

CLI.—*The Formation and Stability of spiro-Compounds.*
Part VI. New Derivatives of cycloPropane and
cycloHexanespirocyclopropane.

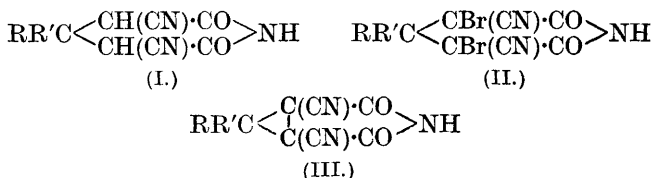
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THE results recently attained from a study of dialkyl- and *spirocyclo*-propane compounds made it appear desirable to extend our knowledge of the methods by which such compounds can be obtained. Up to the present they have usually been prepared in these laboratories by the action of hydrolysing agents on the esters of the bromo-substituted glutaric acids (compare Beesley, Ingold, and Thorpe, T., 1915, **107**, 1080; Becker and Thorpe, T., 1920, **117**, 1579; Perkin and Thorpe, T., 1899, **75**, 48) and although a fair variety of starting material was thus available, the products consisted of a few types only.

It was therefore decided to search for new sources of such compounds and also to endeavour to increase the variety of the compounds obtainable, with the object of comparing their stability.

An examination of the literature revealed a possible source of *cyclopropane* derivatives in the bridged piperidine compounds described by Guareschi (*Mem. R. Accad. Sci. Torino*, 1901, **50**, 235; *Atti R. Accad. Sci. Torino*, 1910–1911, **46**, 662; Guareschi and Grande, *ibid.*, 1898–1899, **34**, 924). These compounds are formed in almost quantitative yield when the imides of the general type

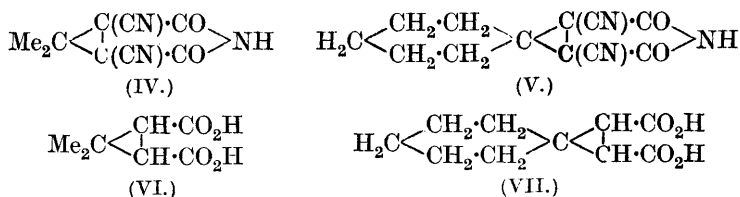
(I), obtained by the condensation of ketones with ethyl cyanoacetate and ammonia, are brominated and the resulting dibromo-compounds (II) are subjected to the action of heat, or treated with some agent capable of eliminating bromine, such as formic acid or even alcohol. Formula III was assigned by Guareschi to these compounds,



although no proofs of its correctness, beyond the elementary analysis, were supplied by him.

At first it appeared unlikely that this constitution could be correct owing to the ease with which the "bridging" takes place, this being seldom observed in reactions leading to *cyclopropane* compounds. It was therefore decided to investigate the matter further and, should Guareschi's formula prove correct, to endeavour to utilise these compounds as a source of *cyclopropane* derivatives, more particularly of those which are not obtainable by the methods already in use.

Two typical examples were chosen, namely, the dimethyl compound (IV) and the *cyclohexane* compound (V), which should, if Guareschi's formula is correct, be convertible respectively into caronic acid (VI) and *cyclohexanespirocyclopropanedicarboxylic acid* (VII) or their derivatives :



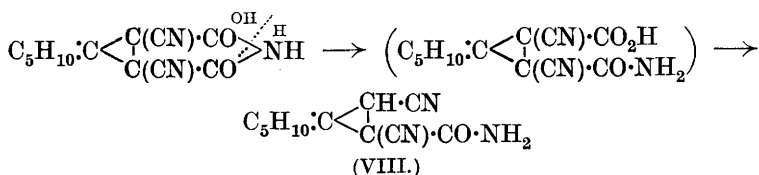
The latter two acids have already been studied in detail (Beesley, Ingold, and Thorpe, *loc. cit.*), especially with regard to their stability. It was clearly shown that the *cyclohexane*-compound is the more readily formed and the more stable, which points to the influence of the *cyclohexane* ring in conferring stability on a *cyclopropane* ring having a carbon atom in common with it.

It was most important definitely to establish the constitution of Guareschi's bridged imides, but the problem proved to be one of considerable difficulty owing, particularly, to the large number of products which could be obtained from these compounds by the

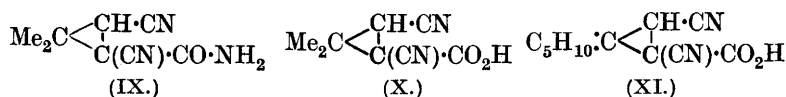
action of various reagents; ultimately, however, it was possible to demonstrate the correctness of the general constitution (III) assigned to them.

It was soon discovered that the use of acid hydrolysing agents caused deep-seated changes, but regulated hydrolysis with alkali led to the formation of a variety of products according to the conditions of the experiment.

It was found that the *cyclohexane* compound (V) was somewhat more readily hydrolysed than the dimethyl compound (IV). If it is boiled for a few minutes with one molecular proportion of 10 per cent. aqueous potassium hydroxide, the imino-ring is broken and at the same time a molecule of carbon dioxide is eliminated, the amide (VIII) being obtained in almost quantitative yield:



An exactly analogous compound (IX) is produced from the imide (IV), except that some of the original substance is always recovered unchanged.



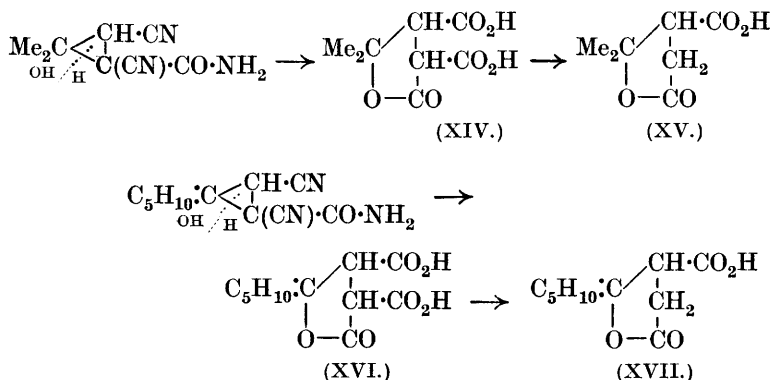
On further hydrolysis with alkali, these compounds undergo fission (see below); it is, however, possible to obtain from them the acids (X) and (XI) by the action of nitrous acid. The yields are not good, but the unchanged material can be recovered.

The dicyano-acids (X) and (XI) can also be prepared directly from the imides by acting on the latter with two molecular proportions of potassium hydroxide in dilute solution, but the best conditions are difficult to establish, and the use of nitrous acid is preferable.

Although the amides are not affected by heating with water under pressure at 180° , the corresponding acids readily lose carbon dioxide under these conditions and are converted into the dinitriles (XII) and (XIII), from which the dicarboxylic acids (VI and VII) can be obtained by digestion with alcoholic potassium hydroxide.



It is noteworthy that no fission occurs, although the action of potassium hydroxide on the amides (VIII) and (IX), no doubt owing to the presence of two quaternary carbon atoms, leads rapidly to the splitting of the *cyclopropane* ring with the formation of the lactonic acids (XIV) and (XVI) :



At first the nature of these fission products was not clear, but it was found that they readily lose a molecule of carbon dioxide on heating, or on boiling with dilute sulphuric acid.

In the case of the dimethyl compound the product was the well-known terebic acid (XV), so that the fission of the original amide must have taken place in the manner indicated, that is, between the two quaternary carbon atoms.

The ready fission of the amides on hydrolysis is quite analogous to the behaviour of the hydroxy-*spiro*-acid recorded by Beesley, Ingold, and Thorpe (*loc. cit.*). This substance undergoes fission between the two quaternary carbon atoms on heating with water under pressure, whereas the unhydroxylated *spiro*-acid is quite stable under the same conditions.

In the reactions described above there is little difference between the behaviour of the dimethyl- and the *cyclohexane*-compounds and no inferences can be drawn as to their relative stability.

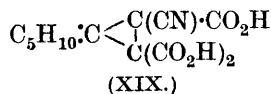
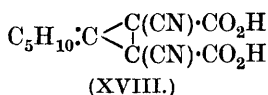
Evidence bearing on the question is, however, readily obtained on studying the behaviour of the two bridged imides on treatment with three or more molecular proportions of alkali.

In the first place, if these two compounds are subjected to the action of very concentrated alkali at a high temperature, the main product obtained from the *cyclohexane* compound is the lactonic acid (XVI), but an appreciable amount of the *spiro*-acid (VIII) is also formed. Not a trace of caronic acid (VI) could, however, be isolated in similar experiments with the dimethyl compound and

it must be concluded that here the *cyclopropane* ring is too unstable to survive the experimental conditions.

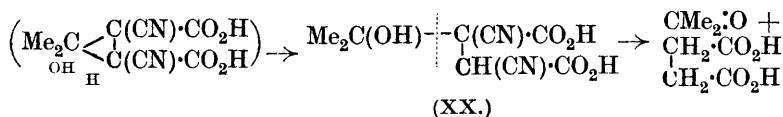
Such drastic treatment is not, however, necessary to demonstrate the difference of stability between the two series of compounds.

The most striking evidence on this point is afforded by the hydrolysis of the original imides by means of three molecular proportions of potassium hydroxide in aqueous solution. Under these conditions the *cyclohexane* compound yields the acid (XVIII) almost quantitatively; if the boiling is very prolonged, the substance (XIX) is also produced.



It is interesting to note, in passing, that if sufficient alkali (3 mols. is used in the hydrolysis, carbon dioxide is not eliminated and substances with three quaternary carbon atoms are produced; otherwise the amide (VIII) or its products of hydrolysis are formed in greater or smaller amount.

When the amide (IV) is hydrolysed in the same way, an analogous acid is obtained in fair yield, but this acid has the expected composition with the addition of one molecule of water. The constitution of this substance (XX) follows clearly from the fact that on boiling with dilute sulphuric acid it is rapidly and quantitatively split into acetone and succinic acid, the latter being produced by the hydrolysis of the dicyanosuccinic acid first formed :



It is certainly remarkable that the acid (XX), which is a γ -hydroxy-acid, does not pass into a lactone under the experimental conditions used; * but its behaviour on hydrolysis is, we think, sufficient proof of its constitution. That the substance represented by the formula (XVIII) is not the lactone of a hydroxy-acid similar to the acid (XX) is clearly proved by the fact that it forms an anhydride from which the original acid is readily regenerated.

It will thus be seen that the results described in the present paper strongly support the views expressed by Beesley, Ingold, and Thorpe regarding the stability of *spirocyclopropane* compounds.

* For other examples of γ -hydroxy-acids not forming lactones, see Kiliani and Loeffler, *Ber.*, 1905, **38**, 3624; Kiliani and Matthes, *ibid.*, 1907, **40**, 1238.

EXPERIMENTAL.

Preparation of Guareschi's Bridged Imides (IV and V).

The method used was a modification of that described by Guareschi (*Atti R. Accad. Sci. Torino*, 1910-1911, **46**, 662).

One-tenth of a gram-molecule of the finely powdered dicyanamide (obtained by Guareschi's method; compare Kon and Thorpe, T., 1919, **115**, 686; Kon, this vol., 818) is suspended in 160 c.c. of water and 32 grams of bromine are gradually added with vigorous shaking. Hydrogen bromide is evolved and the liquid finally assumes a permanent yellow tinge, due to excess of bromine. The suspension of the dibromo-compound is treated with 160 c.c. of formic acid (80 per cent.) and the mixture slowly heated to boiling with constant stirring to prevent frothing; it is finally allowed to boil for a few minutes. On cooling, the bridged compound separates out; it is collected, and a further small amount can be recovered by diluting the mother-liquors with water.

The dimethyl compound (IV) was found to melt at 242° (Found : C=56.99; H=3.81; N=22.41. Calc., C=57.11; H=3.73; N=22.22 per cent.) and the cyclohexane compound (V) at 233° (Found : N=18.54. Calc., N=18.38 per cent.).

2 : 3-Dicyano-1 : 1-dimethylcyclopropane-2-carboxylamide (IX).

The imide (IV) was boiled with 10 per cent. aqueous potassium hydroxide (1 mol.) for five minutes and then cooled in ice. The amide crystallised out and was collected, further quantities being recovered by extracting the mother-liquors with ether. On acidifying the mother-liquors, some of the imide was precipitated; it is usually preferable to repeat the heating once or twice before recovering the unchanged material.

The *amide* obtained in this way crystallises from hot water,* dilute alcohol, or benzene in long, flattened needles melting at 163.5° (Found : C=58.77; H=5.73; N=25.93. $C_8H_9ON_3$ requires C=58.85; H=5.76; N=25.74 per cent.).

2 : 3-Dicyano-1 : 1-dimethylcyclopropane-2-carboxylic Acid (X).

The amide (5 grams) was dissolved in cold concentrated sulphuric acid (100 c.c.), the mixture cooled in ice, and a saturated solution of sodium nitrite in water added drop by drop with stirring until the mixture became nearly solid. It was allowed to remain for

* This solvent is not to be recommended, as it tends to hydrolyse the amide.

half an hour, poured into water, and the aqueous fluid repeatedly extracted with ether, which dissolved both the new acid and the unchanged material; the acid was then separated from the latter by shaking the extract with a solution of sodium carbonate and liberated from the alkaline solution by acidifying and extracting with ether in the usual way. It should be remembered, however, that both the acid and its amide are somewhat sparingly soluble in ether.

The *acid* slowly crystallises from water in large, transparent, rhombic laminae melting at 168–169°. It is almost insoluble in benzene, chloroform, or light petroleum, and does not decolorise alkaline permanganate in the cold (Found: C=58·83; H=5·10; N=17·18. $C_8H_8O_2N_2$ requires C=58·50; H=4·94; N=17·05 per cent.).

The acid can also be obtained by boiling the imide (IV) with 7·5 * per cent. aqueous potassium hydroxide (2 mols.) for about one hour. The liquid gradually assumes a purplish-brown colour with a green fluorescence and ammonia is evolved. After being cooled, it is extracted with ether to remove any amide produced (by partial hydrolysis) and acidified, the colour changing to deep violet; a 20 per cent. yield of the acid can be obtained by extracting the solution with ether.

It was thought desirable to investigate the nature of the by-products formed in this reaction, and therefore the mother-liquors from several experiments were combined and kept for about three weeks. At the end of that time a considerable amount of crystalline solid had separated, which was collected and recrystallised from water. It was found to melt with vigorous decomposition at 195–196° and to consist of the acid XX (see below).

The mother-liquor from this substance was neutralised with ammonia, evaporated to dryness, ground with concentrated hydrochloric acid, and allowed to evaporate to dryness in an exhausted desiccator over sodium hydroxide. The solid was extracted with acetone and the residue obtained on removing the solvent spread on porous porcelain, and then crystallised from water with the use of animal charcoal. The crystals which separated consisted of a mixture of two compounds, which were separated by boiling chloroform.

The substance soluble in chloroform was non-nitrogenous and crystallised from water in small, colourless prisms melting at 173–174°. It was proved to consist of terebic acid (XV) by direct comparison (mixed melting point) with a specimen of that substance.

The second substance contained nitrogen and crystallised from

* The use of 5 per cent. potassium hydroxide is to be preferred.

water in fine, long needles melting not very sharply at 234—235° with slight decomposition (Found : C=53·24; H=5·58. $C_8H_{10}O_3N_2$ requires C=53·31; H=5·60 per cent.). This substance is probably represented by the formula $OH \cdot CMe_2 \cdot CH(CN) \cdot CH(CN) \cdot CO_2H$.

Nitrile of 1 : 1 Dimethylcyclopropane-2 : 3-dicarboxylic Acid (XII).

Four grams of the acid (X) were heated with a little water in a sealed tube for an hour at 180—200°, when a light yellow oil was found floating on the surface of the water. The products of three such experiments were combined, the oil taken up in ether, the ethereal solution carefully washed, first with aqueous potassium hydroxide and then with water, dried, and evaporated.

The residual oil, representing a yield of 50 per cent. of the theoretical, boiled at 158°/12 mm. and solidified on keeping for some time. On crystallising the solid from ether and light petroleum (b. p. 30—40°), it separated in long, flattened needles melting at 50° (Found : N=23·28. $C_7H_8N_2$ requires N=23·32 per cent.).

The alkaline washings obtained above were found to contain a very small amount of a mixture of acids (probably the original acid with caronic acid) and an *imide* melting, after purification, at 163·5°, and doubtless consisting of *caronimide* (Found : N=10·40 $C_7H_9O_2N$ requires N=10·07 per cent.).

cis- and trans-1 : 1-Dimethylcyclopropane-2 : 3-dicarboxylic Acids (Caronic Acids) (VI).

A solution of the dinitrile (2 grams) in 25 per cent. aqueous potassium hydroxide (20 c.c.) and warm alcohol was boiled for four hours, the alcohol then allowed to evaporate, and the liquid, after being cooled, extracted with ether to remove any unchanged nitrile, then strongly acidified, and again extracted with ether. The second extract, on evaporation, yielded 2·2 grams of crude mixed acids. The separation into *cis*- and *trans*-forms was carried out as described by Perkin and Thorpe (*loc. cit.*), 1·3 grams of the *trans*- and 0·5 gram of the *cis*-acid being obtained.

The former separated from water in feathery needles and melted at 213° (Found : C=52·91; H=6·38. Calc., C=53·12; H=6·39 per cent. Titration with 0·0264N-barium hydroxide : Found, 24·4 c.c. Calc., 24·3 c.c.).

The *cis*-acid separated from water in plates melting and decomposing at 174—175° (Found : C=52·93; H=6·40 per cent.).

There is some evidence to show that the use of more concentrated potassium hydroxide favours the formation of the *trans*-modification.

Lactone of β -Hydroxy- β -methylbutane- $\gamma\delta\delta$ -tricarboxylic Acid (XIV).

The amide (3.8 grams) was dissolved in aqueous potassium hydroxide (6 grams in 45 c.c. of water) and the solution boiled until ammonia ceased to be given off (three to four hours). The solution was cooled, acidified, and repeatedly extracted with pure ether. On removing the ether, about 2 grams of a solid acid were obtained. The purification of this substance presented very considerable difficulties, as it proved to be very soluble in water. It separated from a small quantity of water in large, colourless prisms melting and decomposing at 157° (Found : C=47.72; H=5.08. $C_8H_{10}O_6$ requires C=47.50; H=5.00 per cent.).

The *silver* salt is very soluble in water and was not analysed for this reason, but the constitution of the substance follows from its ready conversion into terebic acid, as well as its similarity to the cyclohexane compound (see p. 1326).

Lactone of β -Hydroxy- β -methylbutane- $\gamma\delta$ -dicarboxylic Acid (Terebic Acid) (XV).

When the acid described above is warmed for a short time with sulphuric acid (25 per cent.), it readily loses 1 molecule of carbon dioxide and is converted into terebic acid. The change appears to take place even on boiling with water. The boiling was usually continued until no further evolution of gas occurred; the liquid on cooling deposited spherical clusters of prisms which, after one crystallisation from water, melted sharply at 174° and answered the usual tests for terebic acid (Perkin and Thorpe, *loc. cit.*) (Found : C=53.01; H=6.49. Calc., C=53.12; H=6.39 per cent.).

 $\alpha\beta$ -Dicyano- γ -hydroxy- γ -methylbutane- $\alpha\beta$ -dicarboxylic Acid (XX).

The imide (IV) was dissolved in 10 per cent. aqueous potassium hydroxide (3 mols.) and the solution boiled for half an hour. The purple fluorescent solution was cooled and acidified, when the above acid slowly separated, the yield being about 70 per cent. of the theoretical.* The acid slowly crystallises from water, forming thick, transparent, rhombic plates melting and decomposing at 195 – 196° (Found : C=47.67; H=4.46; N=12.45. $C_9H_{10}O_5N_2$ requires C=47.75; H=4.47; N=12.39 per cent.). It is very sparingly soluble in ether, but dissolves readily in hot water. The *silver* salt appears to be very soluble in water and is not precipitated by alcohol.

The acid cannot be titrated satisfactorily (Found : 13.5 c.c. of

* The mother-liquors appear to contain more of the same substance.

$N/10NaOH$. Calc., 14.3 c.c.), although the result clearly indicates that it is dibasic.

Five grams of the acid were boiled with 50 c.c. of 50 per cent. sulphuric acid. The flask was provided with an air condenser, the end of which was bent over and dipped into a solution of semicarbazide acetate. Almost as soon as the liquid began to boil a precipitate was formed in this solution and gradually increased, while the liquid in the flask evolved a quantity of carbon dioxide. The action appeared to be over in less than an hour, the sulphuric acid solution remaining almost colourless. On cooling, the characteristic crystals of succinic acid separated from this solution, a small additional amount being recovered by means of ether. The yield was nearly quantitative; after two crystallisations from water, the acid melted at 185° and was identified in the usual way (Found : $C=40.76$; $H=5.42$. Calc., $C=40.70$; $H=5.08$ per cent.).

The semicarbazone precipitated melted at 187° and had the characteristic appearance of acetonesemicarbazone; it did not depress the melting point of a genuine specimen of that substance (Found : $N=36.85$. Calc., $N=36.48$ per cent.).

Action of Concentrated Potassium Hydroxide on the Imide IV.

Forty-eight grams of potassium hydroxide were heated with 12 c.c. of water until dissolved and 4 grams of the imide were gradually added. Each addition caused much frothing, and the mixture was finally heated for a few minutes until this subsided. When cold, the mass was dissolved in a small quantity of water, the solution extracted with ether to remove any neutral substances formed, strongly acidified, and again extracted eight times with an equal bulk of ether. The ethereal extract gave on evaporation a very small amount of an oil which solidified when kept in a vacuum. It was very soluble in water, and obviously consisted of the acid XIV (see above, p. 1323), but it could not be induced to crystallise from its solution. It was therefore boiled with a little 10 per cent. aqueous sulphuric acid, when the characteristic crystals of terebic acid were readily obtained on cooling the solution. The acid melted at 174° , and was identified by direct comparison with a specimen of that substance. In spite of a diligent search, no trace of *cis*- or *trans*-caronic acid could be isolated from the products of the above reaction.

cycloHexanespiro-2 : 3-dicyanocyclopropane-2-carboxylamide (VIII).

This was obtained from the *spiro*-imide (V) by the method described for the dimethyl compound (p. 1320). It separates in

almost quantitative yield on cooling; extraction with ether is not necessary.

The compound crystallises best from dilute alcohol or benzene, and is obtained in fine, glistening plates or sometimes in colourless, felted needles. It melts at 141° (Found: C=65.34; H=6.56; N=20.94. $C_{11}H_{13}ON_3$ requires C=65.00; H=6.45; N=20.67 per cent.).

cycloHexanespiro-2 : 3-dicyanocyclopropane-2-carboxylic Acid (XI).

The acid is best obtained from the above amide by means of nitrous acid, in the same way as the corresponding dimethyl compound (p. 1320). The yield is about 30 per cent. of the theoretical, the unchanged amide being recovered.

The acid can also be prepared by the direct hydrolysis of the imide (V) with potassium hydroxide (2 mols.). It is necessary, in this case, to use an alcoholic solution of potassium hydroxide, otherwise the amide melting at 141° will tend to separate, being quite insoluble in aqueous alkali. This method of preparation is not to be recommended, as the yield is only 20 per cent. of the theoretical, and a considerable quantity of the lactonic acid (XVI) is produced as the result of hydrolytic fission.

The dicyano-acid obtained by either method forms colourless prisms melting at 159° . It crystallises best when it is dissolved in a small quantity of water and an equal volume of concentrated hydrochloric acid is added to the solution (Found: C=65.03; H=5.99; N=13.73. $C_{11}H_{12}O_2N_2$ requires C=64.69; H=5.93; N=13.72 per cent. Titration with 0.0264N-barium hydroxide: Found: 3.97 c.c. Calc., 3.96 c.c.).

The Nitrile of cycloHexanespirocyclopropane-2 : 3-dicarboxylic Acid.

On heating the above dicyano-acid with water in a sealed tube in the way described for the dimethyl compound, the nitrile was obtained as a semi-solid mass. It solidified completely when treated with sodium hydrogen carbonate solution, which removed the unchanged acid, and was purified by crystallisation from dilute alcohol. It separated in lustrous, colourless plates melting at 86° . The yield was about 45 per cent. of the theoretical (Found: N=17.75. $C_{10}H_{12}N_2$ requires N=17.49 per cent.).

cycloHexanespirocyclopropane-2 : 3-dicarboxylic Acid (VII).

A quantitative yield of this acid was obtained when the above nitrile was hydrolysed under the condition described for the preparation of *cis*- and *trans*-caronic acids (see p. 1322).

Only a small quantity of the *cis*-modification appeared to be formed, and this was not isolated in a pure state (m. p. 195—196° with decomp.).

The *trans*-acid was readily obtained and corresponded in all its properties with the description given by Beesley, Ingold, and Thorpe (*loc. cit.*); it melted at 238°, and gave an anilide melting at 291° (these authors give 237° and 292° respectively); the identity of these compounds was further confirmed by direct comparison with the original specimens (mixed melting points).

γ-Lactone of 1-Hydroxycyclohexylethane-αββ-tricarboxylic Acid (XVI).

The amide (4.5 grams) was boiled with 45 c.c. of 15 per cent. aqueous potassium hydroxide until ammonia ceased to be evolved (four hours). On acidifying the cooled solution and allowing it to remain over-night, the new acid separated in characteristic spherical aggregates of buff-coloured crystals; a further quantity was obtained on extracting the mother-liquors with ether, the total yield being about 3 grams.

The acid crystallises best from water with the addition of hydrochloric acid. It does not melt sharply, probably because it tends to lose carbon dioxide on boiling with water; usually it melts and decomposes at 183—184°, although melting points up to 191° have been observed (Found: C=54.66; H=6.12. $C_{11}H_{14}O_6$ requires C=54.53; H=5.82 per cent.).

The proof of its structure was obtained by boiling a solution of the acid in dilute ammonia until neutral and adding an excess of silver nitrate solution, when the *silver* salt of the corresponding tribasic hydroxy-acid separated (Found: Ag=55.94. $C_{11}H_{14}O_7Ag_3$ requires Ag=55.72 per cent.).

The acid is not affected by boiling with acetyl chloride and is therefore probably the *trans*-isomeride.*

On heating to a temperature just above its melting point, the acid decomposes vigorously and a molecule of carbon dioxide is eliminated without any charring. The product consists of the lactonic acid described below.

γ-Lactone of 1-Hydroxycyclohexylethane-αβ-dicarboxylic Acid (XVII).

The lactonic acid XVI (6 grams) was boiled with 20 per cent. sulphuric acid (200 c.c.) until all was dissolved and the evolution of carbon dioxide had ceased. On cooling, a new acid was obtained

* An anilide melting at 278° was prepared from this acid by heating it with aniline, but the quantity was not sufficient for analysis.

in good yield; this was repeatedly crystallised from water and separated in plates melting at 184–185°. It is almost insoluble in cold water (Found: C=60·30; H=7·05. $C_{10}H_{14}O_4$ requires C=60·57; H=7·12 per cent.).

The *silver* salt of the lactonic acid is readily obtained in the usual way (Found: Ag=35·64. $C_{10}H_{13}O_4Ag$ requires Ag=35·38 per cent.).

The *silver* salt of the dibasic hydroxy-acid was prepared by dissolving the lactonic acid in an excess of boiling *N*/10-sodium hydroxide; the excess of alkali was neutralised with nitric acid and an excess of silver nitrate added (Found: Ag=50·63. $C_{10}H_{14}O_5Ag_2$ requires Ag=50·19 per cent.).

The lactonic acid is stable to permanganate. If it is heated to boiling in a test-tube for a few moments and then cooled, the residue, dissolved in a little aqueous sodium hydrogen carbonate, instantly reduces permanganate. This property is also characteristic of the similarly constituted terebic acid (Perkin and Thorpe, *loc. cit.*).

The acid gives a characteristic *anilide* when heated with aniline at 200° for a short time, but the compound appears to be abnormal, being formed from equimolecular proportions of the acid and the base by the elimination of one molecule of water and one of carbon dioxide. It crystallises from dilute alcohol in iridescent plates melting at 113° (Found: C=77·85; H=8·30; N=6·20. $C_{15}H_{19}ON$ requires C=78·58; H=8·33; N=6·11 per cent.).

cycloHexanespiro-2 : 3-dicyanocyclopropane-2 : 3-dicarboxylic Acid
(XVIII).

A solution of the imide V in 10 per cent. aqueous potassium hydroxide (3 mols.) was boiled for thirty to forty minutes, and then cooled and acidified, when the above acid was deposited in almost quantitative yield. It crystallises from dilute alcohol in small plates melting and decomposing at 207° (Found: C=58·20; H=5·03; N=11·32. $C_{12}H_{12}O_4N_2$ requires C=58·07; H=4·88; N=11·28 per cent.). The acid, although evidently dibasic, did not give satisfactory figures on titration.

The acid was heated just above its melting point until the evolution of vapour ceased (twenty minutes). The residue set to a stiff gum on cooling; it was taken up in ether, the solution washed with sodium carbonate solution, dried, and evaporated, the solid residue being crystallised from benzene. It separated in distinctly coloured, microscopic crystals melting at 99°, and proved to be the *anhydride* of the above acid, as it was transformed into the latter

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on hydration (Found : $N=12\cdot30$. $C_{12}H_{10}O_3N_2$ requires $N=12\cdot17$ per cent.).

cycloHexanespiro-2-cyanocyclopropane-2 : 3 : 3-tricarboxylic Acid
(XIX).

If either the imide (V) or the dicyano-dicarboxylic acid (XVIII) is hydrolysed with an excess of potassium hydroxide for some hours, the potassium hydrogen salt of the above acid separates on acidifying the solution. The salt crystallises well from alcohol in needles melting and decomposing at 237° ; on grinding with hydrochloric acid, the free acid is obtained. The acid crystallises from water in stellate clusters of prisms melting and decomposing at 169° (Found : $C=53\cdot83$; $H=4\cdot94$; $N=5\cdot38$. $C_{12}H_{13}O_6N$ requires $C=53\cdot91$; $H=4\cdot90$; $N=5\cdot24$ per cent.). The study of this acid is not yet completed.

Action of Concentrated Potassium Hydroxide on the Imide V.

The imide was treated with concentrated potassium hydroxide in exactly the same way as the dimethyl compound (see p. 1320). The mixture of acids obtained was dissolved in hot water, boiled with animal charcoal, filtered, and cooled, when a small amount of a crystalline solid separated. This melted at 229° and gave, on crystallisation from dilute alcohol, the flattened needles of the *trans-spiro*-acid melting at 238° . Its identity was confirmed by analysis (Found : $C=60\cdot85$; $H=7\cdot25$. Calc., $C=60\cdot57$; $H=7\cdot12$ per cent.), and by direct comparison with a genuine specimen. The anilide melting at 291° was also prepared from it.

The filtrate, on the addition of mineral acid, deposited the characteristic crystalline nodules of the lactonic acid (XVI).

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