

CXIX.—*The Formation and Stability of spiro-Compounds. Part I. spiro-Compounds from cyclo-Hexane.*

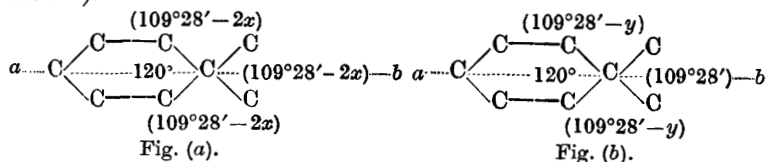
By RICHARD MOORE BEESLEY, CHRISTOPHER KELK INGOLD,  
and JOCELYN FIELD THORPE.

IN the series of investigations of which this communication is Part I, it is intended to ascertain the effect which is produced by the alteration of the tetrahedral angle, consequent on ring-formation, on the formation and stability of a second ring joined to the existing ring by a quaternary carbon atom common to both.

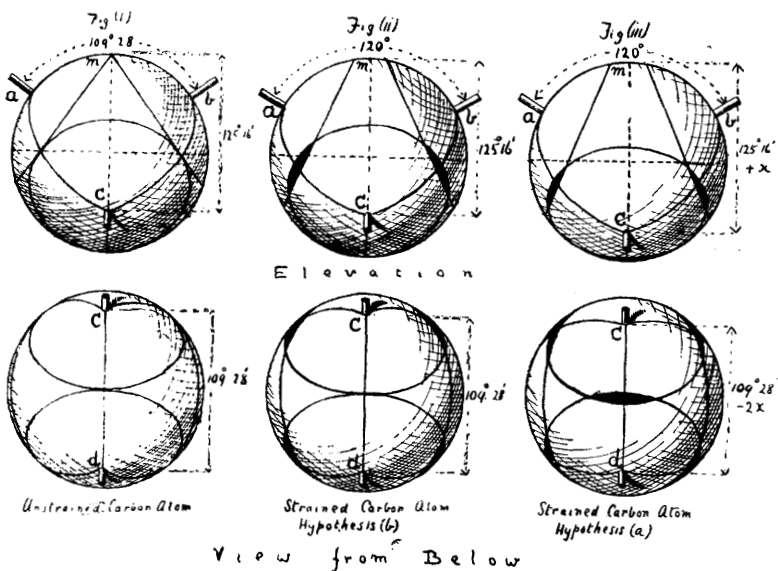
In accordance with Baeyer's strain hypothesis, the normal angle of the tetrahedron has to be altered in order to produce the *cyclohexane* ring, and the amount of change necessary to produce ring-structure, generally, is dependent on the character of the ring formed. It is possible, therefore, that the angle formed by two side-chains attached to any one carbon atom of, for example, the *cyclohexane* ring, will be altered in proportion to any change in the angle between those valencies which participate in the ring-formation. In other words, the groups attached to two side-chains emanating from the same carbon atom of a *cyclohexane* derivative will be closer together than in a corresponding compound having an open-chain structure.

This can be illustrated, roughly, by means of Fig. (a), in which it is assumed that the bending outwards of the two valencies, participating in the ring, causes the other two to distribute themselves equally in the remaining space. The angles will then no longer be  $109^{\circ}28'$ , but  $109^{\circ}28' - 2x$  (hypothesis a). On the other hand, if the two remaining valencies of the carbon atom participating in the ring-structure retain the tetrahedral angle (Fig. b), the space remaining would have to be distributed equally between the

other two angles, which would then be  $109^{\circ}28' - y$  (hypothesis *b*).



It is, of course, assumed that there is no distortion of the angle of the hexagon caused by the attachment of groups to any one carbon atom of the *cyclohexane* ring, and that the substituted derivative retains the plane of symmetry on the dotted line *ab*.



The value of the angles  $x$  and  $y$  can be calculated in the following manner. In the accompanying diagram, Fig. i shows the carbon atom in its normal state. For the sake of simplicity, it is assumed to be of spherical form, its four valency points, *a*, *b*, *c*, *d*, being situated at the apices of the inscribed regular tetrahedron, and being, therefore, at an angular distance of  $109^{\circ}28'$  from one another. According to Werner's mode of representation, the forces, the resultant of which we regard as a valency, emanate from points on the sphere lying within the spherical cap of diameter  $109^{\circ}28'$ , the centre or pole of which is the valency point in question.

Fig. ii is drawn to represent the case (hypothesis *b*) where the forcing apart of the valencies *a* and *b* to an angular distance

of  $120^\circ$  by the closing of the *cyclohexane* ring may possibly not involve the convergence towards one another of the valencies  $c$  and  $d$ . Here, then, whilst the angular distance between  $a$  and  $b$  is now  $120^\circ$ , that between  $c$  and  $d$  is still  $109^\circ 28'$ . This means, as the figure shows, that the spherical caps surrounding  $a$  and  $b$  do not now merely touch, but actually overlap, the caps surrounding  $c$  and  $d$ . It follows, therefore, that the angular distances between  $a$  and  $c$ , and between  $b$  and  $c$ , must be less than  $109^\circ 28'$  by the breadth of the overlapping portions, and by considering the right-angled spherical triangle,  $bcm$ , we see that

$$\cos(bc) = \cos(mc) \cdot \cos(mb) = \cos 125^\circ 16' \cdot \cos 60^\circ = -0.2887,$$

whence  $(bc) = 106^\circ 47'$ , or  $2^\circ 41'$  ( $=y$ ) less than the normal value.

The other possible case (hypothesis  $a$ ), and the one which actually receives experimental support in the present paper, is illustrated in Fig. iii. Here the separation of the valencies  $a$  and  $b$  to an angular distance of  $120^\circ$  involves the convergence of  $c$  and  $d$  towards one another until each of the overlappings of the caps around  $a$  and  $b$  with those around  $c$  and  $d$  is equal to the overlapping of the cap around  $c$  with that around  $d$ . This is equivalent to saying that the divergence of  $a$  and  $b$  will cause  $c$  and  $d$  to approach one another until the angular distances,  $ac$ ,  $bc$ ,  $ad$ ,  $bd$ , are all equal to the angular distance of  $c$  from  $d$ . Each will then be less than  $109^\circ 28'$  by the breadth of an overlapping area. The exact angular distance,  $x$ , through which  $c$  will approach  $d$  and  $d$  approach  $c$  may be determined by considering the spherical right-angled triangle  $bcm$ , in which  $mc$  is  $125^\circ 16' + x$ , and  $cb = cd = 109^\circ 28' - 2x$ ;  $mb$  is, of course,  $60^\circ$ . Hence,

$$\cos(109^\circ 28' - 2x) = \cos(125^\circ 16' + x) \cdot \cos 60^\circ,$$

or

$$\sin(19^\circ 28' - 2x) = \frac{1}{2} \sin(35^\circ 16' + x).$$

Putting  $\alpha = 19^\circ 28'$  and  $\beta = 35^\circ 16'$ , and using Taylor's expansion,

$$\sin \alpha - 2x \cdot \cos \alpha + \dots = \frac{1}{2} \sin \beta + \frac{1}{2} x \cdot \cos \beta + \dots;$$

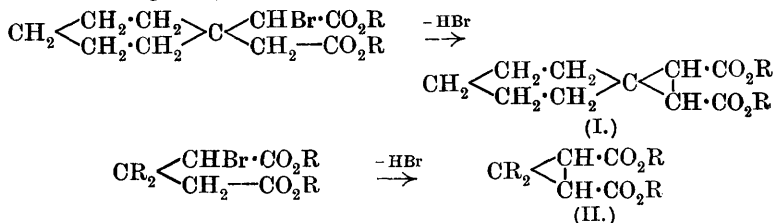
since  $x$  is small compared with  $\alpha$  and  $\beta$ , we may neglect all terms after the second and obtain

$$x = \frac{\sin \alpha - \frac{1}{2} \sin \beta}{2 \cos \alpha + \frac{1}{2} \cos \beta} = \frac{\sin 19^\circ 28' - \frac{1}{2} \sin 35^\circ 16'}{2 \cos 19^\circ 28' + \frac{1}{2} \cos 35^\circ 16'} = 0.0194 \text{ radians.} \\ = 1.06'.$$

It follows, therefore, that the angular distance between each pair of valencies, namely,  $ac$ ,  $bc$ ,  $ad$ ,  $bd$ , and  $cd$ , is  $109^\circ 28' - 2^\circ 12' = 107^\circ 16'$ . Experimental evidence on the correctness of either one or other of these hypotheses should be readily obtainable by a comparison of the conditions of *spiro*-ring-formation from these cyclic structures with the corresponding open-chain derivatives.

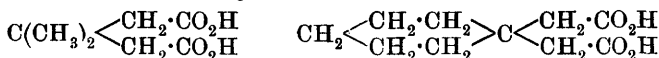
If the conditions represented by Fig. (b) are present, it is obvious that no difference would be apparent between the two types. If, however, Fig. (a) shows the actual condition of the molecule, then there must be a greater tendency to form ring-compounds from the cyclic structure, owing to the closer proximity of the groups attached to the carbon atoms of the side-chains, through the agency of which (elimination of water, hydrogen bromide, and so forth) the ring-formation is effected.

For example, if hypothesis (a) is correct, there should be a greater tendency to form the *spiro*-compound I than there is to form the ring-compound II:



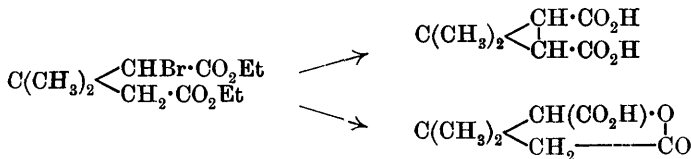
whereas if hypothesis (b) is right, then the tendency should be the same in both cases.

In the present paper, a comparison is drawn between the conditions controlling ring-formation from derivatives of  $\beta\beta$ -dimethylglutaric acid and from *cyclohexane*-1:1-diacetic acid:



and the general conclusions reached are clearly in favour of the hypothesis represented by Fig. (a).

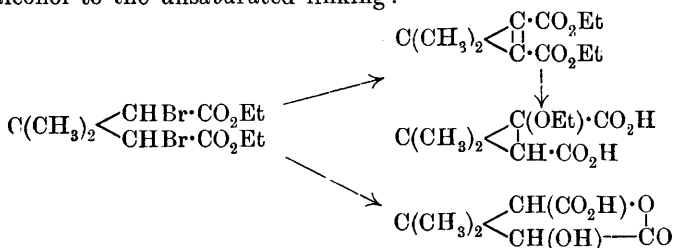
Some years ago (T., 1899, 75, 48), one of us, in conjunction with W. H. Perkin, studied the conditions of ring-formation by the elimination of hydrogen bromide from  $\beta\beta$ -dimethylglutaric acid brominated on either one or both of the  $\alpha$ -carbon atoms. The general conclusions reached were that the mono-brominated derivative gave a mixture of the *cyclopropane* compound and corresponding lactone when treated with alcoholic potassium hydroxide:



but that aqueous sodium carbonate yielded the lactone only.

The investigation of the dibromo-derivative was carried out later (T., 1901, 79, 729), during an attempt to isolate the corresponding unsaturated ring-compound. It was found that the

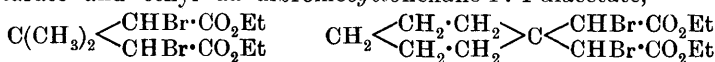
action of alcoholic potassium hydroxide produced a mixture of the hydroxy-lactone and ethoxycaronic acid, formed by the addition of alcohol to the unsaturated linking:



Recently (T., 1911, **99**, 422), a method has been devised by which *cyclohexane*-1:1-diacetic acid can be prepared in large quantities, and it was decided to use this substance as the starting point in our series of comparative experiments.

In the first place, there is a marked difference in the behaviour of the cyclic compound and the open-chain derivative when subjected to the Hell, Volhard, Zelinski method of bromination. In the case of the derivative of dimethylglutaric acid, it is possible to obtain the mono-brominated ester by using the theoretical quantity of bromine, but with the *cyclohexane* derivative under the same conditions, the chief product consists of the dibromo-compound mixed with unbrominated ester. It was only when sufficient bromine was used to form the dibrominated ester that an acid by-product was isolated, which proved on investigation to be the acid ester of the monobromo-derivative.

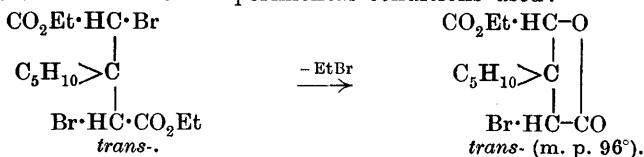
A comparison of the behaviour of ethyl  $\alpha\alpha'$ -dibromo- $\beta\beta$ -dimethylglutarate and ethyl  $\alpha\alpha'$ -dibromocyclohexane-1:1-diacetate,



supplied the first evidence in favour of the view that a greater tendency to ring-formation exists in the latter than in the former.

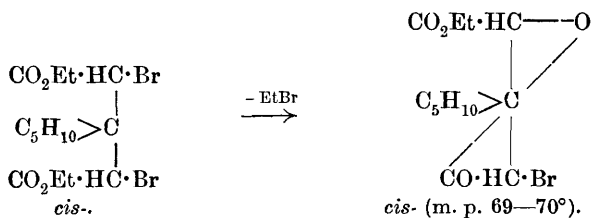
Ethyl dibromodimethylglutarate is a stable substance, which can be distilled without change at  $194^\circ/30$  mm. It is, moreover, a homogeneous compound, a fact which is clearly shown by its reactions (*loc. cit.*).

Ethyl dibromocyclohexanediacetate, on the other hand, is always obtained as a mixture of *cis*- and *trans*-forms. The *trans*-modification is, for the most part, transformed into the bromolactone ester under the experimental conditions used:



A certain amount, however, remains unchanged, and accompanies the stable *cis*-dibromodicarboxylic ester. They can be separated by the action of boiling pyridine, which removes ethyl bromide from the *trans*-modification, and leaves the *cis*-isomeride unattacked.

The *cis*-dibromo-ester is completely converted into a mixture of bromo-lactones on distillation, from which the above *trans*-bromo-lactone ester can be readily isolated. The second substance present is the *cis*-bromo-lactone ester, formed from the *cis*-dibromo-ester without change of configuration :



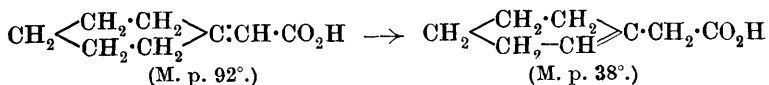
It is significant that these substances, which are, strictly speaking, derivatives of the glutaric acid type, since the end-groups are separated by three carbon atoms, are actually more closely related to compounds of the succinic type. Thus, for example, *trans-αα'*-dimethylglutaric acid does not show any tendency to form its own anhydride, but passes into the anhydride of the *cis*-modification on distillation (Auwers and Thorpe, *Annalen*, 1895, **285**, 310). *trans-αα'*-Dimethylsuccinic acid, on the other hand, yields its own anhydride, which readily passes into the anhydride of the *cis*-modification (Bone and Perkin, T., 1896, **69**, 266).

The action of alkali on the two forms of the bromo-lactone supplies further evidence of their structure. According as the conditions of the alkaline hydrolyses are varied, four different substances are produced, the proportion in which they are formed depending on the strength of the hydrolysing agent. This can be shown by the tables on p. 1086.

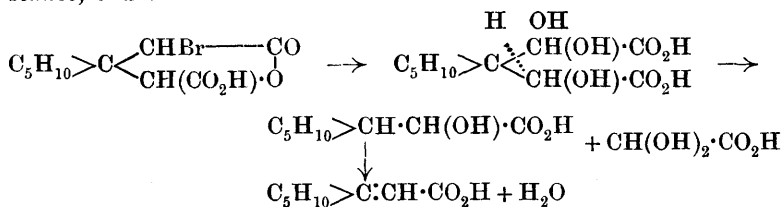
In the first place, it will be noticed that a remarkable degradation of both bromo-lactones occurs through treatment with the alkaline reagent. At first sight, apart from any question as to the mechanism that determines this degradation, it seemed difficult to explain why the action of 15 per cent. alkali should yield *cyclohexylideneacetic acid* (m. p. 92°), whilst the action of 64 per cent. alkali produced only *cyclohexeneacetic acid*, melting at 38°. This difficulty was removed, however, when it was found that *cyclohexylideneacetic acid* undergoes isomeric change when heated with 64 per cent. aqueous potassium hydroxide, yielding, in the



course of a few minutes, its own weight of *cyclohexeneacetic acid*, thus:



The formation of these acids involves the parting of the quaternary carbon atom of the *cyclohexane* ring in the bromo-lactone with one of the four groups directly attached to it. The fact was communicated by the authors to Dr. J. Kenner, and was discussed by him in a recent paper (T., 1914, **105**, 2690). The reaction in all probability involves the elimination of the side-chain as glycollic acid, or some product derived from this substance, thus:

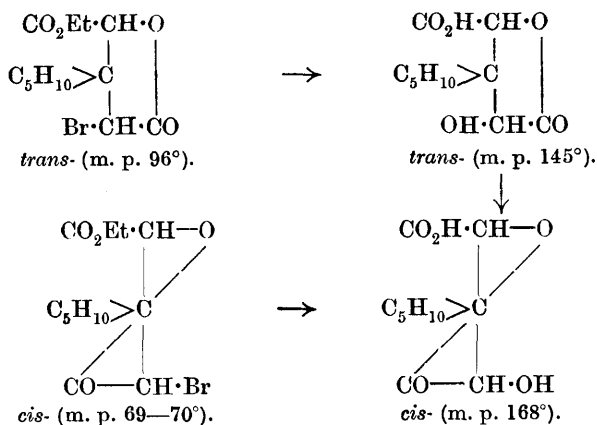


although no experimental evidence could be found to support this view.

It is certain, however, that the production of the unsaturated acids is in no way connected with the instability of the *cyclopropane* ring in the *spiro*-hydroxy-acid, melting at 217°. This acid is quite stable towards boiling alkali, and cannot, therefore, be regarded as an intermediate product in the formation of the unsaturated acids. In consequence, it must be assumed that their formation is determined by some such scheme as that outlined above.

It will be noticed from the tables that the *cis*- and *trans*-forms of the bromo-lactone yield different hydroxy-lactones under the same experimental conditions. For this reason, we have assigned the same configuration to the hydroxy-lactone as that possessed by the bromo-lactone from which it is derived. In this way, the hydroxy-lactone, melting at 145°, which is derived from the *trans*-bromo-lactone, melting at 96°, is given the *trans*-configuration, whilst the prefix *cis*- is given to the hydroxy-lactone, which is derived from the *cis*-bromo-lactone under the same experimental conditions:



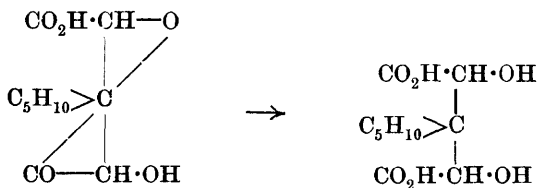


It is remarkable that the *trans*-hydroxy-lactone should be completely converted into the *cis*-modification when it is heated with water at  $240^\circ$ . This is, of course, unusual, since the *trans*-modifications are generally the more stable.

It will be noticed, however, that the process of ring-formation from the *trans*-dibromo-ester (p. 1085) produces actually a compound having the *cis*-configuration in so far as the positions of the bromine and carbethoxy-groups are concerned. From this point of view, the names *cis*- and *trans*-, as applied to the hydroxy-lactones, should be reversed, and hence the compound melting at  $168^\circ$  would be expected to have the greater stability.

At one time it was thought that these configurations ought to be reversed, owing to the fact that the hydroxy-lactone, melting at  $148^\circ$ , exists in a well-defined, hydrated form, which melts at  $100^\circ$ , with immediate loss of water.

If this compound were the free dihydroxy-acid, it follows that it must have the *cis*-configuration, since the corresponding dihydroxy-acid from the hydroxy-lactone, melting at  $168^\circ$ , cannot be isolated:

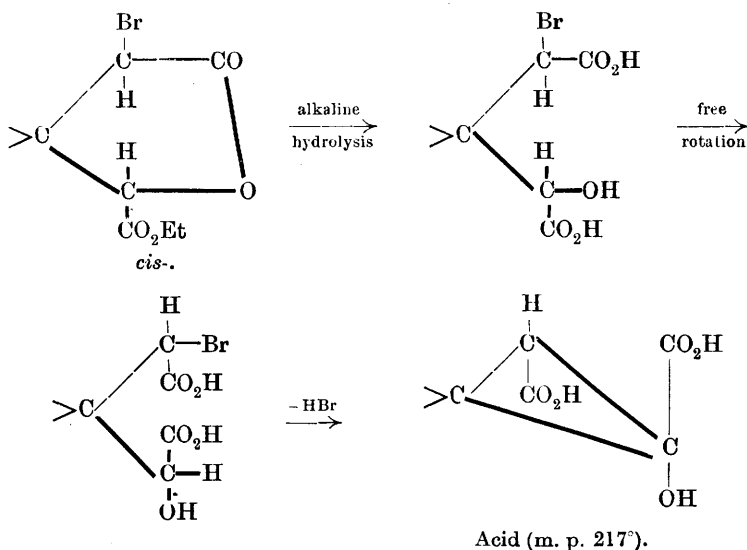


A complete study of the properties of this hydrated form led us, however, to the conclusion that it was not the dihydroxy-acid, but the hydroxy-lactone, crystallising with one molecule of water.

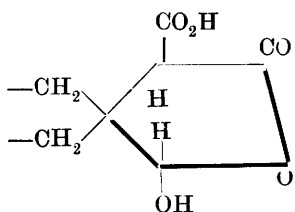
The correctness of the view expressed above as to the configura-

tion of the hydroxy-lactones is strongly supported by their behaviour towards acetyl chloride. The hydroxy-lactone, melting at 145°, is quite unaltered by this reagent, even at a high temperature, whereas the hydroxy-lactone, melting at 168°, is rapidly converted into the acetyl derivative at 100°. As this behaviour conforms with that of the hydroxy-*spiro*-acid, melting at 217°, it is advisable to deal with the two types at the same time.

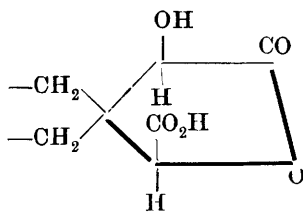
The hydroxy-*spiro*-acid is formed in small quantities from the *trans*-bromo-lactone, melting at 96°, but in very much larger yield from the *cis*-bromo-lactone, melting at 69–70°, under the same experimental conditions. The *spiro*-acid gives neither a lactone nor an acetyl derivative when heated with acetyl chloride. Moreover, it cannot be converted into an anhydride when treated with dehydrating agents. The acid could be isolated in only one form, and that this form has the *trans*-configuration, as is suggested by its inability to form an anhydride, can also be readily shown by the following scheme:



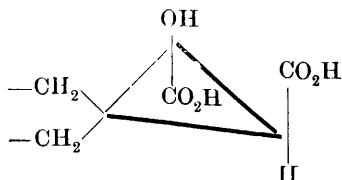
It follows, therefore, that the hydroxy-lactone, which does not yield an acetyl derivative, has the same configuration as the *spiro*-hydroxy-acid, melting at 217°, and that steric inhibition towards acetylation is caused by the presence in both of them of the hydroxyl and carboxyl groups on the same side of the plane of the ring, thus:



*cis*-Hydroxy-lactone, m. p. 168°.  
(Can be acetylated.)



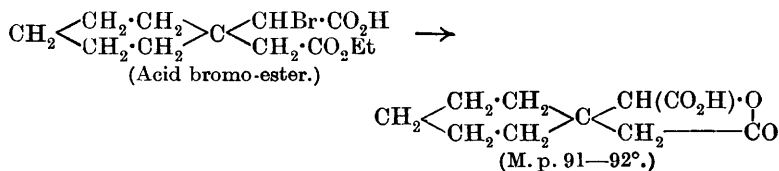
*trans*-Hydroxy-lactone, m. p. 145°.  
(Cannot be acetylated.)



*trans*-Hydroxy-spiro-acid.  
(Cannot be acetylated.)

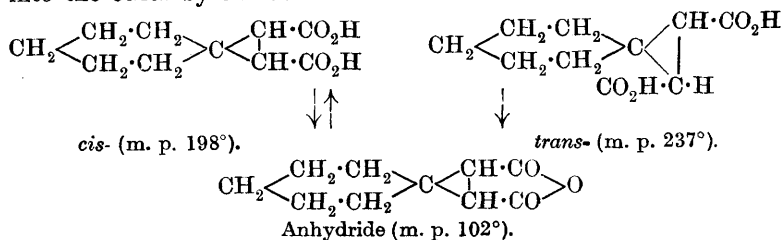
Here, again, it is evident that the use of the terms *cis*- and *trans*- leads to some confusion. As already mentioned, we have used the terms to indicate the configuration of the open-chain forms from which the ring-structures are derived.

It has been already stated that during the dibromination of *cyclohexane-1:1*-diacetic acid considerable quantities of an acid ester of the mono-brominated product is formed. This substance cannot be purified by distillation, and analysis gave no clue as to its structure, beyond the fact that it contained approximately one atom of bromine. That it is mainly composed of the bromo-acid ester is shown by the fact that, when boiled with sodium carbonate, it gives an excellent yield of the corresponding lactone:



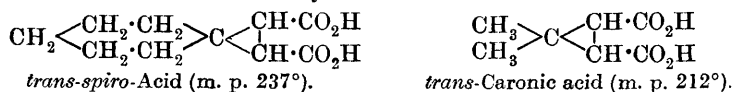
When the bromo-acid ester is treated with very concentrated potassium hydroxide solution, the *trans*-modification of the *spiro*-acid, mixed with a small amount of the *cis*-isomeride, is formed. The structure of the acid ester from which these acids are derived is of too indefinite a character to warrant any conclusions being drawn as to their ease of formation as compared with that of the corresponding caronic acids, which are produced from the similar acid bromo-ester which accompanies ethyl  $\alpha$ -bromo- $\beta\beta$ -dimethyl-

glutarate when  $\beta\beta$ -dimethylglutaric anhydride is brominated. The two stereoisomeric acids are similar to the caronic acids, but seem to possess greater stability. They are convertible the one into the other by the usual means:

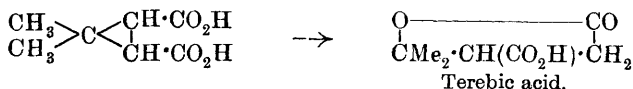


### The Stability of spiro-cycloPropane Acids.

It is to be expected that if the hypothesis represented by Fig. (a), p. 1081, is correct, then the stability of ring-structures derived from *cyclohexane* will be greater than that of the corresponding ring-compounds obtained from open-chain derivatives. A comparison of the *spiro*-acid mentioned above with *trans*-caronic acid shows that this is actually the case:



Both these acids are remarkably stable towards boiling acid permanganate. In fact, the *spiro*-acid can be boiled for some considerable time without undergoing change. The chief difference between them is seen, however, when the two acids are heated with concentrated hydrochloric acid in a sealed tube at 240°. Under these conditions, the *spiro*-acid is quite unaltered, whereas *trans*-caronic acid is completely converted into terebic acid:

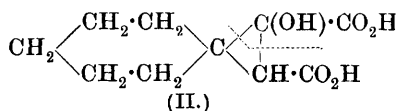
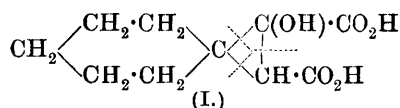


There is, therefore, very definite evidence that the *spiro*-acid has the greater stability.

So far as the hydroxy-*spiro*-acid melting at 217° is concerned, we have been unable to prepare any open-chain analogue with which to compare it. The acid is very stable to acid permanganate and to reducing agents, but, owing presumably to the presence of the quaternary carbon atom which carries the hydroxyl group, it readily undergoes fission when heated with water at 240°.

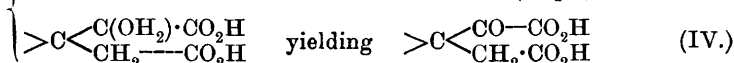
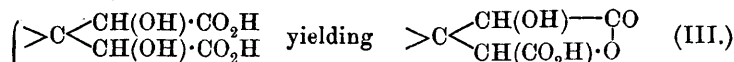
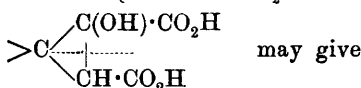
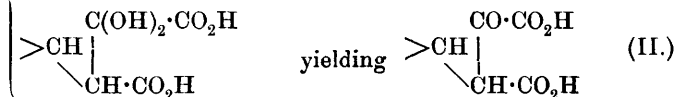
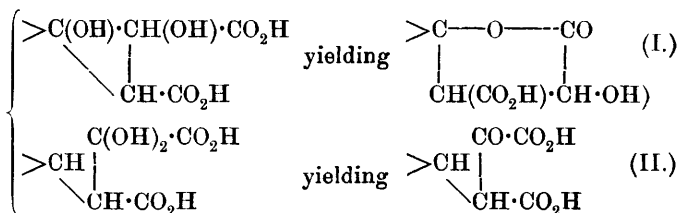
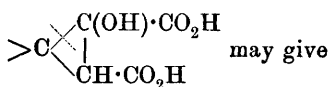
The fission of the *cyclopropane* ring in an acid of this character can, of course, take place between any one of the three carbon

atoms forming the ring, as in I, and it is evident that the elements of water can add on in two directions, yielding six products in all:



From the fact, however, that the unhydroxylated *spiro*-acid, melting at 237°, does not undergo fission when heated with water, it is reasonable to assume that the fission of the ring takes place between the carbon atoms, as represented in II.

This will lead to the production of four compounds, thus:



Of these, substances II and IV are ketones, and could be readily detected. Substance III is the hydroxy-lactone, the *cis*- and *trans*-forms of which have already been described. Substance I is therefore the only product that could not be immediately identified.

As a matter of fact, the fission of the hydroxy-*spiro*-acid takes place in two directions, yielding 20 per cent. of an hydroxy-lactone, melting at 168°, which was proved by direct comparison to be identical with the hydroxy-lactone of formula III, and 80 per cent. of another hydroxy-lactone, melting at 131°, which must, therefore, have the structure represented by formula I.

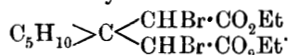
EXPERIMENTAL.

*Bromination of cyclohexane-1:1-diacetic Acid.*

The bromination was effected by bromine and phosphorus pentabromide in the following way. Fifty grams of the acid, contained in a Perkin flask, were mixed with 224 grams of phosphorus pentabromide, and warmed on the water-bath until the evolution of hydrogen bromide had ceased; 86 grams of bromine were then added from a dropping funnel, and the product was warmed until free from bromine, a process which requires five hours. After cooling, the whole was poured into absolute alcohol, and when the vigorous reaction had subsided, water was added, and the brominated product extracted by ether. Aqueous sodium carbonate extracted some acid material from the ethereal solution, and the residue, on evaporation, yielded the neutral ester, which constituted 90 per cent. of the total amount.

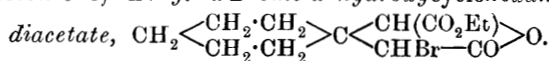
(1) *The Neutral Products of Bromination.*

*Ethyl αα'-Dibromocyclohexane-1:1-diacetate,*



The neutral product described above is a mixture of three substances, namely, the *cis*- and *trans*-forms of the dibrominated ester and the bromo-lactone formed by the elimination of ethyl bromide from the *trans*-modification under the experimental conditions employed. Separation can be effected by adding an equal volume of light petroleum (b. p. 60—70°) to the mixture, when the solid bromo-lactone slowly separates, but the separation is never complete, and since the dibromo-ester cannot be distilled without decomposition, it was not found possible to obtain this substance in a pure condition. A specimen which had been freed from the bromo-lactone as far as possible gave a bromine content of 34.1 per cent. (C<sub>14</sub>H<sub>22</sub>O<sub>4</sub>Br<sub>2</sub> requires Br=38.6 per cent.)

*The Lactones of Ethyl α-Bromo-α'-hydroxycyclohexane-1:1-*



*The trans-Lactone.* This lactone has been prepared in three ways: (a) by means of light petroleum in the manner described above; (b) by boiling the mixture of *cis*- and *trans*-ethyl αα'-dibromocyclohexane-1:1-diacetate with pyridine, when only the *trans*-modification is converted into the lactone, leaving the *cis*-form unaltered; (c) by the distillation of the mixed *cis*- and

*trans*-forms of the dibromo-ester, whereby both modifications are converted into the lactone.

*Process (a)* is mechanical, and yields the *cis*-lactone in a very pure form.

*Process (b)*.—The mixed *cis*- and *trans*-esters are boiled with 1.5 times their weight of pyridine for five hours, and the cooled product poured into dilute hydrochloric acid. The oil is extracted by ether, and treated with light petroleum in the manner already described. The quantity of lactone formed in this way is about 15 per cent., and the remaining 85 per cent. of unchanged dibromo-ester can be recovered. Further treatment with pyridine fails to produce more of the lactone, and it is therefore evident that pyridine can only bring about the elimination of ethyl bromide from the *trans*-modification.

*Process (c)*.—Distillation of the dibromo-ester under diminished pressure constitutes by far the best method for preparing the bromo-lactone in quantity. As the temperature rises, much ethyl bromide is eliminated, but this ceases after a time, and it is this phase that involves the transformation of the *trans*-form of the ester into the bromo-lactone. At a higher temperature, that is, in the neighbourhood of 200°/20 mm., the evolution of ethyl bromide again commences, indicating the phase during which the *cis*-modification is converted into the *trans*-, and thence into the lactone. After this reaction has ceased, the bromo-lactone distils at 225—230°/20 mm., and solidifies on cooling.

By all of these methods, the bromo-lactone was obtained as a white, crystalline solid, which crystallised from light petroleum (b. p. 100—110°) or from alcohol in prisms, melting at 96°. It possesses a remarkable tendency to crystallise:

0.1756 gave 0.3062 CO<sub>2</sub> and 0.0893 H<sub>2</sub>O. C=47.50; H=5.61.

0.2038 „ 0.1262 AgBr. Br=26.32.

C<sub>12</sub>H<sub>17</sub>O<sub>4</sub>Br requires C=47.2; H=5.6; Br=26.2 per cent.

*The cis-Lactone*.—This substance is formed to the extent of about 10 per cent. by the distillation of the mixed *cis*- and *trans*-esters, and also to the extent of about 25 per cent. when the ester from which the *trans*-form has been removed by pyridine, is distilled. It can be readily separated from the *trans*-modification of the lactone by fractional recrystallisation from a mixture of benzene and light petroleum (b. p. 60—70°). It forms small needles, which melt at 69—70°:

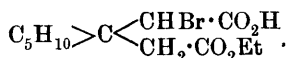
0.1680 gave 0.2907 CO<sub>2</sub> and 0.0836 H<sub>2</sub>O. C=47.23; H=5.52.

0.2033 „ 0.1254 AgBr. Br=26.23.

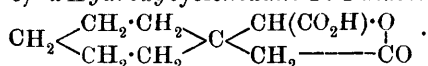
C<sub>12</sub>H<sub>17</sub>O<sub>4</sub>Br requires C=47.2; H=5.6; Br=26.2 per cent.

(2) *The Acid Product of Bromination*.—The acid product,

which is extracted by aqueous sodium carbonate, is obtained as a heavy oil when the alkaline solution is acidified, and can be extracted by ether. It cannot be purified by distillation, and could not, therefore, be obtained in a pure condition. Its reactions show, however, that it was composed, for the most part, of the acid bromo-ester,



*Lactone of α-Hydroxycyclohexane-1:1-diacetic Acid,*



This lactone is the sole product of the action of boiling sodium carbonate solution on the above acid product of bromination. One and a-half molecular proportions of sodium carbonate were used, and the whole was boiled for six hours. The solution was then acidified, and extracted with ether. The ethereal residue distilled at 240—241°/18 mm., and the distillate set to a very viscous gum on cooling. The compound could not be induced to crystallise for many months, until a crystal was obtained by the slow evaporation of its alcoholic solution, when the whole bulk solidified on seeding. It crystallises from a mixture of benzene and light petroleum in small needles, melting at 91—92°:

0·1900 gave 0·4203 CO<sub>2</sub> and 0·1234 H<sub>2</sub>O. C=60·33; H=7·22.

C<sub>10</sub>H<sub>14</sub>O<sub>4</sub> requires C=60·6; H=7·1 per cent.

The *silver* salt is precipitated on the addition of silver nitrate solution to a boiled solution of the ammonium salt. It is a white, amorphous powder:

0·3861 gave 0·1377 Ag. Ag=35·62.

C<sub>10</sub>H<sub>13</sub>O<sub>4</sub>Ag requires Ag=35·4 per cent.

*α-Hydroxycyclohexane-1:1-diacetic Acid.*—This acid is stable only in the form of its salts; it could not be isolated in the free condition. The lactone dissolves in one molecular proportion of *N*/10-sodium hydroxide, forming a neutral solution. When a second molecular proportion of the alkali is added, the solution becomes alkaline, but is rendered neutral by boiling, and retains its neutrality on cooling. The cautious addition of hydrochloric acid to this solution yields the lactone only, but the addition of silver nitrate solution gave a white, amorphous precipitate of the *silver* salt of the dibasic acid:

0·2997 gave 0·3070 CO<sub>2</sub> and 0·0886 H<sub>2</sub>O. C=27·93; H=3·31.

0·2835 „ 0·1435 Ag. Ag=50·60.

C<sub>10</sub>H<sub>14</sub>O<sub>5</sub>Ag<sub>2</sub> requires C=27·9; H=3·3; Ag=50·3 per cent.



When the lactone is treated with 4*N*-sodium hydroxide solution, a crystalline sodium salt separates. It can be purified by rubbing with 80 per cent. alcohol:

0.1342 gave 0.0733  $\text{Na}_2\text{SO}_4$ .  $\text{Na}=17.7$ .

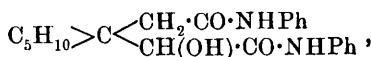
$\text{C}_{10}\text{H}_{14}\text{O}_5\text{Na}_2$  requires  $\text{Na}=17.7$  per cent.

*Aniline Derivatives.*—A characteristic *aniline* salt of the lactone is formed by the interaction of the two constituents in benzene solution. It crystallises from benzene in long, silky needles, melting at  $104^\circ$ :

0.1503 gave 0.3631  $\text{CO}_2$  and 0.0944  $\text{H}_2\text{O}$ .  $\text{C}=65.89$ ;  $\text{H}=7.01$ .

$\text{C}_{16}\text{H}_{21}\text{O}_4\text{N}$  requires  $\text{C}=66.0$ ;  $\text{H}=7.2$  per cent.

*The dianilide of the hydroxy-acid,*

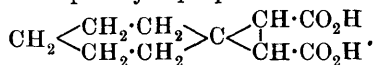


is formed when the lactone is heated with an excess of aniline for a few minutes at  $200^\circ$ . It can be isolated by treating the product first with acid and then with alkali, and can be purified by recrystallisation from alcohol. It forms small clusters of needles, which melt at  $97^\circ$ :

0.1202 gave 0.3179  $\text{CO}_2$  and 0.0756  $\text{H}_2\text{O}$ .  $\text{C}=72.09$ ;  $\text{H}=7.03$ .

$\text{C}_{22}\text{H}_{26}\text{O}_3\text{N}_2$  requires  $\text{C}=72.1$ ;  $\text{H}=7.1$  per cent.

*trans-cycloHexane-spiro-cyclopropane-1:2-dicarboxylic Acid,*



This acid is best produced from the acid product of bromination by the action of very concentrated potassium hydroxide at a high temperature.

Sixty grams of potassium hydroxide are dissolved in 50 c.c. of water, and the solution is evaporated until the boiling point reaches  $150^\circ$ . Twenty grams of the acid bromo-ester are now added to the boiling solution as rapidly as possible consistent with safety, and the very vigorous reaction is allowed to subside. The solution is then cooled, diluted, and acidified, the acid which separates being collected. The acid crystallises from dilute alcohol in flattened needles, melting at  $237^\circ$ :

0.1555 gave 0.3456  $\text{CO}_2$  and 0.0993  $\text{H}_2\text{O}$ .  $\text{C}=60.59$ ;  $\text{H}=7.08$ .

$\text{C}_{10}\text{H}_{14}\text{O}_4$  requires  $\text{C}=60.6$ ;  $\text{H}=7.1$  per cent.

The *silver* salt, prepared in the usual way, is a white, crystalline powder:

0.1567 gave 0.0814  $\text{Ag}$ .  $\text{Ag}=51.93$ .

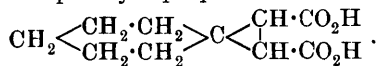
$\text{C}_{10}\text{H}_{12}\text{O}_4\text{Ag}_2$  requires  $\text{Ag}=52.4$  per cent.

The yield of acid prepared in this way was 5 grams; the mother liquor contained 8 grams of the lactone, melting at 91—92°, and 0·7 gram of the *cis*-modification of the *spiro*-acid. The separation of these substances is described in the next paragraph.

The dianilide of the *trans*-acid,  $C_5H_{10}:C \begin{matrix} \text{CH} \cdot \text{CO} \cdot \text{NHPh} \\ | \\ \text{CH} \cdot \text{CO} \cdot \text{NHPh} \end{matrix}$ , is formed when the acid, mixed with excess of aniline, is heated at 200°. It crystallises from alcohol in small needles, melting at 292°:

0·0992 gave 0·2751  $CO_2$  and 0·0616  $H_2O$ . C = 75·62; H = 6·89.  
 $C_{22}H_{24}O_2N_2$  requires C = 75·9; H = 6·9 per cent.

*cis*-cycloHexane-spiro-cyclopropane-1 : 2-dicarboxylic Acid,



The filtrate from the *trans*-acid was extracted with ether, and the crude product obtained in this way fractionated under diminished pressure. Under 18 mm. pressure, a small fraction was obtained, boiling at 220—240°, whilst the lactone distilled at 240—241°; the former was redistilled, and the fraction boiling at 220—225° collected. This was treated with a little water, and the solid material thus obtained was freed from a small quantity of the gummy lactone by means of chloroform.

The *cis*-acid can, however, be more readily prepared by distilling the *trans*-modification, when it is completely converted into the anhydride of the *cis*-modification. The *trans*-acid is boiled in an open tube until water ceases to be evolved, an operation which, owing to the great stability of these substances, can be conducted under the ordinary pressure. The product, after treatment with cold aqueous sodium hydrogen carbonate solution to remove unchanged acid, yields the crude anhydride of the *cis*-modification, from which the acid can be prepared by solution in alkali and acidification. The acid is much more readily soluble in water than the *trans*-modification, and can be recrystallised from this solvent, forming small needles, which melt at 198°, with immediate elimination of water vapour:

0·1759 gave 0·3922  $CO_2$  and 0·1123  $H_2O$ . C = 60·81; H = 7·09.  
 $C_{10}H_{14}O_4$  requires C = 60·6; H = 7·1 per cent.

The anhydride of the *cis*-acid,  $C_5H_{10} \left\langle \begin{matrix} CH \cdot CO \\ | \\ CH \cdot CO \end{matrix} \right\rangle O$ . The *trans*-acid is not acted on by acetyl chloride or acetic anhydride, but is converted into the anhydride of the *cis*-acid on distillation, in the manner described above. The crude anhydride

formed in this way can be purified by recrystallisation from light petroleum (b. p. 80—100°), and is obtained in long, glistening needles, melting at 102°. The anhydride is also readily formed by the action of acetyl chloride on the *cis*-acid:

0.1098 gave 0.2685 CO<sub>2</sub> and 0.0658 H<sub>2</sub>O. C=66.70; H=6.68.

C<sub>10</sub>H<sub>12</sub>O<sub>3</sub> requires C=66.7; H=6.7 per cent.

The *anilic acid*, C<sub>5</sub>H<sub>10</sub>>C< $\begin{matrix} \text{CH}\cdot\text{CO}_2\text{H} \\ | \\ \text{CH}\cdot\text{CO}\cdot\text{NHPH} \end{matrix}$ , separates at once when a benzene solution of the anhydride is mixed with a solution of aniline in the same solvent. It crystallises from alcohol in small needles, which melt and decompose at 207°:

0.897 gave 0.2323 CO<sub>2</sub> and 0.0551 H<sub>2</sub>O. C=70.59; H=6.81.

C<sub>16</sub>H<sub>19</sub>O<sub>3</sub>N requires C=70.3; H=7.0 per cent.

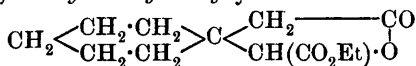
The *anil*, C<sub>5</sub>H<sub>10</sub>>C< $\begin{matrix} \text{CH}\cdot\text{CO} \\ | \\ \text{CH}\cdot\text{CO} \end{matrix}$ >NPh, is obtained by heating the anilic acid above its melting point until water vapour ceases to be evolved. The product is then rubbed with dilute aqueous sodium carbonate, and recrystallised from alcohol. It forms small crystals, which melt at 119°:

0.1108 gave 0.3052 CO<sub>2</sub> and 0.0668 H<sub>2</sub>O. C=75.08; H=6.72.

C<sub>16</sub>H<sub>17</sub>O<sub>2</sub>N requires C=75.3; H=6.7 per cent.

The *cis*-acid, when heated in a sealed tube with 50 per cent. concentrated hydrochloric acid and water at 180° for five hours, is partly converted into the *trans*-modification.

*Lactone of Ethyl α-Hydroxycyclohexane-1:1-diacetate,*



This substance was obtained as the result of an attempt to displace the bromine in the lactone of ethyl *α*-bromo-*α'*-hydroxycyclohexane-1:1-diacetate by hydroxyl through the agency of moist silver hydroxide.

Ten grams of the bromo-lactone (m. p. 96°) were melted under 400 c.c. of hot water, and sufficient hot alcohol was added to render the solution clear. The solution was then boiled with an excess of silver hydroxide (freshly precipitated and washed) for forty-eight hours on the water-bath. At the end of that time, the hot liquid was run through a filter into three volumes of water, and the precipitated ester extracted by ether. The residue from the ether distilled as a colourless oil at 210°/21 mm., the yield being about 70 per cent.:

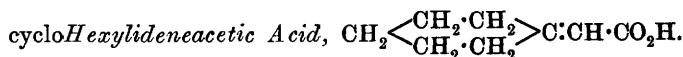
0.1380 gave 0.3230 CO<sub>2</sub> and 0.0997 H<sub>2</sub>O. C=63.78; H=8.01.

C<sub>12</sub>H<sub>18</sub>O<sub>4</sub> requires C=63.7; H=8.0 per cent.

The hydrolysis of this ester yields the lactone, melting at 91—92°.

*Hydrolysis of the Bromo-lactone Esters.*

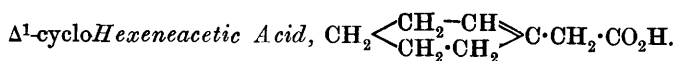
The remarkable difference in the nature of the products formed by hydrolysing these lactones under different conditions has been commented on in the introduction. The experimental details are summarised below.



Five grams of the bromo-lactone (m. p. 96° or 69—70°) were boiled for five hours with 30 c.c. of 15 per cent. aqueous sodium hydroxide. On cooling and acidifying, a white solid separated, which, on recrystallisation from dilute alcohol, melted at 92°. The yield was 1 gram.

The same acid was obtained by the hydrolysis with alcoholic potassium hydroxide, and in this case 10 grams of either of the bromo-lactones were added gradually to 100 c.c. of a boiling, saturated solution of alcoholic potassium hydroxide, and the heating was continued for ten minutes after the first vigorous reaction had subsided. The precipitate formed on acidifying, which weighed about 2 grams, consisted of about equal proportions of the hydroxy-*spiro*-acid, melting at 217° (see p. 1103), and the unsaturated acid. They were separated by treatment with dry ether, in which the *spiro*-acid is quite insoluble. The chief products of these reactions are summarised on p. 1086.

The identity of the acid melting at 92° with the *cyclohexylideneacetic acid* of Wallach was shown in the following way. By analysis, which gave C=68·3; H=8·4 ( $\text{C}_8\text{H}_{12}\text{O}_2$  requires C=68·5; H=8·5 per cent.); by titration with standard alkali, which gave figures in good agreement with those required for Wallach's acid; by the formation of *cyclohexanone* when the acid was oxidised by alkaline permanganate; and, lastly, by the formation of a dibromide, which, on recrystallisation from a mixture of ether and light petroleum, melted at 135—136° (Wallach gives 91—92° as the melting point of his acid and 133—134° as the melting point of its dibromide).



As already mentioned, the acid melting at 92° can be quantitatively converted into the above acid (m. p. 38°) by the action of boiling 64 per cent. aqueous potassium hydroxide. This acid

occurs, therefore, as one of the products formed by the action of this reagent on the bromo-lactones.

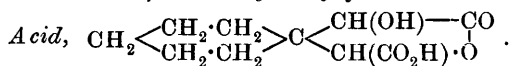
Forty grams of either bromo-lactone were added in small quantities, as rapidly as possible consistent with safety, to a boiling solution of 140 grams of potassium hydroxide in 80 grams of water. The extremely vigorous reaction which ensued after each addition soon subsided, and when all had been added, the solution was diluted and acidified. The viscid precipitate which separated was extracted by ether, and the considerable quantity of solid acid which separated from the ethereal solution on drying and concentrating was collected. This substance proved to be the hydroxy-*spiro*-acid, dealt with on p. 1103. The viscid residue left on the complete evaporation of the ether yielded a further quantity of this acid when rubbed with dry ether. The ultimate ethereal residue was etherified by alcohol and sulphuric acid in the usual way, and the neutral esters were fractionally distilled under diminished pressure, when complete separation into two chief fractions was effected, one boiling at 118—122° and the other at 206—210°/25 mm.

The fraction boiling at 118—122°/25 mm. was hydrolysed both by acid and by alkali. The product in each case was extracted by ether, and the solid residue distilled. It boiled at 151—152°/23 mm., and set to a solid mass, melting at 37—38° on cooling.

The identity of this acid with Wallach's *cyclohexeneacetic* acid was proved by analysis, which gave C=68·4; H=8·5 (C<sub>8</sub>H<sub>12</sub>O<sub>2</sub> requires C=68·5; H=8·5 per cent.), and by the action of bromine in glacial acetic acid, when a dibromide was obtained, which, after recrystallisation from ether and light petroleum, melted at 120—121° (Wallach gives the melting point of the dibromide as 119—120°).

*The Ethyl Ester.*—On redistillation, the pure substance was found to boil at 124—125°/38 mm. (Auwers and Ellinger, *Annalen*, 1912, **387**, 200, give 100°/12 mm.), and to be a colourless, mobile oil. (Found, C=71·01; H=9·17. C<sub>10</sub>H<sub>16</sub>O<sub>2</sub> requires C=71·4; H=9·5 per cent.)

*trans-Lactonic Acid of αα'-Dihydroxycyclohexane-1:1-diacetic*



This substance is formed by the hydrolysis of the *trans*-bromo-lactone, melting at 96°, either by 15 per cent. aqueous potassium hydroxide or by a solution of 64 per cent. strength, and is contained in the form of its ethyl ester in the higher fraction boil-

ing at 206—210°/25 mm., produced in the manner described in the last experiment.

The ester obtained in the experiment with 15 per cent. potassium hydroxide yields on hydrolysis the hydroxy-lactonic acid in a fairly pure condition, but the ester formed in the same manner from the experiment with 64 per cent. potassium hydroxide contains some of the ester of the hydroxy*spiro*-acid (see p. 1103). The hydrolysis is effected by boiling the ester with concentrated hydrochloric acid for forty-five minutes. The residue, on cooling, deposits a mass of crystals, which consist, for the most part, of the lactonic acid in its hydrated form, mixed with a small quantity of the hydroxy*spiro*-acid, melting at 217°. The separation is effected by dehydrating the lactonic acid by drying in the air at 90° and treating the mixture several times with small quantities of hot benzene, in which the *spiro*-acid is insoluble. The residue left on evaporating the benzene is then re-crystallised four times from water.

*The hydrated form of the lactonic acid* produced in this way forms small prisms, which melt at 100°, with immediate elimination of water vapour:

0·2889, on being dried at 90°, lost 0·230.  $H_2O = 8\cdot0$ .

$C_{10}H_{14}O_5 \cdot H_2O$  requires  $H_2O = 7\cdot8$  per cent.

*The dehydrated lactonic acid* melts at 145°:

0·1598 gave 0·3289  $CO_2$  and 0·0950  $H_2O$ .  $C = 56\cdot12$ ;  $H = 6\cdot61$ .

$C_{10}H_{14}O_5$  requires  $C = 56\cdot1$ ;  $H = 6\cdot5$  per cent.

The *disodium* salt is formed as a crystalline precipitate when the lactonic acid is dissolved in about 3 molecular proportions of 4/*N*-sodium hydroxide solution. It can be purified by washing with 80 per cent. alcohol:

0·1856 gave 0·930  $Na_2SO_4$ .  $Na = 16\cdot3$ .

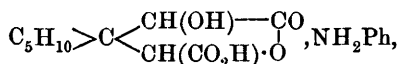
$C_{10}H_{14}O_6Na_2$  requires  $Na = 16\cdot6$  per cent.

The *disilver* salt is a white powder, which is formed by the action of silver nitrate solution on an aqueous solution of the sodium salt:

0·1959 gave 0·0953  $Ag$ .  $Ag = 48\cdot60$ .

$C_{10}H_{14}O_6Ag_2$  requires  $Ag = 48\cdot4$  per cent.

The *aniline* salt of the lactonic acid,



is formed by the interaction of molecular proportions of the two components in benzene solution. It separates from benzene in small crystals, which melt at 133—134°:

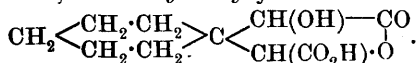
0.1335 gave 0.3042 CO<sub>2</sub> and 0.0846 H<sub>2</sub>O. C = 62.21; H = 7.02.  
C<sub>16</sub>H<sub>21</sub>O<sub>5</sub>N requires C = 62.5; H = 6.8 per cent.

The *dianilide*, (C<sub>5</sub>H<sub>10</sub>)>C< $\begin{matrix} \text{CH(OH)·CO·NHPh} \\ \text{CH(OH)·CO·NHPh} \end{matrix}$ , is obtained by heating the lactonic acid with a slight excess of aniline at 200°, and is isolated in the usual way. It crystallises from dilute alcohol in short needles, which melt at 169°:

0.1410 gave 0.3550 CO<sub>2</sub> and 0.0886 H<sub>2</sub>O. C = 68.71; H = 6.91.  
C<sub>22</sub>H<sub>26</sub>O<sub>4</sub>N<sub>2</sub> requires C = 69.1; H = 6.8 per cent.

The lactonic acid does not react with acetyl chloride even when heated with the reagent in a sealed tube at 100°. When it is distilled under diminished pressure, or when it is heated in a sealed tube with water, it passes into the stereoisomeric form, melting at 168°. It is not reduced by silver hydroxide.

*cis-Lactonic Acid of αα'-Dihydroxycyclohexane-1:1-diacetic Acid,*



This lactone may be obtained by the hydrolysis of the *cis*-bromolactone, melting at 69–70°. The isolation is effected by the same method as that used for preparing the lactone melting at 145° up to the point where the lactonic acid is dissolved away from the admixed hydroxy-*spiro*-acid and is etherified. The fraction of high boiling point obtained on distilling the esters is then hydrolysed by dilute hydrochloric acid, and the product evaporated completely to dryness. The residue, when rubbed with dry ether, leaves most of the *spiro*-acid undissolved. The residue from the ethereal filtrate is then extracted with hot benzene, and the residue from the benzene rubbed with chloroform. The solid thus obtained is finally purified by dissolving in dry ether, filtering, and precipitating by the addition of light petroleum (b. p. 40–60°). The lactonic acid can also be prepared by distilling the stereoisomeric lactonic acid (melting at 145°), but the process leads to much decomposition. The change from one form to the other is best effected in the following way. One gram of the lactonic acid is dissolved in 2 c.c. of water, and heated in a sealed tube at 240° for fifteen minutes. The residue left on evaporating to dryness gave 0.95 gram of the lactonic acid melting at 168° on recrystallisation from ether and light petroleum.

The *cis-lactonic acid* separates in short prisms, which melt at 168°. It is readily soluble in water and in all organic solvents, excepting chloroform and light petroleum:

0.1269 gave 0.2588 CO<sub>2</sub> and 0.0724 H<sub>2</sub>O. C = 55.58; H = 6.51.  
C<sub>10</sub>H<sub>14</sub>O<sub>5</sub> requires C = 56.1; H = 6.5 per cent.

The *disilver* salt is formed by the addition of silver nitrate solution to a solution of the lactone neutralised by the addition of two molecular proportions of sodium hydroxide solution:

0.1964 gave 0.0946 Ag.  $Ag = 48.21$ .

$C_{10}H_{14}O_6Ag_2$  requires  $Ag = 48.4$  per cent.

The *dianilide*,  $C_5H_{10} > C \begin{matrix} \text{CH(OH)·CO·NHPh} \\ \text{CH(OH)·CO·NHPh} \end{matrix}$ , is prepared by

heating the lactonic acid with a slight excess of aniline at  $200^\circ$ . It crystallises from dilute alcohol in small needles, which melt at  $169^\circ$ . This is the same melting point as that of the dianilide from the *trans*-lactonic acid, but a mixture of equal proportions of the two melted at about  $145^\circ$ :

0.0987 gave 0.2496  $CO_2$  and 0.0623  $H_2O$ .  $C = 68.91$ ;  $H = 7.02$ .

$C_{22}H_{26}O_4N_2$  requires  $C = 69.1$ ;  $H = 6.8$  per cent.

The *acetyl* derivative,  $C_5H_{10} > C \begin{matrix} \text{CH(OAc)·CO} \\ \text{CH(CO}_2\text{H)·O} \end{matrix}$ , is readily

formed when the lactonic acid is boiled with acetyl chloride for ten minutes. The residue left on evaporation crystallises from a mixture of benzene and light petroleum, and melts at  $156^\circ$ :

0.0962 gave 0.1971  $CO_2$  and 0.0534  $H_2O$ .  $C = 55.89$ ;  $H = 6.19$ .

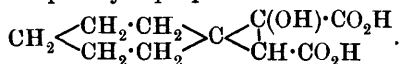
$C_{12}H_{16}O_6$  requires  $C = 56.2$ ;  $H = 6.2$  per cent.

The *silver* salt, prepared in the usual way, is a white, crystalline powder:

0.2424 gave 0.0727 Ag.  $Ag = 29.99$ .

$C_{12}H_{15}O_6Ag$  requires  $Ag = 29.8$  per cent.

*cycloHexane-spiro-cyclopropanol-2: 3-dicarboxylic Acid*,



The best yields of this acid were obtained by hydrolysing the bromo-lactones with boiling 64 per cent. potassium hydroxide solution, the isolation being effected in the manner already described. From 40 grams of the bromo-lactone melting at  $96^\circ$ , only 7.5 grams of the acid (or 27 per cent.) were obtained. On the other hand, the bromo-lactone melting at  $60-70^\circ$  gave a yield of 40 per cent. of the *spiro*-acid under the same experimental conditions. In spite of the poor yield, the acid was always obtained from the bromo-lactone of higher melting point, on account of the fact that this is by far the easiest modification to prepare. The acid separates from water in colourless, pearly plates, which melt at  $217^\circ$ :



0·1928 gave 0·3940 CO<sub>2</sub> and 0·1104 H<sub>2</sub>O. C=55·72; H=6·51.

C<sub>10</sub>H<sub>14</sub>O<sub>5</sub> requires C=56·1; H=6·5 per cent.

0·1525 required 14·25 c.c. N/10-NaOH.

C<sub>10</sub>H<sub>14</sub>O<sub>5</sub> (dibasic) requires 14·25 c.c.

The *silver* salt, prepared in the usual manner, is a white, crystalline powder:

0·2071 gave 0·2102 CO<sub>2</sub> and 0·0503 H<sub>2</sub>O. C=27·69; H=2·71.

0·1888 ,, 0·0946 Ag. Ag=50·11.

C<sub>10</sub>H<sub>12</sub>O<sub>5</sub>Ag<sub>2</sub> requires C=28·0; H=2·8; Ag=50·4 per cent.

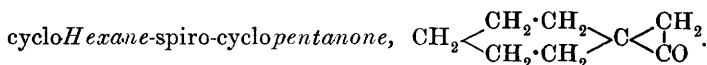
The *anilide*, C<sub>5</sub>H<sub>10</sub>>C  $\begin{matrix} \text{C(OH)·CO·NHPH} \\ \text{CH·CO·NHPH} \end{matrix}$ , is produced by heating

the acid with a slight excess of aniline at 200° for a few minutes. It separates from alcohol in colourless needles, melting at 202°:

0·0833 gave 0·2217 CO<sub>2</sub> and 0·0509 H<sub>2</sub>O. C=72·58; H=6·81.

C<sub>22</sub>H<sub>24</sub>O<sub>3</sub>N<sub>2</sub> requires C=72·5; H=6·6 per cent.

The acid does not react with either acetic anhydride or with acetyl chloride, and can be recovered unchanged after having been boiled with four molecular proportions of phosphorus pentachloride for two hours, and the acid chloride converted into the free acid by means of formic acid. The hydroxy-acid does not show the slightest tendency to be converted into a lactone when heated.



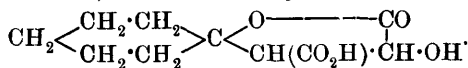
This substance can be prepared in small quantities by the action of concentrated sulphuric acid on the hydroxy*spiro*-acid. The acid, dissolved in five times its weight of sulphuric acid, was heated at 95—100° until the evolution of carbon monoxide had ceased. The product was then poured into six volumes of water, and distilled in a current of steam. The distillate contained a solid substance, melting at 105°, which is not a ketone, and has not yet been investigated. The ketone itself was obtained as an oil when the filtrate from the solid was saturated with salt, but the yield was only about 2 per cent., and the quantity was too small to distil. It was therefore converted into the semicarbazone, which crystallises from alcohol in long, colourless needles, melting and decomposing at 175°:

0·1238 gave 0·2720 CO<sub>2</sub> and 0·0924 H<sub>2</sub>O. C=59·89; H=8·31.

0·0882 ,, 18·4 c.c. N<sub>2</sub> at 16° and 728 mm. N=23·2.

C<sub>9</sub>H<sub>15</sub>ON<sub>3</sub> requires C=59·7; H=8·3; N=23·2 per cent.

*The Lactonic Acid of  $\alpha$ -Hydroxy- $\alpha'$ -cyclohexan-1-olsuccinic Acid,*



Five grams of the hydroxyspiro-acid, melting at  $217^\circ$ , were heated with 5 grams of water in a sealed tube at  $240^\circ$  for half an hour. The aqueous solution of the very readily soluble fission product was then made alkaline with 4/*N*-sodium hydroxide solution, and a further 5 c.c. of the same alkali were added. The solution was evaporated on the water-bath until a crust of sodium salt formed, when the solution was allowed to cool and crystallise. The pasty mass was then spread on porous porcelain, and the crystals, after being treated with the minimum quantity of concentrated hydrochloric acid, were extracted by ether. After recrystallisation from chloroform, the lactonic acid was obtained in hard, cubical prisms, which melted at  $131^\circ$ . It is very readily soluble in water and in all organic solvents excepting light petroleum and chloroform:

0.0928 gave 0.1902  $\text{CO}_2$  and 0.0530  $\text{H}_2\text{O}$ .  $\text{C}=55.87$ ;  $\text{H}=6.41$ .

$\text{C}_{10}\text{H}_{14}\text{O}_5$  requires  $\text{C}=56.1$ ;  $\text{H}=6.5$  per cent.

The *disodium* salt separates when the lactonic acid is dissolved in three molecular proportions of 4/*N*-sodium hydroxide solution, and can be purified by washing with alcohol:

0.1502 gave 0.0782  $\text{Na}_2\text{SO}_4$ .  $\text{Na}=16.89$ .

$\text{C}_{10}\text{H}_{14}\text{O}_6\text{Na}_2$  requires  $\text{Na}=16.7$  per cent.

The *disilver* salt is a crystalline powder formed by the action of silver nitrate solution on an aqueous solution of the sodium salt:

0.1241 gave 0.0604  $\text{Ag}$ .  $\text{Ag}=48.69$ .

$\text{C}_{10}\text{H}_{14}\text{O}_6\text{Ag}_2$  requires  $\text{Ag}=48.4$  per cent.

The monobasic silver is apparently too soluble to be precipitated in the ordinary manner, but a characteristic monobasic *aniline* salt is formed by the interaction of the two components in benzene solution. It melts at  $123^\circ$ :

0.1307 gave 0.2986  $\text{CO}_2$  and 0.0829  $\text{H}_2\text{O}$ .  $\text{C}=62.29$ ;  $\text{H}=7.10$ .

$\text{C}_{16}\text{H}_{21}\text{O}_5\text{N}$  requires  $\text{C}=62.5$ ;  $\text{H}=6.8$  per cent.

The liquid absorbed by the porous porcelain in the foregoing experiment was found to contain a more readily soluble sodium salt, which was extracted by boiling with water. The aqueous solution was evaporated to dryness, treated with concentrated hydrochloric acid, and extracted by ether. The gummy, ethereal

residue gave a solid substance on being rubbed with chloroform, and this was proved, by direct comparison, to be identical with the lactonic acid of  $\alpha\alpha'$ -dihydroxycyclohexane-1:1-diacetic acid, melting at 168°.

THE IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,  
SOUTH KENSINGTON, S.W.

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