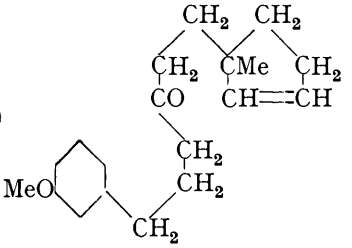
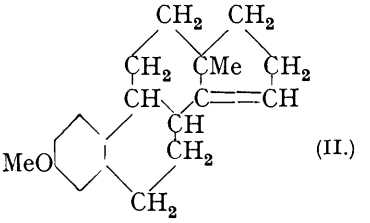
## 364. *Experiments on the Synthesis of Substances Related to the Sterols. Part VII.*

By William Sage Rapson and Robert Robinson.

(*A*) A synthetical objective in this group is a ketone such as (I), which might undergo double cyclisation with formation of (II).

(I.)





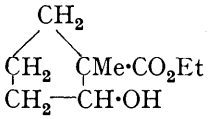
(II.)

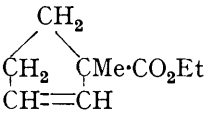
There is no doubt that (I) could be obtained from ethyl 1-methyl-$\Delta^2$-*cyclo*pentenyl-1-methylacetoacetate by a method similar to that outlined in Part III (this vol., p. 1288); unfortunately this derivative of ethyl acetoacetate could not be obtained, though the requisite *methylcyclopentenylmethyl chloride* has been prepared.

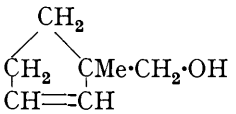
By reduction with sodium amalgam in the presence of carbon dioxide, ethyl 1-methyl-*cyclo*pentan-2-one-1-carboxylate was only partly converted into the corresponding hydroxy-ester (III). By the action of phosphoric oxide in boiling benzene, however, the keto-ester remained unattacked, whereas the hydroxy-ester yielded the lower-boiling *ethyl 1-methyl-*$\Delta^2$-cyclo*pentene-1-carboxylate* (IV), which was separated by fractionation. Since this yielded α-methylglutaric acid on oxidation with alkaline permanganate, the possibility of a rearrangement during the dehydration was excluded.

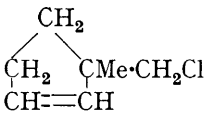
1-*Methyl-*$\Delta^2$-cyclo*pentenyl-1-carbinol* (V) resulted in 70% yield on reduction of the ester with sodium and anhydrous alcohol. Its conversion into a halide derivative gave some difficulty. Neither thionyl chloride nor phosphorus tribromide with pyridine could be employed, but the action of phosphorus pentachloride in light petroleum solution afforded a reasonably pure *chloride* (VI). In the attempted condensation of this with ethyl sodio-

acetoacetate all but a small proportion of the chloride reacted with auto-elimination of hydrogen chloride. The use of the *p*-toluenesulphonate of the alcohol (cf. Slotta and Franke, *Ber.*, 1930, **63**, 678; Tabern and Volwiler, *J. Amer. Chem. Soc.*, 1934, **56**, 1140) proved equally impracticable.

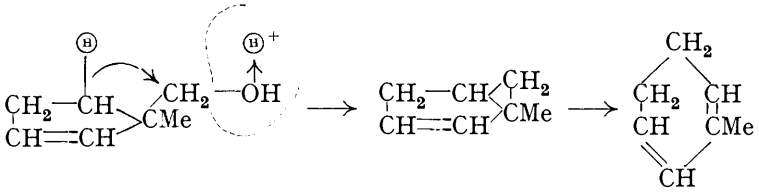

(III.)


(IV.)


(V.)

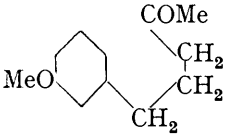

(VI.)

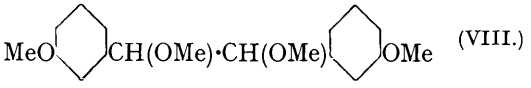
The isolation of the product of the elimination of hydrogen chloride in these reactions was not feasible. By heating the alcohol (V) with potassium hydrogen sulphate, however, a hydrocarbon, b. p. 112°, was isolated, from which the 2 : 4-dinitro- and the pentabromo-derivative of toluene were readily obtained. Although the hydrocarbon was not isolated in an analytically pure condition, there can be little doubt but that it is a dihydrotoluene formed in accordance with some such scheme as :



There are numerous alternative mechanisms.

We next attempted the use of the ester (IV) directly in a β-diketone synthesis with γ-m-*methoxyphenylpropyl methyl ketone* (VII) as the other component.

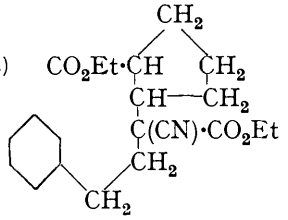
(VII.) 

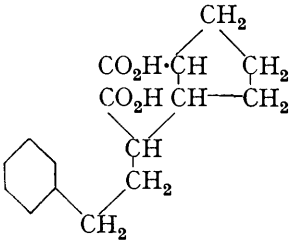

(VIII.)

The preparation of *m*-methoxybenzyl alcohol (Pschorr, *Annalen*, 1912, **391**, 44) has been improved. *m*-Hydroxybenzaldehyde in alkaline solution is reduced smoothly by an electrolytic method to *m*-hydroxybenzyl alcohol, which can then be methylated *in situ* by the addition of methyl sulphate. A by-product of this reaction is the *αα'-dimethyl* ether of 3 : 3'-*dimethoxyhydrobenzoin* (VIII).

*m*-Methoxybenzyl chloride and the corresponding nitrile have been obtained in improved yields (cf. Pschorr, *loc. cit.*), and from the latter ethyl *m*-methoxyphenylacetate was obtained directly by the action of sulphuric acid and alcohol. The series of reactions is more convenient than the preparation through *m*-methoxyphenylacetic acid (Robinson and Zaki, J., 1927, 2411).

β-*m*-Methoxyphenylethyl alcohol was converted through the chloride into the iodide, and this condensed with ethyl sodioacetoacetate to *ethyl* β-m-*methoxyphenylethylacetoacetate*. The required ketone (VII) was readily obtained on hydrolysis. From the condensation of this ketone with the unsaturated ester (IV), however, it has not been possible to isolate a pure β-diketone.

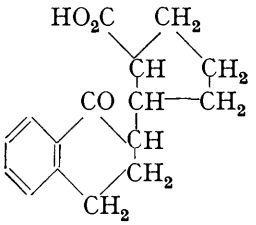
(IX.) 


(X.)

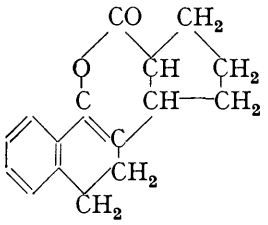
(*B*) Another line of work which has given interesting results starts with the introduction of the β-phenylethyl group into ethyl *trans-cyclo*pentane-1-carboxylate-2-cyanoacetate (Cook and Linstead, J., 1934, 956; this work was published whilst ours was in progress). Although the failure to alkylate the related malonic ester is on record, we experienced little difficulty in the preparation of (IX).

The hydrolysis to (X) was difficult and best effected in stages; the *acid* was obtained as the *trans*-form and it gave a crystalline trans-*anhydride*. The latter, heated at 240° for 15 minutes, was converted into the cis-*anhydride*, from which the *cis*-form of the acid was obtained.

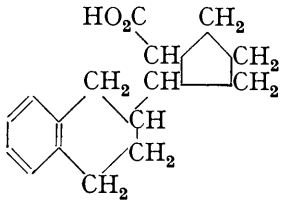
The ring-closure of the *trans*-form of (X) to yield the *keto-acid* (XI) was effected in good yield by 80% sulphuric acid at 100° and the resulting *trans*-keto-acid, on heating with acetic anhydride and sodium acetate, afforded the *cis*-form of lower melting point.



(XI.)



(XII.)



(XIII.)

The methyl ester of (XI) (*trans*-form) could not be brought into reaction with ethyl bromoacetate and zinc, and no alternative method has yet been found by means of which the carbon atoms necessary for the building up of ring (III) can be introduced.

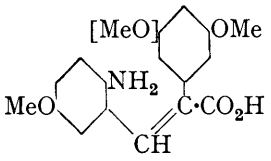
By the action of thionyl chloride, both the *cis*- and the *trans*-form of (XI) are readily dehydrated to the unsaturated *lactone* (XII) in its two possible stereoisomeric forms. In view of the similarity of the ring systems with those of the *cyclo*pentenophenanthrene group, Miss D. Crowfoot has kindly examined these substances by *X*-ray and crystallographic methods. In an attempt to obtain the corresponding saturated lactones, the hydrogenation of the *trans*-unsaturated lactone has been carried out in the presence of a 1% palladium–strontium carbonate catalyst, but four atoms of hydrogen were introduced and the *acid* (XIII) was the product. Jacobs and Scott (*J. Biol. Chem.*, 1930, **87**, 601) have already observed the fission of similarly constituted unsaturated lactones on reduction and were unable to isolate the saturated lactones even when the hydrogenation was interrupted at an intermediate stage.

Ruhemann and Wragg (J., 1901, **79**, 1190) and Fichter and Schwab (*Annalen*, 1906, **348**, 251) have shown that ethyl β-chlorocrotonate reacts with sodio-derivatives of certain enols, and it was hoped that *ethyl 2-chloro-*$\Delta^1$*-cyclopentene-1-carboxylate* might behave in a similar fashion. The ester was obtained by the action of phosphorus pentachloride on ethyl *cyclo*pentan-2-one-1-carboxylate, but it did not react with ethyl sodioacetoacetate, in either alcohol or benzene, or with ethyl sodiomalonate. Accordingly the projected condensation with ethyl sodio-α-acetyl-γ-*m*-methoxyphenylbutyrate was not attempted.

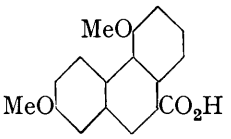
Structures of the kind which might be built up in this way are in fact more readily constructed by the method of Part II (this vol., p. 1285).

(*C*) The extension of the method of Miller and Robinson (J., 1934, 1535), for the introduction of the group $CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3$ in the α-position of β-naphthol, to the phenanthrene series would be of considerable interest. We therefore attempted the synthesis of 2-hydroxy-7-methoxyphenanthrene by Pschorr's method, using m-*benzyloxyphenylacetic acid* as one component in the first stage; de-benzylation could not be avoided, however, and methoxylated intermediates were used in further experiments.

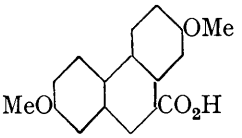
2-*Amino*-5-*methoxy*-α-(m-*methoxyphenyl*)*cinnamic acid* (XIV) yields, on diazotisation and decomposition of the diazo-compound, phenanthrene derivatives in 63% yield, of which about 56% was 2 : 5-*dimethoxyphenanthrene*-9-*carboxylic acid* (XV) and about 44% was 2 : 7-*dimethoxyphenanthrene*-9-*carboxylic acid* (XVI).



(XIV.)



(XV.)

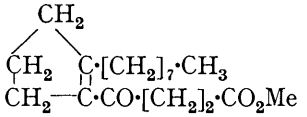


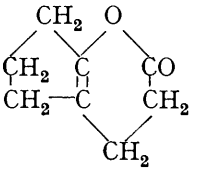
(XVI.)

The orientation of the substituents follows from the identity of the decarboxylation product of (XVI) with 2 : 7-dimethoxyphenanthrene which Fieser (*J. Amer. Chem. Soc.*, 1929, **51**, 2471) prepared by a series of processes from phenanthrene and related to 2 : 7-dinitrophenanthraquinone which has been converted into benzidine (Strasburger, *Ber.*, 1883, **16**, 2346; Schultz, *Annalen*, 1879, **196**, 29).

The formation of the isomeride (XV) in preponderating amount was unexpected, and we have not been able to find a parallel case in the literature (cf. Mayer and Balle, *Annalen*, 1914, **403**, 167). Theoretically it may be related to such cases as the nitration of *m*-methoxybenzaldehyde and other examples of a phenomenon discussed by Jones and Robinson (J., 1917, **111**, 903).

(*D*) An account is included of the preparation of some *cyclo*pentane derivatives bearing moderately long aliphatic chains, for example, (XVII), and also of some experiments due to Dr. R. Hirt, for example, the preparation of (XVIII) and its derivative.

(XVII.) 

(XVIII.)

## Experimental.

(A) *Ethyl* 1-*Methyl*-$\Delta^2$-cyclo*pentene*-1-*carboxylate* (IV).—Dieckmann's method of preparation of ethyl 1-methyl*cyclo*pentan-2-ol-1-carboxylate (III) (*Annalen*, 1901, **317**, 70) was used, but contrary to his results, complete reduction of ethyl 1-methyl*cyclo*pentan-2-one-1-carboxylate, even with a large excess of sodium amalgam, did not occur. Reductions with aluminium amalgam and by electrolytic methods were slower and even less efficient.

Water (300 c.c.) was stirred vigorously over sodium amalgam (900 g. of 3·5%) in a rapid stream of carbon dioxide for 2—3 minutes. A solution of the keto-ester (43 g.) in alcohol (60 c.c.) was then added, the stirring continued during 5—6 hours, and the product isolated (38 g. of b. p. 105—110°/14 mm.).

Dobson, Ferns, and Perkin (J., 1909, **95**, 2016) attempted to obtain the ester (IV) by the conversion of the hydroxy-ester into the chloro-ester by means of phosphorus pentachloride, and subsequent treatment with boiling diethylaniline, but all attempts to remove hydrogen chloride failed. The unsaturated ester was readily obtained, however, as follows: a mixture of the above reduction product (38 g.), benzene (40 c.c.), and phosphoric oxide (10 g.) was refluxed for 1·5 hours; the benzene layer was then decanted, and the products separated by fractionation. (a) 13 g., b. p. 70—80°/13 mm., gave on redistillation pure *ethyl* 1-*methyl*-$\Delta^2$-cyclo*pentene*-1-*carboxylate*, b. p. 70—71°/13 mm., a mobile liquid of strong but pleasant odour (Found: C, 70·3; H, 8·7. $C_9H_{14}O_2$ requires C, 70·1; H, 9·1%). (b) 14·5 g., b. p. 105—110°/14 mm., were identified as ethyl 1-methyl*cyclo*pentan-2-one-1-carboxylate.

1-*Methyl*-$\Delta^2$-cyclo*pentene*-1-*carboxylic acid* was obtained only by prolonged refluxing of its ester with alcoholic potash, followed by acidification. It is a relatively mobile oil, b. p. 110°/14 mm. (Found: C, 66·8; H, 8·1. $C_7H_{10}O_2$ requires C, 66·7; H, 7·9%).

1-*Methyl*-$\Delta^2$-cyclo*pentenyl*-1-*carbinol* (V).—Vigorous reduction of ethyl methyl-$\Delta^2$-*cyclo*penetenecarboxylate (30 g.) with sodium (35 g.) and absolute alcohol (450 c.c.) yielded this alcohol (15 g.) as a clear liquid, b. p. 162—165°/760 mm. (Found: C, 74·9; H, 10·8. $C_7H_{12}O$ requires C, 75·0; H, 10·7%). The p-*nitrobenzoate* crystallised from ethyl alcohol in needles, m. p. 67° (Found: C, 64·4; H, 6·0. $C_{14}H_{15}O_4N$ requires C, 64·4; H, 5·8%).

1-*Methyl*-$\Delta^2$-cyclo*pentenylmethyl Chloride*.—The interaction of the alcohol with thionyl chloride and pyridine (or dimethylaniline) yields chiefly high-boiling resins. The alcohol

(7 g.) was dissolved in light petroleum (15 c.c., b. p. 30—40°) and added during 30 minutes to phosphorus pentachloride (14 g.) under light petroleum (15 c.c.) at − 5°. The mixture was kept for 12 hours, and then mixed with ice and ether; the organic layer was well washed with aqueous sodium carbonate, dried, and distilled, b. p. 40—56°/18 mm. (4·7 g.). The product was not quite homogeneous (Found: Cl, 23·5. $C_7H_{11}Cl$ requires Cl, 27·1%). In the crude state the substance suffered rapid decomposition on attempted distillation under atmospheric pressure.

Attempts to condense 1-methyl-$\Delta^2$-*cyclo*pentenylmethyl chloride with ethyl sodioacetoacetate either in hot alcoholic solution or in a benzene medium failed. Although almost the theoretical amount of sodium chloride separated, the amount of high-boiling material in the product was negligible. In the presence of sodium iodide, and in alcohol, however, a small yield was obtained. The crude chloride (10 g.) was boiled with a solution of sodium (2 g.), acetoacetic ester (12·3 g.), and sodium iodide (3 g.) in absolute alcohol (35 c.c.) for 30 hours. On working up in the usual way, only 2 g. of crude material, b. p. 105—125°/0·2 mm., could be obtained.

The reaction between 1-methyl-$\Delta^2$-*cyclo*pentenylcarbinol (5 g.), *p*-toluenesulphonyl chloride (9 g.), and pyridine (9 c.c.) was complete in 10 hours, and the product was worked up by the addition of ether and washing with both acid and alkali. The residue after the evaporation of the ether was heated in a vacuum at 60° for ½ hour and the residual viscous oil (10 g.) was used in the condensations with acetoacetic ester, as its purification by distillation was impossible. Even after boiling for 48 hours with an excess of ethyl sodioacetoacetate, however, a quantity of unreacted sulphonate remained, which decomposed during subsequent attempts to distil the product. This difficulty was not overcome by the use of potassium.

*Dehydration of* 1-*Methyl*-$\Delta^2$-cyclo*pentenylcarbinol*.—The alcohol (6 g.) was boiled with potassium hydrogen sulphate (3 g.) for 10 hours, and the reaction mixture then distilled. The distillate (b. p. 100—120°) was dried over sodium sulphate and distilled from sodium. Yield, 1·5 g., b. p. 112—113°/760 mm. The substance was unsaturated and not identical with toluene. (a) The hydrocarbon (0·3 g.) was gradually introduced into an ice-cold mixture of nitric acid (1 g.) and sulphuric acid (2 g.). Vigorous reaction occurred, and after 4 hours the mixture was heated on the water-bath for 1 hour. On pouring into water, the product crystallised. It was washed, and recrystallised from alcohol, forming needles, m. p. 70° alone or mixed with 2 : 4-dinitrotoluene.

(b) The hydrocarbon (0·1 g.) was treated with ice-cold bromine (1·2 g.) and a few crystals of aluminium bromide, and kept over-night. The product, washed free from bromine, crystallised from benzene in needles, m. p. 285°, not depressed on admixture with pentabromotoluene.

m-*Methoxybenzyl Alcohol*.—*m*-Hydroxybenzaldehyde (35 g.), dissolved in 10% aqueous sodium hydroxide (200 c.c.), was reduced electrolytically with a current of 4 amps. (*C.D.*, 0·025 amp./sq. cm.) for 3·5 hours. The solution was then taken from the cell, and sodium hydroxide (15 g.) and methyl sulphate (85 g.) successively added, the latter in two portions and with vigorous shaking. An oil that separated was collected in ether and distilled, b. p. 125°/12 mm. (20 g.). A residue (9 g.) remained in the flask and 3 : 3′-*dimethoxyhydrobenzoin* αα′-*dimethyl ether* (VIII) crystallised readily from aqueous ethyl alcohol or from acetic acid in colourless prisms, m. p. 112—113° (Found: C, 71·5; H, 7·3. $C_{18}H_{22}O_4$ requires C, 71·3; H, 7·5%).

*Ethyl* m-*Methoxyphenylacetate*.—*m*-Methoxybenzyl alcohol (170 g.) was converted into the chloride (170 g.) by the Darzens method, thionyl chloride and pyridine being used (cf. Pschorr, *loc. cit.*). This was refluxed with a solution of potassium cyanide (200 g.) and sodium iodide (30 g.) in alcohol (1000 c.c.) for 8 hours, forming *m*-methoxyphenylacetonitrile (125 g.), b. p. 154°/16 mm. The nitrile (88 g.) was boiled with sulphuric acid (26 c.c.) and ethyl alcohol (150 c.c.) for 6 hours and gave the required ethyl *m*-methoxyphenylacetate in almost quantitative yield (83 g.). The reduction of this ester (50 g.) with sodium (35 g.) and absolute alcohol (300 c.c.) gave low yields (18 g., 46%) of β-*m*-methoxyphenylethyl alcohol, b. p. 135—137°/12 mm., which was transformed into β-*m*-methoxyphenylethyl chloride (17 g., b. p. 128—130°/14 mm.) by the method of Darzens. This reacted sluggishly with ethyl sodioacetoacetate in alcoholic solution, and was therefore refluxed (45 g.) on the steam-bath for 12 hours with a solution of sodium iodide (86 g.) in ethyl alcohol (430 c.c.). The alcohol was then distilled, and the residue taken up in ether, washed with a dilute solution of sodium thiosulphate, and dried. On evaporation of the ether and distillation of the residue, there resulted 61 g., b. p. 147—155°/15 mm. (chiefly at 154°).

*Ethyl* β-m-*Methoxyphenylethylacetoacetate*.—β-*m*-Methoxyphenylethyl iodide (30 g.) was

refluxed for 6 hours with the ethyl potassioacetoacetate prepared from ethyl acetoacetate (15 g.) and powdered potassium (4·5 g.) in toluene (150 c.c.). The reaction mixture was worked up in the known manner, affording 20 g. of material, b. p. 180°/2 mm. (Found: C, 68·0; H, 7·5. $C_{15}H_{20}O_4$ requires C, 68·2; H, 7·5%).

*γ*-m-*Methoxyphenylpropyl Methyl Ketone* (VII).—The above acetoacetate (19 g.) was shaken with a cold solution of sodium hydroxide (8 g.) in water (400 c.c.) for 24 hours. A small quantity of neutral material was then extracted, the alkaline layer acidified, and the *m*-methoxyphenylethylacetoacetic acid collected in ether. The extracts were concentrated without drying, and the residue heated in a boiling water-bath for 15 minutes. Hydrochloric acid (10%) was then added, and the heating continued for another 15 minutes. The product was taken up in ether and washed with alkali, the neutral material dried, and the ether evaporated. The residue (10 g.) was almost pure and had b. p. 168°/19 mm. (Found: C, 75·0; H, 8·4. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·3%). The semicarbazone crystallised from alcohol in long, shining, thin plates, m. p. 109°.

An attempt to condense this ketone with ethyl 1-methyl-$\Delta^2$-*cyclo*pentene-1-carboxylate was made in benzene solution in the presence of alcohol-free sodium ethoxide. The acidic material eventually isolated was identified as 1-methyl-$\Delta^2$-*cyclo*pentene-1-carboxylic acid and the neutral product was a viscous oil with a weak ferric reaction. After the removal of the unchanged ester, this reaction product was found to be concentrated in a small fraction of high b. p./1 mm. (bath at 200—300°). No ketone was recovered, but there was a considerable residue of material which exhibited no ferric reaction.

(B) 1-*Cyano*-$\Delta^1$-cyclo*pentene*.—Thionyl chloride (315 g.) was added gradually with shaking and cooling to pure distilled *cyclo*pentanonecyanohydrin (196 g.) mixed with pyridine (420 g.) and dry ether (500 c.c.). The whole was refluxed for 3 hours with frequent shaking, water added, and the clear, light yellow ethereal layer washed free from pyridine salts with dilute acid and then with alkali; it was dried, the ether evaporated, and the residue distilled, b. p. 69°/15 mm. (123 g. or 75%).

Ethyl $\Delta^1$-*cyclo*pentene-1-carboxylate was then obtained by the method of Cook and Linstead (*loc. cit.*). Their directions for the preparation of ethyl *trans-cyclo*pentane-1-carboxylate-2-cyanoacetate gave much better yields than those quoted (*loc. cit.*). Ethyl $\Delta^1$-*cyclo*pentene-1-carboxylate (20 g.), ethyl cyanoacetate (20 g.), sodium (3·5 g.), and alcohol (40 c.c.) gave 24 g. of product, b. p. 146°/1 mm. In our experience the criticism of Cook and Linstead's method by Bardhan and Banerji (this vol., p. 474) is decidedly not valid, provided that anhydrous alcohol is employed and water is excluded from the apparatus.

*Ethyl* α-*Cyano*-α-(trans-2-*carbethoxy*cyclo*pentyl*)-*γ*-*phenylbutyrate* (IX).—Ethyl *trans-cyclo*pentane-1-carboxylate-2-cyanoacetate (96 g.) was added to potassium (14·7 g.), powdered under toluene, and the mixture refluxed until a clear straw-coloured solution of the potassio-derivative was obtained. β-Phenylethyl bromide (71 g.) was then added, and the mixture refluxed for 8 hours. The toluene layer was washed with alkali and water, dried, and distilled, b. p. 195—200°/1 mm. (100 g.) (Found: C, 71·5; H, 7·3. $C_{21}H_{27}O_4N$ requires C, 70·6; H, 7·6%). The *ester* was evidently not quite homogeneous.

α-*Cyano*-α-(trans-2-*carboxy*cyclo*pentyl*)-*γ*-*phenylbutyric Acid*.—The above ester (66 g.) was only partly hydrolysed after boiling for 30 hours with concentrated hydrochloric acid. It was therefore collected and boiled vigorously for 6 hours with 25% alcoholic potash. The acidic material was collected in ether and crystallised from acetic acid, forming colourless rectangular prisms (28 g.), which melted with evolution of gas at 210°, and contained nitrogen (Found: C, 67·6; H, 6·6. $C_{17}H_{19}O_4N$ requires C, 67·8; H, 6·3%). A considerable proportion of the material failed to crystallise.

α-(trans-2-*Carboxy*cyclo*pentyl*)-*γ*-*phenylbutyric Acid* (X).—The above *cyano-dicarboxylic acid* (23 g.) was boiled for 7 hours with a mixture of sulphuric acid (50 c.c.), acetic acid (70 c.c.), and water (70 c.c.), and the product then taken up in ether. On evaporation of the solvent and treatment of the residue with acetic acid, a crystalline mass was obtained. It separated slowly from acetic acid in colourless prisms (15 g.), m. p. 160—161° (Found: C, 69·9; H, 7·0. $C_{16}H_{20}O_4$ requires C, 69·5; H, 7·2%).

α-(cis-2-*Carboxy*cyclo*pentyl*)-*γ*-*phenylbutyric Acid*.—The *trans*-acid (1 g.) was boiled with acetic anhydride (7 c.c.) for 15 minutes and the anhydride was then removed in a vacuum. The corresponding trans-*anhydride* remained as a solid residue; it crystallised from petroleum (b. p. 100—120°) in shining plates, m. p. 112° (Found: C, 73·9; H, 7·1. $C_{16}H_{18}O_3$ requires C, 74·4; H, 7·0%), yielding the original acid on hydrolysis. This *trans*-anhydride was heated

in an oil-bath at 250° for 15 minutes. On cooling, it would not crystallise again, and was therefore hydrolysed by means of dilute aqueous sodium hydroxide on the steam-bath. After acidification, extraction, and evaporation of the ethereal extracts, the residue crystallised from aqueous acetic acid in colourless prisms, m. p. 133° (mixed with the *trans*-isomeride, m. p. 115°) (Found: C, 69·5; H, 7·5. $C_{16}H_{20}O_4$ requires C, 69·5; H, 7·2%).

1-*Keto*-2-(trans-2′-*carboxy*cyclo*pentyl*)-1 : 2 : 3 : 4-*tetrahydronaphthalene* (XI).—The above *trans*-acid (40 g.) was heated in portions of 6 g. with a mixture of sulphuric acid (36 c.c.) and water (12 c.c.) on the steam-bath for 3 hours. The reaction mixture was poured into water, and the product collected by means of ether; it crystallised from acetic acid in colourless plates, m. p. 164—165° after several recrystallisations (yield, 24 g.) (Found: C, 74·3; H, 6·9. $C_{16}H_{18}O_3$ requires C, 74·4; H, 7·0%).

1-*Keto*-2-(cis-2′-*carboxy*cyclo*pentyl*)-1 : 2 : 3 : 4-*tetrahydronaphthalene*.—A mixture of the corresponding *trans*-acid (2 g.), acetic anhydride (10 c.c.), and anhydrous sodium acetate (4 g.) was refluxed for 8 hours. The anhydride was decomposed with water, and an uncrystallisable oil separated, which was taken up in ether. The residue, after removal of the solvent, solidified on rubbing, and crystallised from acetic acid in prisms of hexagonal outline, m. p. 155—156° (mixed with *trans*-acid, m. p. 135—140°) (Found: C, 74·4; H, 7·0. $C_{16}H_{18}O_3$ requires C, 74·4; H, 7·0%).

1-*Keto*-2-(trans-2′-*carbomethoxy*cyclo*pentyl*)-1 : 2 : 3 : 4-*tetrahydronaphthalene*.—An ethereal solution of diazomethane (10 g. of nitrosomethylurea) was added to 1-keto-2-(*trans*-2′-carboxy-*cyclo*pentyl)-1 : 2 : 3 : 4-tetrahydronaphthalene (10 g.) and after decomposition of the excess of diazomethane with acetic acid, the ethereal solution was washed with alkali, dried, and the ether evaporated. The residue was freely soluble in most organic solvents, but separated from its chilled solution in methyl alcohol in colourless plates, m. p. 45° (Found: C, 75·2; H, 7·4. $C_{17}H_{20}O_3$ requires C, 75·0; H, 7·4%).

1-*Hydroxy*-2-(trans-2′-*carboxy*cyclo*pentyl*)-3 : 4-*dihydronaphthalene Lactone* (XII).—A mixture of 1-keto-2-(*trans*-2′-carboxy*cyclo*pentyl)-1 : 2 : 3 : 4-tetrahydronaphthalene (3 g.), thionyl chloride (5 g.), and chloroform (20 c.c.) was refluxed for 30 minutes. The chloroform was removed in a vacuum, and the residue crystallised twice from light petroleum and then from ethyl acetate, forming glistening needles, m. p. 162° (Found: C, 80·2; H, 6·6. $C_{16}H_{16}O_2$ requires C, 80·0; H, 6·7%).

1-*Hydroxy*-2-(cis-2′-*carboxy*cyclo*pentyl*)-3 : 4-*dihydronaphthalene Lactone*.—1-Keto-2-(*cis*-2′-carboxy*cyclo*pentyl)-1 : 2 : 3 : 4-tetrahydronaphthalene yielded this substance in a manner similar to that already described for its isomeride. The product was easily soluble in most solvents, but crystallised from light petroleum (b. p. 30—40°) in rhombohedra, m. p. 66° (Found: C, 79·5; H, 6·5%).

Miss D. Crowfoot has kindly submitted the following report on the properties of crystals of the *trans*- and the *cis*-lactone described above:

(a) trans-*Lactone*.—The compound crystallises in monoclinic needles elongated along *a*, with the faces {021}, {100} developed. The dimensions of the unit cell are: $a = 8{\cdot}2$; $b = 23{\cdot}4$; $c = 13{\cdot}6$; $\beta = 68°$. With a density of about 1·315, the number of molecules in the cell is 8. The only halving is (0*k*0), absent for *k* odd, and the space group may therefore be $P2_1$ or $P2_1/m$. In the first case, there are four molecules in the asymmetric unit, in the second only two. In any case the crystal is presumably a racemate of two optically active molecules—with the 5-ring addition up at A down at B in one form, down at A up at B in the other. Actually the planes (*h*0*l*) are weak where *h* is odd and therefore there appears to be a pseudo-*a* glide plane, so that the space group should probably be given as $P2_1$ simulating $P2_1/a$. Morphologically the crystal is not one of the sterol types, but perhaps this could hardly be expected in view of both its racemic character and the presence of the lactonic linking. The crystal optics, however, do point to an interpretation of the cell dimensions in terms of molecular dimensions very similar to those of the oestrin group. Thus the sign of the double refraction is positive, *b* is the $\gamma$ direction and $\alpha$ is not more than about 6° from *a*; *b* may therefore be taken to represent twice the molecular length—about 11·7 Å.; *a* twice the molecular thickness—about 4·1 Å.; and $c \sin \beta$ twice the molecular width—6·2 Å.

(b) cis-*Lactone*.—This crystallised from light petroleum in fairly thick triclinic plates. The following unit cell dimensions were measured: $a = 7{\cdot}27$; $b = 16{\cdot}75$; $d(001) = 11{\cdot}0$; $\gamma = 75°$. The density determined by flotation was 1·267, which gives the number of molecules in the unit cell as 4. The space group is C1 or C$\bar{1}$.

As in the case of the *trans*-compound, the crystal is presumably a racemate of both optically

active *cis*-forms, which gives the number present in the asymmetric unit as actually 2, there being 2 of each kind of molecule in the cell.

Through the *c* face a positive biaxial figure could be observed with the slow extinction ($\beta$) along *a* and $\gamma$ inclined at a moderate angle to the normal to the *c* plane. This suggests that the molecules may be placed roughly with their thickness four times over in the *b* plane, particularly as the (040) reflexion is very strong, their lengths being along $\gamma$. The determination can only be very approximate, but the dimensions so found are not dissimilar from those of the *trans*-compound.

The most interesting fact about this compound is the great difficulty with which it crystallises at all. Immediately after it had been dissolved in light petroleum some of the solution was scattered on a slide so that the solvent rapidly evaporated; a viscous liquid was left which had not crystallised after several weeks, even where a nucleus crystal was introduced. Similarly, after the crystals had been melted and warmed for some time to destroy all arrangement before cooling, the melt did not recrystallise. In the ordinary way the crystals form very slowly from a supersaturated ligroin solution in the course of a day or longer. It seems natural to connect this property with the fact that owing to the presence of the double bond between rings B and C the 5-membered ring fused in the *cis*-position must turn nearly at right angles to the main ring system. This must enormously increase the difficulty with which the molecules can move over one another to build up a regular crystalline arrangement.

In the main group of the sterols and oestrin derivatives the bond common to rings B and C is hydrogenated and in this case it is possible to achieve a fairly flat configuration of the 5-ring with respect to the rest of the molecule, whether it is attached in the *cis*- or in the *trans*-position. On the analogy with this *cis*-lactone we might expect that a compound where this becomes a double bond should show marked differences in behaviour on crystallisation, according to whether the fusion of the 5-ring is *cis* or *trans*. In the oestrin series such a compound is equilenin (crystallographic examination by Gaudefroy, *Compt. rend.*, 1932, **193**, 981), in the sterol series *neo*ergosterol (Windaus and Borgeaud, *Annalen*, 1928, **460**, 235). Equilenin according to Gaudefroy crystallises beautifully in orthorhombic plates, much elongated in one direction. There is evidently no difficulty of crystallisation here. Of *neo*ergosterol we have already made *X*-ray measurements showing a structure which, if somewhat more complicated than usual, is still of a perfectly normal type. In fact the *X*-ray photographs show in certain directions smear lines which are sometimes associated with ease of movement of molecules over one another, rather than the reverse.

The analogy of the *cis*- and the *trans*-lactone with these compounds is of course not complete, but such as it is, it does support the *trans*-fusion of ring D to ring C in the sterol and oestrin series (Department of Mineralogy, Oxford University).

2-(2′-trans-*Carboxy*cyclo*pentyl*)-1 : 2 : 3 : 4-*tetrahydronaphthalene* (XIII).—The unsaturated *trans*-lactone (0·8 g.) was dissolved in dry ethyl acetate (20 c.c.), a 1% palladium–strontium carbonate catalyst (8 g.) added, and the mixture shaken with hydrogen under 2 atms. until absorption had ceased. The product solidified when freed from solvent and crystallised from light petroleum (b. p. 60—80°) in radiating clusters of prisms, m. p. 107°, soluble in aqueous sodium hydrogen carbonate (Found: C, 78·8; H, 8·3. $C_{16}H_{20}O_2$ requires C, 78·7; H, 8·2%).

*Ethyl* 2-*Chloro*-$\Delta^1$-cyclo*pentene*-1-*carboxylate*.—Phosphorus pentachloride (50 g.) was covered with light petroleum (b. p. 40—60°), and ethyl *cyclo*pentan-2-one-1-carboxylate (31 g.) added gradually with shaking. Reaction set in immediately with evolution of hydrogen chloride at each addition, and the process was completed by heating on the steam-bath at 60° for 30 minutes. The liquid was decanted, shaken with water and with aqueous alkali till neutral, dried, and distilled; the main fraction, b. p. 95—102°/12 mm., was contaminated with acidic material formed during distillation. It was therefore washed with alkali, dried, and redistilled. There resulted 15·5 g. of *ester*, b. p. 95—98°/12 mm. (chiefly at 96°) (Found: C, 55·1; H, 6·3. $C_8H_{11}O_2Cl$ requires C, 55·1; H, 6·3%).

2-*Chloro*-$\Delta^1$-cyclo*pentenecarboxylic Acid*.—Acidification of the alkaline washings from the above preparation furnished a crystalline *acid* (2 g.) which, dried and recrystallised from light petroleum, formed glistening needles, m. p. 115—116° (Found: Cl, 24·6. $C_6H_7O_2Cl$ requires Cl, 24·3%).

(C) m-*Benzyloxybenzaldehyde*.—*m*-Hydroxybenzaldehyde (41 g.) was added to a solution of sodium (6 g.) in alcohol (100 c.c.). Benzyl chloride (45 g.) was then introduced, and the mixture refluxed for 4 hours. The residue after distillation of the solvent was taken up in

ether, washed with alkali, dried, the ether evaporated, and the residue distilled, b. p. 215—218°/20 mm. (yield, 61 g.). The distillate solidified and was recrystallised from alcohol; colourless plates, m. p. 54° (Found: C, 79·0; H, 5·6. $C_{14}H_{12}O_2$ requires C, 79·3; H, 5·6%).

m-*Methoxybenzylidenephenyl*isooxazolone.—A mixture of *m*-benzyloxybenzaldehyde (23·5 g.), hippuric acid (20 g.), and acetic anhydride (37 c.c.) was heated on the steam-bath for 2 hours. The product, isolated in the known manner, crystallised from acetic acid in short yellow needles (29 g.), m. p. 129° (Found: N, 3·8. $C_{23}H_{17}O_3N$ requires N, 3·9%).

m-*Benzyloxyphenylacetic Acid*.—The *iso*oxazolone (85 g.) was hydrolysed by boiling 10% sodium hydroxide solution during 5 hours, and the benzoic acid precipitated with sulphur dioxide (cf. Buck and Perkin, J., 1924, **125**, 1680). When boiled with hydrochloric acid, the filtrate deposited *m*-benzyloxyphenylpyruvic acid. This crystallised from aqueous alcohol in white irregular prisms (47 g.), m. p. 145°, but decomposed on keeping. The keto-acid (47 g.) was dissolved in aqueous sodium hydroxide (300 c.c. in 10%) and hydrogen peroxide (300 c.c. in 3%) was added gradually in the cold. Acidification after 12 hours liberated m-*benzyloxyphenylacetic acid*, which crystallised from alcohol in glistening plates (37 g.), m. p. 126° (Found: C, 74·3; H, 5·9. $C_{15}H_{14}O_3$ requires C, 74·4; H, 5·8%).

2-*Nitro*-5-*methoxy*-α-(m-*benzyloxyphenyl*)*cinnamic Acid*.—A mixture of 6-nitro-3-methoxybenzaldehyde (1 mol.) (Mason, J., 1925, **127**, 1195), the dry sodium salt of *m*-benzyloxyphenylacetic acid (1 mol.), and acetic anhydride (3 mols.) was heated on the steam-bath for 24 hours. On dilution with water an oil was precipitated, which was collected in benzene and crystallised when freed from solvent; dark-coloured impurities were removed by washing on the filter. It then crystallised from benzene in small, faintly yellow prisms, m. p. 148°. The *acid* was freely soluble in alcohol and acetic acid, and after drying in a vacuum desiccator it gave Ramsden's qualitative test for benzene (Found: C, 70·5; H, 5·0; N, 3·0. $C_{23}H_{19}O_6N,0{\cdot}5C_6H_6$ requires C, 70·3; H, 5·0; N, 3·1%).

2-*Amino*-5-*methoxy*-α-(m-*benzyloxyphenyl*)*cinnamic Acid*.—The above acid was reduced smoothly and almost quantitatively by heating on the steam-bath for 1 hour with an excess of a mixture of solutions of ferrous sulphate and ammonia. In order to isolate the amino-compound, it is essential to filter it from a faintly *alkaline* mother-liquid. If the ammoniacal filtrate from the reaction mixture is acidified, the amino-acid separates in an insoluble flocculent form which contains mineral acid, even after thorough washing, and cannot be recrystallised. The pure *acid* crystallises from aqueous alcohol in colourless plates, m. p. 137° (Found: C, 73·4; H, 5·8. $C_{23}H_{21}O_4N$ requires C, 73·6; H, 5·6%).

2-*Nitro*-5-*methoxy*-α-(m-*methoxyphenyl*)*cinnamic Acid*.—A mixture of dry sodium *m*-methoxyphenylacetate (114 g.) (Robinson and Zaki, J., 1927, 2411), 6-nitro-3-methoxybenzaldehyde (125 g.), and acetic anhydride (400 c.c.) was heated on the steam-bath for 24 hours. The anhydride was then decomposed, and the product taken up in benzene and washed free from acetic acid. On evaporation of the benzene, the residue crystallised in part. After being washed free from dark-coloured impurities with benzene, it crystallised from aqueous alcohol in yellow needles (102 g.), m. p. 148° (Found: C, 62·0; H, 4·7. $C_{17}H_{15}O_6N$ requires C, 62·0; H, 4·6%).

2-*Amino*-5-*methoxy*-α-(m-*methoxyphenyl*)*cinnamic Acid* (XIV).—The nitro-acid was reduced by heating on the steam-bath for 1 hour with an excess of solutions of ferrous sulphate and ammonia. The *amino-acid* (quantitative yield) crystallised from aqueous alcohol in colourless plates, m. p. 185° (Found: C, 67·9; H, 5·9. $C_{17}H_{17}O_4N$ requires C, 68·2; H, 5·7%).

2 : 5-*Dimethoxyphenanthrene*-9-*carboxylic Acid* (XV) *and* 2 : 7-*Dimethoxyphenanthrene*-9-*carboxylic Acid* (XVI).—The amino-acid (85 g., 1 mol.) was dissolved in dilute aqueous sodium hydroxide (1 mol.) and added gradually to an excess of ice-cold 8% sulphuric acid with stirring. 5% Sodium nitrite solution (1·05 mols.) was slowly introduced and the mixture was kept for 12 hours, then rendered faintly alkaline with sodium carbonate, and warmed to 50°; nitrogen was evolved, and when the solution no longer coupled with β-naphthol to an azo-compound, it was acidified and the solid collected. Fractional crystallisation gave two isomeric acids: (1) 2 : 7-*dimethoxyphenanthrene*-9-*carboxylic acid*, sparingly soluble in acetic acid, but crystallising from a relatively large volume in pale yellow prisms (22 g.), m. p. 265° (Found: C, 72·6; H, 4·8. $C_{17}H_{14}O_4$ requires C, 72·3; H, 5·0%), the constitution being based on the formation of 2 : 7-dimethoxyphenanthrene on decarboxylation (see below); (2) 2 : 5-*dimethoxyphenanthrene*-9-*carboxylic acid*, moderately readily soluble in acetic acid and crystallising therefrom in long, pale yellow prisms (28 g.), m. p. 191° (Found: C, 72·6; H, 4·8%).

2 : 7-*Dimethoxyphenanthrene*.—The carboxylic acid of m. p. 265° (20 g.) was dissolved in

quinoline (100 c.c.) and heated for 2·5 hours with a " copper chromite " catalyst (0·7 g.) (bath at 230°), and the mixture then added to dilute hydrochloric acid. The solid, washed with alkali and crystallised from pyridine, gave colourless plates (10 g.), m. p. 169—170° (Fieser, *loc. cit.*, gives m. p. 167—168°). The *picrate* crystallised from alcohol in slender brick-red needles, m. p. 144° (Found: N, 9·2. $C_{16}H_{14}O_2,C_6H_3O_7N_3$ requires N, 9·0%).

2 : 7-Dimethoxyphenanthrene (10 g.) was boiled with acetic acid (20 c.c.) and hydriodic acid (40 c.c., *d* 1·6) for 2 hours. The product was extracted with ether, and a phenolic fraction isolated in the usual way. The substance separated from aqueous acetic acid in colourless needles (6 g.). Heated gradually, it darkened and did not melt sharply, but starting in a bath at 245° droplets appeared at 258° and the meniscus formed at 264°. Fieser (*loc. cit.*) gives m. p. 265° for 2 : 7-dihydroxyphenanthrene.

2 : 5-*Dimethoxyphenanthrene*.—2 : 5-Dimethoxyphenanthrene-9-carboxylic acid (6 g.) yielded this substance (4 g.) in a manner similar to that already described for its isomeride. It crystallised very readily from acetic acid in needles, m. p. 117° (Found: C, 80·4; H, 5·7. $C_{16}H_{14}O_2$ requires C, 80·7; H, 5·9%). The *picrate* crystallised from alcohol in glistening orange-red needles, m. p. 154—156° (Found: N, 9·1. $C_{16}H_{14}O_2,C_6H_3O_7N_3$ requires N, 9·0%).

2 : 5-*Dihydroxyphenanthrene*, obtained like the isomeride, was freely soluble in aqueous alcohol and acetic acid, from which it separated as an oil; it crystallised readily from xylene, however, in prisms, m. p. 180° (Found: C, 80·1; H, 4·8. $C_{14}H_{10}O_2$ requires C, 80·0; H, 4·8%).

2 : 5-Diacetoxyphenanthrene crystallised from aqueous acetic acid in colourless transparent plates, m. p. 144°.

2-*Methyl*-5 : 6-(1 : 2-*naphtha*)-γ-*pyran*.—The reaction mixture from the preparation of β-2-hydroxy-1-naphthylethyl methyl ketone (cf. Miller and Robinson, *loc. cit.*) was poured into dilute hydrochloric acid and shaken with ether. The ethereal extracts were dried, and the ether evaporated; the residue distilled as a viscous oil, b. p. 190°/16 mm., which crystallised from ethyl alcohol in stout prisms, m. p. 44—45° (Found: C, 85·4; H, 6·1. $C_{14}H_{12}O$ requires C, 85·7; H, 6·1%). The substance is evidently formed by the dehydration of the hydroxy-ketone; on exposure to air, it quickly darkens owing to autoxidation, and like the hydroxy-ketone it yields a pyrylium salt by the combined action of phosphoryl chloride and chloranil.

(D) *Ethyl* 1-n-*Octyl*cyclo*pentan*-2-*one*-1-*carboxylate*.—Ethyl potassio*cyclo*pentanonecarboxylate was prepared from powdered potassium (13·5 g.) and the keto-ester (55 g.) in xylene (150 c.c.). *n*-Octyl bromide (65 g.) was then added, and the mixture boiled for 7 hours. The xylene solution was well washed with alkali and with water, dried, and distilled, giving 77 g. of b. p. 157—165°/1 mm. (yield, 85%). The *semicarbazone* crystallised from ethyl alcohol in short fine needles, m. p. 117° (Found: C, 62·8; H, 9·5. $C_{17}H_{31}O_3N_3$ requires C, 62·8; H, 9·5%).

α-n-*Octyladipic Acid*.—The above ester (105 g.) was boiled with a solution of baryta (200 g.) in water (600 g.) for 12 hours. A soapy, insoluble barium salt was formed, which was slowly decomposed by hydrochloric acid. The acidic products were collected by ether, and α-n-*octyladipic acid* crystallised readily from light petroleum in prisms, m. p. 74° (Found: C, 64·7; H, 10·0. $C_{14}H_{26}O_4$ requires C, 65·1; H, 10·1%).

2-n-*Octyl*cyclo*pentanone*.—The neutral and the acidic products of the above hydrolysis were combined and distilled slowly at atmospheric pressure. The distillate was taken up in ether and washed with alkali, the neutral extract dried, the ether evaporated, and the residue distilled, giving 50 g. (65%) of the ketone, b. p. 135—138°/11 mm., as a mobile liquid with a strong camphoraceous odour. The *semicarbazone* separated rapidly in the course of its preparation; it was sparingly soluble in alcohol, from which it crystallised in light feathery crystals, m. p. 183° (Found: C, 66·4; H, 10·7. $C_{14}H_{27}ON_3$ requires C, 66·4; H, 10·7%).

2-n-*Octyl*cyclo*pentanol*.—A solution of 2-*n*-octyl*cyclo*pentanone (15 g.) in 95% alcohol (100 c.c.) was poured on sodium (23 g.) in a reflux apparatus, alcohol (120 c.c.) added gradually, and the mixture boiled so as to maintain a vigorous reaction. When all the sodium had disappeared, water was added, and the ethyl alcohol distilled in steam. The product was isolated by means of ether and distilled; b. p. 161°/23 mm. or 140°/8 mm. (yield, 13 g.) (Found: C, 78·6; H, 13·1. $C_{13}H_{26}O$ requires C, 78·8; H, 13·1%). 2-n-*Octyl*cyclo*pentanol* (12 g.) was heated at 80° for 12 hours with a mixture of equal weights of hydrobromic acid (*d* 1·5) and acetic acid saturated with hydrogen bromide, and the mixture was then boiled for 1 hour. Water was added, and the product collected by means of ether and distilled; b. p. 135—140°/8 mm. (yield, 15 g.). Various attempted condensations with this bromide afforded *n*-octyl-$\Delta^1$-*cyclo*pentene, which was also obtained by the action of octylmagnesium bromide on *cyclo*pentanone (cf. Zelinsky, Michlina, and Eventowa, *Ber.*, 1933, **66**, 1423) and dehydration of the product

by boiling with oxalic acid for 4 hours. In all the experiments it was found necessary to fractionate the product (b. p. 125—128°/12 mm.) in order to separate it from hexadecane (b. p. 150°/12 mm.) also formed in the reaction.

2-(β-*Carbomethoxypropionyl*)-1-n-*octyl*-$\Delta^1$-cyclo*pentene* (XVII).—*n*-Octyl-$\Delta^1$-*cyclo*pentene (23 g.), mixed with β-carbomethoxypropionyl chloride (23 g.; cf. J., 1904, **85**, 530), was added gradually to a solution of stannic chloride (33 g.) in carbon disulphide (80 c.c.) cooled in a freezing mixture. After 4 hours, the dark red complex was decomposed with dilute hydrochloric acid, the solution washed and dried, and the solvent removed. Dimethylaniline (17 g.) was then added, and the mixture heated at 180° for 3 hours. The product was taken up in ether, and the base removed by shaking with dilute hydrochloric acid; finally the ethereal layer was dried, the ether evaporated, and the residue distilled, giving 5 g. of crude material, b. p. 205—215°/10 mm., but the major portion of the product was a resinous residue. On redistillation, it had b. p. 173—177°/1 mm., $n_D^{15°}$ 1·4818 (Found: C, 73·1; H, 10·2. $C_{18}H_{30}O_3$ requires C, 73·4; H, 10·4%). Better yields were obtained, however, by the use of aluminium chloride as catalyst. The acid chloride (19 g.) and the hydrocarbon (20 g.) were mixed in carbon disulphide (70 c.c.), and aluminium chloride (16·5 g.) was added slowly with cooling in ice. The reaction mixture was kept in the cold for 12 hours and then refluxed for 3 hours. On working up and distillation of the product there were obtained 5 g. of keto-ester, $n_D^{15°}$ 1·4812, and 7 g. of recovered octyl*cyclo*pentene.

[Experiments made by Dr. R. HIRT.] cyclo*Pentanone*-2-β-*propionic Acid and Derivatives*.—The memoir of Cook and Linstead on this subject appeared (J., 1934, 954) just after our work had been completed (Dr. F. E. King also had prepared the acid for a different purpose; cf. this vol., p. 782). The only points to which reference need be made are the following: We required the acid chloride for an attempted synthesis of γ-*m*-methoxyphenylpropyl *cyclo*pentanone-2-β-ethyl ketone, but it could not be obtained although many methods were tried. When *cyclo*pentanone-2-β-propionic acid (15 g.) was refluxed with acetyl chloride (30 g.) for 8 hours, it was converted into the related *enolic* lactone (XVIII), b. p. 116—117°/17 mm. (10 g.) (Found: C, 69·4; H, 7·4. $C_8H_{10}O_2$ requires C, 69·6; H, 7·2%). This is a colourless oil which readily absorbs bromine; it is insoluble in cold aqueous alkalis, but dissolves on heating. The reduction of this lactone could not be accomplished, but cyclo*pentanol*-2-β-*propionic acid lactone* was obtained as follows: Sodium (40 g.) was added to a solution of *cyclo*pentanonepropionic acid (40 g.) in alcohol (400 c.c.); the mixture was acidified when the sodium had disappeared, and the alcohol distilled. The product was collected in ether and distilled under diminished pressure. When the bath temperature reached 180—200°, the hydroxy-acid decomposed (not before) and the lactone passed over at 134—140°; redistilled, b. p. 138—139°/18 mm. (yield, 10 g.) (Found: C, 68·4; H, 8·7. $C_8H_{12}O_2$ requires C, 68·6; H, 8·6%). This substance has the properties of a δ-lactone; it polymerises on heating and the hydroxy-acid is formed on hydrolysis of the resin thus produced (cf. Fichter and Beisswenger, *Ber.*, 1903, **36**, 1200). In the experiment described, 6 g. of lactone were thus recovered from the residue in the flask. By the action of phosphorus pentachloride at 130—140° on this lactone and subsequent treatment with alcohol, ethyl 2-chloro*cyclo*pentane-1-β-propionate, b. p. 126—127°/15 mm., was obtained. The content of chlorine was always somewhat too high. From this substance ethyl $\Delta^1$-*cyclo*pentene-1-β-propionate was obtained by the action of boiling diethylaniline. This ester had b. p. 102—103°/19 mm. and contained a trace of chlorine which vitiated the analytical results.

1-*Methyl*-3:4-*dihydronaphthalene*.—The formation of this substance is the model for a stage in several contemplated syntheses. γ-Phenylpropyl methyl ketone (semicarbazone, m. p. 125° in accord with Diels and Poetsch, *Ber.*, 1921, **54**, 1587, who first prepared the ketone from benzylidenediacetylmonoxime) is obtained in 92% yield by the hydrolysis of ethyl β-phenylethylacetoacetate (75% yield of product, b. p. 167—168°/14 mm., from β-phenylethyl iodide and ethyl sodioacetoacetate in alcoholic solution) with boiling 10% hydrochloric acid.

The ketone (4 g.) was carefully mixed with 85% sulphuric acid (30 c.c.) at 0°; the homogeneous solution formed at first quickly became orange and an oil separated. After keeping for 30 minutes at room temperature the *hydrocarbon* was isolated (2·6 g. or 74·3%), b. p. 107—108°/14 mm., and redistilled over sodium (Found: C, 91·3; H, 8·6. $C_{11}H_{12}$ requires C, 91·7; H, 8·3%).

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