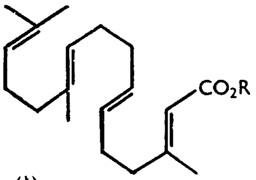
256. *Reduced Cyclic Compounds. Part I. The Preparation and Cyclodehydration of ω-Phenyl Unsaturated Tertiary Alcohols.*

By M. F. Ansell and M. E. Selleck.

The preparations are reported of 2-methyl-9-phenylnon-6-en-2-ol and 2-methyl-13-phenyltrideca-6 : 10-dien-2-ol. These have been converted into 1 : 2 : 3 : 4 : 4*a* : 9 : 10 : 10*a*-octahydro-1 : 1-dimethylphenanthrene and 1 : 2 : 3 : 4 : 4*a* : 4*b* : 5 : 6 : 10*b* : 11 : 12 : 12*a*-dodecahydro-1 : 1-dimethylchrysene respectively.

The formation of reduced cyclic systems from long-chain unsaturated compounds has been suggested as a possible biogenetic route to terpenes and steroids.[1,2] That this type of reaction is possible has been shown by Caliezi and Schinz[3] who converted the unsaturated open-chain ester (I) into the tricyclic ester (II) by treatment with formic acid containing a small amount of sulphuric acid.



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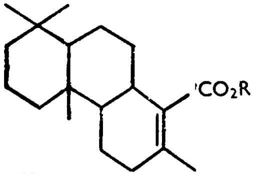

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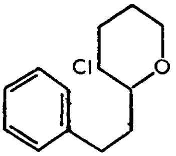

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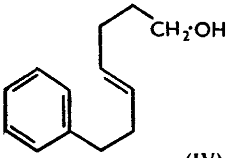

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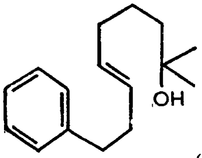

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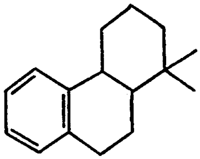
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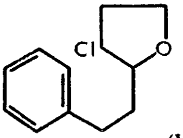

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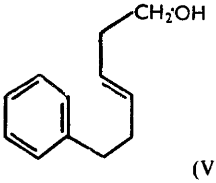

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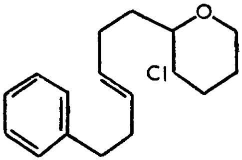

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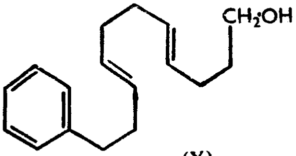

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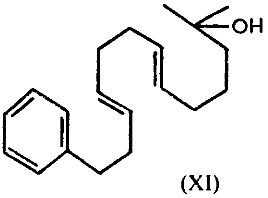

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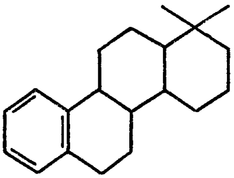
(XII)

The object of the present work was the preparation of completely synthetic unsaturated alcohols capable of undergoing cyclodehydration. For this purpose the method of chain-extension by means of 1 : 2-dichlorotetrahydro-furans or -pyrans, developed by Crombie

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[1] Woodward and Bloch, *J. Amer. Chem. Soc.*, 1953, **75**, 2023.
[2] Ruzicka, *Experientia*, 1953, **9**, 357.
[3] Caliezi and Schinz, *Helv. Chim. Acta*, 1952, **35**, 1649.

and Harper,[4] is satisfactory : a double bond may be introduced at a known position, and a terminal hydroxyl group is available for further chain-extension.

The Grignard reagent from phenethyl bromide, with 2 : 3-dichlorotetrahydropyran, gave smoothly 3-chlorotetrahydro-2-phenethylpyran (III), which on ring scission with sodium gave 7-phenylhept-4-en-1-ol (IV). Conversion of the latter into 7-phenylheptane-1 : 3 : 4-triol followed by oxidation with periodic acid gave 3-phenylpropanol. The other product of the oxidation, 4-hydroxybutanal, could not be isolated. Previous work[5] has shown this to be expected. These results confirm expected position for the double bond. Conversion of the alcohol (IV) into 2-methyl-9-phenylnon-6-en-2-ol (V) was accomplished by reaction of acetone with the Grignard reagent derived from the corresponding bromide. This compound is the *trans*-isomer as the double bond was introduced by opening a 3-chlorotetrahydropyran ring.[4a]

Treatment of the tertiary alcohol (V) with cold concentrated sulphuric acid or hot polyphosphoric acid gave 1 : 2 : 3 : 4 : 4*a* : 9 : 10 : 10*a*-octahydro-1 : 1-dimethylphenanthrene (VI). The structure of the product, which contained no ethylenic double bonds, was established by oxidation to phthalic acid, and dehydrogenation to 1-methylphenanthrene. In addition its ultraviolet spectrum had absorption maxima at 267 and 273 mμ, which are identical with those found by Askew[6] for 1 : 2 : 3 : 4 : 4*a* : 9 : 10 : 10*a*-octahydrophenanthrene.

This synthetic route was extended to the preparation of 2-methyl-13-phenyltrideca-6 : 10-dien-2-ol (XI). 3-Chlorotetrahydro-2-phenethylfuran (VII), obtained from phenethylmagnesium bromide and 2 : 3-dichlorotetrahydrofuran, on treatment with sodium gave 6-phenylhex-3-en-1-ol (VIII). Application of the chain-extension procedure then gave the chloride (IX) and thence 11-phenylundeca-4 : 8-dien-1-ol (X), which was converted in two stages into the required tertiary alcohol (XI). This product was not stereochemically pure, being, from its method of preparation, a mixture of 6 : 7-*trans*-10 : 11-*cis*- and 6 : 7-*trans*-10 : 11-*trans*-forms, the latter probably predominating.

Cyclodehydration of this substituted tridecadienol (XI) with cold sulphuric acid gave 1 : 2 : 3 : 4 : 4*a* : 4*b* : 5 : 6 : 10*b* : 11 : 12 : 12*a*-dodecahydro-1 : 1-dimethylchrysene (XII). This structure is based on the saturated nature of the product, its dehydrogenation (and demethylation) to 1-methylchrysene, and its ultraviolet absorption (max. 267 and 273 mμ) which is similar to that of 1 : 2 : 3 : 4 : 4*a* : 9 : 10 : 10*a*-octahydrophenanthrene.

The above synthetic route is applicable to the preparation of completely aliphatic compounds, and, by the use of suitable methyl-substituted dihydropyrans and dihydrofurans, to the preparation of unsaturated alcohols which on cyclodehydration will yield cyclic systems containing angular methyl groups. Both these aspects are under investigation.

EXPERIMENTAL

7-*Phenylhept*-3-*en*-1-*ol*.—A solution of 2 : 3-dichlorotetrahydropyran[4a] (from 2 : 3-dihydropyran, 45 g.) in ether (150 c.c.) was added dropwise to a stirred (Hershberg wire stirrer) solution of the Grignard reagent prepared from phenethyl bromide[7] (139 g.) and magnesium (18·5 g.) in ether (350 c.c.) at such a rate that steady refluxing was maintained. Before all the 2 : 3-dichlorotetrahydropyran had been added the reaction mixture set solid, addition was stopped, and the mixture left overnight. Excess of Grignard reagent was decomposed with ammonium chloride solution, followed by sufficient concentrated hydrochloric acid to give a clear solution. The ethereal layer was separated and the aqueous layer extracted with ether. The ether was removed from the dried (K_2CO_3) combined ether solutions and the residue distilled, giving, after elimination of lower-boiling material, a mixture of cis- and trans-3-*chlorotetrahydro*-2-*phenethylpyran* (65 g.), b. p. 74—110°/0·006 mm. (Found : C, 70·3; H, 7·7; Cl, 15·3. $C_{13}H_{17}OCl$ requires C, 69·5; H, 7·6; Cl, 15·8%).

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[4] Crombie and Harper, *J.*, 1950, (*a*) 1707, (*b*) 1714.
[5] Paul, *Compt. rend.*, 1941, **212**, 492.
[6] Askew, *J.*, 1935, 512.
[7] Slotta and Altner, *Ber.*, 1931, **64**, 1510.

7-*Phenylhept*-4-*en*-1-*ol*.—Sodium (30 g.) was powdered under xylene, then thoroughly rinsed with dry ether and covered with this solvent (250 c.c.). A little 3-chlorotetrahydro-2-phenethylpyran was added and the suspension stirred until reaction commenced, as shown by the surface of the sodium assuming an indigo-blue colour and by refluxing of the ether. The remaining 3-chlorotetrahydro-2-phenethylpyran (106 g. in all) was then added dropwise so that steady refluxing was maintained. The thick blue suspension was stirred for a further 2 hr. and then kept at room temperature overnight. Next day ice and water were cautiously added. The ether layer was separated and the aqueous layer extracted with ether. After being washed and dried (Na_2SO_4), the ether was removed from the combined extracts, and the residue was distilled, to give 7-*phenylhept*-4-*en*-1-*ol* (74 g.), b. p. 110—118°/0·7 mm., n_D^{20} 1·5237 (Found: C, 82·0; H, 9·7. $C_{13}H_{18}O$ requires C, 82·1; H, 9·5%). The 3 : 5-*dinitrobenzoate* (from light petroleum, b. p. $<40°$) had m. p. 42·5—43·5° (Found: C, 62·5; H, 5·7; N, 7·15. $C_{20}H_{20}O_6N_2$ requires C, 62·5; H, 5·2; N, 7·3%).

7-*Phenylheptane*-1 : 3 : 4-*triol*.—7-Phenylhept-4-en-1-ol (5 g.) was added to a stirred mixture of 100% formic acid (50 c.c.) and 30% hydrogen peroxide (3·5 g.). The temperature rose to 46° and was kept, by heating, at 40° for 2 hr. After cooling, the mixture was diluted with water, and the oil which separated extracted with ether. The ethereal extract was evaporated and the residue boiled with excess of 10% sodium hydroxide solution for 45 min., cooled, neutralised with hydrochloric acid, and extracted with ether. After drying ($MgSO_4$), the ethereal extract was evaporated, to give 7-*phenylheptane*-1 : 3 : 4-*triol* (0·5 g.), m. p. 82—83° after recrystallisation from benzene–light petroleum (b. p. 60—80°) (Found: C, 68·7; H, 9·1. $C_{13}H_{20}O_3$ requires C, 69·6; H, 8·9%).

Periodic acid fission. The triol (0·4 g. in methyl alcohol (5 c.c.) was shaken for 12 hr. with periodic acid (0·5 g.), then diluted with water, and extracted with ether. The residue obtained on evaporation of the ethereal solution was boiled with an aqueous-alcoholic sulphuric acid solution of 2 : 4-dinitrophenylhydrazine, yielding 3-phenylpropanal 2 : 4-dinitrophenylhydrazone as orange plates, m. p. and mixed m. p. 158° after recrystallisation from benzene–light petroleum (b. p. 60—80°) (Found: C, 57·3; H, 4·6; N, 17·9. Calc. for $C_{15}H_{14}O_4N_4$: C, 57·3; H, 4·5; N, 17·8%). Triebs [8] records m. p. 146—147°.

7-*Bromo*-1-*phenylhept*-3-*ene*.—A mixture of 7-phenylhept-4-en-1-ol (45 g.) and pyridine (6 c.c.) was added slowly with stirring to phosphorus tribromide (26 g.), with ice-cooling; after being kept overnight at room temperature the products were distilled (b. p. 110—140°/0·7 mm.) and the distillate shaken with water and then with 10% sodium carbonate solution. The organic layer, dried ($CaCl_2$) and distilled, yielded 7-*bromo*-1-*phenylhept*-3-*ene* (30 g.), b. p. 108—110°/0·37 mm., n_D^{20} 1·5382 (Found: C, 62·3; H, 6·9; Br, 31·6. $C_{13}H_{17}Br$ requires C, 61·7; H, 6·7; Br, 31·6%). The derived *thiuronium picrate* formed yellow plates (from alcohol), m. p. 162—163° (Found: C, 50·3; H, 4·8; N, 14·8. $C_{20}H_{23}O_7N_5S$ requires C, 50·3; H, 5·1; N, 15·3%).

2-*Methyl*-9-*phenylnon*-6-*en*-2-*ol*.—Acetone (7 g.) was added to a stirred solution of the Grignard reagent from 7-bromo-1-phenylhept-3-ene (28 g.) and magnesium (3 g.) in ether (60 c.c.) at such a rate that steady refluxing was maintained. Next morning excess of 10% sulphuric acid was added, the ethereal layer separated, and the aqueous layer extracted with ether. Removal of the ether from the dried (K_2CO_3) combined extracts followed by distillation of the residue gave 2-*methyl*-9-*phenylnon*-6-*en*-2-*ol* (21 g.), b. p. 110—114°/2 × 10^{-3} mm., n_D^{20} 1·5105 (Found: C, 82·3; H, 10·4. $C_{16}H_{24}O$ requires C, 82·8; H, 10·3%).

Cyclodehydration. (*a*) 2-Methyl-9-phenylnon-6-en-2-ol (4 g.) was added dropwise during 40 min. with stirring to ice-cold 90% sulphuric acid (10 c.c.). The ice-bath was removed and stirring continued for a further 2 hr. The mixture was diluted with water to 50 c.c. and extracted with ether. After being washed with water and 10% sodium carbonate solution and dried ($CaCl_2$), the ethereal extract was evaporated and the residue distilled over sodium, yielding 1 : 2 : 3 : 4 : 4a : 9 : 10 : 10a-*octahydro*-1 : 1-*dimethylphenanthrene* (1 g.), b. p. 170°/10 mm., n_D^{20} 1·5454—1·5470 (Found: C, 89·9; H, 10·25. $C_{16}H_{22}$ requires C, 89·7; H, 10·3%). (*b*) The alcohol (10 g.) was heated with phosphoric oxide (10 g.) in 85% phosphoric acid (50 c.c.) at 160° for 3 hr. with stirring. The mixture was diluted with water and extracted with ether. The ethereal extract was worked up as in (*a*), yielding 1 : 2 : 3 : 4 : 4*a* : 9 : 10 : 10*a*-octahydro-1 : 1-dimethylphenanthrene (3·8 g.), b. p. 104—109/0·7 mm., n_D^{20} 1·5464—1·5476. This compound was saturated towards hydrogen at atmospheric pressure in the presence of Adams catalyst.

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[8] Triebs, *Ber.*, 1947, **80**, 97.

Dehydrogenation of 1 : 2 : 3 : 4 : 4a : 9 : 10 : 10a-*Octahydro*-1 : 1-*dimethylphenanthrene.*—The above hydrocarbon (1 g.) was heated with selenium powder (1·5 g.) for 5 hr. at 300—330°, then extracted with alcohol, and the extract was boiled with charcoal and filtered. On concentration the filtrate deposted 1-methylphenanthrene [9] (0·3 g.), m. p. and mixed m. p. 118—119° after recrystallisation from light petroleum (b. p. 40—60°) (picrate, m. p. 135—136°).

3-*Chlorotetrahydro*-2-*phenethylfuran.*—2 : 3-Dichlorotetrahydrofuran [4] (140 g., 1 mole) was added to a stirred solution of the Grignard reagent prepared from phenethyl bromide (277 g., 1·5 mole) and magnesium (36 g., 1·5 g.-atom) in ether (1 l.) at such a rate that steady refluxing was maintained. The mixture was left overnight and then worked up as for 3-chlorotetrahydro-2-phenethylpyran. Distillation, after elimination of lower-boiling material (ethylbenzene), gave a mixture of *cis*- and *trans*-3-chlorotetrahydro-2-phenethylfuran (164 g., 78%) b. p. 70—100°/10^{-2} mm., $n_{\rm D}^{20}$ 1·5319—1·5340 (Found: C, 69·8; H, 7·6; Cl, 16·0. Calc. for $C_{12}H_{15}OCl$: C, 68·4; H, 7·1; Cl, 16·8%).

6-*Phenylhex*-3-*en*-1-*ol.*—Ring scission of 3-chlorotetrahydro-2-phenethylfuran (290 g.) was effected as for the pyran, with sodium (70 g.) in ether (1 l.). The final distillation gave a mixture of *cis*- and *trans*-6-phenylhex-3-en-1-ol (216 g., 88·9%), b. p. 100—110°/0·7 mm., $n_{\rm D}^{20}$ 1·5289 (Found: C, 82·15; H, 8·8. Calc. for $C_{12}H_{16}O$: C, 81·8; H, 9·1%) [3 : 5-dinitrobenzoate, m. p. 63—64°, from light petroleum (b. p. 40°) (Found: C, 61·6; H, 5·3; N, 7·5. Calc. for $C_{19}H_{18}O_6N_2$: C, 61·6; H, 4·9; N, 7·6%)].

1-*Bromo*-6-*phenylhex*-3-*ene.*—A mixture of 6-phenylhex-3-en-1-ol (216 g.) and pyridine (27 c.c.) was added dropwise with stirring to phosphorus tribromide (130 g.), with ice-cooling. The subsequent procedure was as for 7-bromo-1-phenylhept-3-ene. The final distillation gave 1-*bromo*-6-*phenylhex*-3-*ene* (143 g.), b. p. 55—92°/8 × 10^{-2} mm., $n_{\rm D}^{20}$ 1·5446 (Found: C, 60·5; H, 6·4; Br, 32·9. $C_{12}H_{15}Br$ require C, 60·25; H, 6·3; Br, 33·5%) [*thiouronium picrate*, yellow needles (from alcohol), m. p. 164—165° (Found: C, 49·6; H, 4·5. $C_{19}H_{21}O_7N_5S$ requires C, 49·2; H, 4·5%)].

11-*Phenylundeca*-4 : 8-*dien*-1-*ol.*—The Grignard reagent from 1-bromo-6-phenylhex-3-ene (143 g.) and magnesium (16 g.) in ether (250 c.c.) was left overnight, and the clear solution then decanted and treated (stirring) with 2 : 3-dichlorotetrahydropyran (34 g.) in ether (100 c.c.) at such a rate that steady refluxing was maintained. Next morning the mixture was worked up as for the pyran. Distillation gave 6-phenylhex-3-ene (28 g.), b. p. 102/15 mm., $n_{\rm D}^{17\cdot5}$ 1·5050 (Found: C, 89·6; H, 10·5. Calc. for $C_{12}H_{16}$: C, 90·0; H, 10·0%) (Triebs [8] gives b. p. 222°, $n_{\rm D}^{20}$ 1·5039), and 3-chlorotetrahydro-2-(6-phenylhex-3-enyl)pyran (65 g.) b. p. 114—140°/3 × 10^{-3} mm. This crude material was subjected to ring scission as for the pyran, with sodium (13 g.) in ether (300 c.c.). Distillation gave 11-*phenylundeca*-4 : 8-*dien*-1-*ol* (44 g.), b. p. 120—138°/3 × 10^{-3} mm., $n_{\rm D}^{20}$ 1·5219 (Found: C, 83·5; H, 10·1. $C_{17}H_{24}O$ requires C, 83·6; H, 9·8%).

11-*Bromo*-1-*phenylundeca*-3 : 7-*diene.*—A mixture of the preceding alcohol (40 g.) and pyridine (4 c.c.) was added with stirring to phosphorus tribromide (20 g.), with ice-cooling. The subsequent procedure was as for 7-bromo-1-phenylhept-3-ene. Distillation gave 11-*bromo*-1-*phenylundeca*-3 : 7-*diene* (25 g.), b. p. 140—145°/6 × 10^{-4} mm., $n_{\rm D}^{20}$ 1·5325 (Found: C, 67·0; H, 7·7. $C_{17}H_{23}Br$ requires C, 66·45; H, 7·5%). The derived *thiuronium picrate* formed yellow needles (from alcohol), m. p. 162—163° (Found: C, 54·1; H, 5·8. $C_{24}H_{29}O_7N_5S$ requires C, 54·2; H, 5·5%).

2-*Methyl*-13-*phenyltrideca*-6 : 10-*dien*-2-*ol.*—Acetone (4·5 g.) in ether (10 c.c.) was added to a solution of the Grignard reagent from 11-bromo-1-phenylundeca-3 : 7-diene (22 g.) and magnesium (2·5 g.) in ether (10 c.c.) at such a rate that steady refluxing was maintained. The subsequent procedure was as for 2-methyl-9-phenylnon-6-en-2-ol. Distillation gave 2-*methyl*-13-*phenyltrideca*-6 : 10-*dien*-2-*ol* (10 g.), b. p. 130—145°/2 × 10^{-3} mm., $n_{\rm D}^{20}$ 1·5117 (Found: C, 84·15; H, 10·65. $C_{20}H_{30}O$ requires C, 83·9; H, 10·5%).

Cyclodehydration. The alcohol (7·5 g.) was treated with 90% sulphuric acid (15 c.c.) as for 2-methyl-9-phenylnon-6-en-2-ol. The mixture was extracted with light petroleum (b. p. 40—60°), and the extract washed with concentrated sulphuric acid. After being kept over potassium carbonate the extract was filtered and the light petroleum removed by distillation. The residue was distilled over sodium, yielding 1 : 2 : 3 : 4 : 4a : 4b : 5 : 6 : 10b : 11 : 12 : 12a-*dodecahydro*-1 : 1-*dimethylchrysene* (3 g.), b. p. 120—130°/3 × 10^{-3} mm., $n_{\rm D}^{20}$ 1·5520 (Found: C, 89·45; H, 10·7. $C_{20}H_{28}$ requires C, 89·55; H, 10·45%), saturated towards hydrogen at atmospheric pressure in the presence of Adams catalyst.

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[9] Haworth, *J.*, 1932, 1125.

Dehydrogenation of 1 : 2 : 3 : 4 : 4a : 4b : 5 : 6 : 10b : 11 : 12 : 12a-*Dodecahydro*-1 : 1-*dimethylchrysene*.—The above hydrocarbon (1 g.) was heated with selenium powder (2·5 g.) at 350—400° for 5 hr. After cooling, the mixture was extracted with alcohol, and the extract boiled with charcoal and then filtered. On cooling, crystals of 1-methylchrysene were deposited which, crystallised from alcohol and then hexane, sublimed under reduced pressure and, recrystallised from hexane, had m. p. 247—249°. Ruzicka[10] gives m. p. 254—255° (*in vacuo*).

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[10] Ruzicka, *Helv. Chim. Acta*, 1940, **23**, 388.