·4; N, 13·0. C_7H_9N requires C, 78·5; H, 8·4; N, 13·1%).

Hept-4-*ynoic Acid*.—This acid (needles from light petroleum, b. p. <40°), m. p. 57—59° was obtained (67% yield on a 0·16 mole scale) from hept-4-ynonitrile as described for hex-4-ynoic acid. The p-*bromophenacyl ester* (plates from ethanol) had m. p. 99—100° (Found: C, 55·7; H, 4·65. $C_{15}H_{15}BrO_3$ requires C, 55·73; H, 4·6%).

cis- *and* trans-*Hept*-4-*enoic Acid*.—These acids were prepared from hept-4-ynoic acid as described for *cis*- and

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[37] T. L. Jacobs, *Org. Reactions*, 1949, **5**, 48.

[38] M. Bourguel, *Bull. Soc. chim. France*, 1929, **45**, 1067.

[39] M. S. Bainova, R. V. Erstigneeva, R. S. Livshits, K. K. Kuz'mina, and N. A. Preobrazhenskii, *Zhur. obschchei Khim.*, 1952, **22**, 2200.

[40] B. R. Baker, M. V. Querry, S. R. Safir, and S. Bernstein, *J. Org. Chem.*, 1947, **12**, 138.

[41] R. Huisgen and J. Reinertshofer, *Annalen*, 1952, **575**, 174.

trans-hex-4-enoic acid. *cis*-Hept-4-enoic acid (83% on a 0·2 mole scale) had b. p. 114—116°/14 mm., *n* 1·4415 (lit.,[42] b. p. 115—116°/12 mm., *n* 1·4403); its *p*-bromophenacyl ester had m. p. 47·5—48·5° (from methanol) (lit.,[42] 46°). *trans*-Hept-4-enoic acid (79% on 0·24 mole scale) had b. p. 110—111°/11 mm., n^{19} 1·4420 (lit.,[42] b. p. 104—105°/7 mm., *n* 1·4398); its *p*-bromophenacyl ester had m. p. 80—81° (from methanol) (lit.,[42] 78—79°).

trans-*Hept*-2-*enoic Acid*.—A mixture of valeraldehyde (86 g.), malonic acid (104 g.), pyridine (50 ml.), and a few drops of piperidine was stirred and maintained at a temperature of 60—70° for 3 hr. and then at 110° for a further 3 hr. Sufficient sulphuric acid (50%) was added to the cold mixture to give two clear phases, which were separated. The aqueous layer was extracted with ether (3 × 100 ml.). The combined organic material was washed with water (2 × 100 ml.), and then extracted with a saturated solution of sodium carbonate (53 g.). The alkali extract was acidified with 5N-hydrochloric acid and extracted with ether. Evaporation of the dried ($MgSO_4$) extract and distillation of the residue gave *trans*-hept-2-enoic acid (53 g.), b. p. 128—129°/16 mm. (lit.,[43] 120—122°/11 mm.), *n* 1·4550, $\lambda_{max.}$ 10·35 μ (*trans* C=C). The p-*bromophenacyl ester* had m. p. 72—73° (from ethanol) (Found: C, 55·5; H, 5·3. $C_{15}H_{17}BrO_3$ requires C, 55·4; H, 5·3%).

Oct-7-*enoic Acid*.—This acid, b. p. 120°/2 mm., *n* 1·4415 (lit.,[22] b. p. 90—92°/1 mm., n^{27} 1·4340), was obtained (43%) by carboxylation of the Grignard reagent from 7-chlorohept-1-ene [24] as described for hex-4-ynoic acid.

Diethyl Pent-3-*ynylmalonate*.—Pent-3-ynyl toluene-*p*-sulphonate (238 g., 1 mole) (see above) was added during 1 hr. to a hot stirred solution of diethyl malonate (320 g., 2 moles), and sodium ethoxide (58 g., 1 mole) in dry ethanol (400 ml.). The mixture was refluxed for 4 hr., cooled, and filtered, and the residue was washed with water (100 ml.), dried ($MgSO_4$), and distilled to yield (after removal of the ether and diethyl malonate) *diethyl pent*-3-*ynylmalonate* (155 g., 69%), b. p. 100—102°/0·3 mm., *n* 1·4478 (Found: C, 63·5; H, 8·0. $C_{12}H_{18}O_4$ requires C, 63·7; H, 8·0%).

Pent-3-*ynylmalonic Acid*.—Diethyl pent-3-ynylmalonate (74·6 g., 0·33 mole) was stirred into a cold solution of potassium hydroxide (84% purity; 67 g., 1 mole) in water (100 ml.) and sufficient alcohol (*ca*. 5 ml.) to clarify the solution. The solution was left at room temperature for 24 hr., washed with ether (20 ml.), concentrated (under reduced pressure) to two thirds of its original volume, cooled to 0°, made acid (Congo Red) with concentrated hydrochloric acid, and extracted with ether (4 × 20 ml.). Evaporation of the dried ($MgSO_4$) extracts gave *pent*-3-*ynylmalonic acid* (48·5 g., 86%) which readily crystallised when dried *in vacuo*, m. p. 121—123° (decomp.) (from benzene) (Found: C, 56·7; H, 6·0. $C_8H_{10}O_4$ requires C, 56·5; H, 5·9%).

Hept-5-*ynoic Acid*.—Pent-3-ynylmalonic acid (109 g.) was heated at 150° ± 5° for 2 hr. The cooled product was stirred into a saturated aqueous solution of sodium hydrogen carbonate (20 g.) and the resulting solution was extracted with ether (3 × 20 ml.). The aqueous solution was then covered with an equal volume of ether, made acid (Congo Red) with concentrated hydrochloric acid, and the ether layer was separated. The aqueous layer was extracted with ether (3 × 20 ml.). Evaporation of the dried ($MgSO_4$) extracts gave hept-5-ynoic acid (68·4 g., 86%), m. p. 40·5—42° [from light petroleum (b. p. <40°)] (lit.,[14] 36—38°) (Found: C, 66·90; H, 8·1. Calc. for $C_7H_{10}O_2$: C, 66·7; H, 7·9%). The p-*bromophenacyl ester* had m. p. 67—68° (from ethanol) (Found: C, 55·8; H, 4·7. $C_{15}H_{15}BrO_3$ requires C, 55·7; H, 4·6%).

Hept-5-*yn*-1-*ol*.—A stirred suspension of lithium aluminium hydride (12·2 g.) in ether (400 ml.) was refluxed for 2 hr., then cooled, and the solution of hept-5-ynoic acid (31·5 g.) in ether (300 ml.) was added at such a rate that a steady reflux was maintained. After further stirring (2 hr.), saturated aqueous ammonium chloride solution (75 ml.) was added cautiously. The precipitated solid was filtered off and washed with ether. The ethereal filtrate was dried ($MgSO_4$) and distilled, to yield hept-5-yn-1-ol (24 g., 86%), b. p. 104—106°/21 mm., n^{19} 1·4610 (lit.,[26] b. p. 96°/15 mm., n^{25} 1·4590).

cis-*Oct*-6-*enoic Acid*.—Hept-5-yn-1-ol was converted into the toluene-*p*-sulphonate (not purified) and thence to oct-6-ynonitrile (72·2% overall), b. p. 100—102°/14 mm., n^{19} 1·4551 (lit.,[26] b. p. 79°/2 mm., n^{25} 1·4530) as described above for the conversion of pent-3-yn-1-ol into hex-4-ynonitrile. Hydrolysis [26] of the nitrile followed by hydrogenation of the acid in the presence of Lindlar catalyst [cf. *cis*-hex-4-enoic acid (above); use of aged Raney nickel [25]] gave *cis*-oct-6-enoic acid, b. p. 100—102°/0·5 mm., n^{21} 1·4462 (lit.,[25] b. p. 88°/0·8 mm., n^{20} 1·4441). The p-*bromophenacyl ester* had m. p. 46·5—47·5° (from methanol) (Found: C, 56·5; H, 5·6. $C_{16}H_{19}BrO_3$ requires C, 56·6; H, 5·6%).

Oct-5-*ynoic Acid*.—This acid, b. p. 104—106°/0·5 mm., *n* 1·4560 (lit.,[16] b. p. 95—96·5°/0·3 mm., n^{25} 1·4434), *p*-bromophenacyl ester, m. p. 63—64° (lit.,[16] 63·3—64·3°) was obtained from hex-3-yn-1-ol by way of *diethyl hex*-3-*ynylmalonate* (58%); b. p. 92—93°/0·2 mm., *n* 1·4505 (Found: C, 64·71; H, 8·3. $C_{13}H_{20}O_4$ requires C, 65·0; H, 8·3%) and *hex*-3-*ynylmalonic acid* (90%), m. p. 114—118° (from benzene) (Found: C, 58·5; H, 6·6. $C_9H_{12}O_4$ requires C, 58·7; H, 6·6%) as described for the conversion of pent-3-yn-1-ol into hept-5-ynoic acid.

cis- *and* trans-*Oct*-5-*enoic Acid*.—These acids were prepared as described.[16] p-*Bromophenacyl* trans-*oct*-5-*enoate* had m. p. 51—52° (from methanol) (Found: C, 56·6; H, 5·7. $C_{16}H_{19}BrO_3$ requires C, 56·6; H, 5·6%).

Hept-3-*yn*-1-*ol*.—This alcohol, b. p. 90—91°/25 mm., n^{18} 1·4556 (lit.,[26] b. p. 111°/70 mm., n^{25} 1·4530) was obtained (65%, on 3 mole scale) from n-propyl bromide as described for pent-3-yn-1-ol.

Oct-4-*ynonitrile*.—This nitrile, b. p. 90—91°/16 mm., n^{19} 1·4510 (lit.,[26] b. p. 71°/3 mm., n^{25} 1·4492) was obtained (72% overall) from hept-3-yn-1-ol by way of the toluene-*p*-sulphonate as described for pent-3-ynenitrile.

Oct-4-*ynoic Acid*.—Oct-4-ynonitrile (53 g.) was refluxed for 24 hr. with a solution of potassium hydroxide (74 g.) in water (230 ml.) and ethylene glycol (68 ml.), and the product was worked up as described for hex-4-ynoic acid to yield oct-4-ynoic acid (50 g., 81%), m. p. 48—50°. A recrystallised sample (needles from light petroleum, b. p. <40°) had m. p. 49—50° (lit.,[26] 49°). The p-*bromophenacyl ester* had m. p. 100—101° (from aqueous ethanol) (Found: C, 57·3; H, 5·3. $C_{16}H_{17}BrO_3$ requires C, 57·0; H, 5·0%). As reported,[26] this hydrolysis cannot be effected under mild conditions.

cis- *and* trans-*Oct*-4-*enoic Acid*.—These acids, b. p. 94—95°/0·6 mm., *n* 1·4422 (lit.,[25] b. p. 96°/0·8 mm., *n* 1·4417) and b. p. 90—91°/0·5 mm., *n* 1·4436 (lit.,[25] b. p. 93°/1·5 mm., *n* 1·4441), respectively, were obtained (*ca*.

[42] L. Crombie and S. H. Harper, *J. Chem. Soc.*, 1950, 1714.

[43] R. Delaby and S. Guillot-Allegre, *Bull. Soc. chim. France*, 1933, **53**, 301.

80%) from oct-4-ynoic acid as described for *cis*- and *trans*-hex-4-enoic acid. The p-*bromophenacyl esters* (both from methanol) had m. p.s 41—42° (Found: C, 56·6; H, 5·6. $C_{16}H_{19}BrO_3$ requires C, 56·6; H, 5·6%) and 78—79° (Found: C, 56·7; H, 5·7%), respectively.

trans-*Oct-3-enoic Acid*.—This acid, prepared [25] from n-hexanal, malonic acid, and tri-(2-hydroxyethyl)-amine was shown by g.l.c. to contain *trans*-oct-2-enoic acid (8%) and two unidentified components (8%). The p-*bromophenacyl ester* had m. p. 65—66° (from ethanol) (Found: C, 56·7; H, 6·0. $C_{16}H_{19}O_3$ requires C, 56·6; H, 5·6%).

TABLE 7

Lactone	Yield (%)	Constants: Observed	Constants: Lit.	M. p. of hydrazide: Observed	M. p. of hydrazide: Lit.
Hexan-4-olide	71	B. p. 104—105°/20 mm., *n* 1·4390	103°/14 mm.,[a] n^{15} 1·4433	75°	75° [a]
Hexan-5-olide	65	B. p. 108—109°/17 mm., *n* 1·4515	106—107°/14 mm.,[b] *n* 1·452	82—83 [c]	
Heptan-4-olide	65	B. p. 104—105°/12 mm., *n* 1·4411	103°/10 mm.[d]	87—88	88 [d]
Heptan-5-olide	60	B. p. 114—115°/14 mm., *n* 1·4546	68—69°/1 mm.,[e] *n* 1·4545	74—75 [f]	
Octan-4-olide	71	B. p. 123—124°/15 mm., *n* 1·4449	102—105°/5·5 mm.,[g] n^{19} 1·4451	82—83	79—80 [g]
Octan-5-olide	76	B. p. 126°/15 mm., $n^{18·5}$ 14,552	115—117°/12 mm.[h]	88—89 [i]	

[a] Ref. 3. [b] R. Kuhn and D. Jerchel, *Ber.*, 1943, **76**, 413. [c] Found: C, 49·3; H, 9·6; N, 19·4. $C_6H_{14}N_2O_2$ requires C, 49·3; H, 9·6; N, 19·2%. [d] D. Papa, E. Schwenk, and H. F. Ginsburg, *J. Org. Chem.*, 1951, **16**, 253. [e] Ref. 21. [f] Found: C, 52·8; H, 10·2; N, 17·6. $C_7H_6N_2O_2$ requires C, 52·5; H, 10·0; N, 17·5%. [g] Y. Terai and T. Tanaka, *Bull. Chem. Soc. Japan*, 1956, **29**. [h] R. Lukes and M. Cerny, *Coll. Czech. Chem. Comm.*, 1959, **24**, 2722. [i] Found: C, 55·3; H, 10·55; N, 16·0. $C_{13}H_{18}N_2O_2$ requires C, 55·2; H, 10·3; N, 16·1%.

Preparation of γ- and δ-Lactones.—The appropriate oxo-acid (0·1 mole) was dissolved in water (50 ml.) and the solution made neutral (phenolphthalein) by the addition of 10% sodium hydroxide solution. The solution was stirred at room temperature and a solution of potassium borohydride (2·0 g.) in water (50 ml.) was added at such a rate that the temperature was maintained at 20—30°. The solution was stirred for a further 2 hr., the excess of borohydride was decomposed with 2N-sulphuric acid, and the solution was then boiled for 1 hr. The cold solution was extracted continuously with ether for 12 hr.

Distillation of the residue obtained on evaporation of the dried ($MgSO_4$) extract gave the required lactone (Table 7).

Cyclohept-2-enone.—A solution of cyclohept-2-enol [44] (5 g.) [the derived α-naphthylurethane (needles from ethanol) had m. p. 133—134° (Found: C, 76·4; H, 6·7; N, 5·1. $C_{18}H_{19}NO_2$ requires C, 76·9; H, 6·8; N, 5·1%)] in light petroleum (b. p. 60—80°) (250 ml.) was stirred with manganese dioxide [45] (30 g.) for 15 hr., at room temperature. The manganese dioxide was filtered off and washed with light petroleum. Evaporation of the dried ($MgSO_4$) filtrates gave a mixture of equal amounts (g.l.c.) of cyclohept-2-enol and cyclohept-2-enone, which was re-oxidised with manganese dioxide (35 g.) in light petroleum (250 ml.) for 12 hr. After removal of the oxidant as before, distillation gave cyclohept-2-enone (>99% purity by g.l.c.) (2 g., 40%), b. p. 71—72°/10 mm., *n* 1·4690 (lit.,[47] b. p. 73—74°/11 mm., n^{26} 1·4925), $\lambda_{max.}$ 228 and 318 mμ (log ε 4·00 and 1·77), $\lambda_{min.}$ 274 mμ (log ε 1·23) (Found: C, 76·3; H, 9·0. Calc. for $C_7H_{10}O$: C, 76·3; H, 9·1%). The 2,4-dinitrophenylhydrazone (orange plates from ethanol) had m. p. 138—139° [lit., 122° [46] 143—144° [47] (the latter for a bis-derivative)], $\lambda_{max.}$ 375 (log ε 4·32) (Found: C, 53·2; H, 4·8; N, 19·3. Calc. for $C_{13}H_{14}N_4O_4$: C, 53·7; H, 5·0; N, 19·5%).

General Procedures

Reactions in Polyphosphoric Acid.—Polyphosphoric acid (100 g.) was stirred gently and heated in a bath maintained at the desired temperature. The alkenoic acid or lactone (0·04 mole) was then added in one portion and stirring was continued for the desired time. The bath was then replaced by an ice-bath, and when the internal temperature had fallen to 30°, crushed ice (150 g.) was added, followed by ether (70 ml.). The aqueous layer was extracted with ether (2 × 50 ml.) and the combined ethereal solutions were washed with saturated sodium hydrogen carbonate solution and dried ($MgSO_4$). The ether was removed and the residue distilled. The distillate was analysed gas chromatographically.

TABLE 8

Retention times

	Time (min.)	Column
2-Methylcyclopent-2-enone	7·1	A
Cyclohex-2-enone	8·9	A
2-Ethylcyclopent-2-enone	7·0 38·6	B C
2-Methylcyclohex-2-enone	7·0 33·0	B C
2-Ethylidenecyclopentanone	9·3 43·6	B C
Cyclohept-2-enone	11·5	B
2-n-Propylcyclopentanone	23·1	D
2-Ethylcyclohex-2-enone	19·8	D
2-n-Propylidenecyclopentanone	29	D
2-Ethylidenecyclohexanone	35·3 9·24	D E
Hexan-4-olide	17·4	A
Hexan-5-olide	27·8	A
Heptan-4-olide	18·9	B
Heptan-5-olide	28·6	B
Octan-4-olide	17·2	E
Octan-5-olide	20·8	E
Phenol	12·4	A
Phenyl acetate	18·6	A
o-Cresol	12·8	B
*o*Tolyl acetate	17·8	B

A, Apiezon L 25% at 100°; B, Apiezon L 15% at 100°; C, Squalane 25% at 100%; D, Polypropylene sebacate 10% at 100°; E, Polypropylene sebacate at 150°.

Reactions in Trifluoroacetic Anhydride.—The alkenoic

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[45] J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.*, 1952, 1094.

[46] E. H. Braude and E. H. Evans, *J. Chem. Soc.*, 1954, 607.

[47] J. E. Hodgkins and R. J. Flores, *J. Org. Chem.*, 1963, **28**, 3356.

acid (0·04 mole) was added in one portion to trifluoroacetic anhydride (8·5 g., 0·4 mole) and the mixture cooled in an ice-bath. It was left at room temperature for 2 hr., and then heated at 30—40° for 30 min., during which time it turned dark red. It was then poured into saturated aqueous sodium hydrogen carbonate solution (50 ml.) and extracted with ether (2 × 50 ml.). The ethereal solution was dried ($MgSO_4$), evaporated, and distilled. The distillate was analysed gas chromatographically.

Reactions in Acetic Anhydride–Stannic Chloride.—A mixture of the alkenoic acid (0·04 mole), acetic anhydride (40 ml.), and a solution of stannic chloride in acetic acid (20 mg./ml.; 20 ml.) was refluxed gently under nitrogen for 1 hr., during which time the solution became deep red. The mixture was cooled and then carefully poured into a saturated aqueous solution of sodium carbonate (500 ml.); sufficient solid sodium carbonate was then added to complete the neutralisation, and the solution was extracted with ether (3 × 100 ml.). The dry ($MgSO_4$) ethereal solution was evaporated and the residue distilled. The distillate was analysed gas chromatographically.

Reactions in Acetic Anhydride–Sulphuric Acid.—These reactions were carried out as just described, with the stannic chloride solution replaced by concentrated sulphuric acid (1·5 ml.). The solution was heated for 30 min. at 140°.

Gas–Liquid Chromatography.—Gas chromatographic analyses were determined with a Pye Argon chromatograph. The retention times are recorded in Table 8.

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