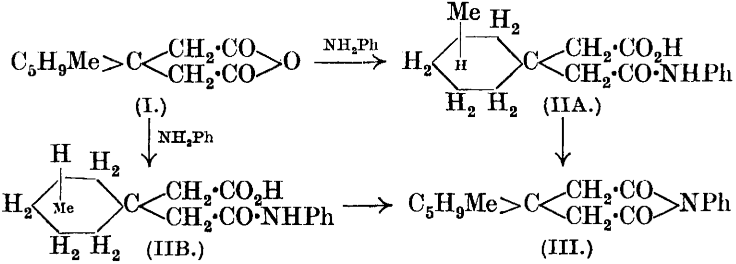
135. *The Formation and Stability of* spiro-*Compounds. Part XIV. The Effect of the Methyl*cyclo*hexane Ring on the Carbon Tetrahedral Angle.*

By RANCHHODJI DAJIBHAI DESAI.

THE recent work of Rao (J., 1930, 1162) and Kandiah (J., 1931, 952) has shown that when *cyclo*hexane, which, as regards the reactions in question, behaves as a strained ring, is interlocked in the *o*-position with a six- or a five-membered ring, the resulting dicyclic nuclei behave like strainless rings. It appeared of interest to examine the effect of a single group with the view of gaining an insight into the character of such a ring on the basis of the valency deflexion hypothesis of Thorpe and Ingold. The methyl*cyclo*hexane ring was chosen for examination, and this communication deals with the hydrolysis products of monobromo- and dibromo-esters of 3-methyl- and 4-methyl-*cyclo*hexane-1 : 1-diacetic acids.

The diacetic acids were prepared by the acid hydrolysis of their respective dicyano-imides, prepared by Guareschi's method from the ketones and ethyl cyanoacetate (compare Kon and Thorpe, J., 1919, **115**, 686). Each anhydride (I) gave two *anilic acids* (IIA and IIB) but only one *anil* (III).

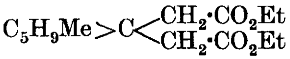


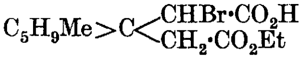
Monobromination of the Diacetic Acids.

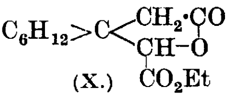
Like their *cyclo*hexane analogue, the diacetic acids on monobromination by the Hell–Volhard–Zelinsky method gave mixtures of *mono-bromo-* (IV), *dibromo-* (V), and unbrominated esters (VI). The monobromo-esters could be prepared by bromination of the *ethyl hydrogen methyl*cyclo*hexane*-1 : 1-*diacetates*, but the *monobromo-acid* esters (VIII) were always formed to the extent of 20—25%. The monobromo-esters were converted into *lactonic* esters (X) on distillation.

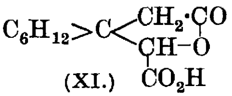
(IV.) 
$C_5H_9Me{>}C{<}\begin{matrix}CHBr\cdot CO_2Et\\ CH_2\cdot CO_2Et\end{matrix}$

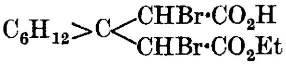
 (V.)
$C_5H_9Me{>}C{<}\begin{matrix}CHBr\cdot CO_2Et\\ CHBr\cdot CO_2Et\end{matrix}$

(VI.) 
$C_5H_9Me{>}C{<}\begin{matrix}CH_2\cdot CO_2Et\\ CH_2\cdot CO_2Et\end{matrix}$

 (VIII.)
$C_5H_9Me{>}C{<}\begin{matrix}CHBr\cdot CO_2H\\ CH_2\cdot CO_2Et\end{matrix}$

 (X.)
$C_6H_{12}{>}C{<}\begin{matrix}CH_2\cdot CO\\ CH-O\end{matrix}$ with CO_2Et on CH

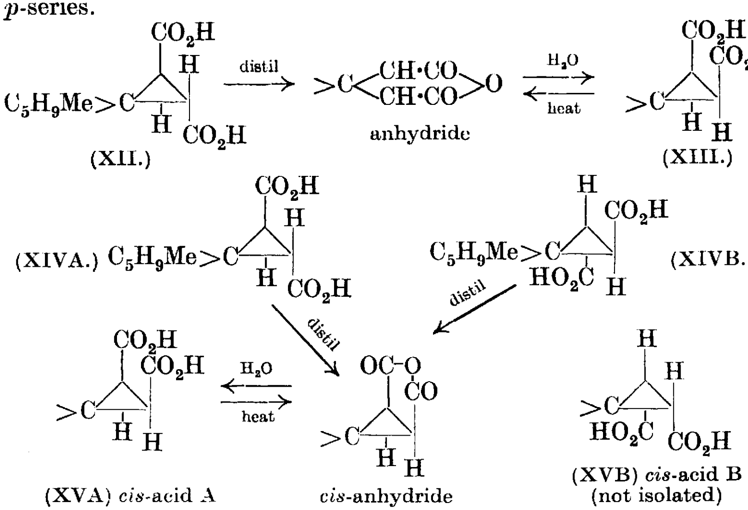
 (XI.)
$C_6H_{12}{>}C{<}\begin{matrix}CH_2\cdot CO\\ CH-O\end{matrix}$ with CO_2H on CH

 (IX.)
$C_6H_{12}{>}C{<}\begin{matrix}CHBr\cdot CO_2H\\ CHBr\cdot CO_2Et\end{matrix}$

cis- *and* trans-spiro-*Acids.*

The neutral monobromo-esters (IV) were hydrolysed by 64% caustic potash solution to mixtures of *spiro*-acids (40%) and lactonic acids (XI), the yields of the *spiro*-acids being the same as in the case of *cyclo*hexane itself. Two spiro-*acids*, one *trans*- (XII) and the other *cis*- (XIII), in the *p*-series and three spiro-*acids*, two *trans*- (XIVA and XIVB) and one *cis*- (XVA), in the *m*-series have been isolated from the hydrolysis products. The separation of the *cis*-acids from their *trans*-isomerides was effected in each case by means of acetyl chloride, and fractional crystallisation from acetone separated the two components of the mixture of *trans*-acids in the *m*-series. Conversion of *trans*- into *cis*-forms was easily done by distillation, and hydration of the *anhydrides*, but in the *m*-series the *trans*-forms both gave the same *cis*-acid.

The lactonic acids of the *m*-series formed in this reaction, and also by the hydrolysis of the monobromo-esters with 2*N*-sodium carbonate, did not solidify in a vacuum during 6 months, but one lactonic acid (XI), m. p. 145°, was isolated in small amount in the *p*-series.



(XII.) (XIII.) (XIVA.) (XIVB.)

(XVA) *cis*-acid A

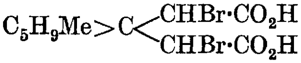
cis-anhydride

(XVB) *cis*-acid B (not isolated)

Stability of the spiro-*Acids*.—All the *trans-spiro*-acids have the same degree of stability, the position of the methyl group having no effect at all: they are stable to 5% hydrochloric acid at 240°, and to 10% hydrochloric acid at 200°, but are decomposed by the latter at 240° and by 20% hydrochloric acid at 200°, their respective diacetic acids remaining unchanged under identical conditions. The stability of these *spiro*-acids is much less than that of the *cyclo*hexane analogue, which is stable to concentrated hydrochloric acid at 240°.

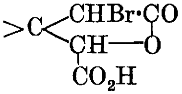
Dibromination of the Diacetic Acids.

The dibromo-esters (V) are conveniently obtained by the usual method, but a much longer time (100 hours) is required for the completion of the reaction. The acid product of bromination, formed in 10—15% yield, consists of a mixture of *dibromo-acid* ester (IX) and monobromo-acid ester (VIII). The dibromo-acid chlorides, which are probably mixtures of stereoisomeric forms, give rise to *dibromo*-acids (XVI) and *bromo-lactonic* acids (XVII) when warmed with anhydrous formic acid.

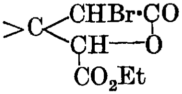


$C_5H_9Me{>}C{<}\begin{matrix}CHBr\cdot CO_2H\\ CHBr\cdot CO_2H\end{matrix}$

(XVI.)



(XVII.)

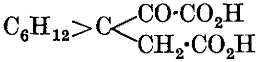


(XVIII.)

As in the *cyclo*hexane series, the dibromo-esters cannot be distilled, since they are thereby converted into *bromo-lactonic* esters (XVIII) with considerable charring.

The dibromo-esters were hydrolysed by 64% caustic potash solution at 150°, mainly to isomeric mixtures of α-*ketomethyl*cyclo*hexane*-1 : 1-*diacetic acids* (40%) (XIX) and a small amount of unsaturated acids (5%) (XX). The rest of the material was possibly changed into mixtures of stereoisomeric hydroxy-lactonic acids (XXI).

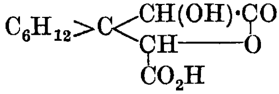
(XIX.)

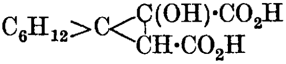


$C_6H_{12}{>}C{<}\begin{matrix}CO\cdot CO_2H\\ CH_2\cdot CO_2H\end{matrix}$

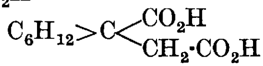
$C_6H_{11}{>}C\cdot CH_2\cdot CO_2H$ (XX.)

(XXI.)





(XXII.)



$C_6H_{12}{>}C{<}\begin{matrix}CO_2H\\ CH_2\cdot CO_2H\end{matrix}$

(XXIII.)

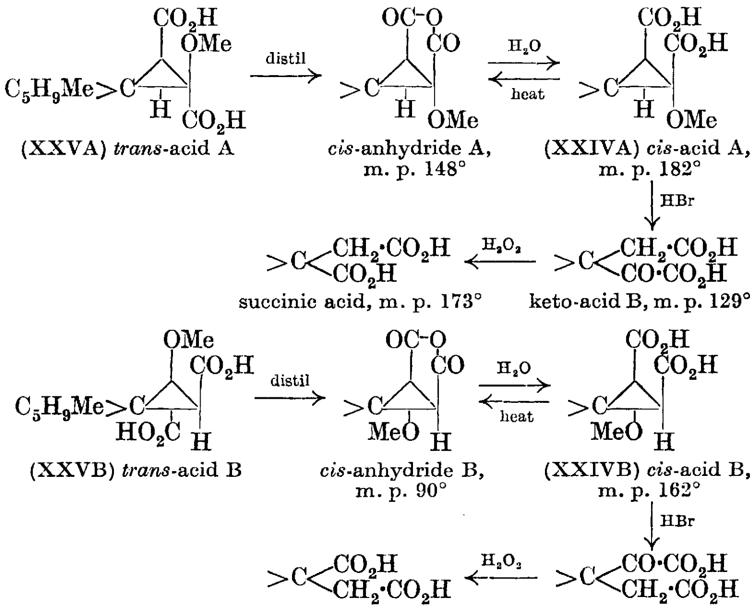
The hydroxy-ring acid (XXII) could not be detected. It was no doubt formed, but owing to its instability under the experimental conditions must have been converted into its open-chain isomeride (XIX). The side chain which was eliminated as glyoxylic acid, leading to the formation of the unsaturated acid (XX), was oxidised to oxalic acid, which was detected among the reaction products.

The isolation of the keto-acids (XIX) presented great difficulty, as the purified fraction which was supposed to contain them only did not solidify unless it was seeded with crystals of the keto-acids. Two keto-acids (A and B forms), isolated both in the *m*- and in the *p*-series, have been characterised as their *quinoxaline* derivatives, 2 : 4-*dinitrophenylhydrazones*, and the *phenylhydrazones* of their *methyl* esters. The acids did not react with semicarbazide acetate, but the sodium salts of the semicarbazones were formed when their aqueous solutions were treated with semicarbazide hydrochloride and sodium acetate. Fuming hydrobromic acid degraded the keto-acids to 1-*carboxymethyl*cyclo*hexane*-1-*acetic acids* (XXIII), which could also be prepared by oxidising them with hydrogen peroxide. The A forms resisted oxidation by this reagent, but almost quantitative yields were obtained from the B forms. All the keto-acids were recovered unchanged after being heated with 64% caustic potash solution at 150° for 12 hours.

The unsaturated acids (XX) formed in this reaction had the βγ-structure, and were identified by means of their derivatives. As the hydroxy-lactonic acids did not solidify in a vacuum after 6 months, no definite solid product could be isolated.

Hydrolysis of the dibromo-esters with methyl-alcoholic potash gave chiefly mixtures of methoxy-*spiro*-acids. Two cis-*methoxy*-acids (XXIVA and XXIVB) and one trans-*methoxy*-acid (XXVA) were isolated in a pure form in the *p*-series; the *trans*-methoxy-acid B (XXVB) had an indefinite m. p. On distillation, the mixture of *trans*-acids gave a mixture of cis-*anhydrides A* and *B*, the separation of which was effected by means of light petroleum (b. p. 60—80°), in which the A form, m. p. 148°, was sparingly, and B form, m. p. 90°, freely soluble.

p-*Series.*



(XXVA) *trans*-acid A

cis-anhydride A, m. p. 148°

(XXIVA) *cis*-acid A, m. p. 182°

succinic acid, m. p. 173°

keto-acid B, m. p. 129°

(XXVB) *trans*-acid B

cis-anhydride B, m. p. 90°

(XXIVB) *cis*-acid B, m. p. 162°

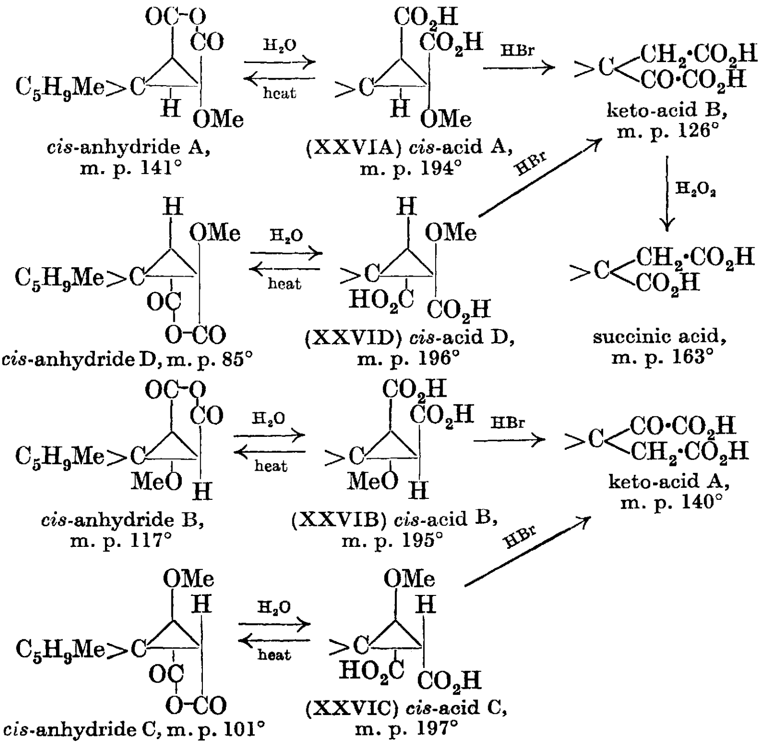
succinic acid, m. p. 136°

keto-acid A, m. p. 147°

Each *cis*-anhydride gave two *anilic acids* but only one *anil*. The *cis*-acids yielded the keto-acids (XIX) when heated with hydrobromic acid; a small amount of 1-carboxy-4-methyl*cyclo*hexane-1-acetic acid was also produced.

One trans-*methoxy-* and four cis-*methoxy*-spiro-acids have been isolated in the *m*-series. The mixture of *cis*-methoxy-anhydrides was fractionally crystallised from light petroleum (b. p. 60—80°) and four *anhydrides*, A, B, C, and D, m. p. 141°, 117°, 101°, and 85° respectively, were isolated. The acids obtained from them melted at 194°, 195°, 197°, and 196° (XXVIA, B, C, and D) respectively, and depressed each other's melting points. Acids A and D gave the same keto-acid B when heated with hydrobromic acid, and the same keto-acid A was obtained from the *cis*-acids B and C. On distillation, the mixture of *trans*-acids gave a mixture of *cis*-anhydrides, in which anhydrides A and D could be identified. Besides these *spiro*-methoxy-acids, which were sparingly soluble in benzene, benzene-soluble products were obtained in amounts insufficient for further investigation.

m-*Series.*

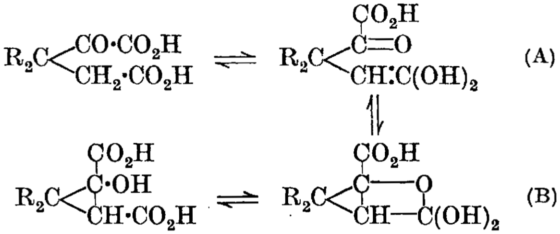


When the hydrolysis products of these dibromo-esters are compared with those of other series, the difference in behaviour of the *cyclo*hexane and the methyl*cyclo*hexane ring becomes manifest. In the former case caustic potash gives mainly the hydroxy-ring acid (type XXII), the unsaturated acid (type XX), and the hydroxy-lactonic acids (type XXI). No keto-acid (type XIX) is obtained. When methyl-alcoholic potash is used, only the hydroxy-ring acids are obtained. In the *cyclo*pentane, *trans*-decalin, and hexahydrohydrindene series, the products of potash hydrolysis are keto-acid, unsaturated acid, and hydroxy-lactonic acids. Methyl-alcoholic potash gives methoxy-*spiro*-acids in all cases, but in the cyclopentane and hexahydrohydrindene series a *cis*-hydroxy-ring acid can be isolated which is stable to 64% potash solution. The hydrolysis of the dibromo-esters with 2*N*-sodium carbonate gives the keto-acid (small amounts) and a mixture of stereoisomeric hydroxy-lactonic acids which does not solidify even after 6 months.

The foregoing evidence from the decomposition products of the monobromo- and the dibromo-esters of 3-methyl- and 4-methyl-*cyclo*hexane-1 : 1-diacetic acids shows that the methyl*cyclo*hexane ring simulates the behaviour of strainless rings such as *cyclo*pentane and especially *trans*-decalin and hexahydrohydrindene. The instability of the *spiro*-*cyclo*propane acids to 10% hydrochloric acid, and the stability of the keto-acids to 64% potash solution, emphasise this resemblance. The imides of 3- and 4-methyl*cyclo*hexane*spiro*-2 : 3-dicyano-2 : 3-dicarboxylic acids behave differently from their *cyclo*hexane analogue when hydrolysed with caustic potash (Birch and Thorpe, J., 1922, **121**, 1821).

If the methyl*cyclo*hexane ring is strainless, the question naturally arises : "How is this strain relieved ?" It might be done by a departure from the uniplanar structure and the assumption of the multiplanar form, but during the present investigation no evidence of this was obtained through the discovery of additional isomeric forms. The difference between the methylated and the unmethylated ring might be due to the stabilisation of one of the two possible strainless forms of the substituted ring. If this were so, a similar difference should appear in the dissociation constants of the diacetic acids (Spiers and Thorpe, J., 1925, **127**, 538; Gane and Ingold, J., 1931, 2153). The dissociation constants of *cyclo*hexane-1 : 1-diacetic acid and of its 3- and 4-methyl analogues are practically identical and are different from that of *cyclo*pentane-1 : 1-diacetic acid (private communication from Dr. R. P. Linstead). No such assumption to account for the anomalous chemical results, therefore, can be entertained.

If the configurations of the *cyclo*hexane and the methyl*cyclo*hexane rings are the same, there must be some factor in the methyl*cyclo*hexane ring which invalidates the methods used to demonstrate strain in other rings. It may be that the stability of the *spiro-cyclo*propane acids to hydrochloric acid of various strengths is dependent upon physical and polar factors. As regards the stability of the keto-acid to 64% caustic potash solution, it may be that the keto-cyclol change is not dependent only on the proximity of the oxalyl and the acetic acid residue, and that Lanfear and Thorpe's explanation (J., 1923, **123**, 1686) is the correct one :



The polar influence of the methyl group in the methyl*cyclo*hexane ring may inhibit the transitory formation of either (A) or (B), which must necessarily be formed as an intermediate.

EXPERIMENTAL.

p-*Methyl Series.*

An ice-cold mixture of 4-methyl*cyclo*hexanone (168 g.) and ethyl cyanoacetate (339 g.) was added to absolute ethyl alcohol (600 c.c.), which was cooled in a freezing mixture and saturated with ammonia. After 24 hours, the precipitated ammonium salt was collected and decomposed with hot dilute hydrochloric acid. The ω-imide of 4-methyl*cyclo*hexane-1 : 1-dicyanoacetic acid obtained, after being washed with hot water and dried (yield, 250 g.), crystallised from dilute alcohol in needles, m. p. 215° (compare Thorpe and Wood, J., 1913, **103**, 1593) (Found : C, 63·5; H, 6·3. Calc. : C, 63·7; H, 6·1%).

The imide was hydrolysed to 4-methyl*cyclo*hexane-1 : 1-diacetic acid by hot dilute sulphuric acid, but when a solution in concentrated sulphuric acid (10 parts) was kept for 24 hours and poured into water, the ω-*imide* of 4-*methyl*cyclo*hexane*-1 : 1-*dicarbamylacetic acid* was obtained; it crystallised from glacial acetic acid in long flattened needles, m. p. 260° (decomp.) (Found : C, 55·4; H, 6·9. $C_{13}H_{19}O_4N_3$ requires C, 55·5; H, 6·8%).

Ethyl 4-*methyl*cyclo*hexane*-1 : 1-*diacetate*, prepared by heating the acid (5 g.) with absolute alcohol (25 c.c.) and concentrated sulphuric acid (2 c.c.) for 6 hours, boiled at 178°/24 mm. (Found : C, 66·5; H, 9·7. $C_{15}H_{26}O_4$ requires C, 66·7; H, 9·6%).

Isomeric Anilic Acids.—The solid obtained from 4-methyl*cyclo*-

hexane-1 : 1-diacetic anhydride (5 g.) and aniline (3 g.) in benzene solution after 24 hours melted at 170—175°. On fractional crystallisation from alcohol, the sparingly soluble anilic acid A separated in flattened needles, m. p. 184° (Thorpe and Wood, *loc. cit.*). The more soluble *anilic acid B* crystallised from dilute alcohol in silky needles, m. p. 148° (Found: C, 70·5; H, 8·2. $C_{17}H_{23}O_3N$ requires C, 70·6; H, 8·0%.)

The *anil* (III), obtained by heating the anilic acid at 200° for 2 hours, and removing the unchanged anilic acid with dilute sodium carbonate solution, crystallised from dilute alcohol in needles, m. p. 140° (Found: C, 75·1; H, 7·9. $C_{17}H_{21}O_2N$ requires C, 75·3; H, 7·7%).

*Ethyl Hydrogen 4-Methyl*cyclo*hexane-*1 : 1-*diacetate.*—4-Methyl*cyclo*hexane-1 : 1-diacetic anhydride (100 g.), dissolved in absolute alcohol (125 c.c.), was gradually added to a solution of sodium (12 g.) in absolute alcohol (300 c.c.) and heated for ½ hour on the water-bath. The alcohol was then removed, and the residue diluted with water, extracted with ether, and acidified. The viscous oil precipitated was isolated by means of ether; it could not be distilled under reduced pressure without conversion into the anhydride (Found: equiv., 241. $C_{13}H_{22}O_4$ requires equiv., 242).

*Monobromination.—Ethyl α-bromo-*4-*methyl*cyclo*hexane-*1 : 1-*diacetate* (IV).—Phosphorus pentachloride (120 g.) and the acid ester (121 g.) were slowly mixed, warmed on the steam-bath for 2 hours, and dry bromine (28 c.c.) added at 50—60°. After 8 hours the mixture was poured into cooled absolute alcohol (450 c.c.), heated on the water-bath for 4 hours, and diluted with water. The oily *bromo*-ester thus precipitated was extracted with ether and washed with 5% sodium carbonate solution (yield, 75%) (Found: Br, 22·4. $C_{15}H_{25}O_4Br$ requires Br, 22·9%). On distillation it lost ethyl bromide and gave the *lactonic* ester (X), b. p. 205°/20 mm. (Found: C, 64·8; H, 8·5. $C_{13}H_{20}O_4$ requires C, 65·0; H, 8·3%).

The *monobromo-acid* ester (VIII) obtained on acidification of the sodium carbonate extract was a dark yellow, viscid oil (Found: Br, 24·5. $C_{13}H_{21}O_4Br$ requires Br, 24·9%).

Hydrolysis of the Neutral Monobromo-ester (IV) *with* 64% *Caustic Potash Solution at* 150°.—The bromo-ester (40 g.) was added as rapidly as possible to a solution of potassium hydroxide (120 g.) in water (66 c.c.) at 150°. The mixture was heated for 20 minutes, cooled, diluted with water, and acidified after removal of neutral impurities in ether. The oil obtained was isolated and dried in ether, recovered, and kept in a vacuum for 3 days; it then partly solidified (20 g.). The solid (5 g.) remaining after trituration with benzene was collected; the benzene solution gave a further quantity

(1 g.) of the *spiro*-acid on addition of light petroleum. The solid (m. p. 195—203°), which was a mixture of *cis*- and *trans*-forms, was heated with acetyl chloride (25 c.c.) for 12 hours, the excess of acetyl chloride removed, and the unchanged acid extracted from an ethereal solution of the residue with dilute sodium bicarbonate solution. The alkaline extract, on acidification, yielded trans-4-*methyl*cyclo*hexane*spirocyclo*propane*-2′ : 3′-*dicarboxylic acid* (XII), which crystallised from acetone in lustrous plates, m. p. 212° (Found : C, 62·1 ; H, 7·5 ; equiv., 106. $C_{11}H_{16}O_4$ requires C, 62·3 ; H, 7·5% ; equiv., 106).

The ethereal solution from which the *trans*-acid was removed left a small quantity of a viscid liquid, which did not solidify but on decomposition with dilute potash solution gave the cis-*acid* (XIII), which crystallised from water in thick plates, m. p. 165° (Found : C, 62·2 ; H, 7·6% ; equiv., 105·5).

The *anhydride*, prepared by refluxing the *cis*-acid with acetyl chloride, solidified when kept over potash for a month, and crystallised from light petroleum (b. p. 60—80°) in laminæ, m. p. 72° (Found : C, 67·8 ; H, 7·3. $C_{11}H_{14}O_3$ requires C, 68·0 ; H, 7·2%).

The syrup obtained from the benzene mother-liquor was esterified with ethyl alcohol and sulphuric acid and distilled. A fraction (4 g.), b. p. 185—188°/18 mm., gave 2 g. of *spiro*-acids, m. p. 180—195°, on hydrolysis with concentrated hydrochloric acid ; and a second fraction (15 g.), b. p. 199—203°/18 mm., gave a small quantity of a lactonic acid, crystallising from benzene in thick plates, m. p. 145°.

Dibromination.—Ethyl αα′-*dibromo*-4-*methyl*cyclo*hexane*-1 : 1-*diacetate* (V). A mixture of phosphorus pentachloride (405 g.) and 4-methyl*cyclo*hexane-1 : 1-diacetic acid (185 g.) was warmed at 50—60° for 3—4 hours, and dry bromine (100 c.c.) then added during 24 hours. After 96 hours, the mixture was poured into cooled absolute alcohol (800 c.c.) and refluxed for 6 hours. The oil precipitated on dilution was extracted with ether, washed with 5% sodium carbonate solution, dried, and recovered (yield, 85%) (Found : Br, 36·9. $C_{15}H_{24}O_4Br_2$ requires Br, 37·4%).

The *dibromo*-ester charred considerably when distilled ; the *bromolactonic* ester (XVIII) formed had b. p. 235°/21 mm. (Found : Br, 25·4. $C_{13}H_{19}O_4Br$ requires Br, 25·1%).

The acid product of the dibromination was a semi-solid viscous mixture of dibromo- and monobromo-acid esters. The monobromo-acid ester (VIII) (Found : Br, 25·1. Calc. : Br, 24·9%) was removed by extraction with benzene–petroleum, in which the *dibromo-acid* ester (IX) was sparingly soluble (Found : Br, 38·8. $C_{13}H_{20}O_4Br_2$ requires Br, 40·0%).

*Lactone of α-Bromo-α'-hydroxy-4-methyl*cyclo*hexane*-1 : 1-*diacetic Acid* (XVII).—The dibromo-acid chloride was warmed with an excess of anhydrous formic acid for 4 hours, and the solid was collected after 24 hours, and extracted with benzene. The residue, consisting mainly of the *lactone*, crystallised from much benzene in long flattened needles, m. p. 210° (Found: C, 45·5; H, 4·9; Br, 27·7; equiv., 290. $C_{11}H_{15}O_4Br$ requires C, 45·4; H, 5·1; Br, 27·5%; equiv., 291).

The benzene extract, on concentration, deposited tiny needles of *αα'-dibromo-4-methyl*cyclo*hexane* - 1 : 1 - *diacetic acid* (XVI), m. p. 185° (decomp.) (Found: Br, 42·8; equiv., 186. $C_{11}H_{16}O_4Br_2$ requires Br, 43·0%; equiv., dibasic, 186).

Hydrolysis of the Dibromo-ester (V) *with* 64% *Caustic Potash Solution at* 150°.—This was done as for the monobromo-ester (p. 1055) (dibromo-ester, 100 g.; caustic potash, 360 g.; water, 200 c.c.). The dried acids (47 g.) recovered from the ethereal extract were esterified with ethyl alcohol and sulphuric acid, and the esters distilled. Three fractions were collected: (1) 120—123°/23 mm. (5 g.); (2) 195—197°/23 mm. (32 g.); (3) 205—210°/23 mm. (15 g.).

Fraction (3) gave nothing definite on hydrolysis with concentrated hydrochloric acid.

Fraction (1) was hydrolysed by 10% aqueous methyl-alcoholic potash; the resulting acid (b. p. 154—155°/18 mm.) solidified when seeded with a crystal of 4-methyl*cyclo*hexenylacetic acid. It crystallised from light petroleum (b. p. 40—60°) in plates, m. p. 42—43° (Found: C, 70·0; H, 9·2; equiv., 154. Calc. for $C_9H_{14}O_2$: C, 70·1; H, 9·1%; equiv., 154), and gave an amide, m. p. 155° (Wallach and Evans, *Annalen*, 1907, **353**, 312).

Fraction (2) was heated with concentrated hydrochloric acid for 24 hours and the resulting acids were extracted with ether, recovered, dried in a vacuum at 100°, and seeded in benzene solution with a crystal of the keto-acid prepared from the methoxy-*spiro*-acid (see later). The solid (15 g.) thus obtained was extracted with benzene; the residue crystallised from chloroform in soft needles, m. p. 147°, of *α-keto-4-methyl*cyclo*hexane*-1 : 1-*diacetic acid* (*A*) (XIX) (Found: C, 57·7; H, 7·1; equiv., 114. $C_{11}H_{16}O_5$ requires C, 57·9; H, 7·0%; equiv., 114).

The *quinoxaline* derivative, readily formed from the keto-acid and *o*-phenylenediamine in glacial acetic acid on the water-bath, crystallised from dilute alcohol (charcoal) in white laminæ, m. p. 226° (Found: C, 67·9; H, 6·8. $C_{17}H_{20}O_3N_2$ requires C, 68·0; H, 6·7%). The 2 : 4-*dinitrophenylhydrazone*, prepared in hot alcohol, crystallised from dilute alcohol in sulphur-yellow needles, m. p. 220°

(decomp.) (Found : C, 50·0; H, 5·0. $C_{17}H_{20}O_8N_4$ requires C, 50·2; H, 4·9%). The *methyl* ester, prepared by means of hot alcoholic sulphuric acid, had b. p. 192°/25 mm. (Found : C, 60·7; H, 7·8. $C_{13}H_{20}O_5$ requires C, 60·9; H, 7·8%), and gave, when heated with a slight excess of phenylhydrazine in benzene solution on the water-bath for 1 hour, a *phenylhydrazone*, precipitated by light petroleum (b. p. 40—60°), which crystallised from benzene in rhombic plates, m. p. 163° (Found : C, 65·6; H, 7·7. $C_{19}H_{26}O_4N_2$ requires C, 65·9; H, 7·5%).

The benzene extract of the acids gave on evaporation a solid, m. p. 120—135°, from which was obtained, by fractional crystallisation from chloroform–benzene, the more soluble *keto-acid B*; this crystallised from benzene in clusters of short needles, m. p. 128—129° (mixed m. p. with its stereoisomeride, 110—115°) (Found : C, 57·9; H, 7·1%; equiv., 114).

The *quinoxaline* derivative crystallised from alcohol (charcoal) in silky needles, m. p. 245° (mixed m. p. with its stereoisomeride, 210—215°) (Found : C, 67·8; H, 6·7%), the 2 : 4-*dinitrophenylhydrazone* in sulphur-yellow silky needles, m. p. 205° (decomp.) (Found : C, 50·1; H, 5·1%), and the *phenylhydrazone*, prepared in hot benzene solution and solidified by rubbing with dry ether, in colourless plates (from benzene), m. p. 204° (decomp.) (Found : C, 63·9; H, 7·0. $C_{17}H_{22}O_4N_2$ requires C, 64·1; H, 6·9%). The *methyl* ester, b. p. 187°/20 mm. (Found : C, 60·8; H, 7·9%), gave a *phenylhydrazone* which crystallised from benzene in colourless plates, m. p. 227° (decomp.) (Found : C, 65·7; H, 7·8%).

Oxidation of the Keto-acids with Hydrogen Peroxide.—The keto-acids in 10% sodium carbonate solution were gently warmed with an excess of 20-vol. hydrogen peroxide and left over-night. The succinic acids that separated on acidification were collected. 1-*Carboxy*-4-*methyl*cyclo*hexane*-1-*acetic acid* (*A*), obtained in very small amount from the keto-acid (A), crystallised from water in plates, m. p. 136° (with previous sintering) (Found : C, 59·8; H, 8·1; equiv., 99·5. $C_{10}H_{16}O_4$ requires C, 60·0; H, 8·0%; equiv., 100). 1-*Carboxy*-4-*methyl*cyclo*hexane*-1-*acetic acid* (*B*), formed in good yield from the keto-acid (B), crystallised from water, containing a little alcohol, in long flattened needles, m. p. 173° (efferv.) (Found : C, 59·9; H, 8·0%; equiv., 100). Its *anhydride*, prepared by heating with excess of acetyl chloride, crystallised from petroleum (b. p. 60—80°) in plates, m. p. 104° (Found : C, 65·7; H, 7·8. $C_{10}H_{14}O_3$ requires C, 65·9; H, 7·7%). The *anilic acid*, prepared in benzene solution, crystallised from alcohol in needles, m. p. 184° (Found : C, 69·5; H, 7·8. $C_{16}H_{21}O_3N$ requires C, 69·8; H, 7·6%).

These two carboxymethyl*cyclo*hexaneacetic acids seem to be identical with the acids A and C prepared by Qudrat-i-Khuda (*J. Indian Chem. Soc.*, 1931, **8**, 277).

Hydrolysis of the Dibromo-ester (V) *with Methyl-alcoholic Potash.*—The dibromo-ester (100 g.) was added as rapidly as possible to a boiling solution of caustic potash (200 g.) in methyl alcohol (600 c.c.), and the reaction completed by heating for 20 minutes. Methyl alcohol having been removed by means of a pump, the aqueous solution was acidified with concentrated hydrochloric acid and the precipitated acids were extracted with ether, dried, recovered (52 g.), and refluxed with acetyl chloride (100 c.c.) for 12 hours. The excess of acetyl chloride was then removed, the residue dissolved in ether, the solution extracted with 5% aqueous sodium bicarbonate, washed, and dried, and the mixture of anhydrides recovered (35 g.), left in a vacuum for 24 hours, and extracted with petroleum (b. p. 60—80°); a part of it dissolved, leaving a residue (15 g.) which crystallised from benzene–petroleum (b. p. 60—80°) in long silky needles, m. p. 148°, of cis-4-*methyl*cyclo*hexane*spiro-2′-*methoxy*cyclo*propane*-2′ : 3′-*dicarboxylic anhydride A* (Found : C, 64·4; H, 7·1. $C_{12}H_{16}O_4$ requires C, 64·3; H, 7·1%). The petroleum extract deposited some anhydride A on standing and then, on concentration, the cis-*anhydride B* (5 g.) in thick rhombic plates, m. p. 90° (Found : C, 64·4; H, 7·2%). Finally, on evaporation, an oil remained which distilled at 185—186°/20 mm. and solidified to a mixture of anhydrides A and B.

Anilic acids and anils. (1) The *cis*-anhydride A and aniline were mixed in benzene, the solvent evaporated, and the residue dissolved in ether and extracted with sodium carbonate solution; the solid obtained on acidification of the alkaline extract was separated by crystallisation from alcohol into thick plates, m. p. 183°, of the less soluble *anilic acid A* (Found : C, 67·9; H, 7·4. $C_{18}H_{23}O_4N$ requires C, 68·2; H, 7·2%) and silky needles, m. p. 160°, of the more soluble *anilic acid B* (Found : C, 68·0; H, 7·3%).

The *anil* crystallised from alcohol in long prismatic needles, m. p. 134° (Found : C, 72·0; H, 6·9. $C_{18}H_{21}O_3N$ requires C, 72·2; H, 7·0%).

(2) An anilic acid was precipitated at once when the *cis*-anhydride B and aniline were mixed in benzene solution; recrystallisation from alcohol gave the *anilic acid A′* in needles, m. p. 193° (efferv.) (Found : C, 68·2; H, 7·3%). The benzene solution on evaporation yielded the *anilic acid B′*, which crystallised from dilute alcohol in tiny plates, m. p. 157° (Found : C, 68·1 ; H, 7·5%).

The *anil* crystallised from alcohol in plates, m. p. 96° (Found : C, 72·5; H, 7·1%).

cis-4-*Methyl*cyclo*hexane*spiro-2′-*methoxy*cyclo*propane*-2′ : 3′-*dicarboxylic acid A* (XXIVA), obtained from the anhydride A, crystallised from water in plates or needles, m. p. 182° (efferv.) (Found : C, 59·6; H, 7·3; equiv., 121. $C_{12}H_{18}O_5$ requires C, 59·5; H, 7·4%; equiv., 121). The corresponding cis-*acid B* (XXIVB), obtained from the anhydride B, crystallised from water in plates containing water of crystallisation; the anhydrous acid melted at 162° (efferv.) (Found : C, 59·4; H, 7·6; equiv., 121).

trans-*Methoxy*-spiro-*acid A* (XXVA). The sodium bicarbonate extract (p. 1059) was acidified with concentrated hydrochloric acid; the recovered liquid acids (15 g.) became semi-solid after being kept for 3 weeks in a vacuum. The solid (5 g.) was obtained by trituration with benzene. After removal of the benzene-soluble portion (from which a very small quantity of a solid, m. p. 145° after softening at 122°, was obtained), the residue was fractionally crystallised from dilute acetone, the trans-*acid A* being obtained in plates, m. p. 190° (previous sintering) (Found : C, 59·3; H, 7·7%; equiv., 121). On distillation it gave the *cis*-methoxy-anhydride A, m. p. 148°. From the remaining mixture of acids, the *trans*-acid B could not be isolated.

Action of Fuming Hydrobromic Acid on the cis-*Methoxy*-spiro-*acids A and B.*—A solution of the *cis*-methoxy-acid A (5 g.) in fuming hydrobromic acid (50 c.c.) was heated under reflux for 6 hours and then diluted with water. The precipitated solid, which proved to be 1-carboxy-4-methyl*cyclo*hexane-1-acetic acid, m. p. 173° (efferv.), was removed, and the filtrate saturated with ammonium sulphate and extracted four times with ether; the gum obtained from the extracts partly solidified after being kept in a vacuum for 3 weeks. The solid, obtained by trituration with benzene, gave α-keto-4-methyl*cyclo*hexane-1 : 1-diacetic acid B (XIX), m. p. 129°, on recrystallisation from this solvent. The benzene solution, on concentration, yielded the succinic acid A, m. p. 173°.

When the *cis*-acid B was similarly treated, the crude keto-acid obtained melted at 142—145°. On crystallisation from chloroform the keto-acid A, m. p. 147°, was obtained; the mother-liquor gave the succinic acid, m. p. 136°.

m-*Methyl Series.*

The preparative methods here are so similar to those used in the *p*-series that descriptive details are omitted.

The ω-*imide* of 3-*methyl*cyclo*hexane*-1 : 1-*dicarbamylacetic acid* crystallised from glacial acetic acid in plates, m. p. 272° (decomp.) (Found : C, 55·7; H, 7·0. $C_{13}H_{19}O_4N_3$ requires C, 55·5; H, 6·8%).

Ethyl 3-*methyl*cyclo*hexane*-1 : 1-*diacetate* had b. p. 174°/22 mm. (Found : C, 66·6; H, 9·8. $C_{15}H_{26}O_4$ requires C, 66·7; H, 9·6%).

Anilic Acids (II).—The less soluble acid A crystallised from alcohol in plates, m. p. 172°, the more soluble *acid B* in tiny needles or plates, m. p. 141° (Found : C, 70·7 ; H, 8·1. $C_{17}H_{23}O_3N$ requires C, 70·6 ; H, 8·0%).

The *anil* crystallised from alcohol in needles, m. p. 137° (mixed m. p. with the anilic acid B, 115—118°) (Found : C, 75·5 ; H, 7·8. $C_{17}H_{21}O_2N$ requires C, 75·3 ; H, 7·7%).

Monobromination.—The monobromination of ethyl hydrogen 3-methyl*cyclo*hexane-1 : 1-diacetate gave *ethyl α-bromo-3-methyl*cyclo*hexane-1 : 1-diacetate* (IV) (75% yield) (Found : Br, 22·5. $C_{15}H_{25}O_4Br$ requires Br, 22·9%), which on distillation was converted into the *lactonic* ester (X), b. p. 196°/16 mm. (Found : C, 64·9 ; H, 8·4. $C_{13}H_{20}O_4$ requires C, 65·0 ; H, 8·3%).

The *monobromo-acid* ester (V) was a dark yellow, viscous liquid (Found : Br, 24·6. $C_{13}H_{21}O_4Br$ requires Br, 24·9%).

Hydrolysis of the Neutral Monobromo-ester (IV) *with* 64% *Caustic Potash at* 150°.—The acids (25 g.) obtained from the monobromo-ester (50 g.) partly solidified in a vacuum. The solid (8 g., m. p. 230—245°) remaining after trituration with benzene was treated with acetyl chloride (40 c.c.) and the *trans*-acids (7·5 g., m. p. 240—248°) ultimately isolated were fractionally crystallised from acetone. The less soluble trans-*3-methyl*cyclo*hexane*spiro*cyclo*propane-2′ : 3′-dicarboxylic acid A* (XIVA) crystallised in short needles, m. p. 270° (Found : C, 62·2 ; H, 7·4 ; equiv., 106. $C_{11}H_{16}O_4$ requires C, 62·3 ; H, 7·5% ; equiv., 106), the *dianilide* of which formed needles, m. p. 280° from alcohol (charcoal) (Found : C, 76·3 ; H, 7·3. $C_{23}H_{26}O_2N_2$ requires C, 76·2 ; H, 7·2%). The more soluble acid (m. p. 235—238°), when extracted with aqueous acetone, mostly dissolved ; the solution slowly deposited a solid which, recrystallised thrice from the same solvent, gave the trans-*acid B* in small plates, m. p. 245° (Found : C, 62·3 ; H, 7·4% ; equiv., 106) ; the *dianilide* crystallised from alcohol in short needles, m. p. 260° (Found : C, 76·5 ; H, 7·1%). cis-*3-Methyl*cyclo*hexane*spiro*cyclo*propane-2′ : 3′-dicarboxylic acid A* (XVA), prepared from the anhydride obtained from the ethereal solution from which the *trans*-acids had been removed, crystallised from water in needles, m. p. 205° (Found : C, 62·2 ; H, 7·5% ; equiv., 106).

*Ethyl αα′-dibromo-3-methyl*cyclo*hexane-1 : 1-diacetate* (V) was obtained in 85% yield in the dibromination of 3-methyl*cyclo*hexane-1 : 1-diacetic acid (Found : Br, 37·6. $C_{15}H_{24}O_4Br_2$ requires Br, 37·4%). On distillation it gave the *bromo-lactonic* ester (XVIII) as a pale yellow, viscous liquid, b. p. 234°/21 mm., which partly solidified. The solid crystallised from benzene–petroleum (b. p. 60—80°) in plates, m. p. 130° (Found : Br, 24·9. $C_{13}H_{19}O_4Br$ requires Br, 25·1%).

The acid product of dibromination became semi-solid when kept ;

the solid obtained by treating it with benzene–light petroleum crystallised from benzene in clusters of thick plates, m. p. 162°, of *ethyl hydrogen* αα′-*dibromo*-3-*methyl*cyclo*hexane*-1 : 1-*diacetate* (Found: Br, 39·8; equiv., 398. $C_{13}H_{20}O_4Br_2$ requires Br, 40·0%; equiv., 400). The mother-liquor gave an almost pure monobromo-acid ester (Found : Br, 25·3. Calc. for $C_{13}H_{21}O_4Br$: Br, 24·9%).

Stereoisomeric Lactones of α-*Bromo*-α′-*hydroxy*-3-*methyl*cyclo*hexane*-1 : 1-*diacetic Acid.*—The gum obtained by decomposing the dibromo-acid chloride with excess of anhydrous formic acid became semi-solid when kept. After trituration with benzene, the solid was removed and crystallised from chloroform, the *bromo-lactonic acid A* (XVII) being obtained in white plates, m. p. 225° (Found : C, 45·7; H, 5·2; Br, 27·6; equiv., 289. $C_{11}H_{15}O_4Br$ requires C, 45·5; H, 5·1; Br, 27·5%; equiv., 291). The chloroform mother-liquor on evaporation left a solid which, recrystallised from benzene, gave the *bromo-lactonic acid B* in needles, m. p. 201° (Found : Br, 27·8%; equiv., 290).

Hydrolysis of the Dibromo-ester with 64% *Caustic Potash Solution at* 150°.—The acids (47 g.) obtained by hydrolysis of the dibromo-ester (100 g.), being liquid, were esterified, and the ethyl esters fractionally distilled : (1) 118—120°/23 mm. (5 g.), (2) 190—193°/23 mm. (30 g.), (3) 200—205°/23 mm. (20 g.).

Fraction (1), on hydrolysis, gave 3-methyl*cyclo*hexenylacetic acid, b. p. 152—153°/20 mm. (Found : C, 70·2; H, 9·3; equiv., 153. Calc. for $C_9H_{14}O_2$: C, 70·1; H, 9·1%; equiv., 154), the amide of which had m. p. 154° (Wallach, *Annalen*, 1906, **347**, 340).

Fraction (2). The acids obtained by hydrolysis were kept in a vacuum for 1 month, benzene was added, and the solution seeded with a crystal of the keto-acid (synthesised from the methoxy-*spiro*-acid). The solid (10 g.) was fractionally crystallised from benzene. The less soluble solid was recrystallised from chloroform, α-*keto*-3-*methyl*cyclo*hexane*-1 : 1-*diacetic acid A* being obtained in needles, m. p. 139—140° (Found : C, 57·8; H, 7·2; equiv., 114. $C_{11}H_{16}O_5$ requires C, 57·9; H, 7·0%; equiv., 114). [The *quinoxaline* derivative crystallised from dilute acetic acid (charcoal) in small plates, m. p. 217° (Found : C, 68·1; H, 6·8. $C_{17}H_{20}O_3N_2$ requires C, 68·0; H, 6·7%), and the 2 : 4-*dinitrophenylhydrazone* from alcohol in yellow needles, m. p. 198° (decomp.) (Found : C, 50·3; H, 5·1. $C_{17}H_{20}O_8N_4$ requires C, 50·3; H, 4·9%); mixed m. p. with the isomeric dinitrophenylhydrazone, 179—183° (decomp.).] The more soluble component was crystallised from chloroform–benzene and then from benzene, α-*keto*-3-*methyl*cyclo*hexane*-1 : 1-*diacetic acid B* being obtained in clusters of small needles, m. p. 126—127° (Found : C, 57·7; H, 7·1%; equiv., 114). [The *quinoxaline* derivative crystallised from dilute alcohol (charcoal) in colourless needles, m. p. 239° (Found: C, 68·2; H, 6·9%), and the 2 : 4-*dinitrophenylhydrazone* in sulphur-yellow flattened needles, m. p. 194° (decomp.) (Found: C, 50·4; H, 5·0%). The *methyl* ester, b. p. 185°/23 mm. (Found: C, 60·9; H, 7·9%), formed a *phenylhydrazone*, which crystallised from benzene in colourless plates, m. p. 220° (decomp.) (Found: C, 65·6; H, 7·9%).]

Oxidation of the keto-acid B with hydrogen peroxide gave 1-*carboxy*-3-*methyl*cyclo*hexane*-1-*acetic acid*, which crystallised from water in plates, m. p. 163° (efferv.) (Found: C, 59·9; H, 8·1; equiv., 100. $C_{10}H_{16}O_4$ requires C, 60·0; H, 8·0%; equiv., 100).

The *anhydride* had b. p. 166°/22 mm. and m. p. 41° (Found: C, 65·8; H, 7·6. $C_{10}H_{14}O_3$ requires C, 65·9; H, 7·7%). The *anilic acid*, which was precipitated at once from benzene solution, crystallised from alcohol in lustrous laminæ, m. p. 170° (efferv.) (Found: C, 69·9; H, 7·7. $C_{16}H_{21}O_3N$ requires C, 69·8; H, 7·6%). The *anil* crystallised from alcohol in needles, m. p. 139° (Found: C, 74·8; H, 7·5. $C_{16}H_{19}O_2N$ requires C, 74·7; H, 7·4%).

Hydrolysis of the Dibromo-ester with Methyl-alcoholic Potash.—The acids (53 g.) obtained from the dibromo-ester (100 g.) gave a mixture of *cis*-methoxy-anhydrides (34 g.) on treatment with acetyl chloride (100 c.c.). The mixture solidified in a vacuum after 2 days and was then treated with light petroleum (b. p. 60—80°); the residue, recrystallised from petroleum containing a little benzene, gave cis-3-*methyl*cyclo*hexane*spiro-2′-*methoxy*cyclo*propane*-2′ : 3′-*dicarboxylic anhydride A* in long needles, m. p. 140—141° (Found: C, 64·3; H, 6·9. $C_{12}H_{16}O_4$ requires C, 64·3; H, 7·1%).

The benzene–petroleum mother-liquor and the petroleum extract were mixed and concentrated and the solid, m. p. 110—125°, obtained was recrystallised from petroleum (b. p. 60—80°). The first crop melted at 140° (previous sintering); the second crop (m. p. 105—110°), after five or six crystallisations, was separated into the *cis*-anhydride A and the cis-*anhydride B*, the latter of which crystallised from petroleum in silky needles, m. p. 116° (Found: C, 64·3; H, 7·2%).

The petroleum solution from which the anhydrides A and B had been removed was concentrated to half its bulk; it then yielded a solid, m. p. 65—75°, which was fractionally crystallised from the same solvent. The first crop, m. p. 95—98°, on recrystallisation yielded the cis-*anhydride C* in fluffy needles, m. p. 101° (Found: C, 64·3; H, 7·0%). The second crop, m. p. 79—82°, when recrystallised from petroleum (b. p. 40—60°) gave thick rhombic plates, m. p. 85°, of the cis-*anhydride D* (Found: C, 64·2; H, 7·1%).

The petroleum mother-liquor from which the solid anhydrides had been removed was evaporated, the residual oil (15 g.) decomposed with dilute potash solution, and the acids recovered. Benzene extracted a solid (2 g.), m. p. 148° after softening at 125°. The benzene-insoluble acids were distilled; a liquid (10 g.), b. p. 175°/20 mm., was obtained which solidified. When it was fractionally crystallised, anhydrides A, B, C, and D were obtained and a small amount of an oil was left.

The *cis*-anhydride A gave *anilic acids A* (insoluble in benzene) and *B* (soluble in benzene), which crystallised from alcohol in lustrous laminæ, m. p. 195° (efferv.) (Found: C, 68·0; H, 7·4. $C_{18}H_{23}O_4N$ requires C, 68·2; H, 7·2%), and plates, m. p. 135° (Found: C, 68·3; H, 7·3%), respectively. The *anil* crystallised from alcohol in plates, m. p. 112° (Found: C, 72·3; H, 7·3. $C_{18}H_{21}O_3N$ requires C, 72·2; H, 7·0%).

The cis-*methoxy-acid A*, obtained by decomposing the anhydride with dilute potash solution, crystallised from water in needles, m. p. 194° (efferv.) (Found: C, 59·7; H, 7·3; OMe, 12·9; equiv., 121. $C_{12}H_{18}O_5$ requires C, 59·5; H, 7·4; OMe, 12·8%; equiv., 121).

The *anilic acid* (insoluble in benzene) obtained from the *cis*-anhydride B crystallised from alcohol in needles, m. p. 215° (efferv.) (Found: C, 69·7; H, 7·8%). The cis-*methoxy-acid B* crystallised from water in long silky needles, m. p. 195° (efferv.) (Found: C, 59·4; H, 7·4%; equiv., 121); mixed m. p. with stereoisomeride A, 175—180°.

The *anilic acid* obtained from the *cis*-anhydride C crystallised from alcohol in flattened needles, m. p. 212° (Found: C, 70·0; H, 7·7%). The cis-*methoxy-acid C* crystallised from water in silky needles, m. p. 197° (efferv.) (Found: C, 59·3; H, 7·4; OMe, 13·3%; equiv., 121); mixed m. p.'s with acids B and A, 175—180° and 173—177°, respectively. Mixtures of the acids A, B, and C melted at 165—170°.

The *anilic acid* obtained from the *cis*-anhydride D crystallised from alcohol in plates, m. p. 192° (efferv.) (Found: C, 68·4; H, 7·2%), and the *anil* in thick plates, m. p. 118° (Found: C, 72·1; H, 7·1%). The cis-*methoxy-acid D* crystallised from water in small plates, m. p. 196° (efferv.) (Found: C, 59·7; H, 7·3; OMe, 13·2%; equiv., 121).

The m. p.'s of all these *cis*-methoxy-acids and anilic acids depend upon the rate of heating. The recorded m. p.'s were taken in a bath previously heated to 140—150°. Even so, a difference of 2—3° was observed with the same sample.

trans-*Methoxy*-spiro-*acids*. The liquid acids, recovered by acidification of the alkaline extract in the separation of the *cis*- and *trans*-methoxy-acids, partly solidified in a vacuum after 2 weeks. The solid, obtained by trituration with benzene, was repeatedly crystallised from aqueous acetone, giving plates, m. p. 201° (previous sintering), of trans-3-*methyl*cyclo*hexane*spiro-2′-*methoxy*cyclo*propane*-2′ : 3′-*dicarboxylic acid A* (Found : C, 59·5; H, 7·3%; equiv., 121). This was converted into the *cis*-methoxy-anhydride A on distillation.

Action of Hydrobromic Acid on the cis-*Methoxy-acids A and D.*—A solution of the *cis*-methoxy-acid (5 g.) in hydrobromic acid (50 c.c.) was heated for 6 hours. The gum produced, isolated from the diluted solution by means of ether, was esterified with methyl-alcoholic sulphuric acid, and two fractions of esters were collected : (1) 150—152°/22 mm., (2) 183—185°/23 mm. The first fraction on alkaline hydrolysis gave 1-carboxy-3-methyl*cyclo*hexane-1-acetic acid, m. p. 163° (efferv.), the second fraction gave α-keto-3-methoxy-*cyclo*hexane-1 : 1-diacetic acid B, m. p. 127°.

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