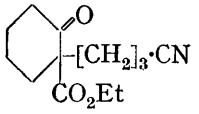
168. *The Synthesis of Polyterpenoid Compounds. Part III.*

By J. W. Cook and C. A. Lawrence.

In Part II (J., 1935, 1637) we gave the first example of a new method of synthesis of polycyclic hydroaromatic ketones by intramolecular condensation of an unsaturated acid chloride of suitable structure. In the further development of our work we have been to some extent anticipated by Chuang, Tien, and Ma (*Ber.*, 1936, **69**, 1494), who adapted our method to the synthesis of hydronaphthalenes containing an "angular" methyl group, and of the hydrindane (perhydroindene) system. We were ourselves occupied with both these projects when the paper of the Chinese authors appeared, and had in fact completed the former scheme, using a simpler route than that taken by Chuang and his collaborators. We now record our own experiments, except in so far as they are duplicated by those of Chuang *et al.* The extension of the synthetic methods to more complex ring systems is in progress.

For the synthesis of γ-Δ^1-*cyclo*hexenylbutyric acid, required for cyclisation to $\Delta^{9:10}$-1-octalone (Part II), we had introduced the butyric acid side chain in two stages, a procedure followed by Chuang. This can, however, be effected in one stage, condensation of ethyl potassio*cyclo*hexanone-2-carboxylate with γ-iodobutyronitrile leading to *ethyl* 2-γ-*cyanopropyl*cyclo*hexanone*-2-*carboxylate* (I), which was hydrolysed by dilute alkali to γ-2-keto-

*cyclo*hexylbutyric acid (II), a compound formerly obtained by Hückel and Naab (*Annalen*, 1933, **502**, 146) by oxidation of $\Delta^{1:9}$-octahydronaphthalene. A by-product of the hydrolysis was *octane-*$\alpha\delta\theta$*-tricarboxylic acid*. The *ethyl* ester of the keto-acid (II) reacted with methylmagnesium iodide to give a product which, after hydrolysis and dehydration, gave γ-(2-methyl-Δ^1-*cyclo*hexenyl)butyric acid (III), which was synthesised by Chuang, Tien, and Ma (*loc. cit.*) by another method. Cyclisation of (III) led to 9-methyl-$\Delta^{4:10\ (or\ 5:10)}$-1-octalone, which was hydrogenated to 9-methyl-1-decalone (IV), the properties of which agreed with those cited by Chuang, Tien, and Ma.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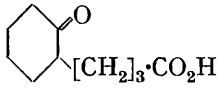
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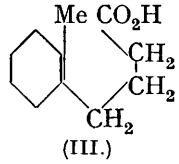
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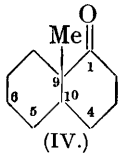
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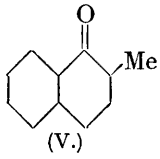
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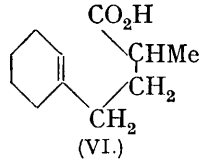

(VI.)

A ketone of type (IV), with a methoxyl group at position 6, would furnish a suitable starting point for the synthesis of a sterol type of molecule. Synthesis of (IV) from *cyclo*hexanone is laborious, and it seemed possible that the angle methyl group might be introduced directly into the molecule of α-decalone. However, treatment of the sodio-derivative of *trans*-1-decalone with methyl iodide led to a complex mixture, from which was isolated only a small amount of the 9-methyl derivative (IV). The principal product was *2-methyl-1-decalone* (V),* and a third *ketone*, probably stereoisomeric with (IV) or (V), was also isolated. The structure of (V) was shown by its synthesis from β-Δ^1-*cyclo*hexenylethyl bromide and ethyl methylmalonate, with subsequent hydrolysis and decarboxylation of the product, and then cyclisation of the resulting γ-Δ^1-cyclo*hexenyl-*α*-methylbutyric acid* (VI), followed by hydrogenation of the *2-methyl-*$\Delta^{9:10}$*-1-octalone*.

In an attempt to extend these reactions to synthesis in the sesquiterpene field we have studied the condensation of β-(4-methyl-Δ^1-*cyclo*hexenyl)propyl bromide with ethyl potassiomalonate, and of ethyl γ-bromovalerate with ethyl potassio-5-methyl*cyclo*hexanone-2-carboxylate. The disappointingly small yields of the products (VII and VIII, respectively) have made it impracticable to attain our objective, although (VII) was transformed through the usual stages into 1 : 6-*dimethyl-*$\Delta^{9:10}$*-4-octalone* (IX), which, if available in sufficient quantity, should be readily convertible into a hydrocarbon (X) differing structurally from α- or β-cadinene only in the disposition of one double bond.

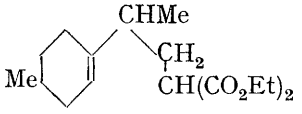
Nenitzescu and Ciorănescu (*Ber.*, 1936, **69**, 1820) have shown that the reaction between acid chlorides and *cyclo*olefins leads to *saturated* ketones if carried out in the presence of aluminium chloride and *cyclo*hexane, the latter acting as a hydrogen donor. This type of reduction did not occur when γ-Δ^1-*cyclo*hexenylbutyryl chloride was treated under similar conditions with aluminium chloride and *cyclo*hexane, the sole ketonic product being $\Delta^{9:10}$-1-octalone. This experience tallies with that of Robinson and Walker (this vol., p. 61), who likewise observed no reduction in an analogous case.

We are also occupied with possible applications of the Diels–Alder diene reaction to the synthesis of polycyclic hydroaromatic compounds. We merely report now that addition

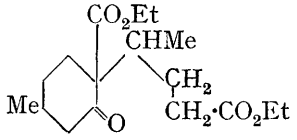
* *Note on Configuration.*—It is probable that our 2-methyl-1-decalone is one of the two possible racemic *trans*-forms. This is supported by the preparation of the compound both by methylation of *trans*-1-decalone and by hydrogenation of 2-methyl-$\Delta^{9:10}$-1-octalone. The hydrogenation of $\Delta^{9:10}$-1-octalone is known to give largely the *trans*-decalone (Hückel and Blohm, *Annalen*, 1933, **502**, 136). The optical exaltation of 2-methyl-1-decalone (+0·25) also accords with a *trans*-fusion of the rings.

In the case of our 9-methyl-1-decalone the synthetic methods warrant no conclusion concerning the configuration, but the slight optical depression (−0·05) suggests the *cis*-configuration.

products could not be obtained from Δ^1-tetrahydrobenzoic acid and butadiene or 2 : 3-dimethylbutadiene, or from Δ^1-tetrahydrobenzaldehyde and 2 : 3-dimethylbutadiene.



(VII.)



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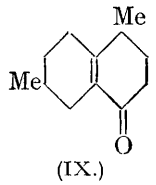

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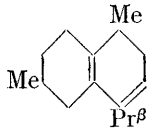
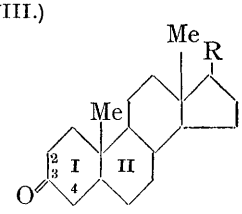
(X.) 



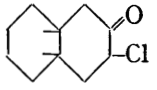
(XI.)

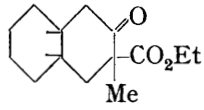
Subsequently, Fieser and Holmes (*J. Amer. Chem. Soc.*, 1936, **58**, 2319) reported the slow formation of adducts from ethyl Δ^1-dihydronaphthoate and butadiene or 2 : 3-dimethylbutadiene. We therefore re-examined one of our examples, and heated ethyl Δ^1-tetrahydrobenzoate with 2 : 3-dimethylbutadiene for 196 hours at 105—110°, but no addition occurred.

Sterol ketones (XI) are brominated at position 2 and oxidised with fission of the 2 : 3-bond when there is a *trans*-fusion of rings I and II, but brominated at position 4 and oxidised with fission mainly of the 3 : 4-bond in the corresponding *cis* series (for references, see *Ann. Reports*, 1936, **33**, 344). If similar differences of reactivity could be shown to hold for simpler dicyclic derivatives of *cis*- and *trans*-2-decalones, then compounds of the *cis*-series, but not of the *trans*-series, could be used in the synthesis of perhydrophenanthrene derivatives by extension of the methods described above (see also Robinson, J., 1936, 1088; du Feu, McQuillin, and Robinson, this vol., p. 54). There can be little doubt that the differences observed in the sterol ketones are due to the different positions favoured by the enolic double bonds in the two stereoisomeric series, in which case different positions should likewise be taken up by the double bonds arising from the dehydration of corresponding series of 3-hydroxy-compounds. There appears to be little available evidence on this point. However, in the case of the β-decalols it has been shown that dehydration of *trans*-2-decalol (m. p. 75°) gives 90% of *trans*-Δ^2-octalin (Hückel and Naab, *Annalen*, 1933, **502**, 151; compare Leroux, *Ann. Chim.*, 1910, **21**, 471), whereas the dehydration of *cis*-2-decalol (m. p. 105°) gives both the Δ^1- and the Δ^2-octalin, the proportion depending to some extent on the dehydrating agent used, but never being predominantly in favour of the Δ^1-compound (Hückel, *Ber.*, 1925, **58**, 1451; Hückel and Friedrich, *Annalen*, 1927, **451**, 147). Also, the formation of the ring system of 1 : 2-benzanthracene to the exclusion of that of 3 : 4-benzphenanthrene by cyclisation of the phenylethyloctalin resulting from the dehydration of 2-β-phenylethyl-*trans*-2-decalol (Cook and Hewett, J., 1934, 375) indicates that the octalin is essentially the Δ^2-compound. Hückel (*Annalen*, 1925, **441**, 17) and Hückel and Friedrich (*loc. cit.*) have also studied the oxidation of the above-mentioned *cis*- and *trans*-2-decalols to the corresponding dicarboxylic acids; presumably the ketones are intermediate products. The results show no clear-cut differences between the two stereoisomeric series, such as is encountered with the sterol derivatives.

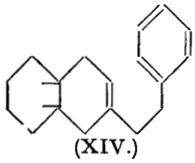
In substitution reactions *trans*-2-decalone is attacked mainly at position 3, the 3-chloro-derivative having been described by Lehmann and Krätschell (*Ber.*, 1934, **67**, 1867), and the ethyl 3-glyoxylate by Hückel and Goth (*Ber.*, 1925, **58**, 449). By monochlorination of *cis*-2-decalone we have obtained 3-*chloro*-cis-2-*decalone* (XII), the orientation of which was shown by its hydrolysis to 3-*hydroxy*-cis-2-*decalone*, followed by oxidation to *cis*-*cyclo*hexane-1 : 2-diacetic acid. *cis*-2-Decalone condensed with ethyl oxalate to give ethyl *cis*-2-ketodecalyl-3-glyoxylate, which was thermally degraded to *ethyl* cis-2-*decalone*-3-

carboxylate. In order to determine the orientation of this keto-ester its sodio-derivative was methylated with methyl iodide, and the resulting *ethyl* 3-*methyl*-cis-2-*decalone*-3-*carboxylate* (XIII) was dehydrogenated with selenium to 3-methyl-2-naphthol, the properties of which agreed with those given by Veselý and Šťursa (*Coll. Czech. Chem. Comm.*, 1934, **6**, 137). The same naphthol was similarly obtained from ethyl *trans*-2-decalone-3-carboxylate.

(XII.) 


(XIII.)

We have also studied the cyclisation with aluminium chloride at 0° of the *phenylethyloctalin* which arises from the dehydration of 2-β-*phenylethyl*-cis-2-*decalol*. The unsaturated hydrocarbon, which could contain (XIV) and (XV), was cyclised to a mixture of hydrocarbons, from which was isolated the same dodecahydro-1 : 2-benzanthracene, m. p. 72°, previously prepared from *trans*-2-decalone (Cook and Hewett, *loc. cit.*).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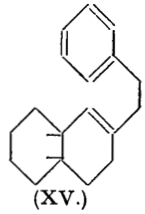
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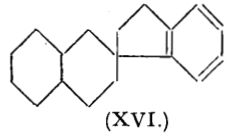
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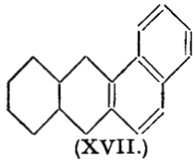
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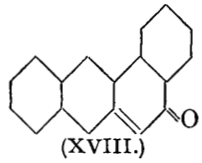
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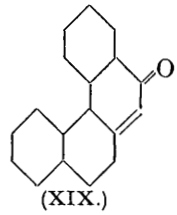
(XIX.)

Evidently change in configuration occurs during cyclisation with aluminium chloride, analogous to the conversion of *cis*- into *trans*-decalin (Zelinsky and Turowa-Pollak, *Ber.*, 1932, **65**, 1299). Dehydrogenation of the mixture of saturated hydrocarbons gave 1 : 2-benzanthracene, 5 : 6 : 7 : 8-tetrahydro-1 : 2-benzanthracene, *octahydro*-1 : 2-*benzanthracene* (XVII), and a small amount of chrysene. There was no evidence of the presence of 3 : 4-benzphenanthrene (from XV). The chrysene probably arises from (XVI) by rearrangement during dehydrogenation (compare Cook and Hewett, J., 1934, 365). Hence, the cyclisation products are mainly stereoisomeric dodecahydrobenzanthracenes, so that the phenylethyloctalin is mainly the Δ^2-compound (XIV), as in the *trans*-series. We cannot exclude the possibility that the *cis*-octalin (XIV) is *completely* converted into its *trans*-isomeride *prior to* ring closure, in which event this argument is not valid.

Additional evidence, not open to such objection, that position 3 is the main position of reactivity of *cis*-2-decalone was secured by utilising the condensation method developed by Rapson and Robinson (J., 1935, 1285; 1936, 757, 759, 763). The sodio-compounds of both *cis*- and *trans*-2-decalones were condensed with acetyl-Δ^1-*cyclo*hexene to give mixtures of ketones, of which the main constituents (in fact the only constituents which could be isolated) were the two stereoisomeric 3-*keto*-Δ^4-*hexadecahydro*-1 : 2-*benzanthracenes* (XVIII), in which the ring systems were established by dehydrogenation to 1 : 2-benzanthracene. In the case of the condensation with *cis*-2-decalone the distilled mixture of ketones was reduced by Clemmensen's method, and the hydrocarbon mixture dehydrogenated with platinum-black. In addition to 1 : 2-benzanthracene, a small amount of 3 : 4-benzphenanthrene was isolated, indicating the presence of the ketone (XIX) in the original mixture.

These results provide ample demonstration that the striking differences in the position of substitution shown by the stereoisomeric sterol ketones (XI) do not hold in the case of the

simpler 2-decalones, both *cis*- and *trans*-compounds being attacked mainly at position 3. Evidently the stability of the alternative Δ^1- and Δ^2-octalin systems present in the enolic forms of the ketones is influenced by the locking of this portion of the sterol molecule with the remainder of the ring system. Incidentally, the method envisaged by Robinson (J., 1936, 1088) for the synthesis of testosterone would appear to be precluded by these results.

Experimental.

Synthesis of α-Decalone Derivatives.

Ethyl 2-*γ-Cyanopropyl*cyclo*hexanone-2-carboxylate* (I).—γ-Chlorobutyronitrile (50 g.) (" Organic Syntheses," Collective Vol. I, p. 150) was converted into the corresponding iodo-compound by refluxing for 12 hours with sodium iodide (100 g.) in ethyl alcohol (400 c.c.). The filtered solution was concentrated under reduced pressure, and the residue extracted with ether, washed free from iodine with sodium thiosulphate solution, dried, and distilled. The γ-iodobutyronitrile (85% yield) had b. p. 109°/10 mm. (Case, *J. Amer. Chem. Soc.*, 1933, **55**, 2929, gives 113—116°/7 mm.). This γ-iodobutyronitrile (79·4 g.) was added to a suspension of the sodio-compound prepared from ethyl *cyclo*hexanone-2-carboxylate (70 g.) and sodium powder (9 g.) in benzene (300 c.c.), and the mixture heated on the water-bath for 50 hours. Water was then added, and the benzene layer washed, dried (calcium chloride), and distilled. *Ethyl* 2-*γ-cyanopropyl*cyclo*hexanone-2-carboxylate* (76·3 g.) formed a colourless viscous liquid, b. p. 163—165°/0·7 mm. (Found: C, 65·5; H, 8·8. $C_{13}H_{19}O_3N$ requires C, 65·8; H, 8·1%). The semicarbazone formed colourless hexagonal plates (from methyl alcohol), m. p. 176—177°.

γ-2-*Keto*cyclo*hexylbutyric Acid* (II).—The foregoing ester (70 g.) was heated for 4 hours on the water-bath with aqueous potassium hydroxide (53 g. in 1400 c.c.). Unhydrolysed material was extracted with ether, and re-treated with potassium hydroxide (6 g. in 160 c.c.). The combined alkaline liquors were acidified, saturated with sodium chloride, and extracted four times with ether. The washed and dried extract gave, on distillation, crude γ-2-keto*cyclo*hexylbutyric acid (33·4 g. = 62%), b. p. 168°/0·8 mm., and a brownish gum, b. p. 280—290°/0·8 mm. The latter fraction was evidently *octane-αδθ-tricarboxylic acid* (Found: C, 54·1; H, 7·5; equiv., 85·4. $C_{11}H_{18}O_6$ requires C, 53·6; H, 7·4%; equiv., 82·0). The *ethyl* ester, formed by refluxing with alcohol and sulphuric acid, was a colourless liquid, b. p. 162—163°/1 mm. (Found: C, 62·4; H, 9·2. $C_{17}H_{30}O_6$ requires C, 61·8; H, 9·2%). An analogous example of fission of the *cyclo*hexanone ring has been given by Haworth and Mavin (J., 1933, 1015), who obtained the corresponding heptanetricarboxylic acid as a by-product in the preparation of β-2-keto*cyclo*hexylpropionic acid.

The distilled keto-acid (II) crystallised on cooling and, after crystallisation from ether–light petroleum, had m. p. 58°. Its semicarbazone had m. p. 185—187°, and its oxime had m. p. 102—104°. The acid obtained by hydrolysis of the semicarbazone had m. p. 60—61°. Hückel and Naab (*loc. cit.*) give m. p. 60—61°, 189°, and 101—103° for this acid and its semicarbazone and oxime, respectively. The p-*phenylphenacyl* ester of γ-2-keto*cyclo*hexylbutyric acid formed colourless irregular plates (from alcohol), m. p. 78—79° (Found: C, 75·9; H, 7·0. $C_{24}H_{26}O_4$ requires C, 76·15; H, 6·9%). The *ethyl* ester (34 g.), prepared from the crude acid (34·7 g.) and sulphuric acid (3 c.c.) in alcohol (140 c.c.), formed a colourless liquid, b. p. 136°/0·4 mm. (Found: C, 67·7; H, 9·5. $C_{12}H_{20}O_3$ requires C, 67·9; H, 9·5%); its semicarbazone had m. p. 103—104°.

γ-(2-*Methyl*-Δ^1-cyclo*hexenyl*)*butyric Acid* (III).—A Grignard solution prepared from methyl iodide (17 g.), magnesium turnings (3·1 g.), and anhydrous ether (100 c.c.) was added dropwise, with stirring, to an ice-cold solution of ethyl γ-2-keto*cyclo*hexylbutyrate (24·5 g.) in ether (60 c.c.). After being kept at 0° for 2 hours, the mixture was decomposed with ice and ammonium chloride. The residue remaining after removal of the ether from the washed ethereal solution was hydrolysed by heating for 7 hours at 100° with potassium hydroxide (20 g.) in water (200 c.c.), with frequent shaking. After being extracted with ether, the alkaline solution was acidified, saturated with sodium chloride, and extracted four times with ether. The extract was dried (sodium sulphate), the ether removed, and the residue heated at 170—180° for 2 hours with potassium hydrogen sulphate (35 g.) in order to dehydrate the hydroxy-acid. The product was extracted and distilled at 0·4 mm. The higher fraction (5·1 g.), b. p. 150—152°, solidified on cooling and was mainly unchanged keto-acid. The lower fraction (12 g.), b. p. 134—142°, was essentially the desired γ-(2-methyl-Δ^1-*cyclo*hexenyl)butyric acid (III), and after redistillation had b. p. 123°/0·3 mm. (Found: C, 71·4; H, 9·7. Calc. for $C_{11}H_{18}O_2$: C, 72·5; H, 9·9%).

Its p-*phenylphenacyl* ester formed thin colourless plates, m. p. 83—84° (from alcohol) (Found: C, 79·5; H, 7·3. $C_{25}H_{28}O_3$ requires C, 79·8; H, 7·7%).

9-*Methyl*-$\Delta^{4:10\ (or\ 5:10)}$-1-*octalone and* 9-*Methyl*-1-*decalone*.—Cyclisation of the unsaturated acid (III) by the action of stannic chloride on its chloride was carried out as described for the lower homologue (J., 1935, 1638; see also Chuang, Tien, and Ma, *loc. cit.*). The semicarbazone of the 9-methyloctalone had m. p. 222—223° (decomp.) (Found: N, 19·2. Calc.: N, 19·0%); Chuang *et al.* give m. p. 226—227°. The 2 : 4-*dinitrophenylhydrazone* formed red plates (from alcohol or aqueous dioxan), m. p. 133° (Found: N, 16·2. $C_{17}H_{20}O_4N_4$ requires N, 16·3%). 9-Methyl-1-decalone (IV) was obtained by hydrogenation of the unsaturated ketone in alcoholic solution with palladium-black. After purification through its semicarbazone, m. p. 224—225° (Chuang *et al.* give 225—226°), the saturated ketone (IV) had b. p. 118°/20 mm., $n_D^{18\cdot8°}$ 1·4903, $d_4^{18\cdot8°}$ 0·9953; whence $[R_L]_D$ = 48·56 (calc., 48·61). The *oxime* formed thin lozenge-shaped plates (from aqueous methyl alcohol), m. p. 108·5—111° (Found: N, 7·85. $C_{11}H_{19}ON$ requires N, 7·7%), and the 2 : 4-*dinitrophenylhydrazone* formed orange tabular crystals (from alcohol containing a little dioxan), m. p. 159—160° (decomp.) (Found: N, 15·9. $C_{17}H_{22}O_4N_4$ requires N, 16·2%).

β-Δ^1-cyclo*Hexenylethylmethylmalonic Acid*.—The yield of β-Δ^1-*cyclo*hexenylethyl alcohol obtained by Bouveault reduction of ethyl Δ^1-*cyclo*hexenylacetate (Cook and Dansi, J., 1935, 500) was increased from 55% to 72% by the use of anhydrous alcohol, dried with magnesium methoxide. β-Δ^1-*cyclo*Hexenylethyl bromide (61·4 g.) was heated on the water-bath for 130 hours with the potassio-compound prepared from ethyl methylmalonate (60 g.) and potassium (13 g.) in pure benzene (350 c.c.). *Ethyl* β-Δ^1-cyclo*hexenylethylmethylmalonate* (53 g.), isolated in the usual manner, formed a colourless liquid, b. p. 134—137°/0·5 mm. (Found: C, 67·4; H, 9·5. $C_{16}H_{26}O_4$ requires C, 68·05; H, 9·3%). β-Δ^1-cyclo*Hexenylethylmethylmalonic acid*, formed by hydrolysis of the ester with alcoholic potash, separated from ligroin–benzene as a colourless crystalline powder, m. p. 141·5—142·5° (Found: C, 63·7; H, 8·4. $C_{12}H_{18}O_4$ requires C, 63·7 H, 8·0%).

γ-Δ^1-cyclo*Hexenyl*-α-*methylbutyric acid* (VI) was obtained in almost quantitative yield by heating the foregoing malonic acid at 180—190° for 20 minutes, and formed a colourless liquid, b. p. 140—145°/0·8 mm. (Found: C, 72·0; H, 10·6; equiv., 199·4, 203·4. $C_{11}H_{18}O_2$ requires C, 72·5; H, 9·9%; equiv., 182·1). The p-*phenylphenacyl* ester crystallised from alcohol in thin colourless plates, m. p. 88—90·5° (Found: C, 79·5; H, 7·7. $C_{25}H_{28}O_3$ requires C, 79·75; H, 7·6%).

2-*Methyl*-$\Delta^{9:10}$-1-*octalone*.—The unsaturated acid (VI) (12·1 g.) was converted into its chloride by the standard procedure (see Part II), by means of 50 c.c. of ether, 5·3 g. of pyridine, and 8·0 g. of thionyl chloride, and the acid chloride was cyclised to the octalone, which was obtained in 43% yield, 2·6 g. of acid being recovered (17 g. of stannic chloride, 20 c.c. of carbon disulphide, and 15 g. of dimethylaniline were employed). 2-*Methyl*-$\Delta^{9:10}$-1-*octalone*, obtained analytically pure by hydrolysis of its semicarbazone with 2*N*-sulphuric acid at 100°, formed a colourless mobile liquid, b. p. 129°/13 mm., $n_D^{11\cdot2°}$ 1·5210, $d_4^{11\cdot2°}$ 1·022; whence $[R_L]_D$ = 48·90 (calc., 48·14) (Found: C, 80·6; H, 10·0. $C_{11}H_{16}O$ requires C, 80·4; H, 9·8%). The *semicarbazone* formed small colourless plates (from alcohol), m. p. 212° (decomp.) (Found: N, 18·9. $C_{12}H_{19}ON_3$ requires N, 19·0%); the *oxime* formed small colourless needles (from methyl alcohol), m. p. 160—161° (Found: N, 7·6. $C_{11}H_{17}ON$ requires N, 7·8%); and the 2 : 4-*dinitrophenylhydrazone* formed small, thick, red plates (from dioxan), m. p. 219—220° (decomp.) (Found: N, 16·2. $C_{17}H_{20}O_4N_4$ requires N, 16·3%).

2-*Methyl*-1-*decalone* (V).—The unsaturated ketone (2·5 g.) was hydrogenated in alcoholic solution (25 c.c.) with palladium-black (0·2 g.). The theoretical volume of hydrogen was absorbed in 2 hours. The *semicarbazone* of the saturated ketone (V) was recrystallised from alcohol until it had a constant m. p., 216—217·5° (decomp.) (Found: N, 19·55. $C_{12}H_{21}ON_3$ requires N, 18·8%). 2-*Methyl*-1-*decalone* (V), obtained by hydrolysis of the semicarbazone, formed a colourless liquid, b. p. 109°/11 mm., which gave an unsatisfactory value for carbon (see, however, p. 824) (Found: C, 78·7; H, 10·8. $C_{11}H_{18}O$ requires C, 79·5; H, 10·9%). Its *oxime* formed long colourless needles (from aqueous methyl alcohol), m. p. 152—153·5° (Found: N, 8·05. $C_{11}H_{19}ON$ requires N, 7·7%), and its 2 : 4-*dinitrophenylhydrazone* formed orange tabular crystals (from aqueous dioxan), m. p. 223—224·5° (Found: N, 16·45. $C_{17}H_{22}O_4N_4$ requires N, 16·2%).

γ-(4-*Methyl*-Δ^1-cyclo*hexenyl*)*valeric Acid*.—By the use of alcohol dried with magnesium methoxide for the Bouveault reduction of ethyl α-(4-methyl-Δ^1-*cyclo*hexenyl)propionate (Cook and Dansi, *loc. cit.*) the yield of β-(4-methyl-Δ^1-*cyclo*hexenyl)propyl alcohol was raised to 80%. Condensation of β-(4-methyl-Δ^1-*cyclo*hexenyl)propyl bromide (55·9 g.) with the potassio-com-

pound from ethyl malonate (55 g.) and potassium (12 g.) in benzene (350 c.c.) (130 hours at 100°) gave only an 8·3% yield of ethyl β-(4-methyl-Δ^1-*cyclo*hexenyl)propylmalonate (VII), b. p. 138°/0·4 mm. Hydrolysis with alcoholic potash yielded an oily acid, which did not crystallise after 14 days in the ice-chest. It was therefore decarboxylated by heating at 180—190° for 20 minutes. The resulting γ-(4-*methyl*-Δ^1-cyclo*hexenyl*)*valeric acid* formed a colourless liquid, b. p. 112—114°/0·4 mm. (Found: C, 72·6; H, 10·45. $C_{12}H_{20}O_2$ requires C, 73·4; H, 10·3%).

1 : 6-*Dimethyl*-$\Delta^{9:10}$-4-*octalone* (IX).—Cyclisation of γ-(4-methyl-Δ^1-*cyclo*hexenyl)valeric acid (2·8 g.) in the usual manner gave the crude *ketone* (IX) (1 g.), b. p. 141°/13 mm., which was not obtained analytically pure (Found: C, 78·8; H, 10·0. $C_{12}H_{18}O$ requires C, 80·9; H, 10·2%). The *oxime* formed a colourless microcrystalline powder (from aqueous methyl alcohol), m. p. 98—102° (Found: N, 7·4. $C_{12}H_{19}ON$ requires N, 7·25%); the *semicarbazone* formed small, colourless, irregular crystals (from aqueous dioxan), m. p. 163—165·5° (clear at 169°) (Found: C, 65·7; H, 8·9; N, 17·7. $C_{13}H_{21}ON_3$ requires C, 66·3; H, 9·0; N, 17·85%); and the 2 : 4-*dinitrophenylhydrazone* formed red, microscopic, lath-shaped crystals (from aqueous dioxan), m. p. 217·5—219° (decomp.) after slight sintering (Found: N, 15·8. $C_{18}H_{22}O_4N_4$ requires N, 15·6%).

γ-(2-*Keto*-4-*methyl*cyclo*hexyl*)*valeric Acid*.—Ethyl γ-bromovalerate was prepared from γ-methylbutyrolactone (Staudinger and Ruzicka, *Helv. Chim. Acta*, 1924, **7**, 249), which was obtained by catalytic hydrogenation of lævulic acid (Schuette and Thomas, *J. Amer. Chem. Soc.*, 1930, **52**, 3010). The bromo-ester (20·4 g.) was heated on the water-bath for 50 hours with the potassio-compound from ethyl 5-methyl*cyclo*hexanone-2-carboxylate (Haworth, Mavin, and Sheldrick, J., 1934, 457) (18 g.) and potassium (3·9 g.) in benzene (120 c.c.). The reaction products were worked up in the usual way and gave 3·4 g. of the desired keto-ester (VIII), b. p. 153—156°/0·5 mm. The combined products from two batches were redistilled, and then heated at 100° for 20 hours with 5% aqueous potassium hydroxide (50 c.c.). From the alkaline solution was obtained 0·7 g. of a yellow liquid, b. p. about 160°/0·8 mm., which gave a crystalline *semicarbazone* of γ-(2-keto-4-methyl*cyclo*hexyl)valeric acid, m. p. 177—178·5° (Found: C, 57·5; H, 8·6. $C_{13}H_{23}O_3N_3$ requires C, 57·9; H, 8·6%).

Attempted Simplification of the Conversion of γ-Δ^1-cyclo*Hexenylbutyric Acid into* 1-*Decalone*.—Powdered anhydrous aluminium chloride (3·4 g.) was slowly added to a solution of γ-Δ^1-*cyclo*hexenylbutyryl chloride (see Part II) (from 2·1 g. of acid) in *cyclo*hexane (5 c.c.), cooled in a freezing mixture. The whole was then allowed to warm to room temperature; a vigorous reaction set in. When this had subsided, the mixture was heated at 70° until hydrogen chloride was no longer evolved. The product was worked up in the usual way, the only ketonic substance isolated being $\Delta^{9:10}$-1-octalone, identified by means of its semicarbazone and its 2 : 4-*dinitrophenylhydrazone*. An authentic specimen of the latter compound was prepared from $\Delta^{9:10}$-1-octalone obtained by the method described in Part II. It formed small, dark red, tabular crystals (from xylene), m. p. 266·5—267° (decomp.) (Found: N, 16·9. $C_{16}H_{18}O_4N_4$ requires N, 17·0%). For comparison, the 2 : 4-*dinitrophenylhydrazone* of *trans*-1-decalone was prepared. This formed small, thin, orange-red plates (from xylene), m. p. 222—222·5° (Found: N, 16·8. $C_{16}H_{20}O_4N_4$ requires N, 16·9%).

Lactone of β-2-*Hydroxy*cyclo*hexylpropionic Acid*.—β-2-Keto*cyclo*hexylpropionic acid was prepared by the method of Haworth and Mavin (J., 1933, 1015), and was further characterised by its *semicarbazone*, which separated from alcohol as a colourless crystalline powder, m. p. 181—182° (decomp.) (Found: N, 18·5. $C_{10}H_{17}O_3N_3$ requires N, 18·5%). The keto-acid (4 g.) was hydrogenated in alcoholic solution (80 c.c.) with platinum-black (0·5 g.). The product, b. p. 145°/10 mm., was the *lactone* of β-2-hydroxy*cyclo*hexylpropionic acid (Found: C, 69·7; H, 9·1. $C_9H_{14}O_2$ requires C, 70·1; H, 9·2%). Our contemplated conversion of this compound into 1-hydrindanone was rendered unnecessary by the publication of the experiments of Chuang *et al.* (*loc. cit.*), whose synthesis of 8-methyl-1-hydrindanone established the point in which we were interested—namely, that the intramolecular Darzens reaction could be utilised for the formation of a five-membered ring.

Methylation of trans-1-*Decalone*.

Finely powdered sodamide (3 g.) was gradually added to a solution of *trans*-1-decalone (7·5 g.) in anhydrous ether (50 c.c.), and the mixture then heated on the water bath for 1½ hours. After cooling, methyl iodide (11 g.) was slowly added, and then heating was continued for 3¼ hours. Vigorous stirring was maintained throughout these operations. After addition of water, the ethereal solution was separated, washed, and dried (sodium sulphate), and the ether removed. The residue was treated with hydroxylamine hydrochloride and sodium acetate in boiling

aqueous-alcoholic solution, and the semi-solid mixture of oximes was fractionally crystallised from methyl alcohol. The predominating product was a crystalline oxime, m. p. 148—149·5°, not depressed by the oxime (m. p. 152—153·5°) of synthetic 2-methyl-1-decalone (see above). 2-Methyl-1-decalone (V), obtained by hydrolysis of this oxime, had b. p. 111°/12 mm., $n_D^{17\cdot7°}$ 1·4812, $d_4^{17\cdot7°}$ 0·969; whence $[R_L]_D$ = 48·86 (calc., 48·61) (Found: C, 79·2; H, 10·9. Calc.: C, 79·5; H, 10·9%). The semicarbazone of this ketone had m. p. 222—225° (decomp.), and did not depress the m. p. (216—217·5°) of the semicarbazone of synthetic 2-methyl-1-decalone (Found: N, 18·4. Calc.: N, 18·8%). Identification was completed by comparison of the 2 : 4-dinitrophenylhydrazones.

The more soluble fractions of the crystalline oximes of the methylated decalone gave a small amount of an *oxime* of a methyl-1-decalone, which crystallised from aqueous methyl alcohol in thin colourless needles, m. p. 139—139·5°, depressed to 133—134° by admixture with the oxime of synthetic 2-methyl-1-decalone (Found: C, 72·95; H, 10·4. $C_{11}H_{19}ON$ requires C, 72·8; H, 10·6%).

The mother-liquors from the first crystallisation of the oximes gave a gum which, after distillation (b. p. 155—156°/13 mm.), was hydrolysed, and the product treated with semicarbazide. Repeated crystallisation from methyl alcohol then gave a small amount of the semicarbazone of 9-methyl-1-decalone (IV), m. p. 223—224°, not depressed by a synthetic specimen.

The use of benzene instead of ether as a solvent in the methylation of *trans*-1-decalone led to substantially the same result.

Comparison of cis- *and* trans-2-*Decalones.*

The *cis*-2-decalone used in these experiments was prepared by chromic acid oxidation of *cis*-2-decalol, m. p. 105°, obtained by hydrogenation of *ar*-β-tetralol (prepared from tetralin by the method of Schroeter, *Annalen*, 1922, **426**, 119) in acetic acid solution with Adams's platinum catalyst at 4 atms.' pressure. For example, in one experiment, in which 115 g. of tetralol, 500 c.c. of acetic acid, and 2·5 g. of platinum oxide were used, hydrogenation was complete in 16 hours, and gave 37 g. of recrystallised *cis*-2-decalol. In all, 195 g. of the pure decalol were obtained from 475 g. of tetralol (compare Hückel, *Annalen*, 1926, **451**, 118).

3-*Chloro*-cis-2-*decalone* (XII).—A solution of chlorine (12 g.) in carbon tetrachloride (140 c.c.) was slowly added, with ice-cooling, to a solution of *cis*-2-decalone (25 g.) in carbon tetrachloride (40 c.c.), a trace of iodine being used for activation. After being kept at room temperature for an hour, the reaction mixture was washed with dilute sodium carbonate solution and water, dried (calcium chloride), and distilled at 10 mm. into fractions having b. p.'s 128—140°, 140—153°, 153—163°, and 163—173°. Crystals were eventually deposited by all four fractions, but in the case of the lowest fraction only after 3 weeks in the ice-chest. The crystals were drained free from oil, washed with light petroleum (b. p. 40—60°), and recrystallised from ligroin (b. p. 80—100°). 3-*Chloro*-cis-2-*decalone* (XII) (1·5 g.) formed long colourless needles, m. p. 107—108° (Found: C, 64·4; H, 8·2. $C_{10}H_{15}OCl$ requires C, 64·3; H, 8·1%).

3-*Hydroxy*-cis-2-*decalone*.—A suspension of the chloro-ketone (XII) (1·4 g.) in aqueous sodium hydroxide (0·4 g. in 25 c.c.) was boiled under reflux for an hour. After being kept overnight in the ice-chest, the crystals were collected and recrystallised from hot water. 3-*Hydroxy*-cis-2-*decalone* formed large, colourless, parallelogram-shaped crystals, m. p. 88—90° (Found: C, 71·5; H, 9·5. $C_{10}H_{16}O_2$ requires C, 71·4; H, 9·6%). The orientation was shown by oxidation of this hydroxy-ketone (0·5 g.) with a boiling solution of potassium permanganate (0·4 g.) in water (70 c.c.) to *cis-cyclo*hexane-1 : 2-diacetic acid, identified by comparison with a specimen prepared by direct oxidation of *cis*-2-decalol, m. p. 105° (Hückel, *Annalen*, 1925, **441**, 17).

Ethyl cis-2-*Decalone*-3-*carboxylate*.—A mixture of *cis*-2-decalone (5 g.) and ethyl oxalate (5 g.), cooled to −15°, was slowly added to a solution of sodium ethoxide (0·8 g. of sodium in 16 c.c. of alcohol), also cooled to −15°. After being kept overnight in the ice-chest, the mixture was treated with ice-cold dilute sulphuric acid, and the oil extracted with ether. This ethyl *cis*-2-ketodecalyl-3-glyoxylate, which could not be obtained crystalline, was characterised by its 2 : 4-*dinitrophenylhydrazone*, ochre-coloured, microscopic, elongated plates which decomposed at 181—186° (Found: C, 55·35; H, 5·4. $C_{20}H_{24}O_7N_4$ requires C, 55·5; H, 5·6%). For conversion into *ethyl* cis-2-*decalone*-3-*carboxylate* the remainder of the crude glyoxylate was heated at 180° for an hour. The keto-ester (4·7 g.) formed a colourless liquid, b. p. 130°/0·7 mm., which gave an intense purple colour with ferric chloride in alcoholic solution (Found: C, 69·0; H, 9·0. $C_{13}H_{20}O_3$ requires C, 69·6; H, 9·0%). The 2 : 4-*dinitrophenylhydrazone* formed a yellow crystalline powder (from alcohol), m. p. 169—170·5° (decomp.) (Found: C, 56·6; H, 5·9; N, 13·6. $C_{19}H_{24}O_6N_4$ requires C, 56·4; H, 6·0; N, 13·9%).

Ethyl 3-*Methyl*-cis-2-*decalone*-3-*carboxylate* (XIII).—A solution of methyl iodide (5 g.) in methyl alcohol (15 c.c.) was added, with ice-cooling, to the sodio-compound prepared by addition of ethyl *cis*-2-decalone-3-carboxylate (5·4 g.) to sodium methoxide (0·55 g. of sodium in 15 c.c. of methyl alcohol). After being kept overnight in the ice-chest, the whole was heated on the water-bath until the methyl alcohol had distilled off, and the residue was extracted with ether and shaken twice with 15% potash solution. The extract was washed, dried (sodium sulphate), and distilled in a vacuum. *Ethyl* 3-*methyl*-cis-2-*decalone*-3-*carboxylate* (XIII) formed a colourless liquid (4·7 g.), b. p. 108·5—110°/0·4 mm., $n_D^{19°}$ 1·4879 (Found: C, 69·8; H, 9·2. $C_{14}H_{22}O_3$ requires C, 70·5; H, 9·3%). The substance gave a purplish coloration with ferric chloride in alcoholic solution, so a little of the unmethylated ester was probably still present. The 2 : 4-*dinitrophenylhydrazone* formed small yellow needles (from methyl alcohol), m. p. 120—121·5° (Found: C, 56·9; H, 6·1; N, 13·4. $C_{20}H_{26}O_6N_4$ requires C, 57·4; H, 6·3; N, 13·4%).

Dehydrogenation of the keto-ester (XIII) with selenium at 300—320° for 7 hours gave, in poor yield, 3-methyl-2-naphthol, which crystallised from dilute alcohol in almost colourless plates, m. p. 156·5—157° (Veselý and Stursa, *loc. cit.*, give 155—156°) (Found: C, 83·3; H, 6·5. Calc.: C, 83·5; H, 6·4%). 1-Methyl-2-naphthol, which would arise if condensation had occurred in position 1 of *cis*-2-decalone, has m. p. 110° (Fries and Hübner, *Ber.*, 1906, **39**, 441).

Ethyl 3-*Methyl*-trans-2-*decalone*-3-*carboxylate*.—In order to complete the comparison with the *cis*-compound, ethyl *trans*-2-decalone-3-carboxylate (Hückel and Goth, *loc. cit.*), which gave a 2 : 4-*dinitrophenylhydrazone* crystallising from alcohol in thin yellow needles, m. p. 181·5—182° (decomp.) (Found: C, 56·3; H, 6·0; N, 13·85. $C_{19}H_{24}O_6N_4$ requires C, 56·4; H, 6·0; N, 13·9%), was methylated as described for its *cis*-isomeride. The resulting *ethyl* 3-*methyl*-trans-2-*decalone*-3-*carboxylate* formed a colourless liquid, b. p. 113°/0·5 mm., which gave only a faint purple colour with alcoholic ferric chloride (Found: C, 69·2; 69·4; H, 9·2, 9·2. $C_{14}H_{22}O_3$ requires C, 70·5; H, 9·3%). The 2 : 4-*dinitrophenylhydrazone* formed small, hexagonal, orange plates (from methyl alcohol), m. p. 102·5—104° (Found: C, 57·2; H, 6·1; N, 13·4. $C_{20}H_{26}O_6N_4$ requires C, 57·4; H, 6·3; N, 13·4%). Selenium dehydrogenation of the methylated keto-ester gave 3-methyl-2-naphthol, in conformity with the orientation established by Hückel and Goth (*loc. cit.*) for ethyl *trans*-2-decalone-3-carboxylate.

2-β-*Phenylethyl*-cis-2-*decalol*.—*cis*-2-Decalone (10 g.), diluted with ether (20 c.c.), was added to an ice-cold Grignard solution prepared from β-phenylethyl chloride (10·8 g.), magnesium turnings (2 g.), and anhydrous ether (80 c.c.). After being kept at 0° for an hour and then at room temperature for an hour, the mixture was heated under reflux for 2 hours and then decomposed with ice and ammonium chloride. The ethereal solution was washed, dried (sodium sulphate), and distilled. The distillate (10·1 g.), b. p. 165—168°/0·5 mm., solidified on cooling, and was recrystallised from ligroin. 2-β-*Phenylethyl*-cis-2-*decalol* (4·7 g.) formed small colourless plates, m. p. 111—112° (Found: C, 83·4; H, 10·1. $C_{18}H_{26}O$ requires C, 83·7; H, 10·15%). Dehydration of the crystalline carbinol (4·2 g.) with potassium hydrogen sulphate (8·5 g.) at 170—180° (2½ hours) gave 2-β-*phenylethyl*-cis-$\Delta^{2:3}$-*octalin* (XIV) (3·4 g.), a colourless liquid, b. p. 148—149°/0·9 mm., $n_D^{16·7°}$ 1·5449 (Found: C, 89·7; H, 10·0. $C_{18}H_{24}$ requires C, 89·9; H, 10·1%).

Cyclisation of 2-β-*Phenylethyl*-cis-$\Delta^{2:3}$-*octalin*.—Finely powdered anhydrous aluminium chloride (4·5 g.) was slowly added to an ice-cold solution of the unsaturated hydrocarbon (XIV) (3·6 g.) in carbon disulphide (35 c.c.). After being kept for 3 hours at 0° and then overnight at room temperature, the mixture was decomposed with ice, and the carbon disulphide solution was washed, dried (calcium chloride), and distilled. The distillate (3·0 g.), b. p. 154°/0·5 mm., deposited crystals when kept in the ice-chest overnight. These were collected, drained on a tile, and recrystallised from methyl alcohol. They had m. p. 68—70°, not depressed by the dodecahydro-1 : 2-benzanthracene similarly prepared from *trans*-2-decalone (Cook and Hewett, *loc. cit.*).

Dehydrogenation of Saturated Hydrocarbons obtained by Cyclisation of (XIV).—(i) The liquid mixture from which the crystalline dodecahydrobenzanthracene had been separated was heated at 300—320° for 7½ hours with platinum-black. The products were extracted with benzene, and the filtered solution was concentrated and treated with alcohol. Crystals separated and these were extracted with boiling alcohol to which a little benzene had been added. A few mg. of material remained undissolved; this, after recrystallisation from benzene, was shown to be chrysene by direct comparison of the hydrocarbon and its 2 : 7-dinitroanthraquinone complex with authentic specimens. The alcohol–benzene liquors gave crystals, m. p. 123—124°, after repeated crystallisation. This product was identical with the octahydrobenzanthracene described under (ii) (Found: C, 90·9; H, 8·4%); when dehydrogenated with selenium at 340—

360°, it gave 1 : 2-benzanthracene, identified by comparison of the hydrocarbon and its 2 : 7-dinitroanthraquinone complex with authentic specimens. The 2 : 7-*dinitroanthraquinone complex* of 1 : 2-benzanthracene, which has not been described hitherto, crystallises from xylene in magenta needles, m. p. 252—253° (decomp.) (Found : C, 73·1; H, 3·4. $C_{18}H_{12},C_{14}H_6O_6N_2$ requires C, 73·0; H, 3·4%).

(ii) Without separating the crystalline dodecahydro-1 : 2-benzanthracene, we heated the distilled mixture of saturated hydrocarbons (2·2 g.) at 300—305° for 5½ hours with palladium-black. About 500 c.c. of hydrogen were liberated. 1 : 2-Benzanthracene (0·6 g.) was isolated from the product by crystallisation from alcohol. The m. p.'s of this hydrocarbon (165—167°; lit., 160°) and its picrate (138—139°; lit., 141·5—142·5°) showed that it was not quite pure; doubtless the contaminant was chrysene, which is much less soluble. In order to remove the last traces of benzanthracene, the oil remaining after removal of the alcohol from the mother-liquors was refluxed for 1½ hours with maleic anhydride (1 g.) in xylene (20 c.c.). 2*N*-Sodium hydroxide (25 c.c.) was then added, the xylene distilled in steam, and the gum extracted and treated in alcoholic solution with picric acid (1·5 g.). The crystalline picrates were recrystallised from alcohol. The first crop formed orange needles, m. p. 150—151°, not depressed by the picrate of tetrahydrobenzanthracene (m. p. 155°; Cook and Hewett, *loc. cit.*). On standing in the ice-chest for 2 days, the mother-liquors deposited light red needles; these were freed from picric acid, and the resulting hydrocarbon recrystallised from alcohol. This *octahydro*-1 : 2-*benzanthracene* (XVII) formed slender colourless needles, m. p. 124·5—125·5° (Found : C, 91·0; H, 8·5. $C_{18}H_{20}$ requires C, 91·45; H, 8·55%). Examination of the mother-liquors from the crystallisation of the picrates did not reveal the presence of any other constituent; there was no indication of 3 : 4-benzphenanthrene, which forms a characteristic, rather sparingly soluble, red picrate (Cook, J., 1931, 2524).

3-*Keto*-Δ^4-*hexadecahydro*-1 : 2-*benzanthracene* (XVIII; trans-*form*).—The sodio-compound of *trans*-2-decalone (5 g.) was prepared by stirring its solution in anhydrous ether (50 c.c.) with finely powdered sodamide (1·3 g.) for 7 hours, the whole being finally refluxed for ½ hour. The ice-cold suspension was then treated slowly with acetyl-Δ^1-*cyclo*hexene (4·1 g.). After being kept at room temperature overnight, the mixture was boiled for an hour, then cooled, and decomposed with dilute sulphuric acid. The ethereal layer was washed, dried (sodium sulphate), and distilled. The fraction (3·3 g.), b. p. 192—195°/1·3 mm., gave a *semicarbazone*, which separated from aqueous dioxan as a colourless microcrystalline powder, m. p. 240·5—241·5° (decomp.) (Found : C, 72·3; H, 9·7. $C_{19}H_{29}ON_3$ requires C, 72·3; H, 9·3%), and a 2 : 4-*dinitrophenylhydrazone*, which formed small reddish-orange needles (from aqueous dioxan), m. p. 201·5—204° (decomp.) (Found : C, 65·5; H, 7·0. $C_{24}H_{30}O_4N_4$ requires C, 65·7; H, 6·9%). The ketone (XVIII; *trans*-form) obtained by hydrolysis of the semicarbazone was a viscous oil which began to crystallise after a month. When dehydrogenated with selenium at 300—320°, it gave 1 : 2-benzanthracene.

3-*Keto*-Δ^4-*hexadecahydro*-1 : 2-*benzanthracene* (XVIII; cis-*form*).—The sodio-derivative of *cis*-2-decalone (10 g.) was treated with acetyl-Δ^1-*cyclo*hexene as described for the *trans*-compound, and yielded 7·5 g. of a fraction, b. p. 184—189°/0·6 mm. This distillate deposited crystals of 3-*keto*-Δ^4-*hexadecahydro*-1 : 2-*benzanthracene* (XVIII; *cis*-form), which were separated from oil, drained on a tile, and recrystallised from ligroin; they formed small colourless needles, m. p. 122—122·5° (Found : C, 83·4; H, 9·95. $C_{18}H_{26}O$ requires C, 83·7; H, 10·15%). The *semicarbazone*, prepared from the crude distilled ketone, crystallised from aqueous dioxan in microscopic prisms, m. p. 258·5° (decomp.) (Found : C, 72·3; H, 9·3. $C_{19}H_{29}ON_3$ requires C, 72·3; H, 9·3%), and the 2 : 4-*dinitrophenylhydrazone* crystallised from dioxan–alcohol in orange-red microscopic needles, m. p. 172·5—179° (decomp.) (Found : C, 65·5; H, 6·9. $C_{24}H_{30}O_4N_4$ requires C, 65·7; H, 6·9%). Hydrolysis of the semicarbazone by boiling dilute sulphuric acid gave the same crystalline ketone which had been separated from the crude mixture, and the structure of this ketone was established by its dehydrogenation to 1 : 2-benzanthracene by selenium at 300—320°.

In another experiment the mixture of ketones (3·8 g.; b. p. 165—175°/0·5 mm.) from *cis*-2-decalone (5 g.) and acetyl-Δ^1-*cyclo*hexene (4·1 g.) was reduced by 6 hours' boiling with acetic acid (50 c.c.), concentrated hydrochloric acid (50 c.c.), and amalgamated zinc wool (15 g.). At the end of the first hour toluene (10 c.c.) and concentrated hydrochloric acid (10 c.c.) were added, further portions of hydrochloric acid (10 c.c.) being then added after each hour. The product (b. p. 136—138°/0·6 mm.; 3·2 g.) was heated with platinum-black (0·25 g.) at 300—320° for 7 hours. 1 : 2-Benzanthracene (0·45 g.) was isolated by crystallisation from alcohol. In order to remove the last traces of this hydrocarbon the material recovered from the mother-

liquors was refluxed for 2 hours with maleic anhydride (2 g.) in xylene (15 c.c.). The xylene was removed in steam in presence of excess of alkali, and the residual oil was extracted with ether, and then, after removal of the ether, treated with alcoholic picric acid. Fractional crystallisation of the picrates gave a small amount of the picrate of tetrahydro-1 : 2-benzanthracene, identified by the method of mixed m. p.'s, and an impure specimen of the picrate of 3 : 4-benzphenanthrene (0·3 g.; m. p. 118—120°; lit., 126—127°). The hydrocarbon regenerated from this picrate was identified by comparison with authentic 3 : 4-benzphenanthrene and by oxidation to the quinone, and conversion of this into the corresponding phenazine. The m. p.'s of these derivatives were not depressed by admixture with authentic specimens (Cook, J., 1931, 2524).

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