The Synthesis and Reactions of Branched-chain Hydrocarbons. Part VII. The Preparation and Pinacol Rearrangement of Some αβ-Acetylenic Ditertiary Glycols.*

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The preparation of three αβ-acetylenic ditertiary glycols is described, and the action of concentrated sulphuric acid at −20° on two of them reported.

αβ-ACETYLENIC ditertiary glycols (II) have been previously prepared by the action of acetylene on α-hydroxy-ketones (I) in ether in the presence of either potassium hydroxide (Favorski and Onischenko, *J. Gen. Chem. U.S.S.R.*, 1941, **11**, 1111) or sodamide (Bernard and Colonge, *Bull. Soc. chim. France*, 1945, **12**, 347). We have now found, in agreement with Davis and Erman (*J. Amer. Chem. Soc.*, 1954, **76**, 3477; published since the completion of this work) that these compounds may be prepared in good yield, in some cases, by the use of sodium acetylide in liquid ammonia. Thus 3-hydroxy-3-methylbutan-2-one (I; R = R′ = Me) and 3-hydroxy-3 : 5 : 5-trimethylhexan-2-one (I; R = Me, R′ = $CMe_3{\cdot}CH_2$) yield respectively 2 : 3-dimethylpent-4-yne-2 : 3-diol (II; R = R′ = Me) and 3 : 4 : 6 : 6-tetramethylhept-1-yne-3 : 4-diol (II; R = Me, R′ = $Me_3C{\cdot}CH_2$) in good yield, while a poorer yield of 3 : 4 : 4 : 5-tetramethylhex-1-yne-3 : 4-diol (II; R = Me, R′ = Bu^t) was obtained from 3-hydroxy-3 : 4 : 4-trimethylpentan-2-one (I; R = Me, R′ = Bu^t). The yield was not improved by the use of lithium acetylide or by employing boiling ether or benzene as solvent. 3-Hydroxy-4-methyl-3-*iso*propylpentan-2-one (I; R = R′ = Pr^i) and 3-hydroxy-3 : 4 : 4 : 6 : 6-pentamethylheptan-2-one (I; R = Me, R′ = $Me_3C{\cdot}CH_2{\cdot}CMe_2$) failed to react with acetylene under any of the above conditions. The structure of each of the αβ-acetylenic glycols prepared was proved by oxidation with periodic acid to but-3-yn-2-one and a saturated ketone.

(I) $HO{\cdot}CRR'{\cdot}COMe$ $HO{\cdot}CRR'{\cdot}CMe(OH){\cdot}C{\equiv}CH$ (II)

The pinacol rearrangement of 2 : 3-dimethylpent-4-yne-2 : 3-diol (III) has been reported by Favorski and Onischenko (*loc. cit.*) to yield 3 : 3-dimethylpentane-2 : 4-dione (VI) in concentrated sulphuric acid at −10° and, subsequent to this work, Davis and Erman (*loc. cit.*) reported that 3 : 3-dimethylpent-4-yn-2-one (V) is produced in the presence of boiling 40% sulphuric acid. We have found that both these products, together with 3-methylbutan-2-one, arise if the rearrangement is performed in concentrated sulphuric acid

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at —20°. We consider that 3 : 3-dimethylpentane-2 : 4-dione (VI) arises by the initial hydration of the ethynyl group of the glycol followed by the rearrangement of the dihydroxy-ketone (IV) produced, as we have been unable to hydrate the ethynyl group of 3 : 3-dimethylpent-4-yn-2-one.

(III) $HO\cdot CMe_2\cdot CMe(OH)\cdot C\equiv CH$ $HO\cdot CMe_2\cdot CMe(OH)\cdot COMe$ (IV)
(V) $Me\cdot CO\cdot CMe_2\cdot C\equiv CH$ $Me\cdot CO\cdot CMe_2\cdot COMe$ (VI)

The rearrangement of 3 : 4 : 6 : 6-tetramethylhept-1-yne-3 : 4-diol (VII) in concentrated sulphuric acid at —20° gave small amounts of 4 : 4-dimethylpentan-2-one and but-3-yn-2-one, which appear to arise by fission of the glycol (cf. Hickinbottom, Hyatt, and Sparke, *J.*, 1954, 2533; Hickinbottom and Pyle, unpublished work). The principal products were the normal rearrangement product, 2 : 2 : 5 : 5-tetramethylhept-6-yn-4-one (IX) (identified by conversion into 2 : 2 : 5 : 5-tetramethylheptan-4-ol), 3 : 5 : 5-trimethylhexan-2-one, and 3 : 4 : 6 : 6-tetramethylhepta-2 : 4-dien-1-al (X). The latter, identified by ozonolysis, may arise through a Meyer–Schuster–Rupe type of rearrangement (A. W. Johnson, " The Chemistry of Acetylenic Compounds," Edward Arnold & Co., London, 1946, Vol I, pp. 124—130), followed by dehydration of the intermediate unsaturated hydroxy-aldehyde (VIII). This type of rearrangement has been previously observed in the action of sulphuric acid on 2 : 3-dimethyl-5-phenylpent-4-yne-2 : 3-diol (XI) which gives 2-hydroxy-2 : 3-dimethyl-5-phenylpent-3-en-5-one (XII) and 2 : 3-dimethyl-5-phenylpenta-1 : 3-dien-5-one (XIII) in addition to the " normal " product (Venus-Danilova, Serkova, and Pavlova, *J. Gen. Chem. U.S.S.R.*, 1951, **21**, 2210).

(VII) $Me_3C\cdot CH_2\cdot CMe(OH)\cdot CMe(OH)\cdot C\equiv CH$ $Me_3C\cdot CH_2\cdot CMe(OH)\cdot CMe{:}CH\cdot CHO$ (VIII)
(IX) $Me_3C\cdot CH_2\cdot CO\cdot CMe_2\cdot C\equiv CH$ $Me_3C\cdot CH{:}CMe\cdot CMe{:}CH\cdot CHO$ (X)

$HO\cdot CMe_2\cdot CMe(OH)\cdot C\equiv CPh$ (XI) $HO\cdot CMe_2\cdot CMe{:}CH\cdot COPh$ (XII) $CH_2{:}CMe\cdot CMe{:}CH\cdot COPh$ (XIII)

The mechanism of the formation, in both of the above rearrangements, of a saturated ketone containing two fewer carbon atoms than the original glycols is a matter of speculation. The subject is under investigation and will be reported later.

EXPERIMENTAL

Preparation of α-Hydroxy-ketones.—(*A*) 3-Hydroxy-3-methylbut-1-yne (Froning and Hennion, *J. Amer. Chem. Soc.*, 1940, **62**, 653) (420 g.) was added during 3 hr. to a vigorously stirred boiling solution of mercuric oxide (7·5 g.) in sulphuric acid (30 g.) and water (500 c.c.), with continuous steam-distillation. The distillate was saturated with sodium chloride, and the upper layer separated and combined with the ethereal extract of the aqueous layer and dried ($MgSO_4$). Distillation gave, after a small forerun, 3-hydroxy-3-methylbutan-2-one (449 g., 88%), b. p. 140—142°, n_D^{20} 1·4150, which yielded a 2 : 4-*dinitrophenylhydrazone*, m. p. 149°, orange needles from benzene–light petroleum (Found : C, 47·0; H, 5·0; N, 20·0. $C_{11}H_{14}O_5N_4$ requires C, 46·8; H, 5·0; N, 19·9%), and a semicarbazone, m. p. 164° (from ethanol). Froning and Hennion (*loc. cit.*) record b. p. 139°, n_D^{20} 1·4150. Scheibler and Fischer (*Ber.*, 1922, **55**, 2903) record a semicarbazone, m. p. 164°.

(*B*) 3-Hydroxy-3 : 4 : 4-trimethylpentan-2-one, 3-hydroxy-3 : 5 : 5-trimethylhexan-2-one, 3-hydroxy-4-methyl-3-*iso*propylpentan-2-one, and 3-hydroxy-3 : 4 : 4 : 6 : 6-pentamethylheptan-2-one were prepared by the method of Hickinbottom, Hyatt, and Sparke (*J.*, 1954, 2529).

Preparation of αβ-Acetylenic Glycols.—The α-hydroxy-ketone (1·5 moles) was added dropwise during 3 hr. to a well-stirred suspension of sodium acetylide (3·0 moles) in liquid ammonia (2 l.) through which a slow stream of acetylene was passing. After 1 hour's stirring the acetylene was shut off and ammonium chloride (200 g.) added. After further stirring (1 hr.) the ammonia was allowed to evaporate overnight. Water (2 l.) was added, and the mixture extracted with ether (10 × 100 c.c.). Distillation of the dried ($MgSO_4$) ethereal extract gave, after a small forerun, the αβ-acetylenic glycol. Thus were prepared : 2 : 3-dimethylpent-4-yne-2 : 3-diol (151 g.), b. p. 82—84°/13 mm., n_D^{20} 1·4626 (Davis and Erman, *loc. cit.*, record b. p. 90—91°/19 mm., $n_{\rm D}^{25}$ 1·4600), 3 : 4 : 6 : 6-*tetramethylhept*-1-*yne*-3 : 4-*diol* (221 g.), b. p. 76—78°/1·5 mm., $n_{\rm D}^{20}$ 1·4650 (Found : C, 71·8; H, 10·9. $C_{11}H_{20}O_2$ requires C, 71·7; H, 10·9%), and 3 : 4 : 5 : 5-tetramethylhex-1-yne-3 : 4-diol (13·6 g.; 183·4 g. of α-hydroxy-ketone recovered), b. p. 70—71°/0·9 mm., $n_{\rm D}^{20}$ 1·4751, m. p. 54—56° (Bernard and Colonge, *loc. cit.*, record b. p. 104—107°/15 mm., $n_{\rm D}^{13}$ 1·4748). No reaction occurred with 3-hydroxy-4-methyl-3-*iso*propylpentan-2-one or 3-hydroxy-3 : 4 : 4 : 6 : 6-pentamethylheptan-2-one under the above conditions or with sodium or lithium acetylide in boiling ether or benzene, nor could the yield of 3 : 4 : 5 : 5-tetramethylhex-1-yne-3 : 4-diol be improved by using these modifications.

Oxidative Fission of the αβ-*Acetylenic Glycols.*—Periodic acid (3 g.) was added to a solution of the glycol (3 g.) in aqueous methanol (20 c.c.), and the mixture shaken (3 hr.). Air was then aspirated through the solution for 3 hr. and passed into a warm solution of 2 : 4-dinitrophenylhydrazine in aqueous-alcoholic sulphuric acid. The precipitate formed was filtered off, dried, and chromatographed in benzene–light petroleum (b. p. 60—80°) (1 : 9) through alumina. Elution with the same solvent gave, in the case of 2 : 3-dimethylpent-4-yne-2 : 3-diol, the 2 : 4-dinitrophenylhydrazone of acetone (m. p. and mixed m. p. 125°) and, in the case of 3 : 4 : 6 : 6-tetramethylhept-1-yne-3 : 4-diol, the 2 : 4-dinitrophenylhydrazone of 4 : 4-dimethylpentan-2-one (m. p. and mixed m. p. 101°). Further elution, with the same solvent plus 10% of ether, gave, in each case, the 2 : 4-dinitrophenylhydrazone of but-3-yn-2-one, m. p. 180°. Bowden, Heilbron, Jones, and Weedon (*J.*, 1946, 39) record m. p. 181°.

Rearrangement of 2 : 3-*Dimethylpent*-4-*yne*-2 : 3-*diol.*—The glycol (100 g.) was added dropwise during 2 hr. to concentrated sulphuric acid (1200 g.) kept at −20°. After about 10 g. of glycol had been added the mixture liquefied and efficient stirring was commenced and continued throughout the addition and for 1 hr. subsequently. The pale yellow syrup was then poured on crushed ice (4 kg.), water (4 l.) added, and the mixture steam-distilled. The organic layer of the distillate was separated, and the aqueous layer extracted with ether. The combined organic material was washed with a little water and dried ($MgSO_4$), and the ether removed. Fractional distillation of the residue gave fractions :

Fraction	B. p.	Wt. (g.)	$n_{\rm D}^{20}$
1	<92°	1·4	1·3802
2	92—100	9·2	1·3877
3	100—105	1·5	1·3982
4	105—117	5·2	1·4182
5	117—119°	39·5	1·4206
6	—55°/13 mm.	0·9	1·4284
7	55—60°/13 mm.	11·6	1·4332
	Residue	1·3	—

Fraction 1 was unsaturated but no pure component could be isolated. Refractionation of fraction 2 gave 3-methylbutan-2-one, b. p. 94°, $n_{\rm D}^{20}$ 1·3875 (semicarbazone, m. p. and mixed m. p. 112—113°; 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 117°). Fraction 5 gave a white precipitate with ammoniacal silver nitrate and on redistillation gave 3 : 5-dimethylpent-4-yn-2-one, b. p. 117—118°, $n_{\rm D}^{20}$ 1·4202 (Found : C, 76·2; H, 9·2. Calc. for $C_7H_{10}O$: C, 76·3; H, 9·2%) [2 : 4-dinitrophenylhydrazone, yellow needles (from ethanol), m. p. 140°; *semicarbazone*, needles (from ethanol), m. p. 130° (Found : C, 57·6; H, 8·1; N, 24·9. $C_8H_{13}ON_3$ requires C, 57·5; H, 7·8; N, 25·1%). Davis and Erman (*loc. cit.*) record b. p. 117·5°, $n_{\rm D}^{25}$ 1·4180, 2 : 4-dinitrophenylhydrazone, m. p. 139°. Hydrogenation of 3 : 5-dimethylpent-4-yn-2-one in alcohol with Adams's catalyst at 50 lb./sq. in. gave 3 : 3-dimethylpentan-2-one, b. p. 128—130°, $n_{\rm D}^{20}$ 1·4101 (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 112°; semicarbazone, m. p. and mixed m. p. 136°).

Fraction 7, when distilled, yielded 3 : 3-dimethylpentane-2 : 4-dione, b. p. 173°, $n_{\rm D}^{20}$ 1·4332, which gave a *disemicarbazone* (purified by boiling with ethanol, benzene, and ether), m. p. and mixed m. p. 220° (Found : C, 44·6; H, 7·2; N, 34·5. $C_9H_{18}O_2N_6$ requires C, 44·6; H, 7·5; N, 34·7%), and a *bis*-2 : 4-*dinitrophenylhydrazone*, orange plates (from ethanol), m. p. and mixed m. p. 146° (Found: C, 46·9; H, 4·1; N, 22·8. $C_{19}H_{20}O_8N_8$ requires C, 46·7; H, 4·1; N, 22·9%). The authentic specimens were obtained from the dione prepared according to Kohler and Erickson (*J. Amer. Chem. Soc.*, 1931, **53**, 2301).

Rearrangement of 3 : 4 : 6 : 6-*Tetramethylhept*-1-*yne*-3 : 4-*diol.*—The glycol (215 g.) was rearranged as for the previous example but with concentrated sulphuric acid (1500 c.c.; 2757 g.). Fractional distillation of the organic material gave 5·3 g. in the cold trap, (*a*) 16·4 g. of b. p. <78°/19 mm., $n_{\rm D}^{20}$ 1·4271—1·4471, (*b*) 40·1 g. of b. p. 78—102°/19 mm., $n_{\rm D}^{20}$ 1·4540—1·4595, and 35·2 g. of residue. All the fractions were unsaturated and had olefinic odours. Material (*a*) was treated with excess of an aqueous-ethanolic solution of semicarbazide hydrochloride and sodium acetate. The solid precipitated overnight was recrystallised from ethanol and hydrolysed by boiling 20% aqueous oxalic acid. The organic material was extracted with ether, washed with aqueous sodium carbonate solution, and water, and dried ($MgSO_4$). Distillation gave 3 : 5 : 5-trimethylhexan-2-one (10·9 g.), b. p. 61°/19 mm., n_D^{20} 1·4172 (Found : C, 76·2; H, 12·5. Calc. for $C_9H_{18}O$: C, 76·0; H, 12·7%) [semicarbazone, needles (from ethanol), m. p. 177°; 2 : 4-dinitrophenylhydrazone, yellow plates (from ethanol), m. p. 65°]. Whitmore and Meunier (*J. Amer. Chem. Soc.*, **1941**, **63**, 2197) record semicarbazone, m. p. 168—169°, and 2 : 4-dinitrophenylhydrazone, m. p. 63—64°. Colonge and Dreux (*Compt. rend.*, 1950, **230**, 1776) record ketone, b. p. 61°/19 mm., and semicarbazone, m. p. 176°.

Material (*b*) was purified *via* the semicarbazone as above to yield 2 : 2 : 5 : 5-*tetramethylhept*-6-*yn*-4-*one* (16·4 g.), b. p. 90°/16 mm., n_D^{20} 1·4652 (Found : C, 79·2; H, 11·2. $C_{11}H_{18}O$ requires C, 79·5; H, 10·9%), which gave a *semicarbazone*, needles (from ethanol), m. p. 206° (Found : C, 64·2; H, 9·2; N, 18·9. $C_{12}H_{21}ON_3$ requires C, 64·5; H, 9·5; N, 18·8%), and a 2 : 4-*dinitrophenylhydrazone*, yellow crystals (from ethanol), m. p. 124° (Found : C, 58·8; H, 6·6; N, 16·3. $C_{17}H_{22}O_4N_4$ requires C, 58·9; H, 6·4; N, 16·2%). Hydrogenation of 2 : 2 : 5 : 5-tetramethylhept-6-yn-4-one in alcohol with Adams's catalyst at 50 lb./sq. in. followed by reduction of the product with lithium aluminium hydride gave 2 : 2 : 5 : 5-tetramethylheptan-4-ol, b. p. 85°/14 mm., n_D^{20} 1·4410 [3 : 5-dinitrobenzoate (from light petroleum, b. p. 40—60°), m. p. and mixed m. p. 108°]. The preparation of this alcohol will be described in Part IX.

The residue was further distilled and all the fractions from it were unsaturated, but none gave a precipitate with ammoniacal silver nitrate. The carbonyl fractions, b. p. 65—100°/2 mm., n_D^{20} 1·4600—1·4770, were treated with excess of aqueous-alcoholic semicarbazide hydrochloride and sodium acetate. The precipitate which was rapidly formed was filtered off, purified by boiling it with ether, and then hydrolysed by shaking it in light petroleum (b. p. 40—60°) for 24 hr. with 20% sulphuric acid. Distillation of the washed (sodium carbonate solution, and water) and dried ($MgSO_4$) ethereal extract gave 3 : 4 : 6 : 6-*tetramethylhepta*-2 : 4-*dien*-1-*al* (9·3 g.), b. p. 75°/2 mm., n_D^{20} 1·4861, which reduced Fehling's solution but not Schiff's reagent and darkened and became viscous on storage (Found : C, 79·5; H, 11·0. $C_{11}H_{18}O$ requires C, 79·5; H, 10·9%), and gave a *semicarbazone* (purified by extraction with ethanol, benzene, and ether), m. p. 238° (Found : C, 64·5; H, 9·5; N, 18·8. $C_{12}H_{21}ON_3$ requires C, 64·5; H, 9·5; N, 18·8%), and a 2 : 4-*dinitrophenylhydrazone*, scarlet crystals [from benzene-light petroleum (b. p. 60—80°)], m. p. 178° (Found : C, 58·9; H, 6·4; N, 16·0. $C_{17}H_{22}O_4N_4$ requires C, 58·9; H, 6·4; N, 16·2%). Ozonolysis of 3 : 4 : 6 : 6-tetramethylhepta-2 : 4-dienal in chloroform gave trimethylacetaldehyde and diacetyl which were isolated as the 2 : 4-dinitrophenylhydrazones, m. p.s and mixed m. p.s 210° and 243° respectively, the separation being effected by chromatography on alumina from light petroleum–benzene–ether (9 : 1 : 1).

Material from the cold trap, on redistillation, gave (*A*) but-3-yn-2-one, b. p. 80—86°, n_D^{20} 1·4050 [2 : 4-dinitrophenylhydrazone, yellow needles (from ethanol), m. p. 180°] [Bowden *et al.* (*loc. cit.*) record b. p. 84·5—86°, n_D^{22} 1·4050 (2 : 4-dinitrophenyhydrazone, m. p. 181°)], and (*B*) a liquid, b. p. 110—125°, n_D^{20} 1·4043. The latter was treated with a solution of 2 : 4-dinitrophenylhydrazine (see above), and the orange oil formed was extracted with benzene and chromatographed to yield 4 : 4-dimethylpentan-2-one 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 100°.

Attempted Hydration of 3 : 3-*Dimethylpent*-4-*yn*-2-*one and* 2 : 2 : 5 : 5-*Tetramethylhept*-6-*yn*-4-*one*.—The acetylenic ketone (0·05 mole) was added dropwise during 30 min. to well-stirred boiling solution of mercuric oxide (0·25 g.) in 10% dilute sulphuric acid. After a further hour's heating and stirring the mixture was steam-distilled. Distillation of the dried ($MgSO_4$) and washed (water) ethereal extract of the distillate gave only unchanged acetylenic ketone. The same result was obtained when the amount of mercuric oxide was increased, the reaction time extended (10 hr.), or the solution made homogeneous with ethanol.

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