192. *The Synthesis and Reactions of Branched-chain Hydrocarbons. Part X.*† *The Rearrangement of α-Ethynyl Alcohols to Unsaturated Carbonyl Compounds.*

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Rearrangement of α-ethynyl alcohols in the presence of formic acid or phosphoric oxide in benzene has been studied. αβ-Unsaturated aldehydes and vinylacetylenes are formed, besides αβ-unsaturated ketones. Some observations on the course of the reaction are made.

The rearrangement of α-ethynyl alcohols (I) to unsaturated carbonyl compounds is sometimes called the Rupe rearrangement.[1] This reaction has now been applied to eight α-ethynyl alcohols, formic acid or phosphoric oxide suspended in benzene being used as reagents. In all the cases studied the unsaturated ketone (II) was formed together with the unsaturated aldehyde (III) and, except in two instances, also the vinylacetylene (IV). Our results are shown in Table 1.

$\mathrm{RR'CH{\cdot}CR''(OH){\cdot}C{\vdots}CH}$ (I) $\mathrm{RR'C{:}CR''{\cdot}COMe}$ (II) $\mathrm{RR'CH{\cdot}CR''{:}CH{\cdot}CHO}$ (III) $\mathrm{RR'C{:}CR''{\cdot}C{\vdots}CH}$ (IV)

a : R = R′ = H, R″ = Me.
b : R = R′ = H, R″ = Bu^t.
c : R = H, R′ = Me, R″ = Bu^t.
d : R = R′ = Me, R″ = Bu^t.
e : R = R′ = H, R″ = $\mathrm{CMe_2Et}$.
f : R = H, R′ = Me, R″ = $\mathrm{CMe_2Et}$.
g : R = R′ = Me, R″ = Pr^i.
h : R = H, R′ = Pr^i, R″ = Bu^i.

Table 1. *Rearrangement of ethynyl alcohols.*

Ethynyl alcohol	Yield of ketone (%)		Yield of aldehyde (%)		Yield of vinylacetylene (%)	
	By $\mathrm{H{\cdot}CO_2H}$	By $\mathrm{P_2O_5}$	By $\mathrm{H{\cdot}CO_2H}$	By $\mathrm{P_2O_5}$	By $\mathrm{H{\cdot}CO_2H}$	By $\mathrm{P_2O_5}$
(I*a*)	*ca.* 2	—	*ca.* 4·5	—	35·0	—
(I*b*) *	33·0	21·0	16·7	7·5	18·3	29·6
(I*c*) *	41·0	27·8	9·6	5·7	17·2	33·2
(I*d*)	Trace	Trace	31·8	15·3	7·5	30·4
(I*e*)	20·3	10·1	8·5	4·3	9·0	34·0
(I*f*)	48·0	12·0	7·0	2·0	6·0	46·0
(I*g*) *	6·8	—	2·5	—	0	—
(I*h*)	5·5	—	10·5	—	0	—

* In these rearrangements fission of the ethynyl alcohol to the parent ketone was observed.

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† Part IX, *J.*, 1955, 2705.

[1] Johnson, "Chemistry of Acetylenic Compounds," E. Arnold and Co., London, 1949, Vol. I, pp. 127—130.

[2] Hurd and McPhee, *J. Amer. Chem. Soc.*, 1949, **71**, 398.

The rearrangement of 2-methylbut-3-yn-2-ol (I*a*) has been shown by Hurd and McPhee [2] to yield 3-methylbut-3-en-1-yne (IV*a*) and a trace of 3-methylbut-3-en-2-one (II*a*), and Takeshima [3] has isolated a small amount of 3-methylbut-2-enal (III*a*). We confirmed these results and in addition showed the presence of 3 : 7-dimethylocta-2 : 4 : 6-trienal in the product. The last material is formed by self-condensation of 3-methylbut-2-enal.[4]

In the rearrangement of 3 : 4 : 4-trimethylpent-1-yn-3-ol (I*b*) our results are contrary to those of Rupe and Giesler [5] who state that the main product is 3 : 4 : 4-trimethylpent-2-enal (III*b*) together with a small amount of an isomeric aldehyde. We find that the main product is 3-*tert.*-butylbut-3-en-2-one (II*b*), with the unsaturated aldehyde (III*b*) as a minor product. In this reaction fission of the ethynyl alcohol to 3 : 3-dimethylbutan-2-one occurred : such a fission has not previously been recorded under these conditions.

The other six rearrangements (see Table 1) have not been previously reported. The structures of the unsaturated aldehydes were proved by ozonolysis of the aldehydes or the corresponding acids, and the identities of the vinylacetylenes established by hydration to the unsaturated ketones whose structures were proved by ozonolysis. Of these ketones, 3-*tert.*-butylpent-3-en-2-one (II*c*) has been previously reported [6] as the product of the condensation of acetaldehyde with 4 : 4-dimethylpentan-2-one in the presence of alcoholic potassium hydroxide. Our ketone and the corresponding saturated alcohol differ from the compounds thus obtained. It has been shown by Mr. M. A. Davis (in our laboratories), and since the completion of this work,[7] that the condensation of acetaldehyde with 4 : 4-dimethylpentan-2-one occurs at the methyl group of the latter and not at the methylene group as claimed by the earlier workers.

A survey of our results leads us to suggest that although the main product of the Rupe rearrangement is usually the unsaturated ketone [8] (II), this is not invariably so. The formation of an unsaturated aldehyde appears to be favoured by an acumulation of alkyl groups adjacent to the hydroxyl group of the ethynyl alcohol, *e.g.*, in 4 : 4-dimethyl-3-*iso*-propylpent-1-yn-3-ol (I*d*). Isolation of the aldehydes is hampered by their tendency to undergo self condensation (cf. the isolation of 3 : 7-dimethyl-2 : 4 : 6-trienal) and by their ease of oxidation which is shown by the isolation of 4 : 4-dimethyl-3-*iso*propylpent-2-enoic acid from the rearrangement of 4 : 4-dimethyl-3-*iso*propylpent-1-yn-3-ol (I*g*).

It was not the original intention of this work to examine the mechanism of the Rupe rearrangement, but our observations are not in accord with some of the hypotheses that have been advanced. It has been suggested [9] that rearrangement in the presence of formic acid depends on the initial dehydration of the ethynyl alcohol (I) to the vinylacetylene (IV) which is then hydrated to the αβ-unsaturated ketone (II). Although this is a possible route we do not consider it to be the exclusive one, because hydration of the vinylacetylenes is slow and incomplete in the presence of formic acid, as is shown in Table 2.

TABLE 2. *Hydration of vinylacetylenes.*

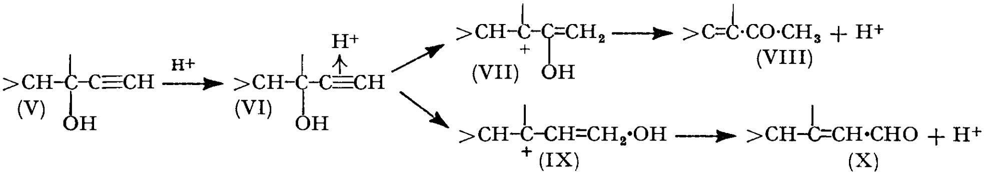
	Formic acid		Mercuric oxide in aq. H_2SO_4	
Vinylacetylene	Unchanged (%)	Unsat. ketone (%)	Unchanged (%)	Unsat. ketone (%)
(IV*b*)	50·5	6·2	—	32·4 *
(IV*c*)	56·4	5·1	32·7	39·7
(IV*d*)	71·1	4·2	21·3	34·9
(IV*e*)	52·8	7·2	26·7	41·0
(IV*f*)	41·1	6·1	16·2	59·0

* 3 : 3-Dimethylbutan-2-one isolated.

The Rupe rearrangement may also be achieved by heating the ethynyl alcohol either with phosphoric oxide in benzene [10, 11] or with a sulphonated resin in aqueous acetic acid.[11]

[3] Takeshima, *J. Sci. Res. Inst. Tokyo*, 1951, **45**, 103.
[4] Fischer *et al.*, *Ber.*, 1935, **68**, 1726; 1937, **70**, 370.
[5] Rupe and Giesler, *Helv. Chim. Acta*, 1928, **11**, 656.
[6] Mosher and Cox, *J. Amer. Chem. Soc.*, 1950, **72**, 3701.
[7] Dubois and Luft, *Compt. rend.*, 1955, **240**, 1540.
[8] Chanley, *J. Amer. Chem. Soc.*, 1948, **70**, 244; Henbest and Woods, *J.*, 1952, 1150.
[9] Price and Meisley, *J. Amer. Chem. Soc.*, 1947, **69**, 1498; Davis and Maloney, *ibid.*, 1949, **71**, 2813.
[10] Saunders, *Org. Synth.*, **29**, 1.
[11] Newman, *J. Amer. Chem. Soc.*, 1953, **75**, 4740.

Under these conditions it does not seem probable that a vinylacetylene would be readily hydrated. We agree with Newman[11] that in these cases the unsaturated ketone arises by an acid-catalysed 1 : 2-shift of the hydroxyl group of the ethynyl alcohol (V ⟶ VIII) and we suggest that the unsaturated aldehyde may arise through a 1 : 3-shift of the hydroxyl group (V ⟶ X), *i.e.*, essentially the mechanism that has been proposed for the Mayer–Schuster rearrangement.[12]



If the Rupe rearrangement occurs as we have suggested, the products of the rearrangement should accompany the normal hydration product obtained by treatment of an ethynyl alcohol with a hot solution of mercuric sulphate in aqueous sulphuric acid. These products have not been previously observed, but, as is shown in Table 3, we have isolated them in six cases. The unsaturated ketone may be partly produced by the hydration of an intermediate vinylacetylene, but it does not seem probable that the unsaturated aldehyde arises in this way as we have not obtained it by hydration of the vinylacetylene under the same conditions.

TABLE 3. *Hydration of ethynyl alcohols.*

Ethynyl alcohol	Hydroxy-ketone	Vinylacetylene	Unsat. ketone	Unsat. aldehyde	Unsat. acid
(I*b*) *	71	42	2·4	—	Trace
(I*c*) *	31·7	3·7	46·9	—	Trace
(I*d*)	—	8·8	—	25·3	4
(I*e*)	Trace †	9·2	65	Trace †	—
(I*g*) *	32	—	28	—	Trace
(I*h*)	58	—	9	—	—

* Small amount of parent ketone isolated. † Isolated as 2 : 4-dinitrophenylhydrazone.

EXPERIMENTAL

Preparation of Ethynyl Alcohols.—3 : 4 : 4-Trimethylpent-1-yn-3-ol gives a 3 : 5-*dinitrobenzoate*, m. p. 111°, plates from light petroleum (b. p. 40—60°) (Found: C, 56·2; H, 4·7; N, 8·8. $C_{15}H_{16}O_6N_2$ requires C, 56·3; H, 5·0; N, 8·7%). 3-*Ethyl*-4 : 4-*dimethylpent*-1-*yn*-3-*ol* (73% yield), b. p. 162—163°, n_D^{20} 1·4458—1·4460 (Found: C, 77·1; H, 11·6. $C_9H_{16}O$ requires C, 77·1; H, 11·5%), 3 : 4 : 4-*trimethylhex*-1-*yn*-3-*ol* (69% yield), b. p. 170—171°, n_D^{20} 1·4535 (Found: C, 77·1; H, 11·6. $C_9H_{16}O$ requires C, 77·1; H, 11·5%), 3-*ethyl*-4 : 4-*dimethylhex*-1-*yn*-3-*ol* (67·3% yield), b. p. 79—80°/20 mm., n_D^{20} 1·4567—1·4569 (Found: C, 77·7; H, 11·8. $C_{10}H_{18}O$ requires C, 77·9; H, 11·8%), and 3-iso*butyl*-5-*methylhex*-1-*yn*-3-*ol* (38·3% yield), b. p. 83—84°/18 mm., n_D^{20} 1·4425 (Found: C, 78·5; H, 11·9. $C_{11}H_{20}O$ requires C, 78·5; H, 12·0%), were prepared by a modification of the method of Froning and Hennion.[13] After evaporation of the ammonia the residue was steam-distilled, the organic layer of the distillate was separated, and the aqueous layer extracted with ether. After drying (Na_2SO_4) of the combined organic material the ether was removed and the residue fractionally distilled.

General Procedure for the Rearrangement of Ethynyl Alcohols.—*Method A*. A mixture of the ethynyl alcohol (2·0 moles) and 80% formic acid (1600 c.c.) was heated under reflux for 3 hr. After cooling, it was poured into water (3 l.), the organic layer separated, and the aqueous layer extracted with light petroleum (b. p. <40°; 3 × 400 c.c.). The combined organic material was washed with 10% sodium hydroxide solution (500 c.c.), then with water (500 c.c.), and dried (Na_2SO_4). After removal of the solvent the residue was fractionally distilled.

Method B. Phosphoric oxide (60 g.) was added to a solution of the ethynyl alcohol (2·0 moles) in dry benzene (1500 c.c.). The vigorously stirred mixture was heated under reflux for 3 hr., then cooled, and the benzene solution decanted from the brown solid residue. After

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[12] Raphael, " Acetylenic Compounds in Organic Synthesis," Butterworths, London, 1955, p. 77.
[13] Froning and Hennion, *J. Amer. Chem. Soc.*, 1940, **62**, 653.

filtering, the solvent was removed and the residue fractionally distilled. The products are recorded in Table 1.

Rearrangement of 2-*Methylbut*-3-*yn*-2-*ol*.—2-Methylbut-3-yn-2-ol (2·0 moles) was rearranged by method A with the following modifications: the reaction mixture, containing a small amount of quinol, was heated under reflux for 1 hr., after which 3-methylbut-3-en-1-yne (46 g.), b. p. 30—35°, n_D^{20} 1·4100 (Hurd and McPhee[2] record b. p. 31—34°, n_D^{20} 1·4105), was distilled off before working up of the residue. Fractional distillation gave: (*a*) 3-methylbut-3-en-2-one (3·5 g.), b. p. 93—96°, n_D^{20} 1·4234 [semicarbazone, m. p. 177—178° (Hurd and McPhee[2] record m. p. 178°; Morgan and Griffiths[14] record b. p. 96—97°, n_D^{20} 1·4224): (*b*) 3-methylbut-3-enal (7·8 g.), b. p. 130—136°, n_D^{20} 1·4538 (semicarbazone, m. p. 220°; 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 179°) (lit.,[15] b. p. 132—133°/730 mm., n_D^{20} 1·4526); (*d*), a black residue, with an odour of lemons, which on distillation gave a fraction, b. p. 95—110°/1 mm., from which 3 : 7-dimethylocta-2 : 4 : 6-trienal was isolated as the *p*-nitrophenylhydrazone, m. p. 193° (Fischer *et al.*[4] record m. p. 193—194°).

Rearrangement of 3 : 4 : 4-*Trimethylpent*-1-*yn*-3-*ol*.—*Method A*. The combined material from three 1·5-molar-scale experiments was fractionally distilled, to yield, with a small forerun and intermediate fractions, (*a*) 2-*tert*.-butylbut-1-en-3-yne (29·8 g.), b. p. 98—98·5°, n_D^{20} 1·4297 (Found: C, 88·7; H, 11·3. Calc. for C_8H_{12}: C, 88·8; H, 11·2%) (lit.,[16] b. p. 98°); (*b*) 3 : 3-dimethylbutan-2-one (9·1 g.), b. p. 105—107° (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 126°); (*c*) 3-*tert*.-butylbut-3-en-2-one (186·5 g.), b. p. 142—143·5°, n_D^{20} 1·4340 (semicarbazone, m. p. 169°; 2 : 4-dinitrophenylhydrazone, m. p. 116—116·5°), for which Hickinbottom, Hyatt, and Sparke[17] record b. p. 142—143°, n_D^{20} 1·4340, semicarbazone, m. p. 165°, and 2 : 4-dinitrophenylhydrazone, m. p. 116°; (*d*) 3 : 4 : 4-trimethylpent-2-enal (95 g.), b. p. 78·5—82°/20 mm., n_D^{20} 1·4675—1·4680 (b. p. 79—80°/20 mm., n_D^{20} 1·4674, on redistillation) [2 : 4-*dinitrophenylhydrazone*, red needles (from acetic acid), m. p. 238° (Found: C, 54·9; H, 6·0; N, 18·0. $C_{14}H_{18}O_4N_4$ requires C, 54·9; H, 5·9; N, 18·3%); p-*nitrophenylhydrazone*, yellow needles (from aqueous alcohol), m. p. 187° (Found: C, 64·4; H, 7·1; N, 16·0. $C_{14}H_{19}O_2N_3$ requires C, 64·3; H, 7·3; N, 16·1%); semicarbazone, needles (from aqueous alcohol), m. p. 204°] (Wouseng[19] records b. p. 75—78°/15 mm., semicarbazone, m. p. 204—205°; Rupe and Giesler[5] record n^{20} 1·46718, semicarbazone, m. p. 193°).

Reduction of the ketone (*c*) by lithium aluminium hydride gave 3-tert.-*butylbut*-3-*en*-2-*ol*, b. p. 156—157°, n_D^{20} 1·4417 (Found: C, 75·2; H, 12·5. $C_8H_{16}O$ requires C, 75·0; H, 12·6%) {3 : 5-*dinitrobenzoate*, needles [from light petroleum (b. p. 40—60°)], m. p. 104·5° (Found: C, 56·2; H, 5·4; N, 8·9. $C_{15}H_{18}O_6N_2$ requires C, 55·9; H, 5·6; N, 8·7%)}. Reduction of the ketone (*c*) by sodium in moist ether gave 3 : 4 : 4-trimethylpentan-2-ol, b. p. 159—160°, n_D^{20} 1·4355 (lit.,[18] b. p. 70—73°/25 mm., n_D^{20} 1·4343). Its 3 : 5-*dinitrobenzoate*, plates [from light petroleum (b. p. 40—60°)], had m. p. and mixed m. p. 72—72·5° (Found: C, 55·5; H, 6·4; N, 8·4. $C_{15}H_{20}O_6N_2$ requires C, 55·6; H, 6·2; N, 8·6%): an authentic specimen was prepared from the alcohol obtained by the reduction of 3 : 4 : 4-trimethylpentan-2-one with lithium aluminium hydride.

Oxidation of the aldehyde (*d*) by exposure to air or treatment with ammonical silver nitrate solution gave 3 : 4 : 4-trimethylpent-2-enoic acid, m. p. 84—85°, which when heated with 80% sulphuric acid for 1 hr. gave the lactone, m. p. 99·5°, of 3-hydroxy-3 : 4 : 4-trimethylpentanoic acid; Loquin and Wouseng[20] record the acid, m. p. 85°; Petschnikoff[21] records the lactone, m. p. 99·5°.

Rearrangement of 3-*Ethyl*-4 : 4-*dimethylpent*-1-*yn*-3-*ol*.—*Method A* (*on a* 2-*molar scale*). Distillation gave the following fractions: (*a*) 48·2 g., b. p. 122—124°, containing some 2 : 2-dimethylpentan-3-one (isolated as the 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 174—175°) which on distillation over sodium gave 3-tert.-*butylpent*-3-*en*-1-*yne* (42 g.), b. p. 123—124°, n_D^{20} 1·4470 (Found: C, 88·3; H, 11·6. C_9H_{14} requires C, 88·4; H, 11·6%); (*b*) 3-tert.-*butylpent*-3-*en*-2-*one* (114·8 g.), b. p. 161—161·5°, n_D^{20} 1·4389—1·4390 (Found: C, 77·3; H, 11·4. $C_9H_{16}O$ requires C, 77·1; H, 11·5%) [2 : 4-*dinitrophenylhydrazone*, m. p. 115·5°, orange-yellow plates (from alcohol) (Found: C, 56·4; H, 6·4; N, 17·3. $C_{15}H_{20}O_4N_4$ requires C, 56·3; H, 6·3; N, 17·5%]; (*c*) 3-*ethyl*-4 : 4-*dimethylpent*-2-*enal* (27 g.), b. p. 83°/16 mm.,

[14] Morgan and Griffiths, *J.*, 1937, 841.
[15] Fischer, Ertel, and Lowenberg, *Ber.*, 1931, **64**, 30.
[16] Favorskya, *J. Gen. Chem. U.S.S.R.*, 1948, **18**, 52.
[17] Hickinbottom, Hyatt, and Sparke, *J.*, 1954, 2529.
[18] Wheeler, *Univ. Microfilm* (*Ann. Arbor, Mich.*), 1941, Publ. No. 380.
[19] Wouseng, *Ann. Chim.* (*France*), 1924, **1**, 343.
[20] Loquin and Wouseng, *Compt. rend.*, 1922, **174**, 1711.
[21] Petschnikoff, *J. prakt. Chem.*, 1902, **65**, 178.

n_D^{20} 1·4672 (Found : C, 77·2; H, 11·5. $C_9H_{16}O$ requires C, 77·1; H, 11·5%), colours Schiff's reagent, reduces Fehling's solution [2 : 4-*dinitrophenylhydrazone*, m. p. 197·5°, red needles (from acetic acid) (Found : C, 56·2; H, 6·4; N, 17·4. $C_{15}H_{20}O_4N_2$ requires C, 56·2; H, 6·3; N, 17·5%) ; *semicarbazone*, m. p. 186° (Found : C, 61·1; H, 9·5; N, 21·4. $C_{10}H_{19}ON_3$ requires C, 60·9; H, 9·7; N, 21·3%)].

Reduction of the ketone (*b*) with sodium in moist ether gave 3-*ethyl*-4 : 4-*dimethylpentan*-2-*ol*, b. p. 66°/12 mm., n_D^{20} 1·4436 (Found : C, 75·0; H, 13·9. $C_9H_{20}O$ requires C, 74·9; H, 14·0%) [3 : 5-*dinitrobenzoate*, m. p. 89·5° (Found : C, 56·7; H, 6·4; N, 8·0. $C_{16}H_{22}O_6N_2$ requires C, 56·8; H, 6·5; N, 8·3%)]. Reduction of the ketone (*b*) with lithium aluminium hydride gave 3-tert.-*butylpent*-3-*en*-2-*ol*, b. p. 68·5°/14 mm., n_D^{20} 1·4560 (Found : C, 75·8; H, 12·6. $C_9H_{18}O$ requires C, 76·0; H, 12·7%) [3 : 5-*dinitrobenzoate*, m. p. 106° (Found : C, 56·9; H, 5·9; N, 8·3. $C_{16}H_{20}O_6N_2$ requires C, 57·1; H, 6·0; N, 8·3%)].

Oxidation of the aldehyde (*c*) by exposure to air or with aqueous-alcoholic ammoniacal silver nitrate gave 3-*ethyl*-4 : 4-*dimethylpent*-2-*enoic acid*, m. p. 70° (Found : C, 69·5; H, 10·5. $C_9H_{16}O_2$ requires C, 69·2; H, 10·3%), ozonolysis of which gave 2 : 2-dimethylpentan-3-one (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 174—175°). Reduction of the aldehyde (*c*) with lithium aluminium hydride gave 3-*ethyl*-4 : 4-*dimethylpent*-2-*en*-1-*ol*, b. p. 88·5°/14 mm., n_D^{20} 1·4590 (Found : C, 76·0; H, 12·8. $C_9H_{18}O$ requires C, 76·0; H, 12·8%) [3 : 5-*dinitrobenzoate*, m. p. 75° (Found : C, 57·1; H, 6·1. $C_{16}H_{20}O_6N_2$ requires C, 57·1; H, 6·0; N, 8·3%)].

Rearrangement of 4 : 4-*Dimethyl*-3-iso*propylpent*-1-*yn*-3-*ol*.—*Method A* (*on a* 1·5-*molar scale*). Distillation gave the following fractions : (*a*) 3-tert.-*butyl*-4-*methylpent*-3-*en*-1-*yne* (15·2 g.), b. p. 43°/23 mm., n_D^{20} 1·4428 (b. p. 131°, n_D^{20} 1·4430, after redistillation over sodium) (Found : C, 88·3; H, 12·0. $C_{10}H_{16}$ requires C, 88·2; H, 11·8%) ; (*b*) 3-tert.-*butyl*-4-*methylpent*-3-*en*-2-*one* (6·1 g.), b. p. 75—75·5°/23 mm., n_D^{20} 1·4487 (Found : C, 78·0; H, 12·0. $C_{10}H_{18}O$ requires C, 77·9; H, 11·8%) [2 : 4-*dinitrophenylhydrazone*, m. p. 101·5—102°, yellow-orange plates from aqueous alcohol (Found : C, 57·3; H, 6·5; N, 16·4. $C_{16}H_{22}O_4N_4$ requires C, 57·5; H, 6·6; N, 16·7%] ; (*c*) 4 : 4-*dimethyl*-3-iso*propylpent*-2-*enal* (73·4 g.), b. p. 98—98·5°/19 mm., n_D^{20} 1·4687—1·4690 (Found : C, 77·7; H, 11·8. $C_{10}H_{18}O$ requires C, 77·9; H, 11·8%) [2 : 4-*dinitrophenylhydrazone*, m. p. 200·5°, red needles from benzene (Found : C, 57·3; H, 6·7; N, 16·6. $C_{16}H_{22}O_4N_4$ requires C, 57·5; H, 6·6; N, 16·7%) ; *semicarbazone*, m. p. 208° (Found : C, 62·6; H, 9·9; N, 19·8. $C_{11}H_{21}ON_3$ requires C, 62·5; H, 10·0; N, 19·9%)].

Reduction of the aldehyde by lithium aluminium hydride gave 4 : 4-*dimethyl*-3-iso*propylpent*-2-*en*-1-*ol*, b. p. 101°/13 mm., n_D^{20} 1·4626 (Found : C, 76·6; H, 12·8. $C_{10}H_{20}O$ requires C, 76·8; H, 12·9%) [3 : 5-*dinitrobenzoate*, m. p. 92° (Found: C, 58·2; H, 6·4; N, 8·2. $C_{17}H_{22}O_6N_2$ requires C, 58·3; H, 6·3; N, 8·0%)]. Oxidation of the aldehyde as for 3 : 4 : 4-trimethylpent-2-enal gave 4 : 4-*dimethyl*-3-iso*propylpent*-2-*enoic acid*, m. p. 128° (Found : C, 70·6; H, 10·6%; *M*, 170. $C_{10}H_{18}O_2$ requires C, 70·6; H, 10·7%; *M*, 170), ozonolysis of which gave 2 : 4 : 4-trimethylpentan-3-one (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 165—166°). This acid (5·4 g.) was also obtained by extraction of the residual tar from the distillation with 10% sodium hydroxide solution.

Rearrangement of 3 : 4 : 4-*Trimethylhex*-1-*yn*-3-*ol*.—*Method A* (*on a* 2-*molar scale*). Distillation gave the following fractions : (*a*) 3-(1 : 1-*dimethylpropyl*)*but*-3-*en*-1-*yne* (23·8 g.), b. p. 127—128°, n_D^{20} 1·4413 (b. p. 128°, n_D^{20} 1·4410, on redistillation over sodium) (Found : C, 88·3; H, 11·8. C_9H_{14} requires C, 88·4; H, 11·6%) ; (*b*) a fraction, b. p. 163—166°, which when shaken with excess of aqueous ammoniacal silver nitrate and redistilled gave 3-(1 : 1-*dimethylpropyl*)*but*-3-*en*-2-*one* (57 g.), b. p. 163—163·5°, n_D^{20} 1·4395 (Found : C, 77·2; H, 11·4. $C_9H_{16}O$ requires C, 77·1; H, 11·5%) [2 : 4-*dinitrophenylhydrazone*, m. p. 135°, yellow needles from aqueous alcohol (Found : C, 56·2; H, 6·4; N, 17·7. $C_{15}H_{20}O_4N_4$ requires C, 56·2; H, 6·3; N, 17·5%)] ; (*c*) 3 : 4 : 4-*trimethylhex*-2-*enal* (26·1 g.), b. p. 87—89°/18 mm., n_D^{20} 1·4722 (b. p. 90—91°/20 mm., n_D^{20} 1·4728, for an analytical sample) (Found : C, 76·8; H, 11·6. $C_9H_{16}O$ requires C, 77·1; H, 11·5%), colours Schiff's reagent and reduces Fehling's solution [*semicarbazone*, plates (from aqueous alcohol), m. p. 172° (Found : C, 61·2; H, 9·6; N, 21·0. $C_{10}H_{19}ON_3$ requires C, 60·9; H, 9·7; N, 21·3%) ; 2 : 4-*dinitrophenylhydrazone*, red needles (from acetic acid), m. p. 196·5° (Found : C, 56·1; H, 6·2; N, 17·5. $C_{15}H_{20}O_4N_4$ requires C, 56·3; H, 6·3; N, 17·5%)].

Oxidation of the aldehyde as for 3 : 4 : 4-trimethylpent-2-enal gave 3 : 4 : 4-*trimethylhex*-2-*enoic acid*, m. p. 71—72° (Found : C, 69·3; H, 10·3. $C_9H_{16}O_2$ requires C, 69·2; H, 10·3%), ozonolysis of which gave 3 : 3-dimethylpentan-2-one (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 112°).

Rearrangement of 3-*Ethyl*-4 : 4-*dimethylhex*-1-*yn*-3-*ol*.—*Method A* (*on a* 1·5-*molar scale*). Distillation gave fractions : (*a*) 3-(1 : 1-*dimethylpropyl*)*pent*-3-*en*-1-*yne* (14·9 g.), b. p. 41—42°/12 mm., n_D^{20} 1·4507 (b. p. 148°, n_D^{20} 1·4500, after distillation over sodium) (Found : C, 88·2; H, 11·9. $C_{10}H_{16}$ requires C, 88·2; H, 11·8%); (*b*) 3-(1 : 1-*dimethylpropyl*)*pent*-3-*en*-2-*one* (110·9 g.), b. p. 64—65°/12 mm., n_D^{20} 1·4457 (Found: C, 78·0; H, 11·8. $C_{10}H_{18}O$ requires C, 77·9; H, 11·8%); (*c*) 3-*ethyl*-4 : 4-*dimethylhex*-2-*enal* (16·2 g.), b. p. 92—93°/12 mm., n_D^{20} 1·4724 (Found : C, 78·4; H, 11·8. $C_{10}H_{18}O$ requires C, 77·9; H, 11·7%), colours Schiff's reagent, reduces Fehling's solution [*semicarbazone*, needles (from aqueous alcohol), m. p. 169° (Found : C, 62·6; H, 9·9; N, 20·0. $C_{11}H_{21}ON_3$ requires C, 62·5; H, 10·0; N, 19·9%); 2 : 4-*dinitrophenylhydrazone*, bright red (from acetic acid), m. p. 156° (Found : C, 57·4; H, 6·5; N, 16·8. $C_{16}H_{22}O_4N_4$ requires C, 57·5; H, 6·6; N, 16·7%)], giving on ozonolysis 4 : 4-dimethylhexan-3-one (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 86°).

Reduction of the ketone with lithium aluminium hydride gave 3-(1 : 1-*dimethylpropyl*)*pent*-3-*en*-2-*ol*, b. p. 91°/22 mm. (Found : C, 77·1; H, 13·0. $C_{10}H_{20}O$ requires C, 76·9; H, 12·9%) [3 : 5-*dinitrobenzoate*, m. p. 88·5°, plates from light petroleum (Found : C, 58·1; H, 6·2; N, 8·2. $C_{17}H_{22}O_6N_2$ requires C, 58·3; H, 6·3; N, 8·0%)].

Rearrangement 4-*Methyl*-3-iso*propylpent*-1-*yn*-3-*ol*.—*Method A* (*on a* 2·0-*molar scale*). Distillation gave the following fractions : (*a*) di*iso*propyl ketone (6·0 g.), b. p. 121—124°, n_D^{20} 1·4010 (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 95—96°); (*b*) 4-methyl-3-*iso*propylpent-3-en-2-one (190·5 g.), b. p. 169—169·5°, n_D^{20} 1·4448—1·4450 (Hickinbottom, Hyatt, and Sparke [17] record b. p. 67·5°/15 mm., n_D^{20} 1·4450; (*c*) 4-*methyl*-3-iso*propylpent*-2-*enal* (7·2 g.), b. p. 85—86°/12 mm., n_D^{20} 1·4728 (Found : C, 76·9; H, 11·4. $C_9H_{16}O$ requires C, 77·1; H, 11·5%), colours Schiff's reagent, reduces Fehling's solution [*semicarbazone*, plates (from aqueous alcohol), m. p. 166° (Found: C, 61·1; H, 9·6; N, 21·1. $C_{10}H_{19}ON_3$ requires C, 60·9; H, 9·7; N, 21·3%); 2 : 4-*dinitrophenylhydrazone*, m. p. 180° (Found : C, 56·1; H, 6·2; N, 17·4. $C_{15}H_{20}O_4N_4$ requires C, 60·9; H, 9·7; N, 21·3%)], giving on ozonolysis di*iso*propyl ketone (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 95—96°).

Rearrangement of 3-iso*Butyl*-5-*methylhex*-1-*yn*-3-*ol*.—*Method A* (*on a* 1·5-*molar scale*). Distillation gave the following fractions : (*a*) 3-iso*butyl*-5-*methylhex*-3-*en*-2-*one* (138·8 g.), b. p. 84—84·5°/14 mm., n_D^{20} 1·4500 (Found : C, 78·7; H, 11·9. $C_{11}H_{20}O$ requires C, 78·5; H, 12·0%) [2 : 4-*dinitrophenylhydrazone*, m. p. 130°, orange plates from aqueous alcohol (Found : C, 58·5; H, 6·9; N, 16·2. $C_{17}H_{24}O_4N_4$ requires C, 58·6; H, 6·9; N, 16·1%)]; (*b*) 3-iso*butyl*-5-*methylhex*-2-*enal* (27·7 g.), b. p. 102—103°/14 mm., n_D^{20} 1·4650 (Found : C, 78·3; H, 11·9. $C_{11}H_{20}O$ requires C, 78·5; H, 12·0%) colours Schiff's reagent, reduces Fehling's solution [*semicarbazone* (from aqueous alcohol), m. p. 115—116° (Found: C, 64·3; H, 10·2; N, 18·8. $C_{12}H_{23}ON_3$ requires C, 64·0; H, 10·3; N, 18·6%); 2 : 4-*dinitrophenylhydrazone*, red needles (from alcohol), m. p. 137° (Found : C, 58·4; H, 6·8; N, 16·4. $C_{17}H_{24}O_4N_4$ requires C, 58·6; H, 6·9; N, 16·1%)]. Reduction of the ketone with lithium aluminium hydride gave 3-iso*butyl*-5-*methylhex*-3-*en*-2-*ol*, b. p. 91°/16 mm., n_D^{20} 1·4480 (Found : C, 77·7; H, 12·9. $C_{11}H_{22}O$ requires C, 77·6; H, 13·0%) [3 : 5-dinitrobenzoate, m. p. 53°, needles from light petroleum (b. p. <40°)]; ozonolysis of the aldehyde gave di*iso*butyl ketone (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 92°).

Hydration of Vinylacetylenes.—*Method A*. The vinylacetylene (0·2 mole) was treated as in the rearrangement of ethynyl alcohols by method A.

Method B. The vinylacetylene (0·25 mole) was added to a stirred solution of mercuric oxide (1·8 g.) in concentrated sulphuric acid (12 c.c.) and water (120 c.c.) at 80°. After being heated and stirred for 3 hr. the mixture was steam-distilled. The organic layer of the distillate was separated and the aqueous layer extracted with ether (3 × 20 c.c.). The ether was removed from the dried ($MgSO_4$) combined organic material, and the residue fractionally distilled. The products obtained are in Table 2, and their physical constants are recorded above.

Ozonolysis of the Unsaturated Ketones.—Ozonised air was bubbled through a solution of the unsaturated ketone (5 g.) in dry chloroform (25 c.c.) for 24 hr. The solvent was then removed at 30° and a mixture of zinc dust (2·0 g.) and water (50 c.c.) added. After 1 hr. at room temperature the mixture was heated under reflux while air was aspirated through it into a warm aqueous-alcoholic sulphuric acid solution of 2 : 4-dinitrophenylhydrazine (except in cases marked * when a solution of dimedone was used). The identity of the carbonyl derivative formed (*A*) is shown below. The mixture was then extracted with ether, and, after drying (Na_2SO_4), the ethereal extract was added to lithium aluminium hydride (1 g.) in ether (20 c.c.). After 1 hr. the mixture was worked up in the usual way and the reduction product (*ca.* 1·5 g.) was shaken for 4 hr. with a solution of periodic acid (1·5 g.) in alcohol (5 c.c.) and water (12 c.c.). Air was then aspirated through the solution into 2 : 4-dinitrophenylhydrazine reagent, and the precipitate formed filtered off and chromatographed in light petroleum (b. p. 40—60°)–benzene on alumina.

Elution with the same solvent gave the 2 : 4-dinitrophenylhydrazone B together with acetaldehyde 2 : 4-dinitrophenylhydrazone.

Unsaturated ketone	A	B
$CH_2{:}CBu^t{\cdot}COMe$*	CH_2O	$Bu^t{\cdot}CHO$
$CHMe{:}CBu^t{\cdot}COMe$	$Me{\cdot}CHO$	$Bu^t{\cdot}CHO$
$CMe_2{:}CBu^t{\cdot}COMe$	$COMe_2$	$Bu^t{\cdot}CHO$
$CMe_2Et{\cdot}C({:}CH_2){\cdot}COMe$*	CH_2O	$CMe_2Et{\cdot}CHO$
$CMe_2Et{\cdot}C({:}CHMe){\cdot}COMe$	$Me{\cdot}CHO$	$CMe_2Et{\cdot}CHO$
$CMe_2{:}CPr^i{\cdot}COMe$	$COMe_2$	$Pr^i{\cdot}CHO$
$CHPr^i{:}CBu^i{\cdot}COMe$	$Pr^i{\cdot}CHO$	$Bu^i{\cdot}CHO$

Hydration of Ethynyl Alcohols.—The ethynyl alcohol (1·0 mole) was added dropwise during 2 hr. to a stirred boiling solution of mercuric oxide (15 g.) in concentrated sulphuric acid (100 c.c.) and water (500 c.c.). Heating and stirring were continued for a further 3 hr. and the mixture then steam-distilled. The organic layer was separated and the aqueous layer extracted with ether. The combined organic material was dried (Na_2SO_4), the ether removed, and the residue fractionally distilled. Acidic material was extracted from the residue from the distillation. The products and yields are in Table 3. The physical constants of the products are described above or elsewhere, with the exception of 3-*hydroxy*-4-*methyl*-3-iso*propylpentan*-2-*one*, b. p. 82°/18 mm., n_D^{20} 1·4412 (Found: C, 68·2; H, 11·3. $C_9H_{18}O_2$ requires C, 68·3; H, 11·5%) (no carbonyl derivative could be obtained), and 3-iso*butyl*-3-*hydroxy*-5-*methylhexan*-2-*one*, b. p. 94·5°/14 mm. (Found: C, 71·0; H, 11·9; active H, 0·52. $C_{11}H_{22}O_2$ requires C, 70·9; H, 11·9; active H, 0·54%) [*semicarbazone*, m. p. 152—153°, plates from aqueous alcohol (Found: C, 59·1; H, 10·2; N, 17·0. $C_{12}H_{25}O_2N_3$ requires C, 59·2; H, 10·4; N, 17·3%); 2 : 4-*dinitrophenylhydrazone*, m. p. 162°, yellow needles from alcohol (Found: C, 55·5; H, 7·2; N, 15·3. $C_{17}H_{26}O_5N_4$ requires C, 55·7; H, 7·2; N, 15·3%)].

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