

CXLVIII.—*Studies in "Strainless" Rings. Part II.*
The Effect of the trans-Decalin Nucleus on the
Carbon Tetrahedral Angle.

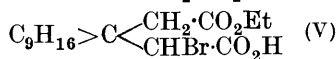
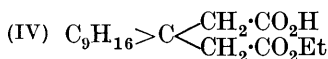
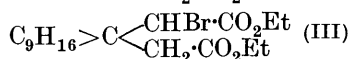
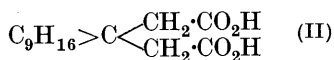
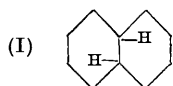
By KESHAVIAH ASWATH NARAIN RAO.

PERHAPS the most successful attempt that has been made to explain the numerous discrepancies in the relative ease of formation and the stability of different types of ring, for which Baeyer's simple conception of strain failed to account satisfactorily, is that of Thorpe and Ingold, on the basis of their "valency-deflexion" hypothesis, which rests on the fundamental assumption that, when the normal angle between two of the valencies of a carbon atom is changed through any cause, *e.g.*, their inclusion in a ring, the other two valencies apparently take up an altered relative position; more definitely, the hypothesis suggested that when the angle between two of the valencies is greater than the normal angle, the angle between the other two valencies will be less than this amount, and *vice versa* (J., 1915, **107**, 1080; 1922, **121**, 650, etc.). Experimental investigation has in general given very good support to the hypothesis.

It seemed desirable, therefore, to examine the rings of dicyclic

compounds on the basis of this hypothesis with the view of gaining an insight into the condition of strain in such rings.

The discovery that five- and six-membered rings can unite together by their *cis*- as well as by their *trans*-valencies satisfied the requirements of Mohr's hypothesis with regard to isomerism. But it is unsound to conclude from the fact of the existence of these isomerides that they are necessarily strainless. As Haworth (*Ann. Reports*, 1927, **24**, 98) has pointed out, the existence of this type of isomerism is in no way inconsistent with the supposition that the isomerides are in a state of strain. *trans*-Decalin [decahydronaphthalene] (I), being the most interesting substance from this point of view, has been chosen in the first instance for examination. If it consists of two uniplanar and strained *cyclohexane* rings interlocked in the ortho-position, and is in consequence itself highly strained, there should be no difference between the effects of *trans*-decalin and *cyclohexane* on the carbon tetrahedral angle; if, on the contrary, it relieves its strain by causing the component *cyclohexane* rings to assume multiplanar and strainless forms, its effect

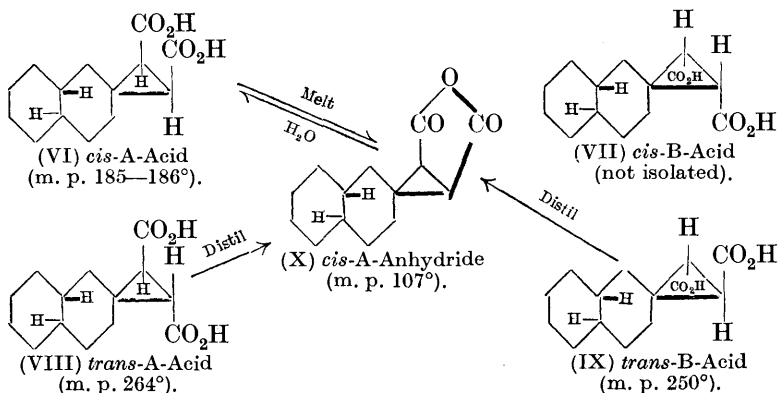


should be similar to that of *cyclopentane* on this angle. The experiments which have been carried out on derivatives of *trans*-decalin-2 : 2-diacetic acid (II) prove conclusively that *trans*-decalin relieves its strain almost completely, diminishing in consequence the convergence of the two acetic acid residues towards each other.

As in the *cyclohexane* and *cycloheptane* series, it has not been possible to prepare the *monobromo-ester* (III) by bromination of *trans*-decalin-2 : 2-diacetic acid. The ester is, however, readily prepared by bromination of *ethyl hydrogen trans-decalin-2 : 2-diacetate* (IV); but it cannot be purified, since it undergoes partial conversion into the lactonic ester on distillation. Some *monobromo-acid ester* (V) is always formed during the bromination. On hydrolysis with concentrated aqueous potassium hydroxide, the neutral and the acid products of bromination lose hydrogen bromide and form the stereoisomeric *spiro-cyclopropane acids*, the yield, about 38% of the theoretical, being the same as in the *cyclohexane* and *cycloheptane* series. The remainder of the material is converted into a mixture of lactonic acids.

trans-Decalin- β -*spiro-cyclopropane*-1 : 2-dicarboxylic acid can

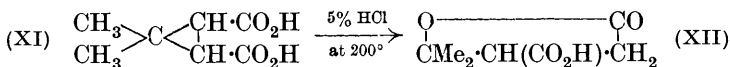
exist in four stereoisomeric forms, two *cis*- (VI and VII) and two *trans*- (VIII and IX). Three of these (the *trans*-A- and -B-acids and the *cis*-A-acid) have been isolated from the products of hydrolysis



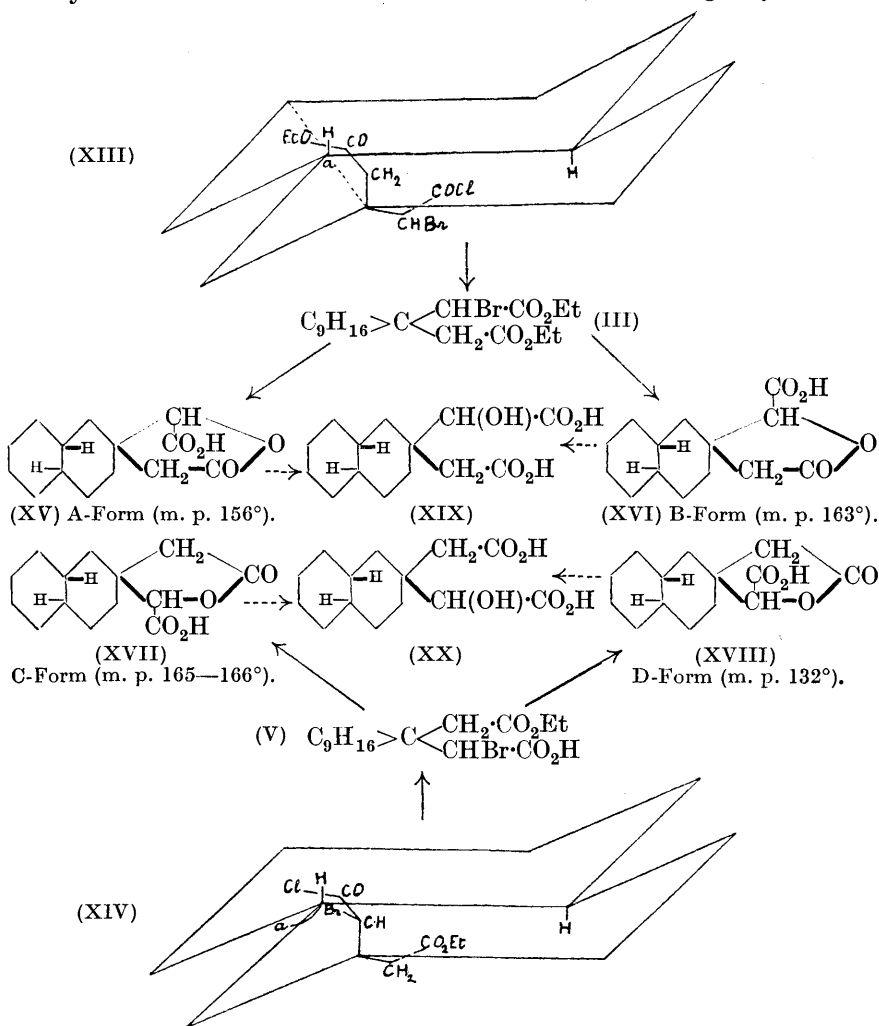
of the neutral and the acid monobromo-esters. The mixture of *trans*-spiro-acids has been separated by repeated fractional crystallisation from aqueous acetone into two acids: (1) the less soluble *A*-acid (VIII), which, as thus obtained, is amorphous, and (2) the more soluble *B*-acid (IX), which is highly crystalline. The two *trans*-spiro-acids should give rise to a mixture of the *cis*-acids (A) and (B) by the directional change of either of the carboxyl groups. Although evidence of the formation of a mixture of *cis*-anhydrides by the distillation of these acids—the *trans*-acids are unchanged on melting—has been obtained, only the *cis*-A-anhydride (X) can be obtained pure from the mixture. The *cis*-A-acid (VI) is formed by hydration of the *cis*-anhydride.

It is in the stability of these *trans*-spiro-acids that the remarkable difference between *trans*-decalin and *cyclohexane* in their effects on the carbon tetrahedral angle is revealed. Both the *trans*-spiro-acids from *trans*-decalin are equally stable (or unstable) towards hydrochloric acid, thus demonstrating that the stability of the spiran-structure depends almost entirely on the ring with which it is associated and very little on other factors. They are unattacked by 5% hydrochloric acid at 240° and by 10% acid at 200°, but are completely decomposed by the latter at 240°; 20% acid decomposes them at a much lower temperature, *viz.*, 200°, within two hours: the *cyclohexane* analogue is unaffected by concentrated hydrochloric acid at 240° during several hours. No definite substance can, however, be isolated, carbon being the chief product of such a decomposition. It is remarkable that of all the analogous compounds, caronic acid (XI) should be the only one to give a definite

product of decomposition, *viz.*, terebic acid (XII). That the observed decomposition of the *trans*-*spiro*-acids is due to the instability of



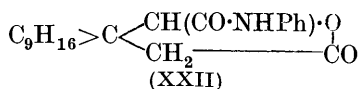
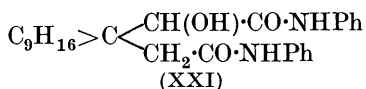
the *spiro*-cyclopropane ring and not of *trans*-decalin *per se* is proved by the fact that *trans*-decalin-2 : 2-diacetic acid, after being subjected



to similar treatment, is recovered unchanged. The *spiro*-acids are stable to cold acid or alkaline permanganate and are decomposed only after prolonged boiling.

It has already been shown (Rao, J., 1929, 1954) that in *cis*- and *trans*-decalins of the type $C_9H_{16} > C < \begin{matrix} X \\ Y \end{matrix}$ only one isomeride corresponding to each decalin is formed when X and Y are identical or are replaced by a symmetrical ring. Further, when X and Y are different, two isomerides (A and B) corresponding to each decalin are obtained, the replacement of X and Y by an unsymmetrical ring not causing any reduction in the number of isomerides. It is therefore to be expected that, when a monosubstituted unsymmetrical ring takes the place of X and Y, four isomerides from each decalin will be produced. This expectation has been realised in the case of *trans*-decalin, for, when the neutral and the acid monobromo-ester (III and V respectively) are hydrolysed with aqueous sodium carbonate, the four stereoisomeric lactones of α -hydroxy-*trans*-decalin-2 : 2-diacetic acids are formed.

The neutral monobromo-ester (III) is converted into the two lactones (A) and (B), the acid monobromo-ester (V) into two other stereoisomerides (C) and (D). The formation of two different pairs of lactones from the two bromo-esters is probably due to the different configurations of the latter. On examining the model of *trans*-decalin-2 : 2-diacetic acid, it is found that the two carboxyl groups are not equidistant from the tertiary carbon atom (*a*), which is in the β -position to the carbon attached to the acetic acid residues. Two bromo-acid chlorides (XIII and XIV) are formed from the stereoisomeric acid esters (IV). In one of these (XIV), the hydrogen attached to the tertiary carbon atom *a*, the bromine, and the acid chloride group are all crowded into a small volume, resulting probably in the development of some sort of steric hindrance. This would resist any further crowding such as would be caused by the introduction of an ethyl group in place of the chlorine. The latter would therefore undergo preferential replacement by hydroxyl, the bromo-acid ester being formed. This would give rise to the two lactones (XVII and XVIII). On the other hand, there is no such abnormal condition in the stereoisomeric bromo-acid chloride (XIII), which would therefore form the neutral ester easily; this neutral bromo-ester forms the two other lactones (XV and XVI).



It was intended to confirm the correctness of this interpretation by the formation of the dianilides (XXI) of the parent hydroxy-acids (XIX and XX) by the interaction of the lactones with aniline.

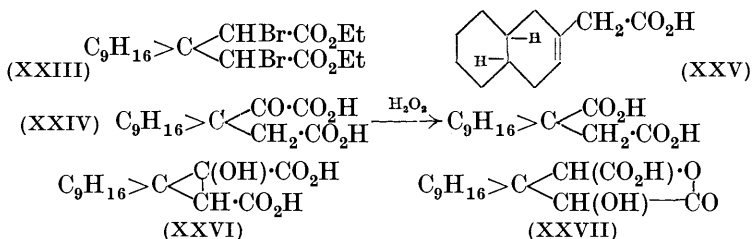
Lactones (A) and (B), which are descended from the hydroxy-acid (XIX), would give one dianilide, different from that produced from the acid (XX) formed from the lactones (C) and (D). But unfortunately all the lactones are converted into their *monoanilides* (XXII) on being heated with *excess* of aniline at 200—220°. The uniform stability of the *spiro-cyclopentane* (heterocyclic) ring in all the isomerides is but another illustration of the stability of the *spiro-cycloid* being dependent only on the ring with which it is associated.

The formation of the monoanilides illustrates an interesting difference between *trans*-decalin and *cyclohexane*, where the dianilide is easily formed by the action of aniline on the lactones at 200°. Since the internal angle of *trans*-decalin (which is a strainless ring) is very nearly the same as the normal angle, the angle between the extracyclic valencies would be of nearly the same value. While this angle (*ca.* 109·5°) makes the associated *cyclopropane* ring (which requires an angle of 60° for stability) unstable (as illustrated by the instability of the *spiro-cyclopropane* acids), it is of the optimum value for the formation of a stable *cyclopentane* ring (stability of the lactones). In *cyclohexane*, on the contrary, the angle between the extracyclic valencies is 107·2°, which is less than the normal angle. This angle increases the stability of *spiro-cyclopropane*, but has a reverse effect on the stability of the associated *cyclopentane*, since it causes the distance between the terminal carbon atoms to increase through overlapping. The work of Dickens, Kon, and Thorpe (J., 1922, **121**, 1499) on *cyclopentanediones* and of Sircar (J., 1927, 1253) on the stability of heterocyclic compounds also illustrates this progressive decrease in stability due to the increased distance between the terminal carbon atoms through overlapping.

So far as the author is aware, this is the first instance in this type of dicyclic ring of the preparation of four stereoisomerides from one parent. Their existence is in complete harmony with Mohr's hypothesis. Orientation of these isomerides is not possible, as there is no known method by which this can be accomplished.

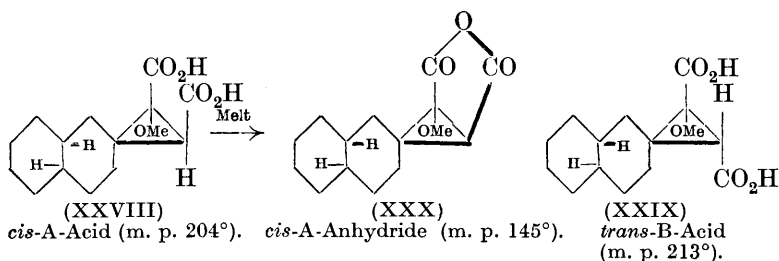
The *dibromo-ester* (XXIII) is readily prepared by the dibromination of *trans*-decalin-2 : 2-diacetic acid, very little acid product being formed when the bromination is carried out under strictly defined conditions. The remarkable difference between *cyclohexane* and *trans*-decalin is again clearly demonstrated by a study of the hydrolysis of the dibromo-ester with potassium hydroxide. When ethyl *trans*-decalin-2 : 2-dibromoacetate is hydrolysed with 64% aqueous potassium hydroxide, there is formed mainly (49%) α -*keto-trans-decalin-2 : 2-diacetic acid* (XXIV), together with a

small quantity (under 4%) of the unsaturated acid (XXV). No trace of the hydroxy-*spiro*-acid (XXVI) could be detected. The



rest of the material is converted into a mixture of the stereoisomeric hydroxy-lactonic acids (XXVII), which cannot be induced to solidify even after 12—18 months. Hydrolysis of the dibromo-ester with 15% sodium hydroxide does not yield any unsaturated acid.

When methyl-alcoholic potash is used for the hydrolysis, the dibromo-ester is converted into a mixture of *cis*- and *trans*-*methoxy*-*spiro*-acids (XXVIII and XXIX respectively).

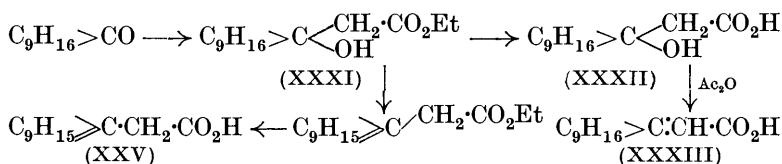


The two acids probably do not belong to the same series, because their melting points lie very close to each other and, moreover, it has not been possible to convert the *trans*-acid into the *cis*-isomeride, which readily gives an *anhydride* (XXX) on melting. The *trans*-*methoxy*-*spiro*-acid (XXIX) is converted into the keto-acid (XXIV) on boiling with hydrobromic acid. The hydroxy-*spiro*-acid (XXVI) is undoubtedly first formed by the hydrolysis of the methoxy-group, but as soon as the necessary mobile hydrogen atom is introduced into the system the ring acid is converted into the stable open-chain isomeride. The stability of the latter is further demonstrated by the fact that after boiling for 4 hours in 64% potassium hydroxide solution, it is recovered entirely unchanged.

It may be recalled that, in the *cyclohexane* series, considerable quantities of hydroxy-*spiro*-acid (type XXVI), unsaturated acid (type XXV), and hydroxy-lactonic acid (type XXVII) were formed by the hydrolysis of the dibromo-ester (or its bromo-lactones);

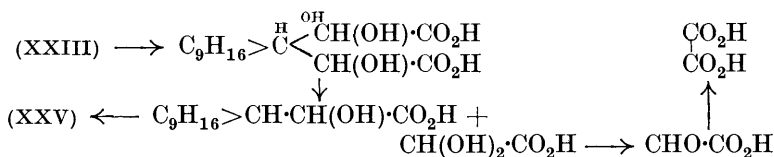
no keto-acid (type XXIV) was formed during the change. In the *cyclopentane* series, on the other hand, the main product of the hydrolysis was the keto-acid (type XXIV), small quantities of *cyclopentylideneacetic acid* (type XXXIII) and the hydroxy-lactonic acid also being formed; no hydroxy-*spiro-acid* was encountered. When methyl-alcoholic potash was used for the hydrolysis, however, a mixture of the hydroxy-*spiro-acid* and its methoxy-derivative was produced, both of which were completely converted into the keto-acid on hydrolysis with hydrobromic acid; moreover, the hydroxy-*spiro-acid* was found to be a *cis-acid*, unlike analogous compounds in the other series. Finally, in the *cycloheptane* series, the product of hydrolysis of the dibromo-ester with aqueous potash consisted of about 90% of the hydroxy-lactonic acid, 3% of the hydroxy-*spiro-acid*, and 7% of the *cycloheptylideneacetic acid* (type XXXIII); the hydroxy-*spiro-acid* or its methoxy-derivatives pass into the keto-acid (99%) on hydrolysis with hydrobromic acid.

trans- β -Decalone condenses with ethyl bromoacetate in presence



of zinc to form the *hydroxy-ester* (XXXI), which on dehydration and subsequent hydrolysis is converted into $\Delta^{2(\text{or } 1)}$ -*trans-octahydronaphthalene-2-acetic acid* (XXV), identical with the unsaturated acid obtained by the hydrolysis of the dibromo-ester. *trans-Decahydronaphthylidene-2-acetic acid* (XXXIII) is prepared by dehydration of the *hydroxy-acid* (XXXII). That the $\alpha\beta$ -acid is first formed during the hydrolysis of the dibromo-ester and is subsequently converted into the $\beta\gamma$ -isomeride by the strong alkali has been proved by boiling a solution of the former in 64% potash, whereby it is completely converted into the $\beta\gamma$ -acid.

The formation of the unsaturated acid from the dibromo-ester probably involves the elimination of one of the (hydroxy)acetic

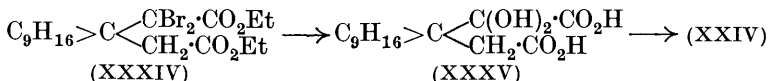


acid residues as glyoxylic acid, which is then oxidised to oxalic acid (see J., 1915, 107, 1080). The last-named substance arising from

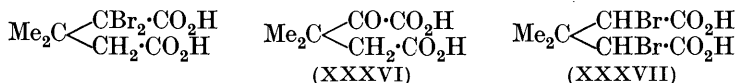
this oxidative fission has actually been isolated from the products of hydrolysis.

Hydrolysis of the dibromo-ester (XXIII) with aqueous sodium carbonate produced a mixture of acids from which a crystalline substance, m. p. 182—183°, having properties usually associated with hydroxy-lactonic acids, was isolated, but the quantity obtained was too small for investigation. From the rest of the material, which showed no tendency to crystallise during several months, small quantities of the keto-acid were isolated by various methods; no other solid product was obtained.

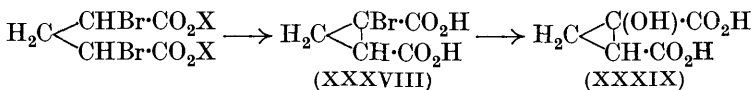
The explanation of this unexpected formation of the keto-acid by the sodium carbonate hydrolysis of the dibromo-ester is not immediately obvious. One simple way is to assume that the product of dibromination is really an unsymmetrical dibromo-ester (XXXIV). This, on replacement of the bromine atoms by hydroxyl, would give the dihydroxy-compound (XXXV), which is the hydrated



form of the keto-acid. But, although numerous substituted glutaric acids have been brominated, in no case has the formation of an unsymmetrical dibromo-derivative been observed. The one substance, *viz.*, ethyl hydrogen dibromo- $\beta\beta$ -dimethylglutarate (Perkin and Thorpe, J., 1901, **79**, 729), which was assumed to be of such a type because it gave the keto-acid (XXXVI) on hydrolysis with alkali, was later considered by Kon, Stevenson, and Thorpe (J., 1922, **121**, 657) to be the $\alpha\alpha'$ -dibromo-derivative (XXXVII).



The explanation must therefore be sought in another direction. Ingold (J., 1921, **119**, 314) has shown that the sequence of changes, dibromo-ester \longrightarrow bromo-ring acid \longrightarrow keto-acid, takes place in presence not only of alkali hydroxide but also of sodium carbonate. It was found that when methyl, ethyl, or *isopropyl* dibromoglutarate was hydrolysed by 2*N*-sodium carbonate a small quantity of the bromocyclopropanedicarboxylic acid (XXXVIII) was produced. On prolonged boiling, however, replacement of the bromine



atom by hydroxyl occurred, with the formation of *cyclopropanoldi*-carboxylic acid (XXXIX).

Such a change is what in all probability occurs in the present instance. It was found necessary to boil the dibromo-ester with a solution of sodium carbonate (saturated at 105°) during 60 hours, before there was appreciable hydrolysis. Under these conditions, the hydroxy-ring acid (XXVI) would be first produced, and, being unstable, be immediately converted into the keto-acid (XXIV).

The hypothetical existence of the two multiplanar forms of *cyclohexane*, (a) the "boat" (XL) and (b) the "arm-chair" (XLI), may be assumed to explain the formation of decalin. The "boat"



is a loose shape which cannot pass into the other form without strain, but is itself capable of passing through a series of vibrating phases by strain-free relative rotations. The number of decalins that can exist by a combination of these forms through their *cis*- as well as their *trans*-valencies is large. But Mohr's postulate is probably applicable, and then all the *cis*-forms can be reduced to one configuration, and the *trans*- to another (Wightman, J., 1925, 127, 1421; Hückel, "Fortschritte der Chemie, Physik und Physikalischen Chemie," Bd. 19, Heft 4, 1927, 27—30). All these forms are probably different phases (the decalin made of two uniplanar *cyclohexanes* is probably one of these, though of much shorter duration) of the vibrating molecule, no phase having more than a transitory existence. The substance behaves stereochemically as if its configuration were the average condition of the limiting states. Moreover, the further the uniplanar form departs from the strainless phase, the more will the molecule behave as a strainless ring.

On examining a model of *trans*-decalin, it is readily seen that it would be very greatly strained if the component *cyclohexanes* were uniplanar; on the other hand, almost complete relief of this strain takes place if the two rings are multiplanar. *trans*-Decalin should therefore be expected to behave like a strainless ring, and this is exactly what has been demonstrated by the present investigation. The instability of the *spiro-cyclopropane* acids, the non-existence of the hydroxy-ring acid, and the stability of the keto-acid all show that *trans*-decalin occupies a place in the table midway between *cyclopentane* and *cycloheptane*, rather than near *cyclohexane*. This evidence is in perfect agreement with that from other sources, including the measurement of the heats of combustion (Roth and Lassé, *Annalen*, 1925, 441, 48).

Brief reference may be made to the strain in *cyclohexane* which has been the subject of controversy in recent years (Hückel, *op. cit.*). The non-existence of two stable strainless forms (Wightman, J., 1926, 2541; Werner and Conrad, *Ber.*, 1899, **32**, 3046) which would be expected on the basis of Sachse's hypothesis (*Ber.*, 1890, **23**, 1363) was explained by Mohr (*J. pr. Chem.*, 1918, **98**, 315; 1922, **103**, 316) by assuming that the temporary strain involved in the interconversion of Sachse's strain-free structures is sufficiently slight to be overcome by forces due to molecular cohesion; yet the fact remains that there is no experimental proof whatever of the existence of strainless *cyclohexane*. Moreover, the data obtained from X-ray examination (Hendricks and Bilicke, *J. Amer. Chem. Soc.*, 1926, **48**, 3007) of benzene hexahalides do not indicate the existence of a multiplanar *cyclohexane*. It has been argued that because decalin exists in *cis*- and *trans*-forms and may therefore be considered fairly free from strain, *cyclohexane* itself should lie in more than one plane. There is no justification for this view, because the condition which exists in dicyclic compounds, e.g., *trans*-decalin, where the strain would be very great if the component *cyclohexanes* were uniplanar, is quite different from that in *cyclohexane*, where the strain would not be excessive.

Hückel (*op. cit.*, p. 90) contends that the "valency-deflexion" hypothesis "steht und fällt mit der willkürlicher Annahme eines ebenen gespannten Sechsrings" and suggests, "eine weitere Ausdehnung des Vergleichs auf substituierte Cyclohexanringe und auf Derivate des *trans*-Dekalins, in denen der Sechsring sicher nicht eben sein kann, wäre von Bedeutung." The marked contrast in the effects of *cyclohexane* and *trans*-decalin on the carbon tetrahedral angle demonstrated by this investigation, which was begun long before Hückel's publication appeared, can only be due to a large difference in strain in the two rings; it should be noted that the polar influences, whatever their nature, would be expected to be similar in the two rings. *trans*-Decalin is obviously strainless, on the evidence from all sources; it seems probable, therefore, that the average condition of the vibrational limits of *cyclohexane* possesses appreciable strain.

One of the characteristics of the analogous derivatives of *cyclopentane* (Becker and Thorpe, J., 1920, **117**, 1584) and *cycloheptane* (Baker and Ingold, J., 1923, **123**, 127) is their remarkable lack of tendency to crystallise. The derivatives of *trans*-decalin display this characteristic even more prominently. This, and the formation of a number of stereoisomerides in all the reactions, has made the experimental investigation extremely difficult. None of the substances described in this paper can be accumulated in any con-

siderable quantity, and even their isolation is possible only when the directions given in the experimental part are closely followed.

EXPERIMENTAL.

Ethyl Hydrogen trans-Decalin-2:2-diacetate (IV).—A solution of sodium (35 g.) in absolute ethyl alcohol (500 c.c.) was added slowly with stirring to a solution of the anhydride of *trans*-decalin-2:2-diacetic acid (356 g.), also dissolved in absolute ethyl alcohol (175 c.c.). After the reaction became slow, the alcohol was removed in a vacuum, and the aqueous solution of the sodium salt acidified with dilute hydrochloric acid. The heavy oil which was precipitated was extracted with pure ether, dried thoroughly, recovered, and kept at 100° under vacuum for 1 hour (420 g.). The *acid ester* [Found: equiv., 280. $C_{10}H_{16}(CH_2 \cdot CO_2Et) \cdot CH_2 \cdot CO_2H$ requires equiv., 282] is a thick, almost colourless syrup; on distillation under reduced pressure, it is reconverted into the anhydride.

Methyl hydrogen *trans*-decalin-2:2-diacetate was prepared in a similar way (Found: Ag in the *silver* salt, 27.0. $C_{15}H_{23}O_4Ag$ requires Ag, 28.8%).

Monobromination. When the ethyl acid ester (420 g.) was cautiously mixed with phosphorus pentachloride (330 g.), a vigorous reaction occurred and hydrogen chloride was evolved: the conversion into the acid chloride was completed by heating on the steam-bath for 1 hour. Dry bromine (82 c.c.; 1.1 mols.) was then added portionwise during 6 hours, the mixture being kept at 50—60°. When the evolution of hydrogen bromide had ceased, the whole was poured into absolute ethyl alcohol (2 l.), kept at 25°. After the vigorous reaction had subsided, the solution was boiled for $\frac{1}{2}$ hour and then mixed with excess of water. The precipitated bromo-ester was extracted with ether, the acid product removed with a 5% solution of sodium carbonate, and the extract then dried over calcium chloride and evaporated. The residual neutral *mono-bromo-ester* (III) was kept over concentrated sulphuric acid in a vacuum during several days (yield, 80—83%) (Found: Br, 19.1. $C_{18}H_{29}O_4Br$ requires Br, 20.5%). On distillation even under 2 mm., it (b. p. 180—200°/2 mm.) was partly converted into the lactonic ester, the distillate being a thick viscid syrup (Found: C, 61.9; H, 8.2. The lactonic ester, $C_{16}H_{24}O_4$, requires C, 68.6; H, 8.6%. The monobromo-ester, $C_{18}H_{29}O_4Br$, requires C, 53.7; H, 7.2%).

The acid product of the monobromination extracted by aqueous sodium carbonate (above) was obtained as a heavy oil on acidification (yield, 17—20%); it could not be purified by distillation (Found: Br, 21.6. $C_{16}H_{25}O_4Br$ requires Br, 22.1%). This acid

monobromo-ester is formed even under conditions most conducive to the complete esterification of the bromo-acid chloride.

Stereoisomeric Lactones of α -Hydroxy-trans-decalin-2 : 2-diacetic Acids.

Lactones (A) (XV) and (B) (XVI).—These lactones are the only products of the action of boiling sodium carbonate solution on the neutral monobromo-ester (III). A suspension of the mixture of the monobromo-ester and lactonic ester (30 g.), obtained by the distillation of the monobromo-ester, in a solution (saturated at 105°) of sodium carbonate (60 g.) was boiled for 72 hours. The solution was diluted and extracted with ether to remove any unchanged ester. The oil precipitated on acidification was thrice extracted with pure ether, dried, recovered, and kept at 90° for 2 hours. After remaining for 2 weeks in a vacuum over sulphuric acid, it was dissolved in benzene, to which was then added as much light petroleum (b. p. 60—80°) as possible without producing a turbidity. The solid which had separated during 1 week was collected (A). On further addition of light petroleum to the filtrate, an oil (B) was precipitated, from which the supernatant liquid was poured off.

After several months, the mother-liquor deposited colourless nodules. These separated from benzene-light petroleum (b. p. 60—80°) in crystalline lumps, m. p. 137—140°. Titration with *N*/20-barium hydroxide showed that this substance was a mixture of lactone and the hydroxy-acid; the latter, however, could not be obtained sufficiently pure for analysis.

Lactone (A) crystallised from benzene in colourless silky needles, m. p. 156° (Found : C, 66.7; H, 7.9; equiv., by titration with *N*/20-barium hydroxide, 256. $C_{14}H_{20}O_4$ requires C, 66.7; H, 7.9%; equiv., for monobasic acid, 252).

When concentrated aqueous solutions of the lactone and aniline were mixed, the *aniline* salt separated in long silky needles, m. p. 126° (Found : C, 69.1; H, 7.9. $C_{14}H_{20}O_4 \cdot C_6H_5 \cdot NH_2$ requires C, 69.6; H, 7.8%).

The lactone and excess of aniline were heated together at 200—210° for 1.5 hours. The gum obtained on cooling was triturated with dilute hydrochloric acid; it then solidified. Crystallised from dilute ethyl alcohol, the *monoanilide* separated in long, colourless, feathered needles, m. p. 154° (Found : C, 73.4; H, 7.8; N, 4.5. $C_{20}H_{25}O_3N$ requires C, 73.4; H, 7.6; N, 4.3%).

Lactone (B) (XVI). The oil (B, above) solidified after some weeks and then separated from benzene in stellate clusters of soft needles, m. p. 163° (Found : C, 66.6; H, 8.1%; equiv., 252). It is sparingly

soluble in cold benzene. A mixture of lactones (A) and (B) melts at 123—125°.

The *aniline* salt of lactone (B) crystallised from benzene in long silky needles, m. p. 147° (Found : C, 69.6; H, 7.5%). The *monoanilide* separated from dilute methyl alcohol in dirty white, spherical nodules, m. p. 172° (Found : C, 73.2; H, 7.9; N, 4.5%).

Lactones (C) (XVII) and (D) (XVIII).—A sodium carbonate solution (25 g. in 225 c.c. of water) of the acid bromo-ester (V) (40 g.) was boiled for 8 hours, diluted and acidified, and the precipitated oil collected in ether. The ethereal solution having been partly dried over calcium chloride, the substance (29 g.) was recovered : it showed no signs of crystallising and therefore was esterified with ethyl alcohol (120 c.c.) and concentrated sulphuric acid (12 c.c.). The product was isolated in the usual way and after two fractional distillations in a vacuum was separated into two fractions : (1) 210—211°/6 mm., (2) 215°/6 mm.

Lactone (C). The ethyl ester, b. p. 210—211°/6 mm., was boiled with concentrated hydrochloric acid for 10 hours. (The hydrolysis of the esters of these acids with hydrochloric acid is extremely slow, chiefly owing to their insolubility in the acid.) The residue obtained on removal of the acid was dried at 90° for 2 hours and dissolved in benzene—light petroleum (b. p. 60—80°). Even after 10 weeks, only a small quantity of the crystalline lactone (m. p. 110°) had separated. On recrystallisation from benzene—light petroleum (b. p. 60—80°), the lactone (C) separated in hard granular cubic masses of thick plates, m. p. 164°. These are hydrated and the anhydrous *lactone (C)*, m. p. 165—166°, is obtained from them by heating at 100° (Found : C, 66.4; H, 8.0%; equiv., 255). This lactone is sparingly soluble in both hot and cold benzene. In admixture with lactone (A) or (B), its m. p. is depressed by 20—30°.

The *monoanilide* crystallised from dilute ethyl alcohol in shimmering leaflets, m. p. 166° (Found : N, 4.4%).

Lactone (D). The ethyl ester, b. p. 215°/6 mm., was boiled with concentrated hydrochloric acid for 8 hours and the lactonic acid produced was isolated in the usual way, dried, and dissolved in benzene—light petroleum (b. p. 60—80°). After 8 weeks, during which time a small quantity of light petroleum was added daily to prevent turbidity in the solution, the *lactone (D)* which had been deposited was collected and recrystallised from benzene; it then separated in short colourless needles, m. p. 132° (Found : C, 66.5; H, 8.0; equiv., 249).

The *aniline* salt crystallised from benzene in silky needles, m. p. 122°.

Hydrolysis of the Neutral Monobromo-ester with Concentrated Potassium Hydroxide Solution at 150°.—A solution of potassium hydroxide (450 g.) in water (250 c.c.) was evaporated until the boiling point reached 150°. The bromo-ester (150 g.) was then added to the boiling solution as rapidly as possible. The reaction was not vigorous, but after 15—20 minutes' boiling the ester dissolved; at the same time a potassium salt separated. The solution was then diluted freely with water and acidified while hot. The precipitated oil was extracted from the cold solution, partly dried over calcium chloride, recovered, and dried at 90° for 3 hours. The mixture of acids (80 g.), which had partly solidified, was mixed with benzene (125 c.c.) and the precipitated *spiro*-acids (29 g.) were collected after 1 hour: the mother-liquor, mixed with light petroleum (b. p. 60—80°) and kept for 1 week, usually deposited a further quantity of the *spiro*-acids (6 g.).

The mixture of acids, m. p. usually 215—220°, was very difficult to separate into its constituents. The best results were obtained by dissolving the mixture in a large excess of acetone and carefully adding water. A small first crop (A) separated in nodules, m. p. 250—253°; the second crop (B) separated in pearly laminae, m. p. 243°. The later crops were mixtures (m. p. 225—230°).

trans-spiro-Acid (A) (VIII). The first crop (A) was amorphous and separated in nodules from most of the solvents in which it was soluble; from a solution in 5% hydrochloric acid at 240°, however, the acid separated, on cooling, in lustrous fern-like forms. After crystallisation from aqueous acetone, *trans-decalin-β-spiro-cyclopropane-trans-1:2-dicarboxylic acid* melted at 264° (Found: C, 66.6; H, 8.0; equiv., 126. $C_{14}H_{20}O_4$ requires C, 66.7; H, 7.9%; equiv., 126).

The *dianilide* crystallised from ethyl alcohol, in which it was very sparingly soluble, in soft colourless needles, m. p. 307° (decomp.) (Found: C, 77.2; H, 7.7. $C_{26}H_{30}O_2N_2$ requires C, 77.6; H, 7.5%).

trans-spiro-Acid (B) (IX). The second crop (B, above) crystallised from aqueous acetone in lustrous ferns, m. p. 250° (Found: C, 66.5; H, 7.9%; equiv., 126). The *trans-spiro-acid (B)* is more soluble in solvents than its stereoisomeride (A) and melts at 220—225° when mixed with it.

The *dianilide*, m. p. 303° (Found: C, 77.4; H, 7.6%), resembled the isomeride (A) in its solubility in alcohol and in its crystalline form and melted at 280° when mixed with it.

Both the *trans-spiro*-acids are insoluble in water, benzene, and chloroform, sparingly soluble in xylene, and moderately easily soluble in acetone, ethyl acetate, and glacial acetic acid. They are

converted into the same *cis*-A-anhydride (see below) on distillation. They are, however, unchanged on melting.

The benzene-light petroleum mother-liquor from which the *trans*-*spiro*-acids had been removed (see p. 1176) was evaporated and the residue, since it showed no tendency to solidify, was esterified with ethyl alcohol and sulphuric acid in the usual way. The ethyl esters produced were twice fractionally distilled; in addition to small quantities of low-boiling esters, the following fractions were then isolated: (1) 200°/7 mm., (2) 214—215°/7 mm., (3) 224°/7 mm.

Fraction (1). This was boiled with concentrated hydrochloric acid for 11 hours, the residue obtained by evaporation of the acid was dissolved in benzene-light petroleum, and after several days the *cis*-*spiro*-acid (A) (VI) which had been deposited (less than 2 g.) was collected; m. p. 183—184°. The rest of the oil could not be induced to solidify.

The same acid was also prepared (a) by boiling *trans*-*spiro*-acid (A) or (B) and decomposing the anhydride thus produced, (b) from the above mixture of *spiro*-acids, m. p. 180—240°, which could not be separated by fractional crystallisation. This mixture was heated as rapidly as possible until it melted and was then boiled at the ordinary pressure for a few minutes. The unchanged acid was removed with sodium carbonate, and the anhydride distilled under reduced pressure. It boiled at 212—225°/14 mm. and the viscous distillate, after being kept in contact with light petroleum (b. p. 40—60°) for several days, deposited needles which on decomposition with alkali gave the *cis*-*spiro*-acid (A), m. p. 183—184°.

Being sparingly soluble in benzene, the *cis*-*spiro*-acid (A) is best crystallised from chloroform-light petroleum (b. p. 60—80°), from which it separates in lustrous prisms, m. p. 185—186° (efferv. and formation of anhydride) (Found: C, 66.7; H, 8.0%; equiv., 131).

The *anhydride* (X), prepared by melting the *cis*-acid or by treating it with acetyl chloride, or by any of the other methods described above, crystallised from light petroleum (b. p. 60—80°) in long silky needles, m. p. 107° (Found: C, 71.8; H, 7.5. C₁₄H₁₈O₃ requires C, 71.8; H, 7.7%).

Fraction (2). The ester was boiled with excess of hydrochloric acid, glacial acetic acid being added until it dissolved: the hydrolysis was complete in 4 hours. The lactone, isolated in the usual way, was kept in a vacuum for several days and then dissolved in benzene-light petroleum (b. p. 60—80°); after 10 weeks, the crystals (m. p. 110°) which had separated were found on recrystallisation to be identical with lactone (C), m. p. 165—166°.

Fraction (3). The lactone which was obtained by the hydrolysis

of this ester was found, on purification, to be identical with lactone (A), m. p. 156°.

Hydrolysis of the Acid Product of Monobromination by Concentrated Potassium Hydroxide Solution at 150°.—The acid monobromom-ester (120 g.) was treated with a boiling solution of potassium hydroxide (360 g.) at 150° in the same way as the neutral bromo-ester, but in this case the reaction was very vigorous. The acids were isolated in the usual way, dried (83 g.), and mixed with benzene (150 c.c.). From the mixture of *spiro*-acids (27 g.) obtained, only the *trans*-*spiro*-acid (A), m. p. 264°, could be separated by crystallisation from aqueous acetone.

The acids soluble in benzene were esterified and the following fractions were collected: (1) 232°/19 mm., (2) 240°/19 mm., (3) 246—248°/19 mm.

Fraction (1) (35 g.) was hydrolysed with hydrochloric acid, and the product treated with benzene–light petroleum (b. p. 60—80°); a small quantity of the *cis*-*spiro*-acid, m. p. 185—186°, was obtained after several weeks.

Fraction (2) (8 g.) gave the lactone (C), m. p. 165—166°, when hydrolysed.

Fraction (3) (25 g.) gave a mixture of lactones (C) and (D).

Dibromination of trans-Decalin-2 : 2-diacetic Acid.

The reaction which started when *trans*-decalin-2 : 2-diacetic acid (200 g.) was mixed with phosphorus pentachloride (400 g.) was completed by gentle heating on the steam-bath for 4—5 hours. Dry bromine (88 c.c., 2·2 mols.) was then added to the mixture, which was kept at 50—60° during 8 hours. After 20 hours, when the evolution of hydrogen bromide had ceased, the mixture was cooled, poured into absolute ethyl alcohol (1300 c.c.) at 0°, and, when the vigour of the reaction had abated, boiled for 1 hour. The whole was then freely diluted with water and the precipitated *dibromo*-ester (XXIII) was extracted with a large volume of ether, freed from the acid product by extraction with a 5% solution of sodium carbonate, dried over calcium chloride, and recovered (350 g.). The specimen for analysis was kept in a vacuum over sulphuric acid for 4 weeks (Found: Br, 32·1. $C_{18}H_{28}O_4Br_2$ requires Br, 34·1%).

The acid fraction (above) never amounted to more than 5 g. In the earlier experiments, where the usual conditions of bromination were followed, considerable quantities of the acid monobromom-ester (V) were obtained (Found: Br, 21·6. Calc.: Br, 22·1%).

trans-Decalin-2 : 2-dibromoacetic Acid (formula as XXIII).—When the dibromo-acid chloride was poured into anhydrous formic

acid, there was a vigorous evolution of hydrogen chloride. The gummy residue obtained on evaporation of the solution was triturated with chloroform–light petroleum (b. p. 40–60°). A small quantity of a dirty white powder was obtained which, after crystallisation from the same solvent mixture, melted at 199° (decomp.) (Found : C, 40.7; H, 5.0. $C_{14}H_{20}O_4Br_2$ requires C, 40.8; H, 4.8%).

Hydrolysis of the Dibromo-ester (XXIII) with 64% Potassium Hydroxide Solution.—When the dibromo-ester (110 g.) was added as rapidly as was consistent with safety to a boiling solution of potassium hydroxide (420 g.) in water (240 c.c.), it dissolved and a potassium salt separated. The solution was boiled for 5 minutes, diluted, and acidified while hot with hydrochloric acid. The precipitated heavy oil was extracted with ether (thrice), partly dried over calcium chloride, and recovered. After being kept at 90° for 2 hours and in a vacuum for 1 week, when it had become partly solid, it was mixed with benzene–light petroleum (b. p. 60–80°) (equal volumes). After 12 hours, the precipitated *α*-keto-trans-decalin-2 : 2-diacetic acid (XXIV) was collected (25 g.). It crystallised from benzene in short colourless needles and from chloroform in long silky needles, m. p. 156° (Found : C, 62.7; H, 7.5; equiv., 135. $C_{14}H_{20}O_5$ requires C, 62.7; H, 7.4%; equiv., 134).

The keto-acid decolorises alkaline permanganate slowly in the cold, but rapidly when hot. It is easily soluble in acetone and ethyl acetate. It is also soluble in hot water, from which it cannot be crystallised since it becomes hydrated and is obtained as a syrup on removal of the solvent. The *quinoxaline* derivative, prepared by heating equal quantities of the keto-acid and *o*-phenylenediamine in glacial acetic acid for 1 hour, was obtained after two crystallisations from ethyl alcohol in dirty white nodules, m. p. 230° (Found : C, 70.6; H, 7.2. $C_{20}H_{24}O_3N_2$ requires C, 70.6; H, 7.1%).

The *semicarbazone* of the monosodium salt* separated in rhombic plates when a mixture of the keto-acid, semicarbazide hydrochloride, and sodium acetate in concentrated aqueous solution was kept for 24 hours. The crystals, after being washed with water and alcohol, were hydrated (Found : H_2O , 3.0. $C_{15}H_{22}O_5N_3Na, 1/2H_2O$ requires H_2O , 2.6%), but became anhydrous when kept at 110°

* It has frequently been observed that some *α*-keto-acids fail to combine with semicarbazide (or other ketonic reagents). The reason for this abnormal behaviour probably lies in the strong acidity of these acids, which act as hydrolysing agents: one molecule forms the semicarbazone and another immediately hydrolyses it. Semicarbazones are readily formed when the carboxyl groups attached to the keto-group are neutralised.

for 3 hours. The semicarbazone then melted with frothing and decomposition at 255° (Found : Na, 6.35. $C_{15}H_{22}O_5N_3Na$ requires Na, 6.6%).

The keto-acid does not combine with semicarbazide, phenylhydrazine, 2 : 4-dinitrophenylhydrazine, or diphenylbarbituric acid.

The *methyl* ester, prepared by boiling a solution of the keto-acid (5 g.) in methyl alcohol (40 c.c.) and concentrated sulphuric acid (4 c.c.) for 4 hours, or from the silver salt and methyl iodide, boiled at 228°/21 mm. (Found : C, 64.5; H, 8.1. $C_{16}H_{24}O_5$ requires C, 64.9; H, 8.1%). It did not give a semicarbazone, nor react with phenylhydrazine in acetic acid or alcohol. The *phenylhydrazone*, however, was obtained by heating a mixture of the keto-ester and phenylhydrazine in benzene solution on the steam-bath for 4 hours. On addition of light petroleum (b. p. 60—80°) to the cooled product, thick plates were obtained. The phenylhydrazone is sparingly soluble in alcohol and benzene, moderately easily soluble in chloroform, and crystallises from dilute acetic acid in long, colourless, rectangular prisms, which are pale yellow in bulk; m. p. 235° (decomp.) (Found : C, 68.3; H, 7.6. $C_{22}H_{30}O_4N_2$ requires C, 68.4; H, 7.8%). After 1 g. of the keto-acid had been boiled with 20 c.c. of 64% potassium hydroxide solution for 4 hours, 0.9 g. was recovered unchanged by dilution, acidification, and extraction with ether.

Oxidation of the Keto-acid with Hydrogen Peroxide.—A solution of the keto-acid in sodium carbonate was warmed during 3 hours, with frequent additions of hydrogen peroxide. Acidification then produced a crystalline precipitate which, after purification, was identified as 2-carboxy-*trans*-decahydronaphthalene-2-acetic acid (A), m. p. 197°, by comparison with a genuine specimen (J., 1929, 1959).

On distillation under reduced pressure, the keto-acid loses carbon monoxide and gives an oily substance, which is probably a mixture of the anhydrides of 2-carboxy-*trans*-decahydronaphthalene-2-acetic acids (A) and (B).

$\Delta^{2(\text{or } 1)}$ -*trans*-Octahydronaphthalene-2-acetic Acid (XXV).—The benzene solution from which the keto-acid had been removed (p. 1179) was evaporated and the residue, which showed no signs of crystallising after several months, was esterified with methyl alcohol (500 c.c.) and concentrated sulphuric acid (50 c.c.). After two fractional distillations of the product, various fractions, b. p. 170—220°/15 mm., were obtained in addition to a fraction, b. p. 154°/15 mm. (1.7 g.). This fraction was mixed with 40 c.c. of cold 10% aqueous potassium hydroxide, and enough alcohol added to form a clear solution. After 4 days, the oil precipitated on acidific-

ation was extracted with ether, dried, and recovered and the mixture of oil and solid obtained was drained. The solid, which separated from light petroleum (b. p. 60—80°) in rhombic plates, m. p. 100—101°, was identified as $\Delta^{2(\text{or } 1)\text{-trans-octahydronaphthalene-2-acetic acid}}$ by analysis (Found: C, 73.9; H, 9.4. $\text{C}_{12}\text{H}_{18}\text{O}_2$ requires C, 74.2; H, 9.3%), and by comparison with a genuine specimen (see later). The dibromide, m. p. 183°, was identical with the dibromide of the above-mentioned acid.

The other fractions were hydrolysed with concentrated hydrochloric acid. From the resulting acids, after standing in benzene solution for 14—18 months, small quantities of the keto-acid were isolated; the remainder did not solidify and decomposed on distillation.

The aqueous solution from which the above acids had been removed by extraction with ether was evaporated to dryness. From the residue, ether extracted a mixture of oil and solid; the latter crystallised from water in prisms, m. p. 102° (not depressed by admixture with crystalline oxalic acid), and gave the usual reactions of oxalic acid.

Hydrolysis of the Dibromo-ester (XXIII) with Methyl-alcoholic Potash.—The dibromo-ester (100 g.) was added as quickly as possible to a boiling solution of potassium hydroxide (200 g.) in methyl alcohol (600 c.c.). The solution was boiled for 20 minutes and then evaporated to dryness. The residue was dissolved in water and acidified, and the precipitated oil extracted with ether. The residue after removal of the dried ether was kept at 100° in a vacuum for 2 hours; it then partly solidified. It was mixed with a small quantity of benzene, and the resulting *trans-decalin- β -spiro-trans-1-methoxycyclopropane-1:2-dicarboxylic acid* (XXIX) collected; crystallised once from ethyl acetate and once from aqueous acetone, this separated in clusters of fine silky needles, m. p. 213° (Found: C, 63.7; H, 8.0; equiv., 141. $\text{C}_{15}\text{H}_{22}\text{O}_5$ requires C, 63.8; H, 7.8%; equiv., 141). When the *trans-methoxy-spiro-acid* was boiled with hydrobromic acid (*d* 1.45; 30 c.c.) for 4 hours, it was converted into the keto-acid (XXIV), m. p. 156° after crystallisation from chloroform.

The low-melting acid, together with the liquid acids obtained by evaporation of the benzene solution, was refluxed with acetyl chloride, the excess of which was then removed. The residue was dissolved in a large volume of ether, and the unchanged acid removed by a dilute solution of sodium bicarbonate. The anhydride distilled at 210—220°/12 mm. It was decomposed with sodium hydroxide and the liquid acid precipitated on acidification of the alkaline solution was triturated with methyl alcohol; it then partly

solidified. The solid was freed from the oil by draining on porous earthenware and crystallised from aqueous acetone. The resulting solid (m. p. 190—193°) was reconverted into the anhydride by melting, the unchanged acid being removed by sodium carbonate. After three crystallisations from light petroleum (b. p. 60—80°), the *anhydride* (XXX) separated in long, colourless, flattened needles, m. p. 145° (Found : C, 68·2; H, 7·5. $C_{15}H_{20}O_4$ requires C, 68·2; H, 7·5%).

The *cis-methoxy-spiro-acid* (A), which was obtained by decomposing the anhydride, crystallised from aqueous acetone in short colourless needles, m. p. 204° (Found : C, 63·7; H, 7·8; equiv., 143). Mixed with the *trans-methoxy-spiro-acid* (B), it melted at 190—194°.

The substances so far described have a great tendency to retain ether, with the result that when they are placed in a vacuum they swell up, filling the whole of the desiccator, leading to considerable loss of material. This difficulty has been overcome by keeping them at 90° or 100° in a vacuum; all the ether is then completely removed. Even if they solidify in the desiccator, the lactonic acids become oils when exposed to the atmosphere or treated with sodium-dried solvents. The only method of getting them as crystalline solids has been to dissolve them in benzene—light petroleum (b. p. 60—80°) and allow the solution to stand during several months; even so, only a fraction of the material is obtained crystalline.

Synthesis of trans-Decahydronaphthylidene-2-acetic and
 $\Delta^{2(\text{or } 1)\text{-trans-Octahydronaphthalene-2-acetic Acids.}$

Condensation of trans- β -Decalone with Ethyl Bromoacetate : Ethyl 2-Hydroxy-trans-decalin-2-acetate (XXXI).—Zinc (75 g.) was added to a mixture of *trans- β -decalone* (152 g.) and ethyl bromoacetate (106 g.) in dry benzene (375 c.c.). The reaction which started after 2 hours' heating on the steam-bath was allowed to proceed without the application of heat and was then completed by heating again for $\frac{1}{2}$ hour. The zinc compound having been decomposed with ice and dilute sulphuric acid, the benzene layer was separated, washed successively with dilute sulphuric acid, 10% sodium hydroxide solution, and water, and dried over calcium chloride. On distillation under reduced pressure, after removal of benzene, the main fraction boiled at 184°/26 mm., small quantities of esters boiling at lower and higher temperatures being also obtained. On redistillation, pure *ethyl 2-hydroxy-trans-decalin-2-acetate* boiled at 179—180°/20 mm. (Found : C, 70·0; H, 10·0. $C_{14}H_{24}O_3$ requires C, 69·9; H, 10·1%); it had d_4^{25} 1·045, n_D^{25} 1·4832, whence $[R_L]_D$ 65·54 (calc., 65·63).

The hydroxy-ester was hydrolysed by boiling with 50% potassium hydroxide solution for a few minutes; the oily acid obtained on acidification partly solidified after a few hours. The solid was isolated by filtration and draining on porous earthenware. *2-Hydroxy-trans-decalin-2-acetic acid* (XXXII) is readily soluble in hot water (from which it separates in long needles) and alcohol, but is best crystallised from benzene; m. p. 102° (Found: C, 67.7; H, 9.9; equiv., 211.7. $C_{12}H_{20}O_3$ requires C, 67.9; H, 9.5%; equiv., 212). The oil, which probably consisted of the stereoisomeride and would not solidify, was used for the preparation of the $\alpha\beta$ -acid.

Dehydration of the Hydroxy-acid: trans-Decahydronaphthylidene-2-acetic Acid (XXXIII).—The hydroxy-acid (84 g.) was dissolved in acetic anhydride (220 g.; 5 mols.) and boiled for 3 hours. The residue obtained on removal of acetic anhydride under reduced pressure was diluted with water and boiled for 2 hours (distillation in steam was extremely slow and tedious). The acid, which partly solidified on cooling, was collected and drained on porous earthenware. Crystallised from light petroleum (b. p. 60–80°), *trans-decahydronaphthylidene-2-acetic acid* separated in long colourless prisms, m. p. 145° (Found: C, 74.3; H, 9.2; equiv., 194. $C_{12}H_{18}O_2$ requires C, 74.2; H, 9.3%; equiv., 194).

The *dibromide*, $C_9H_{16}>CBr\cdot CHBr\cdot CO_2H$, was prepared by keeping a mixture of the acid and bromine in chloroform solution for 2 days. The crystals obtained by evaporation of the solvent were boiled with light petroleum (b. p. 60–80°) to remove the small quantity of the low-melting stereoisomeride that had also been formed. The dibromide separated from benzene–light petroleum (b. p. 60–80°) in diamond-shaped crystals, m. p. 170° (Found: Br, 45.7. $C_{12}H_{18}O_2Br_2$ requires Br, 45.2%).

A solution of the $\alpha\beta$ -acid in sodium carbonate was immediately oxidised by a 1% solution of potassium permanganate. The resulting ketone, which was taken up in ether, was identified as *trans*- β -decalone by its characteristic odour and in the form of its semicarbazone, m. p. and mixed m. p. 193°.

Dehydration of the Hydroxy-ester.—A solution of the hydroxy-ester (100 g.) in dry benzene (100 c.c.) was mixed with phosphorus oxychloride (28 g.) and heated on the steam-bath for 4½ hours; evolution of hydrogen chloride had then ceased. The oil precipitated on dilution with water was extracted with ether, washed with sodium carbonate and water, dried over calcium chloride, and recovered by removal of the solvent. The $\beta\gamma$ -ester obtained (72 g.) boiled at 170°/24 mm.

Alcohol was added to a mixture of the foregoing ester (77 g.)

and a solution of potassium hydroxide (25 g.) in water (100 c.c.) until a clear solution was formed. After 48 hours, the alcohol having been removed, the solution was diluted with water, and any unchanged ester extracted with ether. The oily acid precipitated on acidification partly solidified after a few hours. It was collected, drained on porous earthenware, and crystallised from light petroleum (b. p. 60—80°), $\Delta^{2(\text{or } 1)}$ -*trans*-octahydronaphthalene-2-acetic acid (XXV) separating in colourless rhombic plates, m. p. 100—101° (Found: C, 74.2; H, 9.5%; equiv., 193). The acid decolorised permanganate and instantly absorbed bromine in chloroform solution. The *dibromide*, $\text{C}_9\text{H}_{15}\text{Br} > \text{CBr} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, obtained on evaporation of the solvent crystallised from chloroform-light petroleum (b. p. 60—80°) in thick plates, m. p. 183° (Found: Br, 45.3%).

Conversion of the $\alpha\beta$ -Acid into the $\beta\gamma$ -Isomeride.—The $\alpha\beta$ -acid (m. p. 145°) was boiled with 64% potassium hydroxide solution for 1 hour. The precipitate obtained on acidification of the diluted solution crystallised from light petroleum (b. p. 60—80°) in rhombic plates, m. p. 100—101°, of the $\beta\gamma$ -acid.

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