

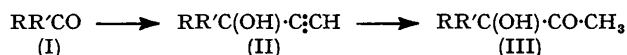
*The Synthesis and Reactions of Branched-chain Hydrocarbons. Part III.**
 α -Hydroxy-ketones with Secondary and Tertiary Alkyl Groups.

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Six branched-chain aliphatic ketones are converted by sodium acetylide in liquid ammonia into alk-1-yn-3-ols. Of these, three are hydrated smoothly and in good yield to the unrearranged ketols. Unsaturated ketone was formed as a by-product from a fourth alk-1-yn-3-ol; from another it constituted the sole product. One of the acetylenic alcohols resisted hydration.

THE work described in this paper explores the limitations of a synthesis of α -hydroxy-ketones by the following scheme when R or R', or both, is a tertiary or secondary alkyl group:



Good yields of the acetylenic alcohol (II) are obtained when the following ketones (I) react with sodium acetylide in liquid ammonia; pinacolone (R = Me, R' = CMe₃); 4:4-dimethylpentan-2-one (R = Me, R' = CMe₃·CH₂); pentamethylacetone (R = Pr^t, R' = Bu^t); hexamethylacetone (R = R' = Bu^t); diisopropyl ketone (R = R' = Pr^t). In view of the smooth reaction of hexamethylacetone, it was unexpected that methyl triptyl ketone (R = Me, R' = CMe₃·CMe₂) should be indifferent to sodium acetylide or lithium acetylide in liquid ammonia or in boiling ether or benzene. It is important that if the quaternary carbon atoms of methyl triptyl ketone are separated by a methylene group, as in 3:3:5:5-tetramethylhexan-2-one (R = Me, R' = CMe₃·CH₂·CMe₂) the acetylenic alcohol can be prepared although only in diminished yield and with some difficulty.

Hydration with boiling 20% aqueous sulphuric acid containing mercuric sulphate gave good yields of the α -hydroxy-ketones (III) from 3:4:4-trimethylpent-1-yn-3-ol (II; R = Bu^t, R' = Me), 3:5:5-trimethylhex-1-yn-3-ol (II; R = CMe₃·CH₂, R' = Me), and 3:4:4:6:6-pentamethylhept-1-yn-3-ol (II; R = CMe₃·CH₂·CMe₂, R' = Me). Hydration is sluggish if R and R' are branched. Thus 4-methyl-3-isopropylpent-1-yn-3-ol (II; R = R' = Pr^t) gives only a 40–50% yield of α -hydroxy-ketone. No ketol is formed from 4:4-dimethyl-3-isopropylpent-1-yn-3-ol: after prolonged boiling, a considerable

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proportion of the alcohol was recovered unchanged and an unsaturated carbonyl compound was formed in poor yield. The alcohol (II; $R = R' = \text{Bu}^t$) was unchanged by a boiling solution of mercuric sulphate in 20% sulphuric acid or aqueous methanol; similar resistance to hydration has been observed with 2 : 2 : 5 : 5-tetramethylhex-3-yne (Hennion and Banigan, *J. Amer. Chem. Soc.*, 1946, **68**, 1202).

It was established that no rearrangement of the ketol occurred in the hydration of the acetylenic alcohols by reduction to a glycol and identification of the products of oxidative fission of this, and confirmation is afforded by a study of the reaction of the ketols with lithium alkyls.

In the hydration of some acetylenic alcohols, limited elimination of acetylene occurred, generally accompanied by formation of unsaturated carbonylic compounds. These are $\alpha\beta$ -unsaturated ketones corresponding to the dehydration product of the normal hydroxy-ketone and have been identified by comparison with authentic specimens from other sources or by ozonolysis. Exceptionally 4 : 4-dimethyl-3-isopropylpent-1-yn-3-ol, on attempted hydration, gave 4 : 4-dimethyl-3-isopropylpent-2-en-1-al as the main product although only in relatively poor yield.

The isolation of β -*tert.*-butylbutyrolactone in small yield from the products of the hydration of 3 : 4 : 4-trimethylpent-1-yn-3-ol suggests that in this case an unsaturated aldehyde is also formed and then oxidised to the corresponding $\alpha\beta$ -unsaturated acid which is known to give the lactone in hot aqueous sulphuric acid.

EXPERIMENTAL

Preparation of 3-Hydroxy-3 : 4 : 4-trimethylpentan-2-one (III; $R = \text{Bu}^t$, $R' = \text{Me}$).—3 : 4 : 4-Trimethylpent-1-yn-3-ol. Pinacolone (*tert.*-butyl methyl ketone) (340 g.) was added, during 3 hr., to sodium acetylide (from sodium, 85 g.) in liquid ammonia (2 l.). The mixture was stirred at -35° for a further $2\frac{1}{2}$ hr., ammonium chloride (220 g.) was then added, and the ammonia allowed to evaporate overnight. Steam-distillation followed by efficient fractionation gave 3 : 4 : 4-trimethylpent-1-yn-3-ol (310 g.), b. p. $142\text{--}144^\circ$, n_D^{20} 1.4440, d_4^{20} 0.868 (Wouseng *Ann. Chim.*, 1924, **1**, 343, gives b. p. 144° , n_D^{11} 1.4441, d_4^{11} 0.8806), and a small solid residue, presumably 2 : 2 : 3 : 6 : 7 : 7-hexamethyloct-4-yne-3 : 6-diol (Wouseng, *loc. cit.*).

Pinacolone (20 g.) and ethynylmagnesium bromide gave 4 g. of the required alcohol and 3 g. of the diol. From sodium acetylide and pinacolone in ether (Wouseng, *loc. cit.*), the yield of alcohol was 24%; it was higher in boiling ether, but the product also contained 2 : 2 : 5 : 6 : 6-pentamethylhept-4-en-3-one (Hickinbottom and Schlüchterer, *Nature*, 1945, **155**, 19). Potassium acetylide in diethylaniline also gave a poor yield of the required product (Distillers Co. Ltd., B.P. 589,350).

The pinacolone required was prepared (a) by rearrangement of pinacol hydrate (Hill and Flosdorf, *Org. Synth.*, Coll. Vol., I, 2nd Edn., p. 462) in 68% yield, and (b) from acetic anhydride and *tert.*-butylmagnesium chloride at -50° (Newman and Smith, *J. Org. Chem.*, 1948, **13**, 592) in 61% yield. Reaction of *tert.*-butylmagnesium chloride with acetyl chloride gave yields averaging 15% (Whitmore *et al.*, *J. Amer. Chem. Soc.*, 1933, **55**, 1564; 1938, **60**, 2900).

3-Hydroxy-3 : 4 : 4-trimethylpentan-2-one (III; $R = \text{Bu}^t$, $R' = \text{Me}$). 3 : 4 : 4-Trimethylpent-1-yn-3-ol (126 g.) was added during 2 hr. to boiling 20% sulphuric acid (300 c.c.) in which were dissolved 10 g. of mercuric oxide. The hydration was completed by a further 2 hours' boiling, and the product was removed by steam-distillation. Distillation of the oil so obtained gave 3-hydroxy-3 : 4 : 4-trimethylpentan-2-one (80%), b. p. $174\text{--}176^\circ/760$ mm., $75\text{--}77^\circ/19$ mm., n_D^{20} 1.4410, d_4^{20} 0.9331 (Locquin and Wouseng, *Compt. rend.*, 1923, **176**, 517, give b. p. 177° , n_D^{11} 1.4442, d_4^{11} 0.9388), fraction (A) (15 g.), b. p. $160\text{--}174^\circ$, and a solid (B) (1.5 g.), not easily volatile in steam.

3-Hydroxy-3 : 4 : 4-trimethylpentan-2-one was characterised as its semicarbazone, m. p. 194° (Found : C, 53.9; H, 9.35; N, 21.0. Calc. for $\text{C}_9\text{H}_{19}\text{O}_2\text{N}_3$: C, 53.7; H, 9.5; N, 20.9%) (Locquin and Wouseng, *loc. cit.*, give m. p. $193\text{--}194^\circ$). With 2 : 4-dinitrophenylhydrazine it gave a compound presumably a pyrazoline, as bright red needles (from glacial acetic acid), m. p. 232° , insoluble in ethanol, ether, or light petroleum, but soluble in benzene or acetic acid (Found : C, 54.9; H, 6.0; N, 18.4. $\text{C}_{14}\text{H}_{18}\text{O}_4\text{N}_4$ requires C, 54.9; H, 5.9; N, 18.3%).

3-Hydroxy-3 : 4 : 4-trimethylpentan-2-one (12 g.) was reduced by lithium aluminium hydride (5 g.) in ether (110 c.c.) at room temperature for 2 hr., then refluxed for 1 hr., and poured on ice. The precipitated hydroxide was dissolved in dilute hydrochloric acid. The material

extracted by ether yielded pure 3 : 4 : 4-trimethylpentane-2 : 3-diol [10.5 g., after crystallisation from light petroleum (b. p. 40—60°)], m. p. 95—96°, b. p. 96°/18 mm. (Found : C, 65.8, 66.0; H, 12.65, 12.4. $C_8H_{18}O_2$ requires C, 65.7; H, 12.4%). This glycol (2.0 g.), methyl alcohol (3 c.c.), water (10 c.c.), and periodic acid (1.0 g.) were shaken together for 4 hr. at room temperature; air was then drawn through the solution into 2 : 4-dinitrophenylhydrazine in aqueous-alcoholic hydrochloric acid. Acetaldehyde 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 168°, separated from this solution overnight after warming. The remaining aqueous solution was extracted with ether; the material in this extract gave *tert.*-butyl methyl ketone 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 126° (after chromatography on alumina).

The lower-boiling fractions (*A*) (above) from a number of hydrations were combined (69 g.) and resolved by fractionation into pinacolone, b. p. 103—107°, n_D^{20} 1.3965—1.3969 (9.1 g.), 3-*tert.*-butylbut-3-en-2-one, b. p. 141—144°, n_D^{20} 1.4339—1.4342 (43 g.), and 3-hydroxy-3 : 4 : 4-trimethylpentan-2-one, b. p. 168—175.5°, n_D^{20} 1.4398—1.4402 (8.2 g.). Redistillation of the second fraction gave the pure ketone, b. p. 142—143°, n_D^{20} 1.4340 (Found : C, 75.9; H, 11.3. Calc. for $C_8H_{14}O$: C, 76.2; H, 11.2%) [semicarbazone, m. p. 165° (Found : C, 58.8; H, 9.3; N, 22.8. Calc. for $C_9H_{17}ON_3$: C, 59.0; H, 9.4; N, 22.9%); 2 : 4-dinitrophenylhydrazone, orange yellow, m. p. 116° (Found : C, 55.4; H, 6.1; N, 18.2. $C_{14}H_{18}O_4N_4$ requires C, 54.9; H, 5.9; N, 18.3%)]. Favorskaya (*J. Gen. Chem. U.S.S.R.*, 1949, 19, 2051) gives 3-*tert.*-butylbut-3-en-2-one, b. p. 80—81°/110 mm. (semicarbazone, m. p. 163—164°). Ozonolysis of this ketone gave formaldehyde and a 1 : 2-diketone, which on reduction by lithium aluminium hydride gave a glycol, m. p. 52° (from light petroleum), oxidised by periodic acid to trimethylacetaldehyde and acetaldehyde (Favorski, *J. Russ. Phys. Chem. Soc.*, 1928, 60, 386, gives m. p. 54° for the glycol). With lithium aluminium hydride in ether the ketone gave 3-*tert.*-butylbut-3-en-2-ol, b. p. 148°, n_D^{20} 1.4418 (Found : C, 74.8; H, 12.5. $C_8H_{16}O$ requires C, 74.9; H, 12.6%) [3 : 5-dinitrobenzoate, m. p. 104° (Found : C, 55.9; H, 5.6; N, 9.0. $C_{15}H_{18}O_6N_2$ requires C, 55.9; H, 5.6; N, 8.7%)].

The solid (*B*) (above) was sparingly soluble in ether or alcohol, but, crystallised from light petroleum (b. p. 80—100°), had m. p. 98.5° (Found : C, 67.0; H, 9.85; active H, 0. Calc. for $C_8H_{14}O_2$: C, 67.55; H, 9.9%). It is soluble in aqueous alkali and acidification of the aqueous solution precipitated 2 : 3 : 3-trimethylbut-1-ene-1-carboxylic acid, m. p. 85° (Found : C, 67.8; H, 9.9. Calc. for $C_8H_{14}O_2$: C, 67.55; H, 9.9%), converted into the original lactone by boiling 50% aqueous sulphuric acid. Locquin and Wouseng (*Compt. rend.*, 1924, 174, 1713) give β -*tert.*-butylbutyrolactone, m. p. 97—98°, and 2 : 3 : 3-trimethylbut-1-ene-1-carboxylic acid, m. p. 85—86°. Petschnikow (*J. pr. Chem.*, 1902, 65, 178) gives m. p. 96—98° for the lactone.

Preparation of 3-Hydroxy-3 : 5 : 5-trimethylhexan-2-one (III; R = $Me_3C\cdot CH_2$, R' = Me).—3 : 5 : 5-Trimethylhex-1-yn-3-ol. Methyl neopentyl ketone (378 g.) with sodium acetylde in liquid ammonia gave 3 : 5 : 5-trimethylhex-1-yn-3-ol (72%), b. p. 159—161°, n_D^{20} 1.4418, d_{20}^{20} 0.8556 (Found : C, 77.4; H, 11.8. $C_9H_{16}O$ requires C, 77.1; H, 11.5%). The ketone was prepared by the oxidation of diisobutylene in 40% yield (Byers and Hickinbottom, *J.*, 1948, 1336; Mosher and Cox, *J. Amer. Chem. Soc.*, 1950, 72, 3701), or of 4 : 4-dimethylpentan-2-ol with dichromate and aqueous sulphuric acid.

3-Hydroxy-3 : 5 : 5-trimethylhexan-2-one. This *ketol* was obtained in 90% yield by the hydration of 3 : 5 : 5-trimethylhex-1-yn-3-ol with boiling 20% aqueous sulphuric acid containing mercuric sulphate. It had b. p. 75°/16 mm., n_D^{20} 1.4354, d_{18}^{18} 0.9152 (Found : C, 68.25; H, 11.3. $C_9H_{18}O_2$ requires C, 68.3; H, 11.5%), and gave a *semicarbazone*, m. p. 160°, very soluble in alcohol (Found : C, 55.6; H, 9.5; N, 19.8. $C_{10}H_{21}O_2N_3$ requires C, 55.8; H, 9.8; N, 19.5%), a 2 : 4-dinitrophenylhydrazone, m. p. 114°, light yellow-orange crystals from aqueous alcohol (Found : C, 53.4; H, 6.9; N, 16.9. $C_{15}H_{22}O_5N_4$ requires C, 53.2; H, 6.5; N, 16.6%), and, in hot aqueous sulphuric acid, a 2 : 4-dinitrophenylpyrazoline, m. p. 161°, orange-red needles (Found : C, 56.0; H, 6.9; N, 17.4. $C_{15}H_{20}O_4N_4$ requires C, 56.2; H, 6.3; N, 17.5%).

Reduction of the *ketol* in ether by lithium aluminium hydride gave 3 : 5 : 5-trimethylhexan-2 : 3-diol, a viscous liquid of faint odour, b. p. 95—96°/12 mm., n_D^{20} 1.4531, d_{17}^{17} 0.9352 (Found : C, 67.0, 67.4; H, 12.2, 12.4. $C_9H_{20}O_2$ requires C, 67.4; H, 12.6%), which with periodic acid in aqueous methanol gave acetaldehyde (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 168—169°) and methyl neopentyl ketone (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 100—101°).

Preparation of 3-Hydroxy-3 : 4 : 4 : 6 : 6-pentamethylheptan-2-one (III; R = $Me_3C\cdot CH_2\cdot CMe_2$, R = Me).—3 : 4 : 4 : 6 : 6-Pentamethylhept-1-yn-3-ol. 3 : 3 : 5 : 5-Tetramethylhexan-2-one (312 g.) was added dropwise to sodium acetylde (from 46 g. of sodium) in anhydrous ammonia (3 l.).

After 3½ hr. an excess of ammonium chloride was added and the ammonia allowed to evaporate. Steam-distillation of the residue gave about equal amounts of unchanged 3 : 3 : 5 : 5-tetramethylhexan-2-one and 3 : 4 : 4 : 6 : 6-pentamethylhept-1-yn-3-ol, b. p. 90/10 mm., n_D^{20} 1.4613, d_4^{20} 0.8842 (Found : C, 78.85; H, 12.15. $C_{12}H_{22}O$ requires C, 79.05; H, 12.15%). A satisfactory yield requires use of very efficient stirring and an excess of ammonia.

3-Hydroxy-3 : 4 : 4 : 6 : 6-pentamethylheptan-2-one. Hydration of the foregoing alcohol (273 g.) as in other preparations gave the required ketol (270 g.), b. p. 85—88/2 mm. This solidified but was too soluble in organic solvents to be recrystallised economically, and was obtained pure by washing with small quantities of ice-cold light petroleum (b. p. 40—60°), then forming waxy white crystals, m. p. 42—43°, b. p. 88°/2 mm. [Found : C, 72.1; H, 11.9; active H, 0.5%; *M* (Rast), 187. $C_{15}H_{24}O_2$ requires C, 71.9; H, 12.1; active H, 0.5%; *M*, 200]. No derivatives could be obtained.

Preparation of 3-Hydroxy-4-methyl-3-isopropylpentan-2-one (III; R = R' = Prⁱ).—4-Methyl-3-isopropylpent-1-yn-3-ol. Reaction of diisopropyl ketone (684 g.) with sodium acetylide in liquid ammonia gave the required alcohol (793 g.), b. p. 162—164°/760 mm., n_D^{20} 1.4470, d_4^{23} 0.8675 (Thompson, Burr, and Shaw, *J. Amer. Chem. Soc.*, 1941, 63, 186, give b. p. 162—164°, n_D^{20} 1.4492), and 2 : 7-dimethyl-3 : 6-diisopropyloct-1-yne-3 : 6-diol (2.5 g.), m. p. and mixed m. p. 108—109° (Iotsitch, *Bull. Soc. chim.*, 1908, 4, 1203, gives m. p. 106—107°).

3-Hydroxy-4-methyl-3-isopropylpentan-2-one. Hydration of 4-methyl-3-isopropylpent-1-yn-3-ol (560 g.) as above yielded the required ketol (246 g.), together with 4-methyl-3-isopropylpent-3-en-2-one, unchanged acetylenic alcohol, and 3-methyl-2-isopropylbut-1-ene-1-carboxylic acid, m. p. 127.5° (3 g.) [Found : C, 69.6; H, 10.3; active H, 0.59%; *M* (Rast), 162. $C_9H_{16}O_2$ requires C, 69.2; H, 10.3; active H, 0.64%; *M*, 156]. Attempts to prepare a lactone from the acid by warming it with 80% sulphuric acid were unsuccessful. Ozonolysis of the acid in chloroform gave diisopropyl ketone (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 95°). By further hydration the lower-boiling fractions gave pure unsaturated ketone (110 g.), the ketol (51 g.), the unsaturated acid (2.2 g.), and diisopropyl ketone (10 g.).

The unsaturated ketone, b. p. 67.5°/17.5 mm., n_D^{20} 1.4450 (Found : C, 77.1; H, 11.7. $C_9H_{16}O$ requires C, 77.1; H, 11.5%), is identical with that obtained by the rearrangement of 4-methyl-3-isopropylpent-1-yn-3-ol with formic acid. It gave no semicarbazone or 2 : 4-dinitrophenylhydrazone. Reduction by lithium aluminium hydride in ether gave 4-methyl-3-isopropylpent-3-en-2-ol, b. p. 77—78°/14 mm., n_D^{20} 1.4591 (Found : C, 76.3; H, 12.6. $C_9H_{18}O$ requires C, 76.0; H, 12.8%) [3 : 5-dinitrobenzoate, m. p. 94°, white needles from light petroleum (b. p. 60—80°) (Found : C, 57.4; H, 6.1; N, 8.5. $C_{16}H_{20}O_6N_2$ requires C, 57.1; H, 6.0; N, 8.3%)]. The unsaturated ketone was identified by ozonolysis in chloroform to acetone (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 126°) and a substance which was reduced by lithium aluminium hydride in ether to a glycol, m. p. 48°. This glycol with periodic acid in aqueous methanol gave acetaldehyde and isobutaldehyde (2 : 4-dinitrophenylhydrazones, m. p.s and mixed m. p.s 165° and 187° respectively). The glycol is therefore 2-methylpentane-3 : 4-diol (Umnova, *J. Russ. Phys. Chem. Soc.*, 1910, 42, 1541, gives m. p. 48—49°).

Pure 3-hydroxy-4-methyl-3-isopropylpentan-2-one is a colourless liquid of ketonic odour, b. p. 85°/20 mm., n_D^{20} 1.4410, d_4^{23} 0.9242 (Found : C, 68.6; H, 11.8. $C_9H_{18}O_2$ requires C, 68.3; H, 11.5%). No semicarbazone or 2 : 4-dinitrophenylhydrazone could be prepared from it. It is reduced by lithium aluminium hydride in ether to 4-methyl-3-isopropylpentane-2 : 3-diol, m. p. 51—52°, b. p. 111°/18 mm. (Found : C, 68.0; H, 12.7. $C_9H_{20}O_2$ requires C, 67.45; H, 12.6%), oxidised by periodic acid in aqueous methanol to diisopropyl ketone (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 96°) and acetaldehyde (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 168°).

Attempted Preparation of 3-Hydroxy-4 : 4-dimethyl-3-isopropylpentan-2-one.—4 : 4-Dimethyl-3-isopropylpent-1-yn-3-ol (I; R = Bu^t, R' = Prⁱ). Pentamethylacetone (269 g.) and sodium acetylide (from 60 g. of sodium) in liquid ammonia (2 l.) gave 4 : 4-dimethyl-3-isopropylpent-1-yn-3-ol (265 g.), b. p. 65—68°/16 mm. Distillation through a highly efficient column gave the pure alcohol as a mobile colourless liquid of powerful odour, b. p. 174.5—176.0°, n_D^{20} 1.4421—1.4423, d_4^{20} 0.8758 (Found : C, 77.65; H, 12.0. $C_{10}H_{18}O$ requires C, 77.85; H, 11.8%).

Attempts to hydrate the alcohol by mercuric sulphate in hot aqueous methanol (Thomas, Campbell, and Hennion, *J. Amer. Chem. Soc.*, 1938, 60, 718) gave only unchanged alcohol. Even when the alcohol (170 g.) was boiled with 20% sulphuric acid containing mercuric sulphate for 10 hr., a considerable amount was recovered unchanged, but there was a fraction (20.5 g.), b. p. 78—85°/25 mm., n_D^{20} 1.4670—1.4690, consisting essentially of 4 : 4-dimethyl-3-isopropylpent-2-enal, and a high-boiling residue (0.5 g.) which solidified and could not be recrystallised

(Found: *M*, 195; active H, 0.58. Calc. for $C_{10}H_{18}O_2$ corresponding to the acid: *M*, 170; active H, 0.59%). The pentenal had b. p. 98°/18 mm., n_D^{20} 1.4689 (Found: C, 77.45; H, 11.7. $C_{10}H_{18}O$ requires C, 77.85; H, 11.8%), and gave a *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%), and 2:4-*dinitrophenylhydrazone*, red needles (from 50% acetic acid), m. p. 200.5° not depressed on admixture with the dinitrophenylhydrazone of 4:4-dimethyl-3-isopropylpent-2-enal obtained by rearrangement of 4:4-dimethyl-3-isopropylpent-1-yn-3-ol with formic acid (J. Hancock, personal communication) (Found: C, 57.75; H, 6.75; N, 16.5. $C_{16}H_{22}O_4N_4$ requires C, 57.45; H, 6.65; N, 16.75%). It is reduced by lithium aluminium hydride in ether to the corresponding *alcohol*, b. p. 91°/13 mm., n_D^{20} 1.4623 (Found: C, 76.75; H, 12.95. $C_{10}H_{20}O$ requires C, 76.85; H, 12.9%).

Preparation of 3-tert.-Butyl-4:4-dimethylpent-1-yn-3-ol.—Hexamethylacetone (45 g.) was added dropwise to a well-stirred suspension of sodium acetylide (from 10 g. of sodium) in liquid ammonia (800 c.c.). Stirring was continued for 3 hr., then the mixture was decomposed by ammonium chloride. After the ammonia had evaporated the product was steam-distilled to remove 3-*tert.-butyl-4:4-dimethylpent-1-yn-3-ol* (36 g.), a colourless mobile liquid with a powerful odour, b. p. 74—75°/14 mm., n_D^{20} 1.4589, d_{25}^{25} 0.8825 (Found: C, 78.8, 78.35; H, 12.35, 12.05. $C_{11}H_{20}O$ requires C, 78.5; H, 12.0%). A small amount of solid material was also obtained (0.5 g.), having m. p. 151° after crystallisation from light petroleum (b. p. 60—80°). It was identified as 3:6-*di-tert.-butyl-2:2:7:7-tetramethyloct-4-yne-3:6-diol* by comparison (m. p. and mixed m. p.) with an authentic specimen prepared by the following method.

3-*tert.-Butyl-4:4-dimethylpent-1-yn-3-ol* (2 g.) was added to sodamide (from 0.5 g. of sodium) in anhydrous ammonia (10 c.c.). After 2 hours' stirring hexamethylacetone (1.5 g.) was added, and stirring continued for another 2 hr. Ammonium chloride was then added, the ammonia allowed to evaporate, and the residue extracted with ether (Soxhlet). Evaporation of the extract left 3:6-*di-tert.-butyl-2:2:6:7-tetramethyloct-4-yne-3:6-diol*, a white volatile crystalline solid, m. p. 152—154° after crystallisation from light petroleum (b. p. 60—80°) (Found: C, 76.95; H, 12.1. $C_{20}H_{38}O_2$ requires C, 77.35; H, 12.35%).

Prolonged heating with 20% aqueous sulphuric acid containing mercuric sulphate or with aqueous methanol containing mercuric sulphate failed to bring about any detectable hydration of 3-*tert.-butyl-4:4-dimethylpent-1-yn-3-ol*: it was recovered unchanged.

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