229. *Reduced Cyclic Compounds. Part III.* The Preparation and Cyclodehydration of Some Unsaturated Tertiary Alcohols.*

By M. F. Ansell and (the late) M. E. Selleck.

Preparations are reported of 2-methyloct-6-en-2-ol, 2-methyldodeca-6 : 10-dien-2-ol, and 2-methylhexadeca-6 : 10 : 14-trien-2-ol. These have been subjected to cyclodehydration with phosphoric acid.

In Part I of this series [1] the preparations of two ω-phenyl unsaturated tertiary alcohols were reported and it was stated that the same synthetical route, namely consecutive chain extensions with 1 : 2-dichlorotetrahydro-furan or -pyran, was applicable to completely aliphatic compounds. This has now been substantiated by the preparation of the unsaturated tertiary alcohols (I), (VII), and (XIII). The cyclodehydration of these alcohols to the reduced monocyclic, bicyclic and tricyclic compounds (II), (VIII), and (XIV) is reported.

trans-2-Methyloct-6-en-1-ol (I) was prepared from *trans*-hex-4-en-1-ol,[2] by reaction of the Grignard reagent from the derived bromide with acetone. Treatment of this alcohol with hot 85% phosphoric acid (cf. ref. 3) gave a 46% yield of substantially monocyclic material (from analysis and catalytic hydrogenation). Of the products to be expected, on the basis of the accepted mechanism [4,5] for such reactions, namely, 2 : 3 : 3- (II) and 3 : 4 : 4-trimethyl*cyclo*hexene (III), the former has been previously prepared [6,7] and was found to be a product of this cyclisation. It was identified by the preparation of its nitrosochloride and by ozonolysis to 5 : 5-dimethyl-6-oxoheptanoic acid (isolated as the semicarbazone). This conclusion is supported by the infrared spectrum of the product which had bands at 5·97 and 12·50 μ (trisubstituted double bond [5]); bands due to *cis*-$\mathrm{CH{=}CH}$ and $\mathrm{C{=}CH_2}$ were not detectable and therefore 3 : 4 : 4-trimethyl*cyclo*hexene must be the predominant product of the cyclisation.

The cyclisation product may contain a little 2-methylocta-2 : 6-diene obtained by dehydration of the alcohol (I), as in one ozonolysis experiment a small amount of succinic acid was isolated, possibly together with a small amount of 3 : 4 : 4-trimethyl*cyclo*hexene. This result is similar to that of Openlander and Day [5] who showed that, contrary to earlier reports,[8] cyclodehydration of 3 : 7-dimethyloct-6-en-3-ol (IV) yields predominantly 1 : 2 : 3 : 3-tetramethyl*cyclo*hexene together with a little 2 : 3 : 4 : 4-tetramethyl*cyclo*hexene.

2-Methyldodeca-6 : 10-dien-2-ol (VII), the precursor of a bicyclic system, was then prepared. 3-Chlorotetrahydro-2-(pent-3-enyl)pyran (V) obtained from 5-bromopent-2-ene [2] and 2 : 3-dichlorotetrahydropyran, gave, on treatment with sodium, deca-4 : 8-dien-1-ol (VI). Conversion of the latter into 2-methyldodeca-6 : 10-dien-2-ol (VII) was accomplished by reaction of acetone with the Grignard reagent derived from the corresponding bromide. The tertiary alcohol (VII) was not stereochemically pure, being from

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* Part II, *J.*, 1956, 4518.

[1] Ansell and Selleck, *J.*, 1956, 1238.

[2] Crombie and Harper, *J.*, 1950, (*a*) 1707, (*b*) 1714.

[3] Linstead, *J.*, 1936, 474.

[4] Stork and Burgstahler, *J. Amer. Chem. Soc.*, 1955, **77**, 5068.

[5] Openlander and Day, *J. Org. Chem.*, 1956, **21**, 961.

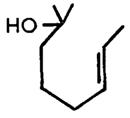
[6] Auwers and Lange, *Annalen*, 1915, **409**, 174.

[7] Godchot and Bedos, *Comp. rend.*, 1925, **181**, 920.

[8] Dupont and Dulou, *ibid.*, 1935, **201**, 219; Escourrou, *Bull. Soc. chim. France*, 1926, **39**, 1126, 1460.

its method of preparation a mixture of 6 : 7-*trans*-10 : 11-*cis*-isomer and the all-*trans*-isomer, with the latter predominating. Treatment of the tertiary alcohol (VII) with hot 85% phosphoric acid gave a mixture of octahydro-1 : 1 : 5-trimethylnaphthalenes (VIII) in which the position of the double bond is uncertain.

For the preparation of a phenanthrene derivative 2-methylhexadeca-6 : 10 : 14-trien-2-ol (XIII) was prepared. Ring scission of 3-chlorotetrahydro-2-(pent-3-enyl)furan (IX), from 5-bromopent-2-ene and 2 : 3-dichlorotetrahydrofuran, gave nona-3 : 7-dien-1-ol (X). Application of the chain-extension procedure with 2 : 3-dichlorotetrahydropyran gave the chloride (XI) and thence tetradeca-4 : 8 : 12-trien-1-ol (XII) which was converted in two stages into the required tertiary alcohol (XIII). This alcohol is not stereochemically pure: the 6 : 7-double bond is *trans*, but the 10 : 11- and 14 : 15-double bonds arise from the non-stereospecific ring scission of furan derivatives. Treatment of the alcohol (XIII) with hot 85% phosphoric acid gave a mixture of dodecahydro-1 : 1 : 8-trimethylphenanthrenes (XIV) in which the position of the double bond is uncertain. The structure of the product was confirmed by hydrogenation (one double bond) and dehydrogenation to 1 : 8-dimethylphenanthrene (XV).



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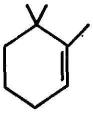

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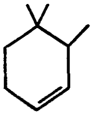

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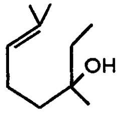

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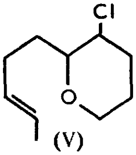

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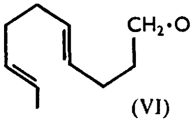

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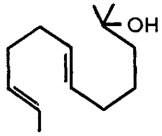

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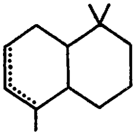

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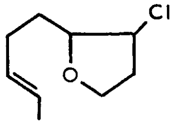

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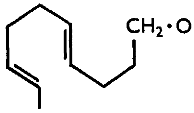

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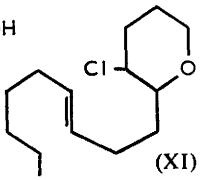

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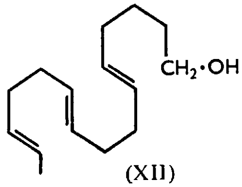

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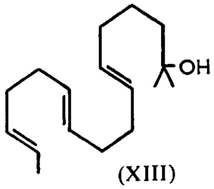

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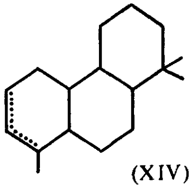

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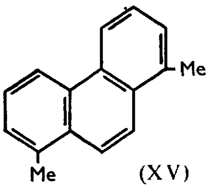

(XV)

The above method for the conversion of long-chain unsaturated alcohols into reduced cyclic systems is limited by the uncertainty as to the final position of the double bond, and also, in the polycyclic cases, the stereochemistry of the product.

EXPERIMENTAL

trans-6-*Bromohex-2-ene*.—This bromide, prepared as previously described,[1] had b. p. 42°/12 mm., n_D^{20} 1·4690 (a redistilled fraction had n_D^{20} 1·4695) (Found: C, 44·1; H, 6·95; Br, 48·95. Calc. for $C_6H_{11}Br$: C, 44·2; H, 6·75; Br, 49·1%). It gave a *thiuronium picrate*, yellow plates (from ethanol), m. p. 152—153° (Found: N, 18·1. $C_{13}H_{17}N_5O_7S$ requires N, 18·1%).

trans-2-*Methyloct-6-en-2-ol*.—The Grignard reagent from the above bromide (0·6 mole) was treated with acetone as in the preparation of 2-methyl-9-phenylnon-6-en-2-ol.[10] Distillation gave 2-*methyloct-6-en-2-ol* (69%), b. p. 82—83°/14 mm., n_D^{20} 1·4444 (Found: C, 76·5; H, 12·9.

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[9] Ansell and Brown, *J.*, 1957, 1788.

[10] Crossley and Renouf, *J.*, 1911, **99**, 1111.

$C_9H_{18}O$ requires C, 76·1; H, 12·7%). In one preparation dehydration occurred during the distillation, to yield 2-*methylhexa*-2 : 6-*diene*, b. p. 144°, $n_{\rm D}^{20}$ 1·4384 (Found: C, 87·0; H, 13·1. C_9H_{16} requires C, 87·1; H, 12·9%).

Cyclodehydration of trans-2-*Methyloct*-6-*en*-2-*ol*.—A stirred mixture of the above alcohol (30 g.) and 85% phosphoric acid (140 ml.) was heated at 100° for 1 hr., cooled, poured into water, and extracted with ether. The extract was washed with water, then sodium hydrogen carbonate solution, and dried (K_2CO_3). After removal of the ether, the residue was refluxed over sodium and distilled. The 2 : 3 : 3-trimethyl*cyclo*hexene fraction (12 g., 46%), b. p. 143—146°, $n_{\rm D}^{20}$ 1·4502—1·4540 was collected (Found: C, 87·1; H, 13·2. Calc. for C_9H_{16}: C, 87·1; H, 12·9%). Auwers and Lange [6] record b. p. 146·2—147·2°, $n_{\rm D}^{20\cdot4}$ 1·456; Godchot and Bedos [7] record b. p. 144—146°, $n_{\rm D}^{14}$ 1·4590. Hydrogen uptake at atmospheric pressure in presence of Adams catalyst was equivalent to 1·1 double bonds.

A mixture of this hydrocarbon (1 g.), glacial acetic acid (1 ml.), and pentyl nitrite (2 ml.) was cooled in ice, and a mixture of 10N-hydrochloric acid (2 ml.) and glacial acetic acid (0·5 ml.) added slowly with shaking. After 3 hr. at 0°, with intermittent shaking, the precipitated nitrosochloride (0·1 g.) was filtered off, and after being washed thoroughly with alcohol and acetone and dried, had m. p. 133—134° (rapid heating). Auwers and Lange [6] record the nitrosochloride of 2 : 3 : 3-trimethyl*cyclo*hexene as having m. p. 133—134° (rapid heating).

Ozonolysis. A solution of the cyclisation product (2 g.) in acetic acid (5 ml.) was treated with ozonised air for 12 hr. Water (5 ml.) and 30% hydrogen peroxide (3 ml.) were then added and the solution was boiled for 30 min. The cold solution was extracted (continuously) with ether, and the ethereal solution extracted with 10% sodium hydroxide solution. After being acidified the aqueous solution was extracted with ether. The residue obtained on evaporation of the dried ($MgSO_4$) extract was boiled for 30 min. with a solution of semicarbazide hydrochloride (0·6 g.) and pyridine (0·6 ml.) in alcohol (2 ml.). The residue obtained on evaporation of this solution partly solidified and was filtered off, washed with a little alcohol, and recrystallised from alcohol, to yield the semicarbazone of 5 : 5-dimethyl-6-oxoheptanoic acid, m. p. 169—171° (Found: N, 18·2. Calc. for $C_{10}H_{19}O_3N$: N, 18·3%). Auwers and Lange [6] record m. p. 167—169°. Crossley and Renouf [10] record m. p. 169°.

2 : 3 : 3-*Trimethyl*cyclo*hexane*-1 : 2-*diol*.—The cyclisation product (12·4 g.) was added to a stirred mixture of 100% formic acid (80 ml.) and 30% hydrogen peroxide (12 g.). The temperature of the mixture rose to 50°, and was then kept at 40° for 2 hr., water (200 ml.) added, and the whole was extracted with ether. After being washed with water the extract was evaporated and the residue boiled with 10% sodium hydroxide solution for 30 min., cooled, neutralised with hydrochloric acid, and extracted with ether. The extract was washed with water and sodium hydrogen carbonate solution and dried ($MgSO_4$). Distillation gave the *glycol* (2 g.), b. p. 110—120°/7—8 mm., which solidified and crystallised from light petroleum (b. p. 60—80°) in needles, m. p. 115—116° (Found: C, 68·3; H, 11·6. $C_9H_{18}O$ requires C, 68·4; H, 11·4%).

It was not possible to repeat this reaction.

3-*Chlorotetrahydro*-2-(*pent*-3-*enyl*)*pyran*.—A solution of 2 : 3-dichlorotetrahydropyran [2a] (from 57 g. of dihydropyran) in ether (100 ml.) was treated with the Grignard reagent from 5-bromopent-2-ene [2b] (149 g.) as in the preparation of 3-chlorotetrahydrophenethylfuran.[1] Distillation gave 3-*chlorotetrahydro*-2-(*pent*-3-*enyl*)*pyran* (63 g., 43·5%), b. p. 123—140°/19 mm., $n_{\rm D}^{20}$ 1·4758—1·4793 (Found: C, 63·6; H, 9·2. $C_{10}H_{17}OCl$ requires C, 63·7; H, 9·0%).

Deca-4 : 8-*dien*-1-*ol*.—3-Chlorotetrahydro-2-(pent-4-enyl)pyran was subjected to ring scission with sodium as in the preparation of 7-phenylhept-4-en-1-ol.[1] Distillation gave *deca*-4 : 8-*dien*-1-*ol* (78%) b. p. 124—126°/17 mm., $n_{\rm D}^{20}$ 1·4654 (Found: C, 77·8; H, 11·8. $C_{10}H_{18}O$ requires C, 77·9; H, 11·7%). The derived 3 : 5-*dinitrobenzoate*, plates from light petroleum (b. p. <40°), had m. p. 43—45° (Found: C, 58·3; H, 5·9; N, 8·2. $C_{17}H_{20}O_6N_2$ requires C, 58·6; H, 5·75; N, 8·05%).

10-*Bromodeca*-2 : 6-*diene*.—A mixture of deca-4 : 8-dien-1-ol (40 g.) and pyridine (6 ml.) was added dropwise with stirring to phosphorus tribromide (28 g.) with ice-cooling. The subsequent procedure was as for 6-bromohex-2-ene.[9] The final distillation gave 10-*bromodeca*-2 : 6-*diene* (36 g., 64%), b. p. 114—116°/10 mm., $n_{\rm D}^{20}$ 1·4845 (Found: C, 55·7; H, 8·0. $C_{10}H_{17}Br$ requires C, 55·3; H, 7·8%); the *thiuronium picrate* had m. p. 130—131° (from ethanol) (Found: N, 15·7. $C_{17}H_{23}O_5N_7S$ requires N, 15·9%).

2-*Methyldodeca*-6 : 10-*dien*-2-*ol*.—This alcohol was prepared from the Grignard reagent of 10-bromodeca-2 : 6-diene and acetone as in the preparation of 2-methyl-9-phenylnon-6-en-2-ol.[1]

Distillation gave 2-*methyldodeca*-6 : 10-*dien*-2-*ol* (29%), b. p. 131—135°/14 mm., n_D^{20} 1·4640 (Found: C, 79·3; H, 12·2. $C_{13}H_{24}O$ requires C, 79·6; H, 12·2%).

Cyclodehydration of 2-*Methyldodeca*-6 : 10-*dien*-2-*ol*.—A stirred mixture of the alcohol (8 g.) and 85% phosphoric acid (50 ml.) was heated at 140° for 1 hr. The subsequent procedure was as for the cyclodehydration of 2-methyloct-6-en-2-ol. Distillation gave octahydro-1 : 1 : 5-trimethylnaphthalene (4 g., 55%), b. p. 100—106°/15 mm., n_D^{20} 1·4803—1·4810 (Found: C, 87·4; H, 12·6. $C_{13}H_{22}$ requires C, 87·6; H, 12·4%). Hydrogen uptake at atmospheric pressure in presence of Adams catalyst was equivalent to 1·01 double bonds.

3-*Chlorotetrahydro*-2-(*pent*-3-*enyl*)*furan*.—2 : 3-Dichlorotetrahydrofuran (0·62 mole) was coupled with the Grignard reagent prepared from 5-bromopent-2-ene [2b] (1 mole) as in the preparation of 3-chlorotetrahydro-2-phenethylfuran.[1] Distillation gave, after elimination of low-boiling material (pent-3-ene), 3-*chlorotetrahydro*-2-(*pent*-3-*enyl*)*furan* (61·5%), b. p. 90—105°/9—11 mm. n_D^{20} 1·4705—1·4745 (Found: C, 61·8; H, 8·8; Cl, 20·0. $C_9H_{15}OCl$ requires C, 62·1; H, 8·6; Cl, 20·4%).

Nona-3 : 7-*dien*-1-*ol*.—Ring scission of 3-chlorotetrahydro-2-(pent-3-enyl)furan with sodium was effected as for the pyran. Distillation gave *nona*-3 : 7-*dien*-1-*ol* (81%), b. p. 98—100°/11 mm., n_D^{20} 1·4657—1·4663 (Found: C, 77·4; H, 11·6. $C_9H_{16}O$ requires C, 77·1; H, 11·4%).

9-*Bromonona*-2 : 6-*diene*.—A mixture of nona-3 : 7-dien-1-ol (40 g.) and pyridine (3 ml.) was added dropwise with stirring to phosphorus tribromide with ice cooling. The subsequent procedure was as for 6-bromohex-2-ene. The final distillation gave 9-*bromonona*-2 : 6-*diene* (33 g., 56·5%), b. p. 86—88°/7—8 mm., n_D^{20} 1·4872 (Found: C, 53·9; H, 7·4; Br, 39·4. $C_9H_{15}Br$ requires C, 53·2; H, 7·4; Br, 39·4%).

9-*Chloronona*-2 : 6-*diene*.—Pure thionyl chloride (225 g.) was added slowly to a stirred mixture of nona-3 : 7-dien-1-ol (212 g.) and pyridine (0·75 ml.), the internal temperature being kept below 20°. The mixture was then slowly heated to boiling and maintained under reflux for 2 hr. It was then cooled, 100% formic acid (20 g.) added slowly, and then the whole was heated under reflux for 30 min., cooled, and poured into saturated brine. The organic layer was separated and the aqueous layer extracted with ether. The combined organic material was washed with 10% sodium hydrogen carbonate solution and water and dried ($MgSO_4$). Distillation gave, after removal of the solvent, 9-*chloronona*-2 : 6-*diene* (192 g., 79·5%), b. p. 86—88°/14 mm., n_D^{20} 1·4668 (Found: C, 68·3; H, 9·5; Cl, 22·7. $C_9H_{15}Cl$ requires C, 68·1; H, 9·5; Cl, 22·4%).

Tetradeca-4 : 8 : 12-*trien*-1-*ol*.—The Grignard reagent from 9-chloronona-2 : 6-diene (1·15 moles) was coupled with 2 : 3-dichlorotetrahydropyran (from 76 g., 0·9 mole, of 2 : 3-dihydropyran) as in the preparation of 3-chlorotetrahydro-2-phenethylpyran.[1] Distillation gave crude 3-chlorotetrahydro-2-(nona-3 : 7-dienyl)pyran (160 g.), b. p. 75—120°/10^{-3} mm., which was not further purified but was subjected to ring scission with sodium as for 3-chlorotetrahydro-2-phenethylpyran.[1] Distillation gave *tetradeca*-4 : 8 : 12-*trien*-1-*ol* (33·5% calc. on chloride), b. p. 100—104°/10^{-3} mm., n_D^{20} 1·4797—1·4801 (Found: C, 81·1; H, 11·5. $C_{14}H_{24}O$ requires C, 80·8; H, 11·5%).

14-*Chlorotetradeca*-2 : 6 : 10-*triene*.—The preceding alcohol (76 g.) was treated with thionyl chloride (66 g.) and pyridine (0·2 ml.) and then formic acid (16 g.) as in the preparation of 9-chloronona-2 : 6-diene. Distillation gave 14-*chlorotetradeca*-2 : 6 : 10-*triene* (57 g., 68·5%), b. p. 98—102°/5 × 10^{-3} mm., n_D^{20} 1·4785—1·4795 (Found: C, 73·9; H, 10·4; Cl, 15·1. $C_{14}H_{23}Cl$ requires C, 74·2; H, 10·15; Cl, 15·7%).

2-*Methylhexadeca*-6 : 10 : 14-*trien*-2-*ol*.—The Grignard reagent from 14-chlorotetradeca-2 : 6 : 10-triene (0·24 mole) was treated with acetone as in the preparation of 2-methyl-9-phenylnon-6-en-2-ol.[10] Distillation gave 2-*methylhexadeca*-6 : 10 : 14-*trien*-2-*ol* (33 g., 49·5%), b. p. 108—110°/10^{-3} mm., n_D^{20} 1·4763—1·4768 (Found: C, 81·5; H, 12·2. $C_{17}H_{30}O$ requires C, 81·6; H, 12·0%).

Cyclodehydration of 2-*Methylhexadeca*-6 : 10 : 14-*trien*-2-*ol*.—A stirred mixture of preceding alcohol (31 g.) and 85% phosphoric acid (200 ml.) was heated at 140° for 1 hr. and then worked up as in the preceding cyclisations. Distillation from sodium gave a mixture of 1 : 1 : 8-trimethyldodecahydrophenanthrenes (21 g., 72·5%), b. p. 91—102°/10^{-3} mm. (Found: C, 87·7; H, 12·45. $C_{17}H_{28}$ requires C, 87·9; H, 12·1%). This product absorbed hydrogen equivalent to one double bond in presence of Adams catalyst at atmospheric pressure.

Dehydrogenation. A mixture of the hydrocarbon (0·5 g.) and selenium (2·5 g.) was heated in a sealed tube at 360° for 24 hr. The product was extracted with chloroform and filtered. The solid left on evaporation of the chloroform was crystallised from benzene, sublimed, and recrystallised from acetic acid. It had m. p. 185—188° not depressed on admixture with an authentic specimen [11] (m. p. 187—190°).

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[11] Robins and Walker, *J.*, 1952, 1615.