The Synthesis and Reactions of Branched-chain Hydrocarbons. Part VIII. The Pinacol Rearrangement of an Aliphatic Tetraol.*

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An attempted preparation of 2 : 3 : 6 : 7-tetramethyloctane-2 : 3 : 6 : 7-tetraol is described, together with the preparation and pinacol rearrangement of 2 : 3 : 8 : 9-tetramethyldecane-2 : 3 : 8 : 9-tetraol.

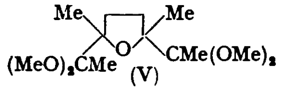
Saturated aliphatic tetratertiary diglycols [*e.g.*, (I)] have not been previously prepared. An attempt was made to obtain 2 : 3 : 6 : 7-tetramethyloctane-2 : 3 : 6 : 7-tetraol (I; $n =$ 2) from 3 : 6-dimethylocta-1 : 7-diyne-3 : 6-diol (II) (Milas, Brown, and Phillips, *J. Amer. Chem. Soc.*, 1948, **70**, 2862) by the method of Hickinbottom, Hyatt, and Sparke (*J.*, 1954, 2529, 2533). Hydration of this compound did not yield the desired diketol but gave instead 2 : 5-diacetyltetrahydro-2 : 5-dimethylfuran (IV) whose structure was shown by its formation when the diethynylfuran (III) (Milas, Brown, and Phillips, *loc. cit.*) was hydrated with mercuric sulphate in aqueous sulphuric acid. In an attempt to avoid furan formation the addition of methyl alcohol to 3 : 6-dimethylocta-1 : 7-diyne-3 : 6-diol (II) under catalysis by boron trifluoride was investigated. This reaction however gave a mixture of the required diol (VI) and the furan derivative (V). The latter was also obtained by the addition of methyl alcohol to the diacetylene (III) in presence of boron trifluoride. Both of these ketals on hydrolysis with dilute acid gave 2 : 5-diacetyltetrahydro-2 : 5-dimethylfuran (IV).

(I) $HO{\cdot}CMe_2{\cdot}CMe(OH){\cdot}[CH_2]_n{\cdot}CMe(OH){\cdot}CMe_2{\cdot}OH$

$[HC{\equiv}C{\cdot}CMe(OH){\cdot}CH_2{\cdot}]_2$ (II)


(III)


(IV)


(V)

An alternative route to 2 : 3 : 6 : 7-tetramethyloctane-2 : 3 : 6 : 7-tetraol that would minimise the possibility of furan formation is hydrogenation of 2 : 3 : 6 : 7-tetramethyloct-4-yne-2 : 3 : 6 : 7-tetraol. The latter compound could not be prepared either by reaction

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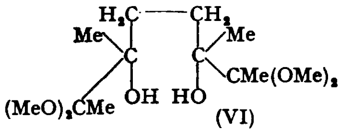
of acetylene with 3-hydroxy-3-methylbutan-2-one (Favorski and Onischenko, *J. Gen. Chem. U.S.S.R.*, 1941, **11**, 1111) or by condensation of 2 : 3-dimethylpent-4-yne-2 : 3-diol (Ansell, Hickinbottom, and Hyatt, *J.*, 1955, 1592) with 3-hydroxy-3-methylbutan-2-one in the presence of sodamide in liquid ammonia.


(VI)

$HO\cdot CMe_2\cdot CMe(OH)\cdot C\equiv CH$ (VII)

$[HO\cdot CMe_2\cdot CMe(OH)\cdot C\equiv C\cdot]_2$ (VIII)

$(Me\cdot CO\cdot CMe_2\cdot CH_2\cdot CH_2\cdot)_2$ (IX)

Attention was then directed to the synthesis of 2 : 3 : 8 : 9-tetramethyldecane-2 : 3 : 8 : 9-tetraol (I; *n* = 4). It was found that 2 : 3-dimethylpent-4-yne-2 : 3-diol (VII) (Ansell *et al.*, *loc. cit.*) undergoes oxidative dimerisation with oxygen in the presence of cuprous chloride–ammonium chloride solution to produce 2 : 3 : 8 : 9-tetramethyldeca-4 : 6-diyne-2 : 3 : 8 : 9-tetraol (VIII) in good yield (cf. Zal'kind and Aizikovitch, *J. Gen. Chem. U.S.S.R.*, 1937, **7**, 227). The latter was obtained in *meso*- and racemic forms. It was readily hydrogenated to the *meso*- and racemic forms of 2 : 3 : 8 : 9-tetramethyldecane-2 : 3 : 8 : 9-tetraol (I; *n* = 4), the structure of which was established by oxidation to octane-2 : 6-dione and acetone. The tetraol (I; *n* = 4) rearranges on dissolution in concentrated sulphuric acid at −10° and subsequent dilution, to give 3 : 3 : 8 : 8-tetramethyldecane-2 : 9-dione (IX). The structure of the dione was established by its non-identity with 2 : 2 : 9 : 9-tetramethyldecane-3 : 8-dione (Fuson and Robinson, *J. Amer. Chem. Soc.*, 1940, **62**, 358) which is a possible product of the rearrangement, and by its oxidation to 2 : 2 : 7 : 7-tetramethylsuberic acid.

The formation of the dione (IX) is the first recorded example, as far as we are aware, of a tetraol undergoing two simultaneous pinacol–pinacolone rearrangements.

EXPERIMENTAL

Hydration of 3 : 6-*Dimethylocta*-1 : 7-*diyne*-3 : 6-*diol*.—The diyne (83 g.) (Milas, Brown, and Phillips, *loc. cit.*) was added in small portions during 1 hr. to a stirred, boiling solution of mercuric oxide (4·5 g.) in 10% sulphuric acid (300 c.c.). After a further hour's heating and stirring the mixture was steam-distilled. The upper layer of the distillate, combined with the ethereal extracts of the lower layer, was washed with water, dried ($MgSO_4$), and distilled, yielding 2 : 5-*di-acetyltetrahydro*-2 : 5-*dimethylfuran* (22·5 g.), b. p. 87—88°/2 mm., n_D^{20} 1·4506 (Found : C, 65·5; H, 8·7. $C_{10}H_{16}O_3$ requires 65·2; H, 8·7%). Its *bis*-2 : 4-*dinitrophenylhydrazone*, yellow needles from pyridine, has m. p. 212° (Found : C, 48·5; H, 4·3; N, 20·4. $C_{22}H_{24}O_9N_8$ requires C, 48·5; H, 4·4; N, 20·5%), and its *disemicarbazone* (purified by boiling with ether and benzene), m. p. 214° (Found : C, 48·5; H, 7·4; N, 28·0. $C_{12}H_{22}O_3N_6$ requires C, 48·3; H, 7·4; N, 28·2%).

2 : 5-*Diethynyl- and* 2 : 5-*Diacetyltetrahydro*-2 : 5-*dimethylfuran*.—3 : 6-Dimethylocta-1 : 7-diyne-3 : 6-diol (10 g.) was heated at 80° with 10% sulphuric acid (50 c.c.) for 2 hr. After cooling, the organic material was extracted with ether and washed with water. Distillation of the dried ($MgSO_4$) ethereal extract gave 2 : 5-diethynyltetrahydro-2 : 5-dimethylfuran, b. p. 62—64°/17 mm., n_D^{20} 1·4559 (Found : C, 80·9; H, 8·4. Calc. for $C_{10}H_{12}O$: C, 81·0; H, 8·2%). Milas, Brown, and Phillips, (*loc. cit.*) record b. p. 63·5—65°/28 mm., n_D^{20} 1·4790. Hydration of this diyne as for 3 : 6-dimethylocta-1 : 7-diyne-3 : 6-diol gave 2 : 5-diacetyltetrahydro-2 : 5-dimethylfuran, b. p. 55°/0·5 mm., n_D^{20} 1·4490.

2:2:7:7-*Tetramethoxy*-3:6-*dimethyloctan*-3:6-*diol and* 2:5-*Di*-(1:1-*dimethoxyethyl*)*tetrahydro*-2 : 5-*dimethylfuran*.—A mixture of mercuric oxide (5 g.), boron trifluoride–ether complex (5 c.c.) (Hennion, Hinton, and Nieuwland, *J. Amer. Chem. Soc.*, 1933, **55**, 2857), dry methanol (5 c.c.), and trichloroacetic acid (1 g.) was heated for 1 min., and then dry methanol (200 g.) was added. To this stirred solution was added 3 : 6-dimethylocta-1 : 7-diyne-3 : 6-diol (112 g.) in dry methanol (300 g.) at such a rate that the temperature was kept at 45—55°. After further stirring (3 hr.) anhydrous potassium carbonate (10 g.) was added, and the mixture kept overnight. The supernatant liquid was decanted off, excess of methanol removed, and the residue distilled, yielding, with a small fore-run and intermediate cuts : (*a*) 2 : 5-*di*-(1 : 1-*dimethoxyethyl*)*tetrahydro*-2 : 5-*dimethylfuran* (87·0 g.), b. p. 62°/1·2 mm., m. p. 42° (after vacuum-sublimation) (Found : C, 60·6; H, 10·5; active H, 0. $C_{14}H_{28}O_5$ requires C, 60·8; H, 10·2%), also obtained from the diacetylenic furan by the same procedure; (*b*) 2 : 2 : 7 : 7-*tetramethoxy*-3 : 6-*dimethyloctane*-3 : 6-*diol* (88·3 g.), b. p. 92°/0·7 mm., n_D^{20} 1·4635 (Found: C, 57·3; H, 10·1; active H, 0·61. $C_{14}H_{30}O_6$ requires C, 57·1; H, 10·3; active H, 0·68%).

Hydrolysis of either ketal by shaking it with excess of cold 2% sulphuric acid gave 2 : 5-diacetyltetrahydro-2 : 5-dimethylfuran, identified by comparison of its derivatives with those prepared above.

Attempted Preparation of 2:3:6:7-*Tetramethyloct*-4-*yne*-2:3:6:7-*tetraol*.—(*a*) (cf. Favorski and Onischenko, *loc. cit.*). Acetylene was passed into an ice-cold stirred suspension of potassium hydroxide flakes (84 g.) in dry ether (800 c.c.). After 20 min. 3-hydroxy-3-methylbutan-2-one (51 g.) was added during ½ hr. Passage of acetylene was continued for a further 6 hr., and the mixture left overnight. Water was then added to the cold mixture to dissolve the solid, and the ether layer was separated and combined with the ethereal extract of the aqueous layer. The combined extracts were saturated with carbon dioxide, and the precipitated solid was filtered off. After drying ($MgSO_4$), the ether was removed and the residue distilled, yielding 3-hydroxy-3-methylbutan-2-one (18 g.) (collected in cold traps) and 2 : 3-dimethylpent-4-yne-2 : 3-diol (23 g.), b. p. 55—56°/0·9 mm., n_D^{20} 1·4620. The residue, a viscous liquid did not solidify, was unsaturated, and was assumed to be mainly condensation products of the ketol.

(*b*) 2 : 3-Dimethylpent-4-yne-2 : 3-diol (128 g., 1 mole) was added during ½ hr. to a well-stirred suspension of sodamide (4 moles) in liquid ammonia (2 l.). After 1 hr. 3-hydroxy-3-methylbutan-2-one (102 g., 1 mole) was added slowly. One hour later, ammonium chloride (250 g.) was added and stirring continued for a further hour. The ammonia was allowed to evaporate overnight, and then water (2 l.) was added. The organic layer was separated and combined with the ethereal extract of the aqueous layer. After drying ($MgSO_4$), the solvent was removed, and the residue distilled, yielding both starting materials unchanged. The same result was obtained with lithium or sodium amide in boiling ether or benzene.

2 : 3 : 8 : 9-*Tetramethyldeca*-4 : 6-*diyne*-2 : 3 : 8 : 9-*tetraol*.—A slow stream of oxygen was passed through a solution of 2 : 3-dimethylpent-4-yne-2 : 3-diol (64 g.) (Ansell *et al.*, *loc. cit.*), cuprous chloride (48 g.), and ammonium chloride (144 g.) in water (600 c.c.) for 24 hr. After removal of the precipitate, passage of oxygen was continued until no further solid was deposited. The combined solids were washed with water, dried *in vacuo*, and dissolved in ethyl acetate by Soxhlet extraction. Evaporation of the extract gave 2 : 3 : 8 : 9-tetramethyl-4 : 6-diyne-2 : 3 : 8 : 9-tetraol (51 g.), m. p. 116—119°, which was purified by washing it with boiling ether and crystallising it from ethyl acetate. The first crop had m. p. 130·5° after recrystallisation. The more soluble material had m. p. 114° after repeated crystallisation from ethyl acetate–light petroleum (b. p. 60—80°). Mixtures of the two fractions melted between 114° and 130·5°. This separation of *meso*- and racemic forms was not pursued; the final purification was effected by recrystallisation of the combined material from ethyl acetate and light petroleum mixtures. The pure material was obtained as cubic crystals, soluble in ethanol or hot water and insoluble n ether, benzene, or light petroleum (Found: C, 62·8; H, 8·8; active H, 1·78%; *M*, 253. Calc. for $C_{14}H_{22}O_4$: C, 66·1; H, 8·7; active H, 1·59%; *M*, 254). A better analysis could not be obtained.

2 : 3 : 8 : 9-*Tetramethyldecane*-2 : 3 : 8 : 9-*tetraol*. The above diyne (38·1 g.) in ethanol (300 c.c.) was hydrogenated at 50 lb. per sq. in., in the presence of Adams catalyst (0·5 g.) (8 hr.). The precipitate was filtered off, washed with ethanol, and dried. Its m. p. (180°) was raised to 185° after removal of the catalyst and repeated crystallisation from ethanol. Evaporation of the initial filtrate gave a solid of m. p. 140° which was 139—140° after recrystallisation from ethanol–light petroleum (b. p. 60—80°). These two solids are the *meso*- and the racemic form of 2 : 3 : 8 : 9-tetramethyldecane-2 : 3 : 8 : 9-tetraol. Final purification was effected by recrystallising the combined fractions from ethanol–light petroleum (Found: C, 64·0; H, 11·3%; *M*, 228. Calc. for $C_{14}H_{30}O_4$: C, 64·1; H, 11·5%; *M*, 262).

Oxidative Fission of 2 : 3 : 8 : 9-*Tetramethyldecane*-2 : 3 : 8 : 9-*tetraol*.—Periodic acid (3 g.) was added to a solution of the above tetraol (3 g.) in water (20 c.c.) and methanol (5 c.c.), and the mixture shaken for 4 hr. Air was then aspirated for 3 hr. through the solution into a trap containing a warm solution of 2 : 4-dinitrophenylhydrazine in aqueous-alcoholic sulphuric acid. The precipitated acetone 2 : 4-dinitrophenylhydrazone had m. p. and mixed m. p. 125° after recrystallisation from ethanol. The remainder of oxidation product was extracted with ether, the extract evaporated, and the residue treated with 2 : 4-dinitrophenylhydrazine in aqueous-alcoholic sulphuric acid, yielding octane-2 : 7-dione 2 : 4-dinitrophenylhydrazone as orange needles, m. p. 218—219° after recrystallisation from ethanol. Shimizu (*J. Agr. Chem. Soc. Japan*, 1950, **23**, 288) records m. p. 219°.

Rearrangement of 2 : 3 : 8 : 9-*Tetramethyldecane*-2 : 3 : 8 : 9-*tetraol*.—The above tetraol (30 g.) was added during 1 hr. to concentrated sulphuric acid (600 g.) at between −5° and −10°. After a further 3 hours' stirring, the mixture was poured on ice (2 kg.). The precipitated solid was filtered off and the filtrate extracted with ether. The combined organic material was washed with water and dried ($MgSO_4$) and the ether evaporated, yielding pale yellow crystals (22·3 g.) which were dissolved in light petroleum (b. p. 40—60°) and passed through a 6-in. column of activated alumina. Evaporation of the solvent gave colourless crystals (20·8 g.). Recrystallisation from light petroleum (b. p. <40°) gave 3 : 3 : 8 : 8-*tetramethyldecane*-2 : 9-*dione*, m. p. 63° (Found: C, 74·2; H, 11·3%; *M*, 193. $C_{14}H_{26}O_2$ requires C, 74·3; H, 11·6%; *M*, 226). Its *disemicarbazone*, colourless needles from ethanol, had m. p. 228 (Found: C, 56·2; H, 9·6; N, 24·7. $C_{16}H_{32}O_2N_6$ requires C, 56·4; H, 9·5; N, 24·7%), and the *bis*-2 : 4-*dinitrophenylhydrazone*, orange-yellow needles from benzene–light petroleum (b. p. 60—80°), had m. p. 204° (Found: C, 53·2; H, 5·8; N, 19·3. $C_{26}H_{34}O_8N_8$ requires C, 53·2; H, 5·8; N, 19·1%) [cf. 2 : 2 : 9 : 9-tetramethyldecane-3 : 8-dione, m. p. 52—52·5° (bis-2 : 4-dinitrophenylhydrazone, m. p. 251—252°) (Fuson and Robinson, *loc. cit.*)].

Oxidation of 3 : 3 : 8 : 8-*Tetramethyldecane*-2 : 9-*dione*.—A well-stirred mixture of the above dione (3 g.), nitric acid (25 c.c.; *d* 1·42), and water (25 c.c.) was heated under reflux for 8 hr., then cooled, the precipitate filtered off, and the filtrate extracted with ether. The combined organic material was extracted repeatedly with aqueous sodium carbonate. After acidification with 5N-sulphuric acid, the solid was extracted with ether, washed with water, and dried ($MgSO_4$). The residue obtained on evaporation of the ether recrystallised from ethyl acetate, yielding 2 : 2 : 7 : 7-tetramethylsuberic acid, m. p. 185—186° (Found: C, 62·6; H, 9·4%; equiv., 110. Calc. for $C_{12}H_{22}O_4$: C, 62·6; H, 9·6%; equiv., 115). Adams and Anderson (*J. Amer. Chem. Soc.*, 1951, **73**, 136) record m. p. 179—181°.

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