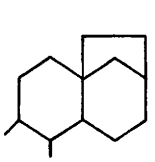
## 244. *Synthesis of Some Angularly Bridged Cyclic Systems. Part I. Perhydrobenz*[d]*indole.*

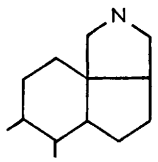
By R. D. HAWORTH and A. F. TURNER.

1-Oxo-*cis*-9-decalylacetic acid (X; R = H) has been prepared from 2-*N*-methylanilinomethylene-1-decalone and ethyl bromoacetate, and converted into perhydrobenz[*d*]indole (III; R = H). The configuration of the acid (X; R = H) has been established by descent and reduction to *cis*-decalin-9-carboxylic acid, identical with a specimen obtained by a second and unambiguous synthesis.

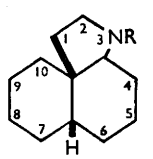
RESEARCHES in progress in these laboratories on cafestol and conessine [1] have emphasised the importance of angular homo- and hetero-cyclic systems (I) and (II) respectively and led to a number of investigations aiming at the synthesis of these and similar ring systems. The present communication describes experiments, based on 1-decalone as starting material, which have culminated in the synthesis of the base (III).



(I)




(II)

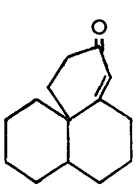



(III)

As α-alkylated ketones are reported [2,3,4] to react with methyl vinyl ketones at the methine rather than the methylene carbon atom, it was expected that 1-decalone would yield the angular system (IV) instead of the isomeric phenanthrene type. However, no success attended attempts to bring about reaction between 1-decalone and 4-diethylaminobutan-2-one methiodide under conditions which have met with success in other fields.[2,3,5] Experiments with 2-*iso*propoxymethylene-1-decalone were equally unsuccessful

[1] Haworth and Johnstone, *J.*, 1957, 1492; Haworth and Michael, *J.*, 1957, 4973.
[2] du Feu, McQuillin, and Robinson, *J.*, 1937, 53.
[3] Robinson and Weygand, *J.*, 1941, 386.
[4] Cornforth and Robinson, *J.*, 1946, 676.
[5] Ghosh and Robinson, *J.*, 1944, 506.

and, when pyridine was used as solvent,[6] condensation occurred and the dodecahydro-3-oxophenanthrene (V) and perhydro-12-hydroxy-3-oxophenanthrene (VI) were isolated, but we are unable to give a satisfactory explanation of the removal of the enol ether group. The structures of these two products were in agreement with spectroscopic data; the ketol (VI) displayed infrared maxima at 3252 and 1715 cm.$^{-1}$ (hydroxy and keto-group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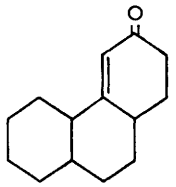
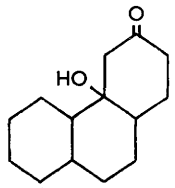
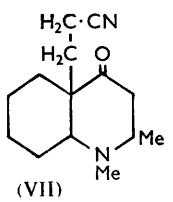

(V)



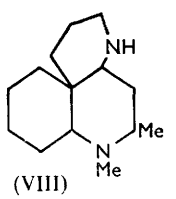
(VI)

respectively [7]), and the αβ-unsaturated ketone (V) showed an ultraviolet absorption maximum at 240 mμ, consistent [8,9] with the ββ-disubstitution and an exocyclic double bond. The ketol (VI) was smoothly dehydrated by ethanolic hydrochloric acid to compound (V), and the latter, after conversion by Huang-Minlon [10] reduction [10] into 1 : 2 : 3 : 5 : 6 : 7 : 8 : 9 : 10 : 11 : 13 : 14-dodecahydrophenanthrene (not purified), was dehydrogenated with selenium in excellent yield to phenanthrene. The ketone (V) and ketol (VI) were also prepared from 2-formyl-1-decalone, condensation in this case being directed to the 2-position by the known [11,12] activating influence of the formyl group.

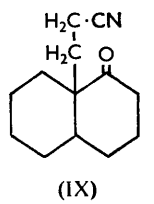
Recently Nazarov *et al.*[13] have described the cyanoethylation of perhydro-1 : 2-dimethyl-4-quinolone to 10-2′-cyanoethylperhydro-1 : 2-dimethyl-4-quinolone (VII), and shown that reductive cyclisation of this product yielded the diacidic base (VIII). 1-Decalone reacted similarly with acrylonitrile in the presence of potassium hydroxide, to give an oil containing the cyanoethyl derivative (IX). The infrared maxima at 2255 and 1695 cm.$^{-1}$ were assigned to the aliphatic nitrile [7] and the keto-group respectively, and the oil gave a crystalline 2 : 4-dinitrophenylhydrazone. The oil also yielded a crystalline 2-piperonylidene derivative with infrared maxima at 2263 (C≡N group [7]) and 1664 cm.$^{-1}$ (conjugated C=O group), and the isolation of this derivative provided evidence of the presence of the 9-cyanoethyl derivative (IX). Hydrolysis of the crude cyano-



(VII)



(VIII)



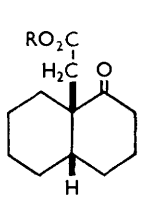
(IX)

ethylation product, however, gave an inseparable mixture of acids; on one occasion a pure β-(1-oxodecalyl)propionic acid was obtained but the experiment could not be repeated, and it was not possible to determine whether this specimen was derived from the nitrile (IX) or from the isomeric nitrile with the cyanoethyl group in position 2.

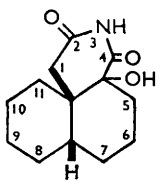
The most fruitful approach discovered during these experiments with 1-decalone is based upon the introduction of an acetic acid residue into position 9. 2-*N*-Methylanilinomethylene-1-decalone was condensed with ethyl bromoacetate in presence of sodamide

[6] McQuillin, *J.*, 1955, 528.
[7] Bellamy, "The Infra-Red Spectra of Complex Molecules," Methuen, London, 1954.
[8] Woodward, *J. Amer. Chem. Soc.*, 1942, **65**, 76.
[9] Fieser, Fieser, and Rajogopalan, *J. Org. Chem.*, 1948, **13**, 800.
[10] Huang-Minlon, *J. Amer. Chem. Soc.*, 1949, **71**, 3301.
[11] Wilds and Werth, *J. Org. Chem.*, 1952, **17**, 1149; 1952, **17**, 1154.
[12] Wilds and Schunk, *J. Amer. Chem. Soc.*, 1949, **71**, 3946; 1950, **72**, 2388.
[13] Nazarov, Schuckhgeimer, and Rudenko, *Zhur. obschei Khim.*, 1954, **24**, 319.

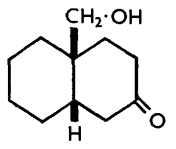
and, after the two-stage hydrolytic procedure [14] for removal of the blocking group, 1-oxo-*cis*-9-decalylacetic acid (X; R = H) was obtained. This keto-acid gave a crystalline oxime and 2 : 4-dinitrophenylhydrazone; attempted conversion into the cyanohydrin gave a compound insoluble in sodium hydrogen carbonate but soluble in sodium hydroxide solution, and its probable imide structure (XI) was supported by the infrared maxima at 3355 (OH group), 3187 (NH group), 1730 and 1694 cm.$^{-1}$ (imide-CO group). Attempted decarboxylation of the acid (X; R = H) to 9-methyl-1-decalone was unsuccessful but structure (X; R = H) was strongly supported by Clemmensen reduction to *cis*-9-decalylacetic acid which on dehydrogenation in the vapour phase over palladium–charcoal [15] gave naphthalene in poor yield instead of 2-methylnaphthalene which would be expected from the isomeric *cis*-2-decalylacetic acid. Final proof of the structure (X; R = H) was obtained by Barbier–Wieland degradation [16] of *cis*-9-decalylacetic acid to *cis*-decalyl-9-carboxylic acid, which differed from the known *trans*-isomer [17] but was identical with a specimen of *cis*-decalin-9-carboxylic acid prepared from 10-hydroxymethyl-*cis*-2-decalone



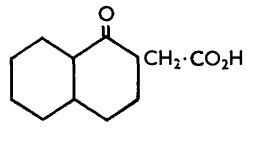
(X)



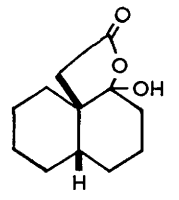
(XI)



(XII)



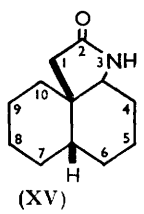
(XIII)



(XIV)

(XII). The *cis*-structure of (XII) has been established by Minckler, Hussey, and Baker,[18] and Clemmensen reduction followed by oxidation with chromic acid gave *cis*-decalin-9-carboxylic acid. (This acid has also been described by Dauben and Rogan [19] after this communication had been prepared.) 1-Oxo-2-decalylacetic acid (XIII) was also synthesised, for comparison, from 2-formyl-1-decalone and ethyl bromoacetate. A peculiar result was obtained during an attempted preparation of the homologue of acid (X; R = H); the sodium salt, on treatment with oxalyl chloride followed by diazomethane, gave a substance, $C_{12}H_{18}O_3$, m. p. 67—69°, which contained neither nitrogen nor chlorine, and was reconverted into 1-oxo-*cis*-9-decalylacetic acid on hydrolysis. The lactone structure (XIV) has been considered but requires confirmation.

When methyl or ethyl 1-oxo-*cis*-9-decalylacetate (X; R = Me or Et) was treated with formamide and formic acid under conditions of the Leuckart reaction, the lactam (XV)



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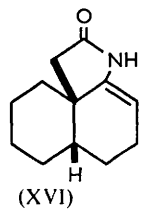
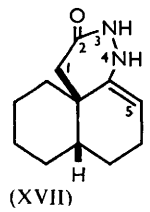
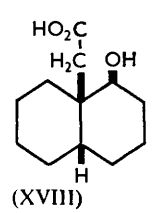


(XVI)



(XVII)



(XVIII)

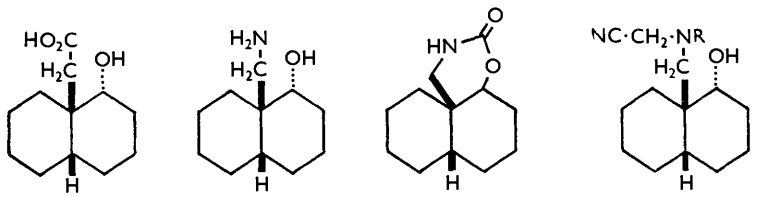
was obtained. The structure (XV) was supported by the infrared maxima at 3219 and 3053 (NH group) and 1694 cm.$^{-1}$ ($\gamma$-lactam CO group).[7] When treated with lithium aluminium hydride, the lactam (XV) was converted into the oily secondary base (III;

[14] Birch and Robinson, *J.*, 1944, 501.
[15] Linstead and Thomas, *J.*, 1940, 1127.
[16] Barbier and Locquin, *Compt. rend.*, 1913, 156, 1443; Wieland, Schlichting, and Jacobi, *Z. physiol. Chem.*, 1926, **161**, 80.
[17] Dauben, Tweit, and MacLean, *J. Amer. Chem. Soc.*, 1955, **77**, 48; Hussey, Liao, and Baker, *ibid.*, 1953, **25**, 4727.
[18] Minckler, Hussey, and Baker, *ibid.*, 1956, **78**, 1009.
[19] Dauben and Rogan, *ibid.*, 1957, **79**, 5002.

R = H), characterised as the hydrobromide and methylated by formaldehyde and formic acid to the oily tertiary base (III; R = Me) which gave a crystalline methiodide.

Methyl 1-oxo-*cis*-9-decalylacetate (X; R = Me) reacted with methanolic ammonia but the amide could not be purified because of its ready conversion into the unsaturated lactam (XVI), which was reduced catalytically to (XV). Similarly methyl 1-oxo-*cis*-9-decalylacetate (X; R = Me) with hydrazine yielded the cyclic hydrazide (XVII) which furnished an *N*-nitroso-derivative; this hydrazide was also obtained by the action of hydrazine on the oxime of methyl 1-oxo-*cis*-9-decalylacetate, but attempts to reduce it to the perhydro-derivative were unsuccessful.

1-Oxo-*cis*-9-decalylacetic acid (X; R = H) was reduced with sodium borohydride, to a mixture of a hydroxy-acid, m. p. 118°, which gave an oily lactone, and a γ-lactone (CO maximum at 1780 cm.$^{-1}$), m. p. 66°. The hydroxy-acid corresponding to the γ-lactone, m. p. 66°, could not be isolated although hydrolysis of the oily lactone readily gave the hydroxy-acid, m. p. 118°. The two isomeric 2-hydroxy*cyclo*hexylacetic acids show a similar behaviour and Newman and VanderWerff [20] have assigned a *cis*-structure to the lactone from which the corresponding hydroxy-acid could not be isolated. On this basis the γ-lactone of m. p. 66° is the lactone of *cis*-1-hydroxy-*cis*-9-decalylacetic acid * (XVIII),




(XIX) (XX) (XXI) (XXII)

and the acid of m. p. 118° is *trans*-1-hydroxy-*cis*-9-decalylacetic acid (XIX). *trans*-1-Hydroxy-*cis*-9-decalylacetic acid (XIX) was also prepared from the keto-acid (X; R = H) either by catalytic reduction or by alkoxide reduction of the methyl ester. The observation that *both* stereoisomers (XVIII) and (XIX) may be lactonised provides further evidence for the *cis*-fusion of the rings, as, if chair conformation of the rings is assumed, a a *trans*-1-hydroxy-*trans*-9-decalylacetic acid must have a diaxial conformation of both substituents and lactonisation would be impossible.

An attempt to convert *trans*-1-oxo-*cis*-9-decalylacetic acid (XIX) into *trans*-9-aminomethyl-*cis*-1-decalol (XX) *via* the hydrazide gave the cyclic urethane (XXI) in poor yield. However the amide of the acid (XIX), prepared from the methyl ester by methanolic ammonia, was successfully degraded to the base (XX) by the Hofmann procedure. Attempts to oxidise *trans*-9-aminomethyl-*cis*-1-decalol (XX) to the corresponding 1-decalone were unsuccessful, but it was converted into *trans*-9-(*N*-cyanomethylaminomethyl)-*cis*-1-decalol (XXII; R = H) by the action of formaldehyde and potassium cyanide. This oily base (XXII; R = H), which gave a crystalline hydrochloride, was methylated to *trans*-9-(*N*-cyanomethyl-*N*-methylaminomethyl)-*cis*-1-decalol (XXII; R = Me), characterised as the methiodide, but again oxidation to the decalone could not be effected.

## Experimental

Light petroleum refers to the fraction of b. p. 40—60°, ligroin refers to the fraction of b. p. 60—80°, and N-aqueous-methanolic potassium hydroxide refers to a solution prepared by dissolving potassium hydroxide (5·65 g.) in water (5 c.c.) and adding methanol to bring the

* Following Minckler *et al.*,[8] the relationship of the angular and peripheral substituents prefixes the name and the nature of the ring fusion is expressed as a prefix to the root of the name. The reference group is the 9-substituent.

[20] Newman and VanderWerff, *J. Amer. Chem. Soc.*, 1945, **67**, 233.

volume to 100 c.c. 1-Decalol, prepared by Birch and Robinson's method [14] using W-7 Raney nickel, was oxidised to 1-decalone as described by Johnson and Posvic.[21]

*Perhydro-12-hydroxy-3-oxophenanthrene* (VI) *and* 1 : 2 : 3 : 5 : 6 : 7 : 8 : 9 : 10 : 11 : 13 : 14-*Dodecahydro-3-oxophenanthrene* (V).—(a) *From* 2-iso*propoxymethylene-1-decalone*. A solution of 2-*iso*propoxymethylene-1-decalone [21] (7·3 g.) in ether (150 c.c.) was heated in dry nitrogen with potassamide prepared from potassium (1·41 g.) and liquid ammonia (30 c.c.) with ferric nitrate (20 mg.) as catalyst. A solution of the methiodide (9·4 g.) of 4-diethylaminobutan-2-one [22] in pyridine (50 c.c.) was added rapidly and with stirring to the deep red suspension at 0°, and the mixture, after 8 hr. at 0° and 12 hr. at room temperature, was refluxed for 5 hr. After addition of water, the mixture was extracted with ether; removal of the solvent gave a thick red oil (4·3 g.), which, after being freed from pyridine at 100°/0·1 mm. (2 hr.), was treated with ferric chloride (15 g.) in methanol (40 c.c.) for 2 hr. at 0°. The product, isolated with ether and washed successively with dilute hydrochloric acid and sodium hydroxide, was a neutral brown oil (3·6 g.).

(b) *From 2-formyl-1-decalone*. To a solution of sodium (4·20 g.) in methanol (30 c.c.) was added 2-formyl-1-decalone [21] (3·00 g.) in methanol (10 c.c.), followed by the methiodide (8·8 g.) of 4-diethylaminobutan-2-one in pyridine (20 c.c.). After 4 days, water was added and the neutral product isolated with ether as a brown oil (3·6 g.).

Chromatography of the products from either (a) or (b) on alumina (100 g.) gave (i), by light petroleum, an oil (0·10 g.), (ii) by light petroleum–benzene (1 : 1), an oil (0·23 g.), (iii) by benzene, an oil (0·48 g.), (iv) by benzene–ether (1 : 1), an oil (0·12 g.), (v) by ether, oily crystals (0·35 g.), (vi) by ether–chloroform (1 : 1), oily crystals (0·65 g.), (vii) by chloroform, oily crystals (0·35 g.), (viii) by chloroform–methanol (1 : 1), a viscous yellow oil (0·75 g.), and (ix) by methanol, a brown tar (0·25 g.). Combination and distillation of the first three fractions gave 1 : 2 : 3 : 5 : 6 : 7 : 8 : 9 : 10 : 11 : 13 : 14-*dodecahydro-3-oxophenanthrene* (V) (0·69 g.), b. p. 120—130° (bath)/0·001 mm., which slowly crystallised as stout needles, m. p. 53—54° (Found: C, 82·0; H, 10·1. $C_{14}H_{20}O$ requires C, 82·3; H, 9·9%), $\lambda_{max.}$ 240 mμ (log ε 4·2 in EtOH). The *semicarbazone* separated from methanol in plates, m. p. 225—226° (Found: C, 69·4; H, 8·6; N, 16·3. $C_{15}H_{23}ON_3$ requires C, 68·9; H, 8·9; N, 16·1%). Fractions (v), (vi), and (vii), combined and crystallised first from light petroleum and then from ligroin, gave *perhydro-12-hydroxy-3-oxophenanthrene* (VI) (0·7 g.) as needles, m. p. 128—129° (Found: C, 75·8; H, 9·9. $C_{14}H_{22}O_2$ requires C, 75·7; H, 9·9%). The infrared spectrum (KBr disc) showed absorption at 1715 and 3525 cm.$^{-1}$. Dehydration of the ketol (VI) (200 mg.) with concentrated hydrochloric acid (0·3 c.c.) in ethanol (3 c.c.) took place at room temperature and yielded the dodecahydro-3-oxophenanthrene (170 mg.) (V), m. p. 53—54°.

*Conversion of the Ketone* (V) *into Phenanthrene*.—The unsaturated ketone (V) (300 mg.) was refluxed for 0·5 hr. with hydrazine hydrate (290 mg.) in diethylene glycol (20 c.c.). Potassium hydroxide (270 mg.) in a little water was added, the mixture was refluxed for another 0·5 hr., concentrated until the temperature of the liquid was 200°, and finally refluxed for 2 hr. 1 : 2 : 3 : 5 : 6 : 7 : 8 : 9 : 10 : 11 : 13 : 14-Dodecahydrophenanthrene, isolated with ether as an oil (183 mg.), b. p. (bath) 180°/10 cm., was heated with selenium (600 mg.) at 320° for 12 hr.; phenanthrene (160 mg.), m. p. 93—94° (picrate, m. p. 143—144°), was obtained.

9-2′-*Cyanoethyl-1-decalone* (IX).—A mixture of 1-decalone (15·7 g.), acrylonitrile (1·88 g.), and 40% potassium hydroxide solution (0·9 c.c.) was stirred for 24 hr. and then set aside for 3 days. Excess of hydrochloric acid was added and the product, isolated with ether, was an oil from which unchanged 1-decalone (13·0 g.) was recovered by distillation. The residue was adsorbed on an alumina (30 g.) column and eluted first with ether–light petroleum (1 : 20) and then with ether. Evaporation of the ether yielded crude 9-2′-cyanoethyl-1-decalone (IX) (1·79 g.), b. p. 120°/0·5 cm.; the infrared spectrum (Nujol mull) showed maxima at 2255 and 1695 cm.$^{-1}$. The 2 : 4-*dinitrophenylhydrazone* crystallised from ethanol in orange needles, m. p. 180° (Found: C, 59·1; H, 6·2; N, 17·9. $C_{19}H_{23}O_4N_5$ requires C, 59·2; H, 6·0; N, 18·2%).

9-2′-*Cyanoethyl-2-piperonylidene-1-decalone*, prepared from 9-2′-cyanoethyl-1-decalone (97 mg.), piperonaldehyde (81 mg.), and 15% sodium hydroxide solution (0·18 c.c.), crystallised from ethanol in yellow plates, m. p. 127° (Found: C, 74·3; H, 7·1; N, 4·0. $C_{21}H_{23}O_3N$ requires C, 74·7; H, 6·9; N, 4·1%). The infrared spectrum (KBr disc) showed maxima at 2263 and 1664 cm.$^{-1}$. Crude 9-2′-cyanoethyl-1-decalone (IX), when hydrolysed for 12 hr. with excess

[21] Johnson and Posvic, *ibid.*, 1947, **69**, 1361.
[22] Wilds and Schunk, *J. Amer. Chem. Soc.*, 1943, **65**, 469; Cornforth and Robinson, *J.*, 1949, 1855.

of boiling 30% sodium hydroxide solution, usually gave an *acid* mixture which after several crystallisations from ligroin had m. p. 78—90°; on one occasion needles, m. p. 130° (Found: C, 69·3; H, 9·1. $C_{13}H_{20}O_3$ requires C, 69·6; H, 9·0%), were obtained.

1-*Oxo*-cis-9-*decalylacetic acid* (X; R = H).—A solution of 2-*N*-methylanilinomethylene-1-decalone [14] (50 g.) in benzene (200 c.c.) was added to a stirred suspension of sodamide, prepared in a nitrogen atmosphere by addition of sodium (4·3 g.) to liquid ammonia (100 c.c.) containing ferric nitrate (50 mg.) in benzene (100 c.c.), the whole being then boiled for 4 hr. Ethyl bromoacetate (31 g.) was added to the cooled suspension, and reaction completed by 2 hours' refluxing. The solvent was removed under reduced pressure and the residual gum refluxed for 1 hr. with water (400 c.c.) and concentrated hydrochloric acid (200 c.c.). The top insoluble layer was taken up in ether and, after removal of the solvent, the hydrolysis was completed by 1 hour's boiling with 20% aqueous sodium hydroxide (300 c.c.). Unchanged 1-decalone (13·6 g.) was removed in ether, and the acid (X; R = H) recovered from the alkaline layer was isolated with ether and purified by distillation; it was obtained as a viscous yellow oil, b. p. 150—180°/0·03 mm. with some decomposition, which separated from carbon tetrachloride or ether–ligroin in rods (5·0 g.), m. p. 100° (Found: C, 68·2; H, 8·8. $C_{12}H_{18}O_3$ requires C, 68·5; H, 8·6%). The yield was not improved by the use of potassamide or triphenylmethylsodium as condensing agent. The 2 : 4-*dinitrophenylhydrazone* crystallised from aqueous acetic acid in pale orange needles, m. p. 203—210° (decomp.) (Found: C, 55·4; H, 5·7; N, 14·0. $C_{18}H_{22}O_6N_4$ requires C, 55·4; H, 5·7; N, 14·3%). The *oxime* crystallised from aqueous ethanol in colourless needles, m. p. 166—169° (decomp.) (Found: C, 63·8; H, 8·6; N, 6·0. $C_{12}H_{19}O_3N$ requires C, 64·0; H, 8·5; N, 6·2%). A mixture of hydrogen cyanide (2·3 g.) and sodium cyanide (180 mg.) in the minimum of water was added to a solution of the keto-acid (X; R = H) (210 mg.) in methanol (7·0 c.c.). After 24 hr. the hydrogen cyanide was removed, dilute hydrochloric acid and chloroform were added, and the chloroform extract yielded a pale brown oil (230 mg.) which was refluxed for 0·5 hr. with 2N-sulphuric acid (10 c.c.). The product was taken up in ether, unchanged keto-acid (X; R = H) (64 mg.) was removed by washing with sodium hydrogen carbonate, and the residual neutral *perhydro-4a-hydroxy*-2 : 4-*dioxobenzo*[e]iso*quinoline* (XI) (113 mg.) separated from benzene in small colourless needles, m. p. 193—194° (Found: C, 65·6; H, 7·9; N, 5·9. $C_{13}H_{19}O_3N$ requires C, 65·8; H, 8·1; N, 5·9%), which dissolved in aqueous sodium hydroxide but not in sodium hydrogen carbonate; the infrared spectrum (KBr disc) showed maxima at 3355, 3187, 1730, and 1694 cm.$^{-1}$. Powdered sodium 1-oxo-9-decalylacetate (856 mg.), prepared from the acid and sodium hydrogen carbonate, was suspended in benzene (15 c.c.) containing pyridine (1 drop), and oxalyl chloride (3·5 c.c.) was added. After 2 hr., the solvents were removed under reduced pressure and the residue was taken up in benzene (15 c.c.) and added to an excess of diazomethane in ether. After another hr. the mixture was washed successively with dilute hydrochloric acid and water, dried, and evaporated. The product, probably the *lactone* (XIV), separated from light petroleum in long needles, m. p. 67—69° (Found: C, 67·8; H, 8·4. $C_{12}H_{18}O_3$ requires C, 68·5; H, 8·6%).

1-*Oxo*-2-*decalylacetic Acid*.—2-Formyl-1-decalone (1·51 g.), dissolved in a little methanol, was added to a solution of sodium methoxide (from sodium, 200 mg.) in methanol (15 c.c.). Ethyl bromoacetate (1·37 g.) in methanol (5 c.c.) was added and after 12 hr. at room temperature the reaction was completed by 3 hours' refluxing. The product, isolated with ether, was refluxed for 1 hour with N-aqueous potassium hydroxide (25 c.c.); 1-decalone (320 mg.) was recovered from the neutral fraction, and the alkaline liquors yielded 1-*oxo*-2-*decalylacetic acid* (320 mg.) which separated from ether–light petroleum as colourless plates, m. p. 153—154° (Found: C, 68·7; H, 8·7. $C_{12}H_{18}O_3$ requires C, 68·5; H, 8·6%).

cis-9-*Decalylacetic Acid*.—Methyl 1-oxo-*cis*-9-decalylacetate (500 mg.), prepared as a colourless oil, b. p. 120° (bath)/0·01 mm., from the acid (X; R = H) by the action of either methanolic sulphuric acid or diazomethane, was reduced during 12 hr. with amalgamated zinc (7 g.), concentrated hydrochloric acid (25 c.c.), and acetic acid (1·5 c.c.). The *product*, isolated with ether, crystallised from aqueous ethanol or light petroleum in colourless needles, m. p. 115° (Found: C, 73·4; H, 10·6. $C_{12}H_{20}O_2$ requires C, 73·4; H, 10·3%). The *anilide* crystallised from aqueous alcohol or light petroleum in slender needles, m. p. 155—156° (Found: C, 79·7; H, 9·3; N, 5·4. $C_{18}H_{25}ON$ requires C, 79·7; H, 9·3; N, 5·2%). *cis*-9-Decalylacetic acid (150 mg.) was dehydrogenated in an apparatus similar to that described by Linstead and Thomas,[15] with 30% palladium–charcoal on glass wool as catalyst at 325°; naphthalene (25 mg.) was isolated and identified by m. p. and mixed m. p.

cis-*Decalin*-9-*carboxylic Acid*.—(a) *From* cis-9-*decalylacetic acid*. Methyl *cis*-9-decalylacetate (415 mg.), prepared by action of diazomethane on the acid, was added in dry ether (25 c.c.) to a solution of phenylmagnesium bromide, prepared from bromobenzene (4·77 g.), magnesium (0·72 g.), and ether (20 c.c.). After 2½ hours' refluxing, the mixture was evaporated, benzene (30 c.c.) was added and the refluxing continued for a further 2½ hr. The mixture was acidified and the neutral product adsorbed on a column of alumina (30 g.) prepared in light petroleum. Elution with the same solvent gave diphenyl (480 mg.) and then an oil (360 mg.) which was heated with acetic anhydride (10 c.c.) for 20 min. The solvent was removed under reduced pressure, and the residue dissolved in acetic acid (15 c.c.) and oxidised during 24 hr. by chromic anhydride (253 mg.) in water (3 c.c.). Excess of oxidising agent was destroyed with ethanol and the solution evaporated under reduced pressure. The residual gum was shaken with ether and water, and the *acid* (75 mg.) removed from the ether layer by sodium hydrogen carbonate was recovered; it crystallised from aqueous ethanol in needles (33 mg.), m. p. 121—122° (Found: C, 72·7; H, 10·1. $C_{11}H_{18}O_2$ requires C, 72·5; H, 10·0%).

(b) *From* cis-10-*hydroxymethyl*-2-*decalone* (XII). The ketone [18] (XII) (1·60 g.) was reduced with amalgamated zinc (10 g.) and concentrated hydrochloric acid (25 c.c.). Extraction with ether gave crude 9-(hydroxymethyl)-*cis*-decalin (1·11 g.), b. p. (bath), 150—170°/10 mm., which crystallised on storage but was not purified further. Oxidation of the oil (350 mg.) in acetic acid (15 c.c.) with chromic anhydride (314 mg.) in water (1 c.c.) gave *cis*-decalin-9-carboxylic acid (30 mg.), m. p. 121—122°, alone or mixed with a specimen prepared by method (a).

*Perhydro*-2-*oxobenz*[d]*indole* (XV).—Methyl 1-oxo-9-decalylacetate (700 mg.), formamide (25 c.c.), and 98% formic acid (5 c.c.) were boiled under conditions which permitted excape of water. When the temperature of the fluid reached 190° the mixture was refluxed for 12 hr., then poured into water. The *product* (XV) (590 mg.) had m. p. 183—185° and separated from *cyclo*hexane in small needles, m. p. 189° (Found: C, 74·6; H, 9·9; N, 7·2. $C_{12}H_{19}ON$ requires C, 74·5; H, 9·9; N, 7·2%).

*Perhydrobenz*[d]*indole* (III; R = H).—A solution of lactam (XV) (460 mg.) in tetrahydrofuran (100 c.c.) was refluxed for 12 hr. with lithium aluminium hydride (410 mg.). After removal of the bulk of the solvent, water was added and the mixture extracted continuously with ether during 4 hr. Unchanged lactam (XV) (123 mg.) was recovered from the ether, and the base (III; R = H) removed in dilute hydrochloric acid and recovered as a brown oil (347 mg.). The *hydrobromide*, prepared with hydrogen bromide in ether, separated from acetone–ether in small colourless needles, m. p. 215° (Found: C, 55·0; H, 8·3; N, 5·7; Br, 30·8. $C_{12}H_{21}N$,HBr requires C, 55·4; H, 8·5; N, 5·4; Br, 30·7%). The base (III; R = H), recovered from the hydrobromide as an oil, gave a positive Liebermann test.

*Perhydro*-3-*methylbenz*[d]*indole* (III; R = Me).—A mixture of the secondary base (III; R = H) (154 mg.), 98% formic acid (2 c.c.), and 40% formaldehyde (2 c.c.) was heated on a steam-bath for 12 hr. Concentrated hydrochloric acid (0·4 c.c.) was added, the solution was evaporated to dryness under reduced pressure, and the residue taken up in water and filtered, and the base recovered and isolated with ether. The crude brown oil (147 mg.), warmed with methyl iodide in hot acetone, gave a *methiodide* which separated from acetone–ether in small needles, m. p. 244° (Found: C, 50·2; H, 7·8; N, 4·2; I, 37·5. $C_{14}H_{26}NI$ requires C, 50·1; H, 7·8; N, 4·1; I, 37·8%).

1 : 2 : 3 : 5 : 6 : 6a : 7 : 8 : 9 : 10-*Decahydro*-2-*oxobenz*[d]*indole* (XVI).—Methyl 1-oxo-9-decalylacetate (from 700 mg. of acid) and ethanolic ammonia (40 c.c.; saturated at 0°) were heated in a sealed tube at 120° for 12 hr. Evaporation gave a brown gum which was adsorbed on a column of alumina (18 g.) prepared in benzene. On elution the column gave, to ether, crystals " a " (145 mg.); to chloroform, crystals " b " (120 mg.) followed by an oil (20 mg.); to methanol–chloroform (5% v/v), crystals " c " (292 mg.); and to methanol, an oil (48 mg.). Crystals " c " separated from *cyclo*hexane in slender rods, m. p. 184°, of the *lactam* (XVI) (Found: C, 74·8; H, 9·0; N, 7·2. $C_{12}H_{17}ON$ requires C, 75·3; H, 9·0; N, 7·3%), which were reduced by hydrogen in presence of 10% palladium–charcoal to perhydro-2-oxobenz[*d*]indole (XV), m. p. 188°. Crystals " a " and " b " were combined; recrystallisation from ligroin gave needles, m. p. 136—138°, which on further recrystallisation from ligroin separated into slender rods, m. p. 184°, of the unsaturated lactam (XVI) mentioned above, and long thin needles, m. p. 138—139°, which could not be purified. These needles were probably the amide of acid (X; R = H) and on attempted purification were converted into the lactam (XVI).

2 : 3 : 4 : 6 : 7 : 7a : 8 : 9 : 10 : 11-*Decahydro*-2-*oxo*-1H-*benzo*[e]*cinnoline* (XVII).—Methyl

1-oxo-9-decalylacetate (120 mg.) and 100% hydrazine hydrate (0·5 c.c.) in sufficient methanol to produce homogeneity were refluxed for 1½ hr., then cooled and the *product* (XVII) (80 mg.) was collected and crystallised first from benzene and then from *cyclo*hexane; it formed small needles, m. p. 204—205° (Found: C, 69·4; H, 8·9; N, 13·7. $C_{12}H_{18}ON_2$ requires C, 69·8; H, 8·8; N, 13·6%). This cyclic hydrazide reacted with nitrous acid in acetic acid solution at 0°, yielding a yellow crystalline *N*-nitroso-compound which gave a positive Liebermann reaction.

*Reduction of* 1-*Oxo*-cis-9-*decalylacetic Acid*.—(a) *With aluminium* iso*propoxide*. A mixture of methyl 1-oxo-*cis*-9-decalylacetate (200 mg.) and a molar solution of aluminium *iso*propoxide in propan-2-ol (15 c.c.) was slowly distilled during 4 hr., then concentrated under reduced pressure and boiled with excess of dilute hydrochloric acid. The product, isolated with ether, was a yellow oil (210 mg.) which yielded to sodium hydrogen carbonate solution unchanged 1-oxo-9-decalylacetic acid (69 mg.) and a neutral oil (91 mg.) which was hydrolysed by 1 hour's boiling with N-aqueous-methanolic potassium hydroxide (20 c.c.) to trans-1-*hydroxy*-cis-9-*decalylacetic acid* (XIX). This hydroxy-acid crystallised from light petroleum containing a little ether in slender needles (88 mg.), m. p. 118° (Found: C, 67·7; H, 9·1. $C_{12}H_{20}O_3$ requires C, 67·9; H, 9·5%), which gave an oily lactone from which the hydroxy-acid was recovered.

(b) *With hydrogen in presence of platinic oxide*. Reduction in acetic acid gave similar results to those outlined in (a).

(c) *With sodium borohydride*. To a solution of 1-oxo-*cis*-9-decalylacetic acid (1 g.) in 0·1N-sodium hydroxide (15 c.c.) was added a solution of sodium borohydride (400 mg.) in water (10 c.c.). The solution was boiled for 1 hr., cooled to 0°, covered with ether, and acidified with dilute hydrochloric acid. The ether extract yielded to sodium hydrogen carbonate solution *trans*-1-hydroxy-*cis*-9-decalylacetic acid (XIX) (540 mg.), m. p. 118°, and retained cis-1-*hydroxy*-cis-9-*decalylacetic lactone* (cf. XVIII) (403 mg.) which separated from light petroleum as prisms, m. p. 66° (Found: C, 74·1; H, 9·4. $C_{12}H_{18}O_2$ requires C, 74·2; H, 9·3%), $\nu_{max.}$ (KBr disc) 1780 cm.$^{-1}$. The lactone dissolved in warm dilute sodium hydroxide solution, but the corresponding hydroxy-acid could not be isolated, and attempts to oxidise the lactone with permanganate, hypobromite, and chromic acid in acetic acid or pyridine were unsuccessful. The lactone was recovered after 5 days at 85° in a sealed tube with methanolic ammonia (saturated at room temperature).

*Perhydro*-3-*oxobenz*[e]1 : 3-*benzoxazine* (XXI).—Methyl *trans*-1-hydroxy-*cis*-9-decalylacetate, prepared from the acid (XIX) (150 mg.) and ethereal diazomethane, was refluxed by 1½ hr. with 100% hydrazine hydrate (7 drops) and a little methanol. After dilution with water and acidification with dilute hydrochloric acid, neutral matter was removed in ether, and the base liberated with aqueous ammonia was taken up in ether and recovered as an oil (145 mg.) which partly crystallised but was not purified. The basic oil (145 mg.) was dissolved in excess of dilute hydrochloric acid, sodium nitrite (58 mg.) was added, the product taken up in ether and washed with sodium hydrogen carbonate solution, and benzene (10 c.c.) added. Evaporation to dryness gave the cyclic urethane (XXI) as crystals (75 mg.), which recrystallised from benzene–ligroin in small needles, m. p. 183° (Found: C, 68·5; H, 9·0; N, 6·8. $C_{12}H_{19}O_2N$ requires C, 68·9; H, 9·1; N, 6·7%).

trans-1-*Hydroxy*-cis-9-*decalylacetamide*.—Methyl *trans*-1-hydroxy-*cis*-9-decalylacetate, prepared from the acid (XIX) (403 mg.), was heated with methanolic ammonia (40 c.c., saturated at room temperature) for 11 hr. at 90° in a sealed tube. The solvent was removed under reduced pressure and the crystalline *amide* recrystallised from acetone in needles (330 mg.), m. p. 223° (Found: C, 68·5; H, 9·7; N, 7·0. $C_{12}H_{21}O_2N$ requires C, 68·2; H, 10·0; N, 6·6%). The amide was also obtained by allowing the ester and methanolic ammonia to react for 10 days at room temperature.

9-*Aminomethyl*-trans-1-*hydroxy*-cis-*decalin* (XX).—A solution of sodium methoxide, from sodium (39 mg.) and methanol (3 c.c.), was added to a suspension of *trans*-1-hydroxy-*cis*-9-decalylacetamide (153 mg.) in methanol (10 c.c.), and a solution of bromine (116 mg.) in methanol (3 c.c.) was introduced. The amide rapidly dissolved and reaction was completed by 15 minutes' boiling, after which 40% aqueous potassium hydroxide (1·5 c.c.) was added, the mixture was refluxed for 12 hr., diluted, and acidified, and neutral matter removed in ether. Basification and continuous ether-extraction of the aqueous layer yielded the *base* (XX) which separated from ligroin in slender needles (90 mg.), m. p. 106—107° (Found, in sample dried over KOH at 56°/0·1 mm.: C, 71·6; H, 11·2; N, 7·8. $C_{11}H_{21}ON$ requires C, 72·0; H, 11·5; N, 7·6%).

The *hydrochloride*, prepared in benzene, separated from ligroin containing a little chloroform in small needles, m. p. 213—214° (Found: C, 59·7; H, 10·1; N, 6·8; Cl, 15·7. $C_{11}H_{21}ON,HCl$ requires C, 60·0; H, 10·1; N, 6·4; Cl, 16·1%). The N-*acetyl derivative* separated from ligroin containing a little benzene in needles, m. p. 128° (Found: C, 69·3; H, 9·7; N, 6·4. $C_{13}H_{23}O_2N$ requires C, 69·3; H, 10·3; N, 6·2%).

9-(N-*Cyanomethylaminomethyl*)-trans-1-*hydroxy*-cis-*decalin* (XXII; R = H).—Aqueous formaldehyde (0·04 c.c. of 40%) was added to a concentrated aqueous solution of the hydrochloride (110 mg.) of base (XX). The solution was covered with ether and cooled to 0°, and concentrated aqueous potassium cyanide (33 mg.) added. After 12 hours' shaking a little saturated sodium chloride solution was added. The product (XXII; R = H), isolated with ether, was an oil (95 mg.). The *hydrochloride*, prepared in ether, separated from methanol–benzene in needles, m. p. 193—194° (decomp.) (Found: C, 59·6; H, 8·8; N, 10·9; Cl, 14·2. $C_{12}H_{22}ON_2,HCl$ requires C, 60·3; H, 9·0; N, 10·8; Cl, 13·7%).

9-(N-*Cyanomethyl*-N-*methylaminomethyl*)-trans-1-*hydroxy*-cis-*decalin* (XXII; R = Me).—The secondary base (XXII; R = H) (164 mg.) was refluxed for 12 hr. with 90% formic acid (1 c.c.) and 40% aqueous formaldehyde (1 c.c.). After addition of concentrated hydrochloric acid (0·1 c.c.) and evaporation to dryness, the residue was taken up in dilute hydrochloric acid, and neutral impurities were removed by filtration and continuous extraction with ether for 2 hr. The base (XXII; R = Me), isolated from the acid layer by basification with ammonia and extraction with ether, was an oil (115 mg.), which with an excess of methyl iodide in boiling acetone gave a methiodide as needles (from acetone), m. p. 242° (Found: C, 47·8; H, 7·3; N, 7·3; I, 33·9. $C_{15}H_{27}ON_2I$ requires C, 47·6; H, 7·2; N, 7·4; I, 33·6%).

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