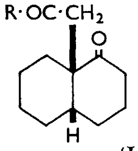
522. *Synthesis of Some Angularly Bridged Cyclic Systems. Part II.*[1]

By R. D. Haworth, B. G. Hutley, (the late) R. G. Leach, and G. Rodgers.

Methods are described for the synthesis of the bridged compounds (XIX), (XXIX), (XXXII), and (XXXIV), and their derivatives.

In Part I [1] of this series some applications of 1-oxo-*cis*-9-decalylacetic acid (I; R = OH) in the synthesis of angular homo- and hetero-cyclic systems were described; some extensions of the work are now reported. Reaction of the dioxolan derivative from ethane-1,2-diol and the keto-ester (I; R = OMe) with ammonia gave the lactam (II) described in Part I, and condensation of the methyl keto-ester (I; R = OMe) with zinc and ethyl bromoacetate gave (III; R = CO_2H) or the *exo*-unsaturated isomer. The dibasic octalin acid (III; R = CO_2H) was reduced to the corresponding decalin derivative but attempts to convert this into the corresponding diamine by reaction with hydrazoic acid were unsuccessful. It was also observed that the lactone of *trans*-1-hydroxy-*cis*-9-decalylacetic acid [1] * was converted by potassium cyanide into $\Delta^{1,2}$-*cis*-9-octalylacetic acid (IV). Further efforts to oxidise *trans*-9-aminomethyl-*cis*-1-decalol * (V) to the corresponding ketone failed and *trans*-9-acetamidomethyl-*cis*-1-decalyl toluene-*p*-sulphonate did not react with potassium cyanide.



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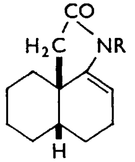

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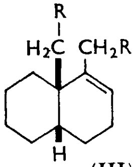

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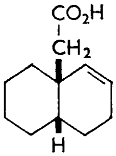

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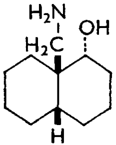

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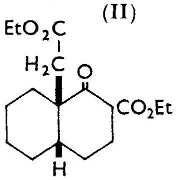

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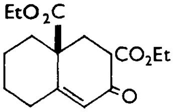

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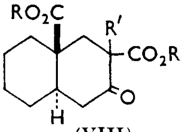

(VIII)

Several attempts were made to prepare 9-dimethylaminomethyl derivatives by using the Mannich reaction on 1-decalone derivatives protected in position 2; but 2-isopropoxymethylene-1-decalone gave 2-dimethylaminomethyl-1-decalone, identical with the base prepared from formaldehyde, dimethylamine, and 2-formyl-1-decalone. 2-Benzylidene-1-decalone with formaldehyde and dimethylamine gave the 9-dimethylamino-base, but attempts to remove the benzylidene group with chlorine followed by sodium ethoxide, or with ozone, led to ill-defined products.

Experiments were then instituted with the object of preparing ethyl 2-ethoxycarbonyl-1-oxo-*cis*-9-decalylacetate (VI), which might have been converted by Dieckmann condensation into derivatives with a 2,9-bridge across the decalin system. Failure to effect a Reformatsky reaction between ethyl γ-bromocrotonate and ethyl 1-ethoxycarbonyl-2-oxocyclohexylacetate,[2] or to condense ethyl carbonate with ethyl 1-oxo-*cis*-9-decalylacetate,[1] prevented these approaches, but some success was encountered in experiments

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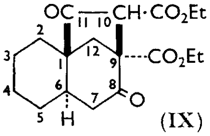
* As in Part I,[1] and following Minckler *et al.* (*J. Amer. Chem. Soc.*, 1956, **78**, 1009), the relationship of the angular and peripheral substituents is given as prefix to the whole name, and the nature of the ring fusion is expressed as a prefix to the root of the name. The reference group is the 9-substituent. Although the formulæ show one stereochemical form, all the compounds were racemates.

[1] Part I, Haworth and Turner, *J.*, 1958, 1240.

[2] Kong Chang and Ming Ma, *Ber.*, 1935, **68**, 871.

starting with ethyl 3-oxo-Δ^4-octalin-9-carboxylate[3] and diethyl oxalate. Heating the intermediate glyoxylate thus produced gave diethyl 3-oxo-Δ^4-octalin-2,9-dicarboxylate (VII), which was reduced catalytically to diethyl 3-oxo-*trans*-decalin-2,9-dicarboxylate (VIII; R = Et, R′ = H). The sodio-derivative of the latter reacted with ethyl bromoacetate, yielding ethyl 3-oxo-2,9-diethoxycarbonyl-*trans*-2-decalylacetate (VIII; R = Et, R′ = $CH_2{\cdot}CO_2Et$) as an oil which with sodium, sodium ethoxide, or potassium t-butoxide gave a poor yield of an oil, probably the bridged compound (IX). The ester (VIII; R = Et, R′ = $CH_2{\cdot}CO_2Et$) is probably stereochemically inhomogeneous at position 2, and the poor yields of the product (IX) may be ascribed to the predominance in the mixture of the isomer in which the acetate and the 9-ethoxycarbonyl group are *trans* to each other. When the ester (IX) was hydrolysed with dilute acid or alkali, it was converted into 9-carboxy-3-oxo-*trans*-2-decalylacetic acid (X; R = H), identical with the dicarboxylic acid obtained by hydrolysis of the ester (VIII; R = Et, R′ = $CH_2{\cdot}CO_2Et$) with concentrated hydrochloric acid. This acid (X; R = H) was esterified with diazomethane, but attempts to bring about a Dieckmann condensation with its dimethyl ester (X; R = Me), by using sodium methoxide or potassium t-butoxide, failed. The ester (VIII; R = Et, R′ = H) readily gave a monobromo-derivative, probably (VIII; R = Et, R′ = Br), but attempts to eliminate hydrogen bromide led to indefinite products.



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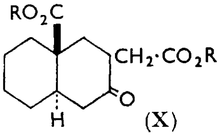
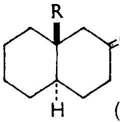
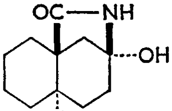


(X)



(XI)

Interesting results were obtained from a study of the reaction of cyanide with $\Delta^{1,9}$-2-octalone.[3] Anhydrous hydrogen cyanide reacted smoothly, giving 50% yields of 9-cyano-*trans*-2-decalone (XI; R = CN), but with aqueous-alcoholic potassium cyanide the principal products were a polymer $(C_{11}H_{15}NO)_x$ together with 2-oxo-*trans*-decalin-9-carboxamide (XI; R = $CO{\cdot}NH_2$), which infrared measurements showed existed in the lactam form (XII). Hydrolysis of the nitrile (XI; R = CN) with hydrochloric acid or the lactam (XII) with potassium hydroxide afforded 2-oxo-*trans*-decalin-9-carboxylic acid (XI; R = CO_2H), which was reduced by Clemmensen's method to *trans*-decalin-9-carboxylic acid, identical with the acid prepared by Dauben, Tweit, and McLean.[4] This identity established the *trans*-configuration of 9-cyano-2-decalone and compounds derived from it. 9-Cyano-*trans*-2-decalone (XI; R = CN) yielded the spiran (XIII) when treated with ethyl cyanoacetate and ammonia, but attempts to hydrolyse this were unsuccessful. Methyl 2-oxo-*trans*-decalin-9-carboxylate (XI; R = CO_2Me) reacted with methyl bromoacetate in presence of zinc, to give the unsaturated ester (XIV; R = Me), which could not be reduced, although the corresponding dibasic acid (XIV; R = H) was readily



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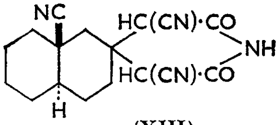

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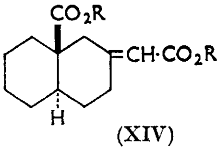

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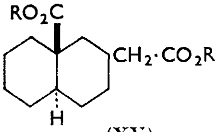

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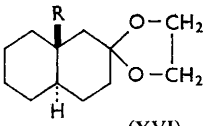

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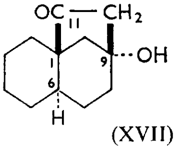

(XVII)

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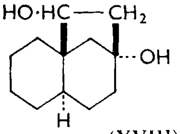
[3] Du Feu, McQuillan, and Robinson, *J.*, 1937, 56.

[4] Dauben, Tweit, and McLean, *J. Amer. Chem. Soc.*, 1955, **77**, 52.

reduced to the decalin acid (XV; R = H). As attempts to effect a Dieckmann condensation with the corresponding dimethyl ester (XV; R = Me) were unsuccessful, the 3-acetate group was probably in the *trans*-position to the angular ester group. An attempt to convert 2-oxo-*trans*-decalin-9-carboxyl chloride into 9-acetyl-*trans*-2-decalone (XI; R = Ac) by reaction with dimethylcadmium failed, but this diketone was eventually prepared from 9-cyano-*trans*-2-decalone (XI; R = CN) by the action of methyl-lithium on the dioxolan derivative (XVI; R = CN). The diketone (XI; R = Ac) was converted by dilute sodium hydroxide solution into the tricyclic hydroxy-ketone (XVII), which was reduced by sodium borohydride to the diol (XVIII); and the dithiolan derivative from the diketone was reduced by Raney nickel to the bridged decalol (XIX; R = OH). The tertiary hydroxyl group of the latter was replaced by chlorine by treatment with phosphorus pentachloride, and the resulting chloride (XIX; R = Cl) was reduced by sodium and alcohol to the tricyclo-parent hydrocarbon (XIX; R = H).



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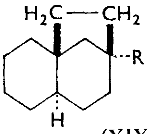

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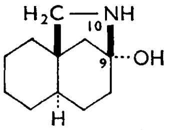

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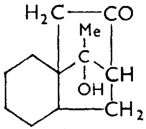
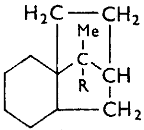


(XXI)



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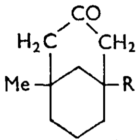

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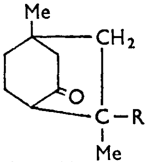

(XXIV)

In view of this formation of homocyclic bridged structures it is interesting to report the conversion of the dioxolan derivative (XVI; R = CN) into the heterocyclic bridged structure (XX) by reduction with lithium aluminium hydride to the 9-aminomethyl derivative, which with hydrochloric acid gave the heterocyclic derivative (XX). However, attempts to condense the 9-aminomethyl derivative with formaldehyde or to cyclise the *N*-formyl derivative of the 9-aminomethyl compound were unsuccessful.

It is necessary to substantiate more fully the structures (XVII) and (XIX) and to exclude the isomeric forms (XXI) and (XXII), respectively. Rabe[5] showed that 3-acetonyl-3-methylcyclohexanone was converted by alkali into a bicyclo-ketone (XXIII; R = OH), and not (XXIV; R = OH). The product and its xanthate resisted dehydration, and the corresponding chloride (XXIII; R = Cl), prepared by the action of phosphorus pentachloride, could not be dehydrochlorinated, both in accordance with the bridged structure (XXIII); ready dehydration and dehydrochlorination would be expected from the isomers (XXIV; R = OH and Cl, respectively). These arguments are equally applicable to the compounds now studied and the proposed structures are also supported by the following evidence: (1) Kuhn–Roth *C*-methyl determinations on the hydrocarbon (XIX; R = H) proved the absence of a *C*-methyl group. (2) Measurements, kindly made for us at Imperial Chemical Industries Limited, Dyestuffs Division, of the nuclear magnetic resonance spectra of the hydrocarbon and of the hydroxy-ketone (XVII) failed to reveal peaks at high field strength which would be produced by the *C*-methyl groups in structures (XXI) and (XXII; R = H); peaks associated with methylene protons in five- or six-membered rings, and with methine protons, were observed at —53 and —84 c./sec., respectively. (3) Infrared measurements of the hydrocarbon failed to reveal the presence of a methyl group, and similar measurements of the dithiolan derivative from the hydroxy-ketone (XVII) proved that a reverse ketol change had not occurred during the preparation of this derivative, because the carboxyl peak was absent and the broad hydroxyl peak at 3615 cm.$^{-1}$ was still present.

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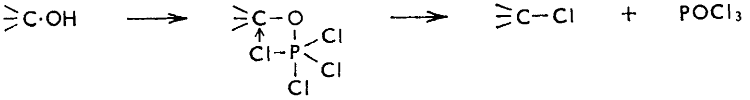
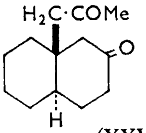
[5] Rabe, *Ber.*, 1904, **37**, 1671.

The ready replacement of hydroxyl by chlorine in compounds (XIX and XXIII; R = OH) requires comment, as normal S_N1 and S_N2 mechanisms cannot operate in these cases; possibly an S_Ni mechanism can be invoked as illustrated.



The success of the ketol condensation in the synthesis of the tricyclic derivatives suggested that similar methods might be applicable in the homologous series with a 2,9-three-carbon bridge. As preliminary attempts to condense $\Delta^{1,9}$-2-octalone with ethyl malonate, acetoacetate, or bromomalonate were not successful, efforts were made to synthesise 9-acetonyl-*trans*-2-decalone (XXV). The decalone ester (XI; R = CO_2Me) was converted by reaction with ethylene glycol into its dioxolan derivative which was reduced by lithium aluminium hydride to the 9-hydroxymethyl compound, but replacement of the hydroxyl group by reaction of the toluene-*p*-sulphonate with sodium cyanide or iodide was not realised, although these methods were effective in the case of neopentyl alcohol.[6]



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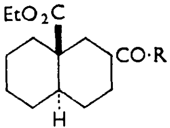

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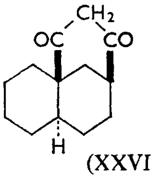
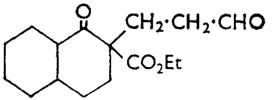


(XXVII)

Then the keto-dicarboxylic ester (VIII; R = Et, R′ = H), in the form of its dithiolan derivative, was reduced by Raney nickel to diethyl *trans*-decalin-2,9-dicarboxylate (XXVI; R = OEt), which was partially hydrolysed to the acid ester (XXVI; R = OH). The derived acid chloride, which did not react satisfactorily with dimethylcadmium, was converted into ethyl 2-chloroacetyl-*trans*-decalin-9-carboxylate (XXVI; R = CH_2Cl) by the action of hydrogen chloride on the crude diazo-ketone, prepared from the acid chloride and diazomethane. Reduction in presence of palladium–charcoal then gave ethyl 2-acetyl-*trans*-decalin-9-carboxylate (XXVI; R = Me), but attempts to convert this into the tricyclic diketone (XXVII) with sodium ethoxide, sodamide, or potassium t-butoxide were unsuccessful.

After unsuccessful attempts to cause the tricyclic hydroxy-ketone (XVII) to react with hydrogen cyanide or sodium cyanide, and to enlarge the ring by reaction with diazomethane, an approach similar to that employed by Cope and Synerholm[7] for an analogous case was examined. Ethyl 1-oxodecalin-2-carboxylate[8] reacted with acraldehyde in presence of sodium ethoxide, yielding compound (XXVIII), which was converted by acids into the tricyclic derivative (XXIX). These structural assignments are based entirely on spectroscopic evidence; in the infrared region the product (XXIX) showed a hydroxyl peak at 3670 cm.$^{-1}$. Unfortunately, crystalline derivatives could not be obtained and the conclusion must be accepted with reserve until further confirmation is obtained.



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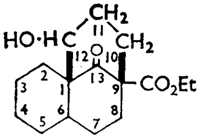

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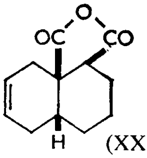

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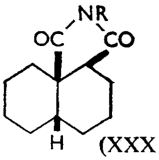

(XXXI)

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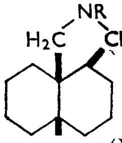
[6] Bordwell, Pitt, and Knell, *J. Amer. Chem. Soc.*, 1951, **73**, 5004.

[7] Cope and Synerholm, *J. Amer. Chem. Soc.*, 1950, **72**, 5228.

[8] Hückel, *Annalen*, 1925, **441**, 39.

Alder and Bachendorf[9] prepared Δ^2-*cis*-octalin-9,10-dicarboxylic anhydride from butadiene and cyclohex-1-ene-1,2-dicarboxylic anhydride, and it has now been found that similar reactions occur with less reactive dienophiles, and the products have been converted into angular ring bases. Thus cyclohex-2-ene-1,2-dicarboxylic anhydride[10] and butadiene yielded $\Delta^{6,7}$-*cis*-octalin-1,9-dicarboxylic anhydride (XXX) which was readily reduced to the decalin derivative. Reaction of the decalindicarboxylic anhydride with ammonia or methylamine led to the perhydrobenzisoindole compounds (XXXI; R = H and Me), respectively. Reduction with lithium aluminium hydride converted the two imides into the oxygen-free analogues (XXXII; R = H and Me), both of which gave crystalline picrates.

In a similar manner cyclopent-1-ene-1,2-dicarboxylic anhydride[11] and butadiene gave the hexahydroindenedicarboxylic anhydride (XXXIII), the reduction product of which with ammonia or methylamine yielded imides whence the tricyclic bases (XXXIV; R = H and Me) were prepared by reduction with lithium aluminium hydride.



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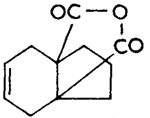

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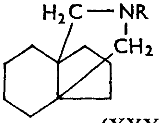

(XXXIV)

EXPERIMENTAL

1,1-*Ethylenedioxy*-cis-*decalyl*-9-*acetic Acid*.—Methyl 1-oxo-*cis*-9-decalylacetate (I; R = OMe) (750 mg.), ethylene glycol (500 mg.), and toluene-*p*-sulphonic acid (50 mg.) were heated in benzene (20 c.c.) for 6 hr. with azeotropic removal of water. The benzene solution, when dried (Na_2SO_4) and evaporated, yielded the *dioxolan* (600 mg.), b. p. 110—115°/0·01 mm. (Found: C, 67·3; H, 8·8. $C_{15}H_{24}O_4$ requires C, 67·2; H, 9·0%). The dioxolan (559 mg.) was heated in a sealed tube with ethanolic ammonia (25 c.c.; saturated at 0°) for 12 hr. at 120°, yielding the lactam (II) as rods (from benzene), m. p. 184°, unchanged when mixed with a sample prepared as described in Part I.[1]

$\Delta^{1,2}$-cis-*Octalin*-1,9-*diacetic Acid* (III; R = CO_2H).—Methyl 1-oxo-*cis*-decalylacetate (I; R = OMe) (11 g.) and ethyl bromoacetate (15 g.) were heated in an atmosphere of nitrogen with zinc (20 g.) in benzene (100 c.c.) and ether (100 c.c.). After 2 hr., further additions of zinc (20 g.) and ethyl bromoacetate (15 g.) were made and heating was continued for 2 hr. more. Acidification of the dried organic layer yielded a pale yellow oil (5 g.), b. p. 160—180°/0·1 mm., which was hydrolysed for 1 hr. with refluxing N-methanolic potassium hydroxide (75 c.c.). The dibasic *acid* (III; R = CO_2H) (4·1 g.) was obtained as needles (from water), m. p. 194° (Found: C, 66·5; H, 8·1. $C_{14}H_{20}O_4$ requires C, 66·6; H, 8·4%), which was not reduced by sodium amalgam in alcohol.

cis-*Decalin*-1,9-*diacetic Acid*.—The dibasic octalin acid (III; R = CO_2H) (60 mg.) was shaken in absolute alcohol (15 c.c.) with hydrogen in presence of platinum oxide (15 g.). Reduction was complete in 1 hr. and the *product* crystallised from acetonitrile in rods, m. p. 218° (Found: C, 65·7; H, 8·5. $C_{14}H_{22}O_4$ requires C, 65·6; H, 8·6%).

$\Delta^{1,2}$-cis-9-*Octalylacetic Acid* (IV).—*trans*-1-Hydroxy-*cis*-9-decalylacetic acid lactone[1] (2 g.) and potassium cyanide (800 mg.) were heated in a sealed tube for 24 hr. at 240—260°. Considerable charring took place; on separation of the products into neutral and acidic fractions, the latter yielded the *acid* (IV) (500 mg.), which crystallised from light petroleum (b. p. 40—60°) in needles, m. p. 97—98° (Found: C, 73·7; H, 8·8. $C_{12}H_{18}O_2$ requires C, 74·2; H, 9·3%).

trans-9-*Acetamidomethyl*-cis-1-*decalyl Toluene*-p-*sulphonate*.—9-Acetamidomethyl-*cis*-1-decalol (54 g.) and toluene-*p*-sulphonyl chloride (53 mg.) in pyridine (2 c.c.) were refluxed for 2 hr. The *product*, isolated with chloroform, crystallised from alcohol in needles, m. p. 168° (Found: C, 62·6; H, 7·5. $C_{20}H_{29}NO_4S$ requires C, 63·4; H, 7·7%).

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[9] Alder and Bachendorf, *Ber.*, 1938, **71**, 2199.
[10] Baeyer, *Annalen*, 1890, **258**, 199.
[11] Willstätter, *Ber.*, 1895, **28**, 685.

2-*Dimethylaminomethyl*-1-*decalone*.—2-Formyl-1-decalone [12,13] (1·5 g.), dimethylamine hydrochloride (1 g.), and paraformaldehyde (1 g.) were refluxed in alcohol for 10 hr. The *base*, liberated by addition of potassium hydroxide and isolated with ether, separated from light petroleum (b. p. 40—60°) in plates, m. p. 78—79° (Found: C, 74·8; H, 10·7; N, 6·3. $C_{13}H_{23}NO$ requires C, 74·6; H, 11·0; N, 6·7%). This compound was also obtained when 2-isopropoxymethylene-1-decalone [12] (1·25 g.), dimethylamine hydrochloride (600 mg.), and paraformaldehyde (500 mg.) were refluxed for 20 hr. in alcohol (12 c.c.); after dilution with water and removal of acidic and neutral material in ether, the base, liberated by addition of potassium hydroxide and isolated with ether, had m. p. and mixed m. p. 78°.

2-*Benzylidene*-9-*dimethylaminomethyl*-1-*decalone*.—2-Benzylidene-1-decalone (8 g.),[14] dimethylamine hydrochloride (3 g.), and paraformaldehyde (2 g.) were refluxed for 7 hr. in alcohol (25 c.c.). After dilution with water and extraction with ether, the aqueous solution was basified with potassium hydroxide (2 g.) and again extracted with ether. Evaporation of the second extract gave the base as an oil, which partly decomposed on attempted distillation at 0·02 mm. but yielded a *picrate* as needles, m. p. 158°, from methanol (Found: C, 59·0; H, 5·8; N, 10·5. $C_{26}H_{30}N_4O_8$ requires C, 59·3; H, 5·7; N, 10·6%). Chlorine was passed through a solution of the base (2·2 g.) in ice-cold carbon tetrachloride (20 c.c.); removal of the solvent then gave 2-*chloro*-2-α-*chlorobenzyl*-9-*dimethylaminomethyl*-1-*decalone hydrochloride* which separated from alcohol in plates, m. p. 212° (Found: C, 59·0; H, 7·2; N, 3·5; Cl, 26·1. $C_{20}H_{27}Cl_2NO,HCl$ requires C, 59·3; H, 6·9; N, 3·5; Cl, 26·3%).

Diethyl 3-*Oxo*-Δ^4-*octalin*-2,9-*dicarboxylate* (VII).—Ethyl 3-oxo-Δ^4-octalin-9-carboxylate [3] (11·1 g.) was added gradually to powdered sodium (1·2 g.) in ether (120 c.c.) containing diethyl oxalate (9·6 g.), and after 12 hr. water was added. The aqueous layer was separated and acidified, and the crude glyoxylate (7·5 g.) was isolated with ether and heated with powdered glass (2 g.) at 200° until evolution of carbon monoxide ceased. The residue (5·9 g.) had b. p. 130—135°/0·01 mm. and separated from light petroleum (b. p. 40—60°) as rhombic plates (5·1 g.), m. p. 81° (Found: C, 65·1; H, 7·4. $C_{16}H_{22}O_5$ requires C, 65·3; H, 7·5%), which gave a deep blue-green ferric test in aqueous alcohol and a 2,4-*dinitrophenylhydrazone*, scarlet plates (from alcohol), m. p. 157·5° (Found: C, 55·6; H, 5·7; N, 11·9. $C_{22}H_{26}N_4O_8$ requires C, 55·7; H, 5·5; N, 11·7%).

Diethyl 3-*Oxo*-trans-*decalin*-2,9-*dicarboxylate* (VIII; R = Et, R′ = H).—The ester (VII) (1 g.) in alcohol (20 c.c.) and acetic acid (2 c.c.) was shaken for 5 hr. with hydrogen in presence of 10% palladium–carbon (60 mg.). The *product* (VIII; R = Et, R′ = H) separated from alcohol in needles (0·9 g.), m. p. 68° (Found: C, 64·7; H, 7·9. $C_{16}H_{24}O_5$ requires C, 64·8; H, 8·1%), which gave a deep violet ferric test. The 2,4-*dinitrophenylhydrazone* crystallised from alcohol in orange needles, m. p. 127° (Found: C, 55·2; H, 6·3; N, 11·4. $C_{23}H_{28}N_4O_8$ requires C, 55·4; H, 5·9; N, 11·7%).

The *ethylene dithioacetal*, prepared by passing hydrogen chloride at 0° through a solution of the ester (3·0 g.) and ethane-1,2-dithiol (5 c.c.) for 3 hr., crystallised from alcohol in rhombic plates (2·8 g.), m. p. 75° (Found: C, 58·1; H, 7·5; S, 17·4. $C_{18}H_{28}O_4S_2$ requires C, 58·1; H, 7·5; S, 17·2%).

The 2-*bromo-derivative* (VIII; R = Et, R′ = Br), prepared by the action of bromine in carbon tetrachloride, separated from alcohol in needles, m. p. 101° (Found: C, 51·0; H, 6·0; Br, 21·1. $C_{16}H_{23}BrO_5$ requires C, 51·2; H, 6·1; Br, 21·3%).

Ethyl 2,9-*Diethoxycarbonyl*-3-*oxo*-trans-2-*decalylacetate* (VIII; R = Et, R′ = $CH_2{\cdot}CO_2Et$).—Diethyl 3-oxo-*trans*-decalin-2,9-dicarboxylate (3·5 g.) in benzene (15 c.c.) was refluxed for ½ hr. with a solution of sodium (0·3 g.) in alcohol (3 c.c.). Ethyl bromoacetate (2·6 g.) was added and the mixture refluxed for a further 5 hr. (until the sodio-derivative redissolved). More ethyl bromoacetate (0·9 g.) was added and after a further 4 hours' refluxing the mixture was neutralised with acetic acid and the solvents were removed. The residue was mixed with water and extracted with ether, and the extract was washed with 5% sodium hydroxide solution and dried. Distillation then gave (*a*) unchanged ester (VIII; R = Et, R′ = H) (0·8 g.) and (*b*) the desired *triester* (2·2 g.), b. p. 156—160°/0·02 mm., n_D^{20} 1·4823 (Found: C, 62·5; H, 7·8. $C_{20}H_{30}O_7$ requires C, 62·2; H, 7·8%).

Diethyl 8,11-*Dioxo*-(trans-1,6-cis-1,9)-*tricyclo*[7,2,1,$0^{1,6}$]*dodecane*-9,10-*dicarboxylate* (IX).—

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[12] Johnson and Posvic, *J. Amer. Chem. Soc.*, 1947, **69**, 1361.

[13] Birch and Robinson, *J.*, 1944, 501.

[14] Johnson, *J. Amer. Chem. Soc.*, 1943, **65**, 1317.

The ester (VIII; R = Et, R′ = $CH_2{\cdot}CO_2Et$) (3·6 g.) was refluxed for 36 hr. with a suspension of powdered sodium (0·2 g.) in ether (30 c.c.). Water was added and neutral material removed with ether, the aqueous layer was acidified, and the precipitated tricyclic *diketo-diester* was taken up in ether and recovered (0·7 g.); it had b. p. 135—138°/0·02 mm., n_D^{20} 1·4973 (Found: C, 64·5; H, 7·6. $C_{18}H_{24}O_6$ requires C, 64·3; H, 7·2%).

9-*Carboxy*-3-*oxo*-trans-2-*decalylacetic Acid* (X; R = R′ = H).—(*a*) The ester (VIII; R = Et, R′ = $CH_2{\cdot}CO_2Et$) (0·2 g.) was refluxed with concentrated hydrochloric acid (22 c.c.) for 30 hr. (*b*) The ester (IX) (0·5 g.) was refluxed either for 5 hr. with dilute hydrochloric acid (20 c.c.) or for 3 hr. with 2N-sodium hydroxide (10 c.c.) and methanol (12 c.c.). In each case, after dilution with water, the acid products were isolated with ether; the *acid* (X; R = R′ = H) obtained by method (*a*) (0·08 g.) and (*b*) (0·2 g.) separated from acetonitrile in prisms, m. p. 214° (decomp.) (Found: C, 61·5; H, 7·4. $C_{13}H_{18}O_5$ requires C, 61·4; H, 7·1%). The *dimethyl ester*, prepared with ethereal diazomethane, crystallised from alcohol as rhombic plates, m. p. 84° (Found: C, 63·8; H, 8·0. $C_{15}H_{22}O_5$ requires C, 63·8; H, 7·8%).

9-*Cyano*-trans-2-*decalone* (XI; R = CN).—A solution of $\Delta^{1,9}$-2-octalone (10 g.), hydrogen cyanide (7 c.c.), and piperidine (1 c.c.) in alcohol (40 c.c.) was left at room temperature for 5 days. Water and dilute hydrochloric acid were added; the ether extract yielded on distillation a small amount (1·5 g.) of unchanged octalone and the *nitrile* (XI; R = CN) (5 g.), b. p. 180°/12 mm. (Found: C, 74·4; H, 8·7; N, 7·5. $C_{11}H_{15}NO$ requires C, 74·5; H, 8·5; N, 7·9%). The *semicarbazone* crystallised from methanol in plates, m. p. 226° (Found: C, 61·6; H, 7·8; N, 24·2. $C_{12}H_{18}N_4O$ requires C, 61·6; H, 7·7; N, 23·9%).

2-*Oxo*-trans-*decalin*-9-*carboxamide* (XI; R = $CO{\cdot}NH_2$).—To a solution of $\Delta^{1,9}$-2-octalone (1 g.) in alcohol (5 c.c.) was added 15% potassium cyanide solution (6 c.c.). After 3 days, the precipitated *polymer* was collected; crystallisation from alcohol gave needles (0·5 g.), m. p. 277—279° (decomp.) [Found: C, 74·4; H, 8·5; N, 8·2. $(C_{11}H_{15}NO)_x$ requires C, 74·5; H, 8·5; N, 7·9%]. Ether-extraction of the filtrate yielded the *amide* (XI; R = $CO{\cdot}NH_2$), which crystallised from ether–light petroleum (b. p. 40—60° in needles (0·3 g.), m. p. 168° (Found: C, 67·9; H, 8·6; N, 7·0. $C_{11}H_{17}NO_2$ requires C, 67·7; H, 8·6; N, 7·1%), $\nu_{max.}$ (in KBr), 1672 cm.$^{-1}$.

2-*Oxo*-trans-*decalin*-9-*carboxylic Acid* (XI; R = CO_2H).—(*a*) The amide (XI; R = $CO{\cdot}NH_2$) (2·0 g.) and 20% potassium hydroxide solution (25 c.c.) were refluxed for 26 hr., and the acid (XI; R = CO_2H) (1·2 g.) was liberated by acidification and isolated with ether. (*b*) A solution of the nitrile (XI; R = CN) (1·5 g.) in concentrated hydrochloric acid (10 c.c.) was saturated at 0° with hydrogen chloride, left in the refrigerator for 6 days with occasional resaturation with hydrogen chloride, and finally kept at room temperature for 24 hr. before dilution with water and extraction with ether. The *acid* (XI; R = CO_2H) prepared by either method crystallised from carbon tetrachloride in needles (1·0 g.), m. p. 117° (Found: C, 67·3; H, 7·8. $C_{11}H_{16}O_3$ requires C, 67·3; H, 8·1%). The acid chloride, prepared by thionyl chloride, had m. p. 56° but was not analysed. The *methyl ester* (XI; R = CO_2Me), prepared with ethereal diazomethane, had b. p. 152—154°/10 mm., n_D^{20} 1·4980 (Found: C, 68·3; H, 8·8. $C_{12}H_{18}O_3$ requires C, 68·6; H, 8·6%), yielding a 2,4-*dinitrophenylhydrazone*, orange prisms (from alcohol), m. p. 175° (Found: C, 55·1; H, 5·8; N, 14·5. $C_{18}H_{22}N_4O_6$ requires C, 55·4; H, 5·7; N, 14·4%).

trans-*Decalin*-9-*carboxylic Acid*.—The keto-acid (XI; R = CO_2H) (0·4 g.) was refluxed with amalgamated zinc (2·5 g.) in concentrated hydrochloric acid (6·5 c.c.) for 17 hr. The product, isolated with ether, separated from aqueous ethanol in needles (0·3 g.), m. p. 133° (Found: C, 72·2; H, 9·6. Calc. for $C_{11}H_{18}O_2$: C, 72·5; H, 9·9%) undepressed on admixture with *trans*-decalin-9-carboxylic acid prepared as described by Dauben, Tweit, and McLean.[4]

3′,5′,9-*Tricyano*-trans-*decalin*-2-*spiro*-4′-*piperidine*-2′,6′-*dione* (XIII).—9-Cyano-*trans*-2-decalone (X) (3·5 g.), ethyl cyanoacetate (2·3 g.), and alcohol (8 c.c.) were saturated with ammonia at −5° and left at 0° for 10 days. The precipitated ammonium salt was collected, dissolved in boiling water, and decomposed by concentrated hydrochloric acid; the *imide* (XIII) separated from alcohol in needles (1·8 g.), m. p. 222° (Found: C, 65·8; H, 5·9; N, 17·9. $C_{17}H_{18}N_4O_2$ requires C, 65·8; N, 18·1%), which were recovered after attempted hydrolysis with concentrated sulphuric or hydrochloric acid.

Methyl 9-*Methoxycarbonyl*-trans-2-*decalylideneacetate* (XIV; R = Me).—Methyl 2-oxo-*trans*-decalin-9-carboxylate (XI; R = CO_2Me) (5 g.), methyl bromoacetate (2 c.c.), benzene (100 c.c.), ether (100 c.c.), zinc (5·0 g.), and iodine (0·1 g.) were refluxed under nitrogen. Five additions of zinc (3 g. each) were made at 45-minute intervals and an additional quantity of methyl bromoacetate (2 c.c.) was added after 1½ hr. After 5 hr., dilute acetic acid was added, and the ether–benzene layer was washed with water and dilute aqueous ammonia, and evaporated, yielding the *ester* (XIV; R = Me) as prisms (2·6 g.), m. p. 103° (from benzene) (Found: C, 67·2; H, 8·2. $C_{15}H_{22}O_4$ requires C, 67·6; H, 8·2%). The *diacid* (XIV; R = H), prepared by refluxing the ester (4·6 g.) with 10% methyl-alcoholic potassium hydroxide (35 c.c.) for 18 hr., crystallised from acetonitrile in prisms (2·1 g.), m. p. 172° (Found: C, 65·4; H, 7·6. $C_{13}H_{18}O_4$ requires C, 65·55; H, 7·55%), $\lambda_{max.}$ 222 mμ (ε 14,500) in ethanol.

9-*Carboxy*-trans-2-*decalylacetic acid* (XV; R = H), prepared by reducing the unsaturated acid (XIV; R = H) (2·0 g.) for 14 hr. in acetic acid (35 c.c.) in presence of platinic oxide (50 mg.), crystallised from acetonitrile in prisms (1·7 g.), m. p. 157° (Found: C, 64·8; H, 8·4. $C_{13}H_{20}O_4$ requires C, 65·0; H, 8·35%). The *methyl ester* (XV; R = Me), prepared by ethereal diazomethane, separated from alcohol in rhombic plates, m. p. 70° (Found: C, 66·8; H, 8·8. $C_{15}H_{24}O_4$ requires C, 67·1; H, 8·9%).

9-*Cyano*-trans-*decalin*-2-*spiro*-2-*dioxolan* (XVI; R = CN).—A solution of 9-cyano-*trans*-2-decalone (1 g.), ethylene glycol (0·8 g.), and toluene-*p*-sulphonic acid (0·07 g.) was refluxed in benzene (30 c.c.) for 5 hr. during azeotropic removal of water. The benzene solution, after being washed with sodium hydrogen carbonate solution, gave a colourless *acetal* (XVI; R = CN) (1·1 g.), b. p. 180°/10 mm., which slowly solidified and then crystallised from light petroleum (b. p. 40—60°) in needles, m. p. 71° (Found: C, 70·3; H, 8·6; N, 6·5. $C_{13}H_{19}NO_2$ requires C, 70·6; H, 8·6; N, 6·4%).

2-*Acetyl*-trans-2-*decalone* (XI; R = Ac).—An ice-cold solution of methyl-lithium, prepared under nitrogen from lithium (2·4 g.) and methyl iodide (23·2 c.c.) in ether (200 c.c.), was added with stirring during ½ hr. to the acetal (XVI; R = CN) (8·8 g.) in ether (50 c.c.). After 12 hr. at room temperature, ice-cold 14% sulphuric acid (500 c.c.) was added, the aqueous layer was warmed on the steam-bath for 1½ hr., and the *diketone* (XI; R = Ac) taken up in ether; it crystallised from light petroleum (b. p. 60—80°) in rhombic plates (3·5 g.), m. p. 68° (Found: C, 74·0; H, 9·5. $C_{12}H_{18}O_2$ requires C, 74·2; H, 9·3%), giving a *mono*-2,4-*dinitrophenylhydrazone*, orange plates, m. p. 183° (from alcohol) (Found: C, 57·5; H, 5·9; N, 15·2. $C_{18}H_{22}N_4O_5$ requires C, 57·75; H, 5·9; N, 15·0%).

9-*Hydroxy*-(trans-1,6-cis-1,9)-*tricyclo*$[7,2,1,0^{1,6}]$*dodecan*-11-*one* (XVII).—A solution of 9-acetyl-*trans*-2-decalone (XI; R = Ac) (0·3 g.) in alcohol (2 c.c.) and 25% aqueous potassium hydroxide (2·5 c.c.) was refluxed for 18 hr. After removal of the solvent, water was added and the *product* (XVII), isolated with ether, crystallised from light petroleum (b. p. 60—80°) in needles (0·2 g.), m. p. 95° (Found: C, 74·0; H, 9·3. $C_{12}H_{18}O_2$ requires C, 74·2; H, 9·3%); this gave a 2,4-*dinitrophenylhydrazone*, separating from benzene–light petroleum (b. p. 60—80°) in orange needles, m. p. 200° (Found: C, 57·6; H, 5·9; N, 14·7. $C_{18}H_{22}N_4O_5$ requires C, 57·75; H, 5·9; N, 15·0%). The *dimethylene dithioacetal*, prepared by the action of hydrogen chloride at 0° on a solution of the ketone (XVII) (1·0 g.) in ethane-1,2-dithiol (2 c.c.), crystallised from light petroleum (b. p. 60—80°)–benzene in rhombic plates (0·9 g.), m. p. 110° (Found: C, 62·3; H, 8·2; S, 24·0. $C_{14}H_{22}OS_2$ requires C, 62·2; H, 8·15; S, 23·7%).

(trans-1,6-cis-1,9)-*Tricyclo*$[7,2,1,0^{1,6}]$*dodecane*-9,11-*diol* (XVIII).—The hydroxy-ketone (XVII) (0·3 g.) in methanol (5 c.c.) was added to sodium borohydride (0·1 g.) and, after dilution with water and extraction with ether, the *diol* (XVIII) was obtained; it crystallised from ether containing a little light petroleum (b. p. 40—60°) in needles, m. p. 164° (Found: C, 73·6; H, 9·9. $C_{12}H_{20}O_2$ requires C, 73·8; H, 9·8%).

(trans-1,6-cis-1,9)-*Tricyclo*$[7,2,1,0^{1,6}]$*dodecan*-9-*ol* (XIX; R = OH).—A solution of the dimethylene dithioacetal (1·5 g.) of the hydroxy-ketone (XVII) in 80% alcohol (60 c.c.) was refluxed for 16 hr. with Raney nickel (18 g.) and, after removal of the catalyst, the alcohol was evaporated, water added, and the product isolated with ether; (trans-1,6-cis-1,9)-*tricyclo*-$[7,2,1,0^{1,6}]$*dodecan*-9-*ol* (XIX; R = OH) was obtained as an oil (0·8 g.), b. p. 180°/10 mm. (Found: C, 79·9; H, 11·2. $C_{12}H_{20}O$ requires C, 80·0; H, 11·1%).

9-*Chloro*-(trans-1,6-cis-1,9)-*tricyclo*$[7,2,1,0^{1,6}]$*dodecane* (XIX; R = Cl).—Phosphorus pentachloride (2·0 g.) was added to a solution of the hydroxy-compound (XIX; R = OH) (1·1 g.) in light petroleum (b. p. 40—60°). After 36 hr., the mixture was decomposed with ice–water, and the *chloride* (XIX; R = Cl) was obtained as an oil (0·8 g.), b. p. 170—175°/10 mm. (Found: C, 72·1; H, 10·0; Cl, 17·9. $C_{12}H_{19}Cl$ requires C, 72·35; H, 9·65; Cl, 17·95%).

(trans-1,6-cis-1,9)-*Tricyclo*$[7,2,1,0^{1,6}]$*dodecane* (XIX; R = H).—Sodium (8·0 g.) was added in 16 portions during 5 hr. to a solution of the chloro-compound (XIX; R = Cl) (2·6 g.) in boiling alcohol (75 c.c.). After 7 hr. the solvent was removed and water added; the *hydrocarbon* (XIX; R = H) (1·4 g.), isolated with ether, had b. p. 160—165°/40 mm., n_D^{20} 1·4998 (Found: C, 87·6; H, 12·0. $C_{12}H_{20}$ requires C, 87·8; H, 12·2%).

9-*Aminomethyl*-trans-*decalin*-2-*spiro*-2′-*dioxolan* (XVI; R = $CH_2{\cdot}NH_2$).—The cyano-spiran (XVI; R = CN) (9 g.) in ether (30 c.c.) was added to a suspension of lithium aluminium hydride (2·5 g.) in ether (50 c.c.), and after 3 days' refluxing in nitrogen, water (4 c.c.), 20% aqueous sodium hydroxide (3 c.c.), and more water (14 c.c.) were added consecutively and dropwise. The dried ether layer yielded the *amine* (3 g.), b. p. 160—165°/8 mm. (Found: C, 69·6; H, 10·4; N, 6·0. $C_{13}H_{23}NO_2$ requires C, 69·3; H, 10·2; N, 6·2%). The N-*formyl derivative* was prepared by addition of the base (3 g.) in ether (50 c.c.) to butyl-lithium (from 3 g. of metal and 2·3 g. of butyl bromide) in ether (50 c.c.), followed by ethyl formate (1·3 g.) in ether (10 c.c.); it separated from light petroleum (b. p. 60—80°) in needles (1·7 g.), m. p. 141—142° (Found: C, 66·0; H, 9·3; N, 5·9. $C_{14}H_{23}NO_3$ requires C, 66·4; H, 9·1; N, 5·5%).

(trans-1,6-cis-1,9)-10-*Azatricyclo*[7,2,1,$0^{1,6}$]*dodecan*-9-*ol* (XX).—Either the crude or the distilled basic spiran (XVI; R = $CH_2{\cdot}NH_2$) (1 g.) was warmed for ½ hr. with 10% hydrochloric acid (10 c.c.). The *base* (XX), liberated by sodium hydroxide solution and isolated with ether, separated from carbon tetrachloride in plates, m. p. 144° (Found: C, 72·7; H, 10·5; N, 7·4. $C_{11}H_{19}NO$ requires C, 72·9; H, 10·5; N, 7·7%).

Methyl trans-*Decalin*-2-*spiro*-2′-*dioxolan*-9-*carboxylate* (XVI; R = CO_2Me).—A mixture of methyl 2-oxo-*trans*-decalin-9-carboxylate (XI; R = CO_2Me) (1·6 g.), ethylene glycol (1·0 g.), and toluene-*p*-sulphonic acid (0·1 g.) was refluxed for 5 hr. in benzene (40 c.c.), water being removed azeotropically. After being washed with sodium hydrogen carbonate solution the benzene was removed under reduced pressure. The residual *acetal* had b. p. 156°/9 mm. and crystallised from light petroleum (b. p. 40—60°) in rhombic plates (1·5 g.), m. p. 78° (Found: C, 66·0; H, 8·6. $C_{14}H_{22}O_4$ requires C, 66·1; H, 8·65%).

9-*Hydroxymethyl*-trans-*decalin*-2-*spiro*-2′-*dioxolan* (XVI; R = $CH_2{\cdot}OH$).—The ester (XVI; R = CO_2Me) (4·0 g.) in ether (60 c.c.) was refluxed under nitrogen with lithium aluminium hydride (0·9 g.) for 24 hr. Decomposition with ice–water and evaporation of the solvent from the dried ether layer gave the *alcohol* (2·8 g.), b. p. 160—163°/9 mm. (Found: C, 69·0; H, 9·8. $C_{12}H_{22}O_3$ requires C, 69·05; H, 9·75%). The *toluene*-p-*sulphonate*, prepared in pyridine at 0°, crystallised from alcohol as prisms, m. p. 96° (Found: C, 63·4; H, 7·6; S, 8·5. $C_{20}H_{28}O_5S$ requires C, 63·1; H, 7·4; S, 8·4%).

9-*Hydroxymethyl*-trans-2-*decalone*.—A solution of the acetal (XVI; R = $CH_2{\cdot}OH$) (3·8 g.) in methanol (15 c.c.) and 0·1N-hydrochloric acid (5 c.c.) was refluxed for 2 hr. Dilution with water and extraction with ether gave 9-*hydroxymethyl*-trans-2-*decalone* (2·2 g.), b. p. 159—163°/9 mm. (Found: C, 72·3; H, 9·8. $C_{11}H_{18}O_2$ requires C, 72·55; H, 9·9%). The 2,4-*dinitrophenylhydrazone* crystallised from alcohol in orange needles, m. p. 171° (Found: C, 56·2; H, 5·8; N, 15·3. $C_{17}H_{22}N_4O_5$ requires C, 56·3; H, 6·0; N, 15·4%).

Diethyl trans-*Decalin*-2,9-*dicarboxylate* (XXVI; R = OEt).—The ethylene dithioacetal (2·5 g.) of the keto-diester (VIII; R = Et, R′ = H) in 80% alcohol (120 c.c.) was refluxed for 16 hr. with Raney nickel (35 g.). The nickel and alcohol were removed and the *ester* (XXVI; R = OEt), isolated with ether, was obtained as an oil (1·6 g.), b. p. 88—90°/0·02 mm., n_D^{20} 1·4727 (Found: C, 68·3; H, 9·2. $C_{16}H_{26}O_4$ requires C, 68·1; H, 9·2%).

9-*Ethoxycarbonyl*-trans-*decalin*-2-*carboxylic Acid* (XXVI; R = OH).—A solution of the diethyl ester (XXVI; R = OEt) (1 g.), methanol (18 c.c.), and N-sodium hydroxide (4·4 c.c.) was refluxed for 22 hr. After removal of the methanol and addition of water, neutral impurities were removed in ether, and acidification of the alkaline aqueous layer gave the *acid* (XXVI; R = OH), which crystallised from light petroleum (b. p. 40—60°) in rhombic plates (0·75 g.), m. p. 129° (Found: C, 66·4; H, 8·6. $C_{13}H_{22}O_4$ requires C, 66·15; H, 8·65%). The acid chloride, prepared with thionyl chloride in benzene, had b. p. 90—95°/0·04 mm.

Ethyl 2-*Chloroacetyl*-trans-*decalin*-9-*carboxylate* (XXVI; R = CH_2Cl).—The chloride (2·0 g.) of the acid (XXVI; R = OH) in ether (10 c.c.) was gradually added to ice-cold ethereal diazomethane (from 6·0 g. of *N*-methyl-*N*-nitrosourea). After 12 hr. at room temperature, the excess of diazomethane was removed, ether (25 c.c.) was added, and the solution was saturated with dry hydrogen chloride. Filtration from polymeric compounds and evaporation of the solvent gave an oily *chloroacetyl compound* which crystallised from light petroleum (b. p. 40—60°) in rhombic plates (1·2 g.), m. p. 58° (Found: C, 62·6; H, 8·0; Cl, 12·7. $C_{15}H_{23}ClO_3$ requires C, 62·8; H, 8·0; Cl, 12·4%).

Ethyl 2-Acetyl-trans-*decalin-9-carboxylate* (XXVI; R = Me).—The chloro-ketone (XXVI; R = CH_2Cl) (4·0 g.) was reduced in alcohol (50 ml.) and pyridine (1·5 c.c.) in presence of 10% palladium–charcoal (80 mg.); absorption of hydrogen was complete in 7 hr. Distillation gave *ethyl 2-acetyl*-trans-*decalin-9-carboxylate* (2·6 g.), b. p. 104—108°/0·05 mm., n_D^{20} 1·4802 (Found: C, 71·1; H, 9·7. $C_{15}H_{24}O_3$ requires C, 71·45; H, 9·5%), which gave a 2,4-*dinitrophenylhydrazone*, orange needles, m. p. 157° (from alcohol) (Found: C, 58·35; H, 6·4; N, 12·9. $C_{21}H_{28}N_4O_6$ requires C, 58·35; H, 6·5; N, 12·9%).

Ethyl 1-Oxo-2-3′-oxopropyldecalin-2-carboxylate (XXVIII).—A mixture of ethyl 1-oxodecalin-2-carboxylate (28·0 g.) and redistilled acraldehyde (9·0 g.) was added at −70° during 1 hr. to a solution from sodium (0·15 g.) in ethanol (50 c.c.), containing quinol (0·2 g.). After a further hour, the mixture was brought to room temperature, glacial acetic acid was added to pH 7, and the solvent removed under reduced pressure. The product, isolated with ether, was fractionated to give some unchanged ester (9·4 g.) and the *aldehydo-ester* (XXVIII) (10·6 g.), b. p. 145—150°/0·05 mm., n_D^{20} 1·5120 (Found: C, 68·7; H, 8·9. $C_{16}H_{24}O_4$ requires C, 68·6; H, 8·55%).

Ethyl 12-Hydroxy-13-oxotricyclo[7,3,1,$0^{1,6}$]*tridecane-9-carboxylate* (XXIX).—The ester (XXVIII) (2·5 g.), acetic acid (8 c.c.), water (4 c.c.), and concentrated hydrochloric acid (3 c.c.) were allowed to react at room temperature for 48 hr. The solution was diluted with water, and neutralised with sodium carbonate; the precipitated tricyclic *product* (1·5 g.) (XXIX), isolated with ether, had b. p. 144—147°/0·05 mm., n_D^{20} 1·5195 (Found: C, 69·1; H, 8·3. $C_{16}H_{24}O_4$ requires C, 68·6; H, 8·55%).

Δ^6-*Octalin-1,9-dicarboxylic Anhydride* (XXX).—Cyclohex-2-ene-1,2-dicarboxylic anhydride[10] (1·0 g.), quinol (0·2 g.), butadiene (3 c.c.), and benzene (3 c.c.) were heated in a sealed tube at 180° for 2 days. The solvent was removed under reduced pressure; the residual oily *anhydride* crystallised from light petroleum (b. p. 60—80°) in rhombic plates (0·4 g.), m. p. 102—103° (Found: C, 69·7; H, 6·4. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·8%). The corresponding *dicarboxylic acid*, prepared by alkaline hydrolysis, crystallised from acetonitrile in prisms, m. p. 160° (Found: C, 64·3; H, 6·8. $C_{12}H_{16}O_4$ requires C, 64·3; H, 7·1%).

cis-*Decalin-1,9-dicarboxylic Anhydride*.—The anhydride (XXX) (1·0 g.) was reduced in acetic acid (25 c.c.) in presence of platinum oxide (0·06 g.). Hydrogen absorption was complete in 6 hr., and the *decalin anhydride* crystallised from light petroleum (b. p. 60—80°) in needles (0·85 g.), m. p. 73° (Found: C, 69·0; H, 7·6. $C_{12}H_{16}O_3$ requires C, 69·25; H, 7·7%). cis-*Decalin-1,9-dicarboxylic acid* crystallised from acetonitrile in prisms, m. p. 195° (Found: C, 63·6; H, 7·95. $C_{12}H_{18}O_4$ requires C, 63·7; H, 7·95%). The *dimethyl ester*, prepared by the action of ethereal diazomethane, had b. p. 110°/0·01 mm., n_D^{20} 1·4900 (Found: C, 66·0; H, 8·7. $C_{14}H_{22}O_4$ requires C, 66·15; H, 8·65%), which on hydrolysis with boiling N-sodium hydroxide for 22 hr. gave 9-*methoxycarbonyl*-cis-*decalin-1-carboxylic acid* as rhombic plates [from light petroleum (b. p. 40—60°)], m. p. 136° (Found: C, 65·0; H, 8·1. $C_{13}H_{20}O_4$ requires C, 65·0; H, 8·35%).

1,3-*Dioxoperhydrobenz*[d]*isoindole* (XXXI; R = H).—*cis*-Decalin-1,9-dicarboxylic anhydride (1·0 g.) was heated at 180° with concentrated aqueous ammonia (2 c.c.). The *imide* (XXXI; R = H), isolated with ether, crystallised from ether–light petroleum (b. p. 60—80°) in hexagonal plates (0·7 g.), m. p. 144° (Found: C, 69·1; H, 8·2; N, 7·0. $C_{12}H_{17}NO_2$ requires C, 69·55; H, 8·2; N, 6·75%).

2-*Methyl*-1,3-*dioxoperhydrobenz*[d]*isoindole* (XXXI; R = Me), prepared similarly but by using 25% methylamine solution (1·5 c.c.), was an oil (0·7 g.), b. p. 200—205°/9 mm., n_D^{20} 1·5198 (Found: C, 70·3; H, 8·8; N, 6·0. $C_{13}H_{19}NO_2$ requires C, 70·6; H, 8·6; N, 6·3%).

Perhydrobenz[d]*isoindole* (XXXII; R = H).—The imide (XXXI; R = H) (1·3 g.) and lithium aluminium hydride (0·3 g.) were refluxed in ether (120 c.c.) for 2 days. After decomposition with water, the ether layer was shaken with dilute sulphuric acid, and the *base* (XXXII; R = H) (0·5 g.) recovered with ether; it had b. p. 175—180°/9 mm., n_D^{20} 1·5305 (Found: C, 80·8; H, 10·7; N, 8·2. $C_{12}H_{21}N$ requires C, 80·4; H, 11·7; N, 7·9%). The *picrate*, crystallised from alcohol in yellow needles, m. p. 219° (decomp.) (Found: C, 52·7; H, 5·9; N, 13·5. $C_{18}H_{24}N_4O_7$ requires C, 52·9; H, 5·9; N, 13·7%).

2-*Methylperhydrobenz*[d]*isoindole* (XXXII; R = Me), prepared similarly, had b. p. 180—185°/10 mm., n_D^{20} 1·5040 (Found: C, 80·4; H, 12·2; N, 7·5. $C_{13}H_{23}N$ requires C, 80·8; H, 11·9; N, 7·3%), giving a *picrate*, yellow needles, m. p. 177° (Found: C, 53·8; H, 6·2; N, 13·1. $C_{19}H_{26}N_4O_7$ requires C, 54·0; H, 6·15; N, 13·3%).

2,3,4,7,8,9-*Hexahydro*-1H-*indene*-8,9-*dicarboxylic anhydride* (XXXIII), prepared from cyclopent-1-ene-1,2-dicarboxylic anhydride[11] (1·0 g.), as described above for the anhydride (XXX), crystallised from light petroleum (b. p. 60—80°) in needles (0·75 g.), m. p. 119° (Found: C, 68·0; H, 6·2. $C_{11}H_{12}O_3$ requires C, 68·7; H, 6·25%). The corresponding dibasic acid crystallised from acetonitrile in prisms, m. p. 154° (Found: C, 62·7; H, 6·65. $C_{11}H_{14}O_4$ requires C, 62·9; H, 6·65%).

Perhydroindene-8,9-*dicarboxylic anhydride*, prepared by reduction of the anhydride (XXXIII) in presence of platinic oxide, crystallised from light petroleum (b. p. 40—60°) in needles, m. p. 74° (Found: C, 68·05; H, 7·3. $C_{11}H_{14}O_3$ requires C, 68·05; H, 7·2%). The corresponding dibasic *acid* crystallised from acetonitrile in prisms, m. p. 171° (Found: C, 62·3; H, 7·9. $C_{11}H_{16}O_4$ requires C, 62·25; H, 7·55%).

The last-mentioned anhydride (2 g.) was heated with concentrated aqueous ammonia as described in the preparation of the imide (XXXI; R = H). The *imide* produced crystallised from ether–light petroleum (b. p. 60—80°) in needles (1·2 g.), m. p. 137° (Found: C, 68·7; H, 8·1; N, 7·4. $C_{11}H_{15}NO_2$ requires C, 68·4; H, 7·8; N, 7·25%).

The *methylimide*, prepared similarly by using 25% methylamine, had b. p. 160—165°/9 mm., n_D^{20} 1·5099 (Found: C, 69·5; H, 8·4; N, 6·8. $C_{12}H_{17}NO_2$ requires C, 69·5; N, 8·2; N, 6·7%).

Perhydro-3a,7a-*propanoisoindole* (XXXIV; R = H).—This *base* was prepared from the corresponding imide (3·5 g.) as described above and had b. p. 145—150°/9 mm., (1·5 g.) (Found: C, 79·5; H, 11·3; N, 8·4. $C_{11}H_{19}N$ requires C, 80·0; H, 11·5; N, 8·5%); its *picrate* formed yellow needles, m. p. 211° from alcohol (Found: C, 51·6; H, 5·9; N, 14·3. $C_{17}H_{22}N_4O_7$ requires C, 51·75; H, 5·6; N, 14·2%).

Perhydro-2-methyl-3a,7a-*propanoisoindole* (XXXIV; R = Me), prepared similarly, had b. p. 148—152°/9 mm., n_D^{20} 1·4930, giving a *picrate*, yellow needles (from alcohol), m. p. 220° (Found: C, 52·8; H, 6·2; N, 13·5. $C_{18}H_{24}N_4O_7$ requires C, 52·95; H, 5·9; N, 13·7%).

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