PRESIDENTIAL ADDRESS.

Delivered at the ANNUAL GENERAL MEETING, MARCH 26TH, 1931.

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PART I. A RETROSPECT.   PART II. THE OUTCOME OF SOME RECENT
RESEARCH WORK.

IN my address to the Society last March I had occasion to refer to
the fact that the Fellows had elected me to a further term of Office,
but it was agreed that I should be allowed to place my resignation
in the hands of the Council at the end of the first year of the new
term.   The Council decided to nominate me for a second period
because it considered that, in view of the decision it had taken to
support the scheme for a Central Building, continuity of policy was
essential until the time should be reached when the scheme had
definitely assumed crystalline form.   As will be explained later in
the address, that state may be said to have been reached with the
formation of the Association of Technical and Scientific Institutions,
and the need which led to my re-appointment as President no
longer exists.   I have therefore placed my resignation in the hands
of the Council, which has accepted it.   Nevertheless, I am in the
curious position—unique as far as this Society is concerned—of
having to deliver a Presidential Address for the third year in
succession.

In his Presidential Address delivered in 1916, Dr. Scott remarks
that during the earlier years of the Society's existence it was thought
sufficient for the President to read extracts from the Report of
Council, sometimes adding comments on the Balance Sheet, but
as time went on more and more was expected from the occupant
of the Chair until now, at each Anniversary Meeting, he is expected
to deliver a formal address on some subject closely connected with
the life of the Society as " a body politic and corporate," or on
some subject of more purely scientific interest.

It is my intention this afternoon to do both of those things, and
to divide my address into two parts.   The first of these, which I
propose to call " A Retrospect," will contain comments on the
progress (or otherwise) of the Society during the ten years in which
I have been in intimate touch with its work, first as Treasurer and
then as President.   The second part, which I propose to call " The
Outcome of some Recent Research Work," will contain comments
on the results obtained in the Organic Chemistry Laboratories of
the Imperial College on two subjects which may be regarded as
of fundamental importance in the development of Organic Chemistry

and have now reached a stage approaching finality. I refer to the " Chemistry of the Glutaconic Acids," a research which I started in Manchester 30 years ago, and to the " Modified Strain Theory of Carbon Ring Formation " with which my name and that of Professor Ingold have been associated since we published the first paper on the subject in 1914.

As, however, time is limited, and many of us have to go to the function this evening, I propose to read only the first part of the address, leaving those who are interested to read the second part at their leisure.

PART I. A RETROSPECT.
" Chemistry House."

A full description of the reasons which led to the elaboration of a scheme for providing a Central Building to house certain Societies connected with Mining, Metallurgy, and Chemistry was given in my address to the Society last March. Details of the scheme were also given, and of the floor space which each of the " Constituent Bodies " required. During the year that has elapsed considerable progress has been made in the development of the scheme. The original intention, outlined in the last report, of creating a Trust by which the funds collected could be administered was, after careful thought, abandoned as unworkable, and ultimately the Board of Trade agreed to register a Company (Limited by Guarantee and not having a share capital) under Section 19 of the " Companies Act 1929." The Articles of Association of the Company provide for the election of a Council of Management composed of not less than 25 and not more than 30 members, of whom 10 shall be Members elected by the Members of the Association. The remaining 15 or 20 are elected by the Councils of the " Constituent Bodies " and are known as " nominated " Members. The nominated members are appointed for so long as the nominating Councils may determine, but of the elected members half retire annually (after 1935) and are not eligible for re-election until one year has elapsed thereafter.

The memorandum and Articles of Association, which were drawn up on the lines of those of the National Trust, are very comprehensive and the memorandum contains no fewer than 17 clauses defining the objects of the Association. Of these clauses, B and C are probably the most important and may be quoted here.

Clause B. To co-ordinate the activities, discussions and researches of scientific and technical societies and institutions dealing with mining, metallurgy, chemistry, fuel, petroleum, and rubber,

and to provide facilities therefor, including a central Library containing scientific, technical, and commercial literature dealing, amongst other things, with the sciences and industries named and to provide conference rooms and lecture halls.

Clause C. To establish in London or elsewhere a central building or buildings for the use and convenience of such Societies and Institutions and the members thereof and to lease portions of any such Central building or buildings to any such Society or Institution and to establish, equip, and maintain therein for the use of such Societies and Institutions, and the members thereof, Libraries, Reading Rooms, Museums, Laboratories, Council and Meeting Rooms, Offices, and other conveniences, and facilities for such co-operation and co-ordination as aforesaid.

Other clauses deal with the power to hold real property and in fact to do all such things as are usually granted in a Royal Charter. In fact, registration under this section of the Companies Act is practically equivalent to the possession of a Royal Charter. Membership of the Association, which is for life, can be obtained subject to the consent of the Council on payment of £20. This sum can, if desired, be spread over four years—membership being conferred on payment of the first instalment.

The present position is, therefore, that an Association has been founded and has been registered by the Board of Trade which will serve as means for collecting funds, erecting the new building and administering it when erected. All funds received by the Association, either by way of donation or membership fee, will be devoted to the purposes of the Association. The Association may make no profits, neither may it give any bonus or distribution of money to its members. The constituent Societies will pay rents up to an amount equal to that which they now pay—our own Society by reason of the transference of the Library being allowed an agreed space—equivalent to its present accommodation—free of rent. The remainder of the building, that is the area not required by the " Constituent Bodies," will be let to " Tenant " Societies, and it is estimated that the sum received by way of rent in this manner will more than cover the cost of upkeep. Since the Association may make no profits, it follows that any excess of income over expenditure will lead to a corresponding reduction in the rents paid by the " Constituent Bodies." Evidently the first thing that our Society will have to do when definite plans have been drawn up for the new building will be to have an agreement drafted defining the conditions under which our Library will be transferred to the new building. These conditions will require the most careful attention of the Council in conjunction with the Society's

solicitors. The present position of affairs is that after careful consideration a proposal to house the Association in the building which has just been erected by Anglo-Properties, Ltd., adjacent to the Imperial Chemical Industries building at Millbank has been definitely rejected as being unsuitable, and recourse has been had to the site originally proposed, which is adjacent to Abbey House in Westminster, being, in fact, Nos. 10—18, Victoria-street.

The lease of this site can be purchased from the Ecclesiastical Commissioners for a term of 99 years, but in order to do this and to buy the sub-leases, etc., a sum of £100,000, in cash, must be paid by June 24th next, when the option the Association possesses expires. Every effort will be made to raise this sum; but conditions are adverse, as the country is passing through a period of acute depression. As I stated in my last address, the appeal to the Treasury failed, and, more recently, a similar appeal made to the Pilgrim Trust has not yet met with any response.

Our Publications.

When I became Treasurer in 1922, the Society was passing through a difficult financial phase. The raising of the subscription from £2 to £3 in 1921, consequent on an adverse balance of £1,310 in 1920, led to a credit balance of £481 for that year. But it must be remembered that the increase in the subscription provided an increased income of no less than £3,400 for that year, and that the relatively small balance was due to the increase of £1,648 in the cost of our publications. During 1922 the cost of publications increased by £464, leading to an adverse balance of £136, and then, although the cost of publications increased during the next year by £74 only, the astonishing debit balance of £1,628 was recorded for 1923.

It is desirable to examine the cause of this occurrence, because up to that time the financial stability of the Society had been determined mainly by fluctuations in the cost of the main item of expenditure, namely, its publications, and it was rather startling to realise that although this item remained constant the financial situation could be so gravely affected.

Fortunately, the explanation was a simple one, because during the year in question it had been decided by the Council to transfer the life composition fees to Capital and not to continue as hitherto to account them as Income—a change which accounted for the loss of £448 as income for that year as compared with the preceding. In addition to this there was an increase in expenditure of nearly £1,000 due mainly to standardisation of salaries, that is, merging of the bonus. Nevertheless the financial position shown

by the balance sheet of 1923 illustrates the point I made at the time and which I wish still further to emphasize, namely, that the Society must increase its capitalised funds so as to be able to meet fluctuations such as the year in question showed. As a means to this end the Council decided at the time to establish a Publication Fund, and during the next few years this amounted to some £10,000, approximately one-half of which was due to the Pedler bequest. This action has undoubtedly been helpful but it is not enough. The Society lives too much from hand to mouth and there is not sufficient margin for contingencies. It should take steps at once to build up a reserve fund which can be drawn upon when occasion demands.

The income of the Society is derived from two chief sources, namely : (a) the contributions of Fellows ; (b) the sales of public-ations. These two items accounted for £15,500 of last year's income, and any serious alteration in the amount received in these ways would have a marked effect on the Society's capacity for useful work. It is a remarkable fact that in 1921 the amount received under (a) was only some £300 less than that received last year, whereas the amount obtained through sales of publications was no less than £2,900 more in 1930 than in 1921. This is a healthy sign and the Society is to be congratulated on having nearly doubled its receipts from sales during the ten-year period. Moreover, this item of income is likely to possess considerable stability and will tend to increase rather than diminish, whereas the same remark cannot be made in regard to the income received from the contributions of Fellows, which may fluctuate within wide limits and is quite beyond control. A period of bad financial depression such as we are now passing through may lead to a large number of resignations and these may easily affect the income of the Society to an extent involving some £1,000 or £1,500—a serious matter under our present mode of existence. A reserve fund is urgently needed to meet such conditions as these.

It is worthy of remark that since 1921 the membership has remained almost constant—fluctuating between 3,912 in 1921 and 4,093 in 1927 ; at the present moment it is 3,840. In effect this means that the number of new Fellows elected is approximately equal to the number of those who cease to be Fellows either through death, resignation, or removal for non-payment of contributions. Actually there is no cause for disquietude here, because it is evident that the Society by this process of replacement obtains a sufficiency of youthful Fellows among its members to ensure its continued and active existence, and it may well be that a number round about 3,900 represents the maximum number of persons to whom

the work of the Society appeals. Indeed, if this were the case it would roughly correspond with the curve representing the output of chemists from the Honours schools of our Universities, which reached a peak some few years after the war and then, after a drop, flattened out to something of the order of a straight line. In this respect the following figures are therefore significant :

Increase.	No. of Fellows.	Year.	
420	{ 2785	1905	
	{ 3205	1914	10 years
714	{ 3198	1916	
	{ 3912	1921	6 years
Decrease.			
72	{ 3912	1921	
	{ 3840	1930	10 years

If this assumption is right it means that we cannot rely on an increase of income from the contributions of our Fellows in future years and that we must bear this in mind when considering the cost of our publications and any increase of expenditure that may be entailed thereby. The remarkable increase of income obtained through the sales of publications, to which reference has already been made, has rather masked the fact that whereas during the past ten years the cost of our publications has increased by £1,300 the income derived from the contributions of Fellows has remained almost constant.

This increase of £1,300 has occurred despite the drastic economy of space in our Journal and Abstracts which had to be effected after the Society had experienced the adverse balance of £1,628 in 1923. The adverse balance of £1,310 in 1920 (which would have been £2,310 had not the Messel bequest of £1,000 been appropriated as income) had led to an increase in the subscription and it was felt that any further increase might lead to so many resignations as to defeat the object desired. The chief means, therefore, of effecting economy lay in decreasing the cost of the chief items of expenditure, namely, the Journal and Abstracts, and this was done to the extent of £797 during the ensuing year—the size of the Journal being diminished from 3,258 pages to 2,698 pages. Nevertheless, although the same measure of restriction was exercised by the Publications Committee, the cost of publications thereafter steadily increased, and during the next seven years (1924—1930) advanced by £1,566. This increase was shared fairly equally by the Journal and the Abstracts for the first four years (1924—1927) and then for the next three years (1928—1930) the astonishing fact emerges that, whereas the cost of the Journal during the period *decreased* by £597, that of the Abstracts *increased* by £1,127. In

consequence the cost of our publications for 1930 is £2,955 more than for 1920.

Year.	Journal.	Increase.	Abstracts.	Increase.
1924	5,140	—	5,660	—
1925	5,363	223	6,055	395
1926	5,769	406	6,124	69
1927	5,792	23	6,045	79 (decrease)
		Decrease.		Increase.
1927	5,792	—	6,045	—
1928	5,657	135	6,429	384
1929	5,297	360	6,513	84
1930	5,195	102	7,172	659

These facts provide some food for thought. It will be generally agreed that the publication of new knowledge in the Journal must be the first care of the Society. As matters now stand, the original papers published in the Journal are sometimes curtailed to such an extent that their value as an aid to practical information is seriously affected. Organic chemists, for example, are continually finding that the experimental details given by authors are not sufficiently definite to enable the work to be repeated and, in consequence, much recrimination occurs, some of which has to be printed. Clearly we are spending more than we can afford on the Abstracts and are thereby deflecting money from the Journal. What is the remedy ? There are, in my opinion, three :

In the first place it must be remembered that no fewer than three periodicals appear covering practically the same field of Chemical Abstracts. They are :—

(1) Our own Abstracts, A and B.

(2) Chemical Abstracts, published by the American Chemical Society.

(3) The *Zentralblatt*, published by the Verlag Chemie.

The difficulty of language will probably prevent the *Zentralblatt* from being included in any scheme for some time to come, but what prevents a fusion of the American and the English Abstracts ? The possibilities have been explored and several efforts have been made on our part to enter into some form of collaboration, but hitherto the general idea has not found acceptance among those controlling American chemical literature. Nevertheless, private conversations have revealed the fact that there is a fairly representative body of opinion in the States in favour of entering into some kind of agreement by which this waste of money and energy would in some way be diminished. We must do everything in our power to strengthen this point of view.

There is, it seems to me, one way in which a commencement

could be made in a scheme of co-operation, and that is in connexion with the Decennial Index. The system at present in vogue is for the American Chemical Society to issue its index every ten years and for our Bureau of Abstracts to do the same. But the ten-year periods do not coincide and the result is to have a general index in the English language every five years. But the American Index is only of use to those who possess the American Abstracts, and our Index to those who have our Abstracts, since each country only refers to its own literature in its index. If it could be arranged that a joint index were published every five years, and by a joint index I mean one which would give references to both sets of abstracts, thus,

Malonic Acid Am. 31, 2141; Br. (A) 31, 1739

it seems to me that not only should we have by this means a thoroughly comprehensive and up-to-date Quinquennial Index, but the sale of this throughout the United Kingdom and the States would more than repay the cost. When it is remembered that the Author and Subject Index of the American Chemical Society for the ten-year period 1917—1926 comprises five volumes containing 6,587 pages and that two of those years are war years, it will be readily understood that any set-off against the cost of such a production ought to be welcomed. As a matter of fact the Subject Index alone for 1930, which is just to hand, contains no less than 1,370 pages. In these days of card-indexing the preparation of a joint index such as I have outlined should not present any insuperable difficulties.

There is also the possibility of acting as the German Chemical Society has acted, that is, by making a separate charge for the Abstracts, but any such change must be fraught with grave possibilities of danger because it is not certain how many purchasers there would be for the Abstracts alone, and a serious drop in income might be experienced if any such scheme were adopted. Indeed the heavily increased charge for the *Zentralblatt* which has had to be made this year by the German Chemical Society seems to suggest that something of the kind has occurred in Germany.

Another alternative and one which can be applied at once is so to arrange matters that the cost of the Abstracts is spread over a wider field than is at present the case. The burden of publication now falls almost exclusively on the Chemical Society and the Society of Chemical Industry, and although it is probably correct to assume that the Journals of these Societies are of interest chiefly to their members, such an assumption cannot be made in the case of the Abstracts, which ought to be of interest to all chemists, and

ought to be supported by all chemists.   There are, roughly speaking, some 4,000 chemists in this country who are not members of either the Chemical Society or the Society of Chemical Industry and therefore do nothing to help in furthering the publication of new knowledge.   The greater proportion of these 4,000 belong to other institutions which do not help to bear the cost arising from this essential service.   Such institutions would doubtless view with concern any possibility of a curtailment of chemical publication owing to lack of funds and would be ready and willing to make such contributions as might be necessary to prevent such an occurrence.   The method of doing this by means of an annual grant is open to objection, because conditions may vary from year to year. The most satisfactory method would be one having a " pro rata " basis, and it is suggested that this could be effected by such institutions as may be concerned paying to the Bureau of Abstracts a sum per head of all those of its members who do not belong either to the Chemical Society or to the Society of Chemical Industry.   It is thus open to the relevant institutions to say to their members, The subscription is £2 provided you are a member of either the Chemical Society or the Society of Chemical Industry; if, however, you are not a member of either of those bodies the subscription is £2 + X, because you are doing nothing to share the cost of publication.   X would then be handed over to the Bureau of Abstracts and every member of the institutions concerned would be entitled to receive a copy of the Abstracts as issued, and the institutions could have the right to appoint a representative to serve on the Bureau of Abstracts.   Personally I do not think this scheme to be as fantastic as, I admit, it appears to be at first sight, and I recommend it for consideration by the Joint Committee which is now sitting.

There is still another and fairly obvious way in which our difficulties could be minimised, and that is by an increase in the Government Grant which is obtained through the Royal Society.   For some years past the Government has allotted a sum of £2,500 to the Royal Society for general publication purposes and this has been increased by a donation of £1,000 from Imperial Chemical Industries.   The Society has received generous grants from this fund : last year £350 was received, and a substantial sum has been promised towards the cost of the Decennial Index.   It has also received a very welcome donation of £100 from Imperial Chemical Industries, so it has little cause to complain in respect of its treatment in this connexion.

The Dyestuffs Act.

In my address last year I pointed out the intimate connexion between a strong and stable Organic Chemical Industry and the continuance of vigorous schools of Organic Research in our Universities and University Institutions, directing particular attention to the fact that without such schools of Research recruitment of the right type of men into the Industry could not be effected, and that any cause leading to the weakening of any one branch of the Industry, such as the dye-making industry, would find repercussion in other branches, such as those dealing with synthetic drugs and fine chemicals generally, upon which the progress of modern biochemistry depends. The Government has prolonged the life of the Act for a further 12 months, and all that I have to do is to call attention to the remarks I made on the last occasion and strongly to emphasise them.

Before concluding, I have to unveil a portrait of our first President, Thomas Graham, which has been subscribed for by twenty Fellows and painted by Mr. H. A. Budd, R.O.I. The portrait has been painted from a lithograph by W. Bosley which was made from a daguerreotype by Claudet. The original lithograph is in the possession of the Royal Society. The picture shows Graham as he was shortly after his first Presidency in 1841—1843, when he was just under 40 years of age. There is a portrait of Graham by G. F. Watts, R.A., in the apartments of the Royal Society. It shows him as a much older man and was, Mr. Budd thinks, painted from the same daguerreotype as that used for the photograph in our Meeting Room.

PART II. THE OUTCOME OF SOME RECENT RESEARCH WORK.

(a) The Chemistry of the Glutaconic Acids.

The first paper on this subject was published thirty years ago and since then 22 communications have appeared in the Journal dealing with various aspects of the problem. One of the chief questions that had to be answered was : Why do those glutaconic acids which contain a hydrogen atom possessing potential three-carbon mobility differ so widely in their properties from those in which this type of hydrogen atom is absent and also from those in which its movement is prevented by the saturation of the double bonds. The three types may be presented in these ways : (a) The true glutaconic acid type (I), (b) the glutaconic acids in which

the " mobile " hydrogen atom is replaced (II), and (c) the saturated type.

$$CO_2H \cdot CH \colon CH \cdot CH_2 \cdot CO_2H \qquad CO_2H \cdot CH \colon CH \cdot CR_2 \cdot CO_2H$$
$$\text{(I.)} \qquad \text{(Glutaconic acid types)} \qquad \text{(II.)}$$

$$CO_2H \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H$$
$$\text{(III.)} \quad \text{(Glutaric acid type)}$$
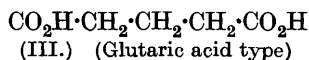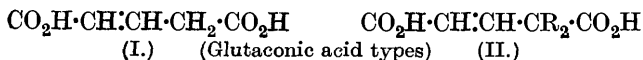
The difference in behaviour between the two unsaturated types (I) and (II) is very marked, for whereas compounds of type (II) possess the following chief properties,

(1) the existence of marked *cis*- and *trans*-forms,

(2) the existence of an anhydride of the *cis*- but not of the *trans*-form,

(3) the occurrence of greater stability in the *trans*- than in the *cis*-modification,

the compounds of type (I) show none of the properties but are characterised as under :

(1) The existence of two forms, one markedly more stable than the other.

(2) The ready manner in which both forms pass into the same anhydride (hydroxy-anhydride).

(3) The anhydride yields the stable acid on hydration under the usual conditions, but can be made to yield the labile acid under special conditions.

It seemed that these differences could be accounted for only by some fundamental difference in the structures of the two types and in order to express this and also to account for the fact that numerous experiments had shown that the α- and γ-positions in glutaconic acid were of equal value the hypothesis was put forward that, whereas the labile modifications of those acids possessed the usual unsaturated structure (I), the stable forms could best be expressed by a symmetrical formula (IV)

$$\text{(IV.)} \qquad CO_2H \cdot \overset{\gamma}{C}H \cdot \overset{\beta}{C}H \cdot \overset{\alpha}{C}H \cdot CO_2H$$
$$\text{(H)}$$
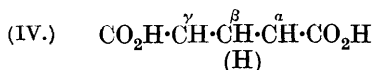
in which the position of the " mobile " hydrogen was left open. This was called the " normal " form.

The correctness of this hypothesis was disputed by Feist, who regarded the facts as being capable of explanation on the lines of usual stereochemical theory. It is, of course, evident that any experimental proof of the identity of the α- and the γ-position falls to the ground if it is assumed that one or other of the two forms

(V) and (VI) is stable and that the labile form passes into the stable form at the moment of formation, but on this point Feist's

(V.) $CO_2H\cdot CR\vdots CH\cdot CH_2\cdot CO_2H$ $CO_2H\cdot CH\vdots CH\cdot CHR\cdot CO_2H$ (VI.)

experimental evidence was not very convincing because on ozonisation he always obtained from simple individuals products derived from both forms. The first striking piece of evidence in favour of Feist's view was found when he was successful in resolving the " cyclic " glutaconic acid (VII) and thus showed that it must

$$CH_3\cdot CH\!\!<\!\!\begin{matrix}C\cdot CO_2H\\C\cdot CO_2H\end{matrix} \qquad CH_3\cdot C\!\!<\!\!\begin{matrix}C\cdot CO_2H\\CH\cdot CO_2H\end{matrix} \qquad CH_3\cdot C(H)\!\!<\!\!\begin{matrix}C\cdot CO_2H\\C\cdot CO_2H\end{matrix}$$
$$\text{(IX.)} \qquad\qquad\qquad \text{(VII.)} \qquad\qquad\qquad \text{(VIII.)}$$

have an asymmetric structure and cannot have the " normal " formula (VIII) unless it can be assumed that the hydrogen atom in this form takes up a position leading to asymmetry.

Curiously enough, all attempts made by either Feist or ourselves to resolve any of the open-chain glutaconic acids were unsuccessful and it is only within the last few weeks that a former student of mine (J. Packer), working in New Zealand with T. H. McCombs, has succeeded in resolving the " normal " form of $\alpha\gamma$-dimethylglutaconic acid (X), which must therefore have an asymmetric

$$CO_2H\cdot CMe\vdots CH\cdot CHMe\cdot CO_2H \qquad CO_2H\cdot CMe\cdot CH\cdot CMe\cdot CO_2H$$
$$\text{(X.)} \qquad\qquad\qquad\qquad\qquad\qquad \text{(H)} \quad \text{(XI.)}$$

structure. The normal form cannot, unless the assumption mentioned above is made, have the normal structure (XI).

Previous to this (in 1926) Packer and I had tried to explain the abnormal reactions of the " mobile " glutaconic acids on the assumption that the normal form did not exist and we then discovered (J., 1926, 1199) the remarkable fact that, although the two hydrogen marked a and b in formula XII are ostensibly of equal value, they are not so in relation to the tautomeric change which leads to formula XIII, because, if hydrogen (a)* takes part in the

$$\text{(XII.)} \quad CO_2H\cdot CH\vdots CH\cdot \overset{\overset{\textstyle H\ (a)}{\displaystyle|}}{\underset{\underset{\textstyle H\ (b)}{\displaystyle|}}{C}}\cdot CO_2H \qquad CO_2H\cdot \overset{\overset{\textstyle H}{\displaystyle|}}{\underset{\underset{\textstyle H}{\displaystyle|}}{C}}\cdot CH\vdots CH\cdot CO_2H \quad \text{(XIII.)}$$

change, an acid of the same configuration is produced, whereas, if hydrogen (b) takes part, a change from the cis- to the trans-form

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* These hydrogen atoms are labelled (a) and (b) for the sake of clearness. It is evident that, if one of them were replaced by the group CH_3 or other group, the same change would be possible owing to the relative positions of the remaining hydrogen atom and the carboxyl group at the time the change is effected.

occurs.   This can be readily seen in the models or by means of the drawing given in the communication cited, and can be expressed on paper as follows :

$$(a) \quad H-\overset{\overset{\displaystyle CO_2H-C-H}{|\ CO_2H}}{\underset{\underset{\displaystyle (b)}{H}}{C}}\overset{\|}{-}C-H$$

$$\underset{cis\text{-}}{}$$

$$CO_2H-\overset{\overset{\displaystyle H\ (a)}{|}}{\underset{\underset{\displaystyle H\ (b)}{C}}{C}}\overset{}{-}C-H$$

$$\underset{cis\text{-}}{}$$

$$(b) \quad H-\overset{\overset{\displaystyle CO_2H-C-H}{|\ (a)\ H}}{\underset{\underset{\displaystyle CO_2H}{C}}{C}}\overset{\|}{-}C-H$$

$$\underset{cis\text{-}}{}$$

$$CO_2H-\overset{\overset{\displaystyle H\ (b)}{|}}{\underset{\underset{\displaystyle CO_2H}{C}}{C}}\overset{}{-}C-H$$

$$\underset{trans\text{-}}{}$$

In other words, if one accepts the modern view that tautomeric change is due to ionisation (a short history of this view is given as an Appendix on page 1015), then it follows that the *cis*- and the *trans*-form of a "mobile" glutaconic acid have the same ion and the rapid interchange between the two forms can be readily understood.   In fact the occurrence of the abnormal reactions enumerated on page 1012 receives adequate explanation.   It would appear, therefore, that the "normal" form has no existence as such but that it may occur as the common ion.

The view that the ion is symmetrical although the acid may contain no plane of symmetry is supported by the experiment of J. Packer already referred to, by which it has been found that the *l*-form of *trans*-$\alpha\gamma$-dimethylglutaconic acid undergoes racemisation with great ease.

Racemisation of *l-trans*-$\alpha\gamma$-Dimethylglutaconic Acid.

Solvent.	Temperature.	k (hr.$^{-1}$).	Half-change period.
Water	100°	0·0388	17·8 hrs.
N-HCl	101·5	0·0325	21·3 hrs.
5N-HCl	101	0·128	5·4 hrs.
N-NaOH..................	101·5	1·70	24·5 mins.
Acetone	56·5	*ca.* 0·0088	*ca.* 80 hrs.

The occurrence of a common ion of this character must happen in quite a number of other cases, as, for example, in the relationship between itaconic (XV), citraconic (XVI), and mesaconic (XVII) acids, in which the common ion is (XVIII).

$$\underset{(XV.)}{\overset{\displaystyle CH_2=CH-CO_2H}{CH_2-CO_2H}} \qquad \underset{(XVI.)}{\overset{\displaystyle CH_3-C-CO_2H}{CH\cdot CO_2H}} \qquad \underset{(XVII.)}{\overset{\displaystyle CO_2H-C-CH_3}{CH\cdot CO_2H}}$$

A normal symmetrical glutaconic ion might be represented in some such way as (XXII).

$$\left[CO_2H : \overset{R}{\underset{\underset{2\ominus}{\curvearrowleft}}{C}} : \overset{R}{\underset{}{C}} : \overset{R}{\underset{\curvearrowright}{C}} : CO_2H \right]^{\ominus} \qquad \left[H : \overset{H}{\underset{\underset{(2\ominus)}{\searrow}}{C}} : \overset{CO_2H}{\underset{}{C}} \ \vdots \ \overset{CO_2H}{\underset{\curvearrowleft}{C}} : H \right]^{\ominus}$$

(XXII.)   (XVIII.)

The oxygen atoms might co-operate in forming some stable association of electrons capable of maintaining a symmetrical arrangement in the three-carbon chain. The common ion from citraconic acid and its isomerides could be similarly represented as (XVIII).

The ready manner in which equilibrium mixtures of all three acids are formed from any one of them is strong evidence in favour of this view (compare Linstead, in the press). Finally there remain the three forms of the cyclic ester (XIX, XX, XXI) which Goss, Ingold, and I obtained in the course of our investigation on the chemistry of glutaconic acid.

$$CH_3 \cdot C(H) \overset{C \cdot CO_2Et}{\underset{C \cdot CO_2Et}{\big\langle} \big|} \qquad CH_3 \cdot C \overset{C \cdot CO_2Et}{\underset{CH \cdot CO_2Et}{\big\langle}} \qquad CH_3 \cdot C \overset{C \cdot CO_2Et}{\underset{C \colon C \overset{OH}{\underset{OEt}{\big\langle}}}{\big\langle}}$$

(XIX.) Normal.   (XX.) Labile.   (XXI.) Enol.
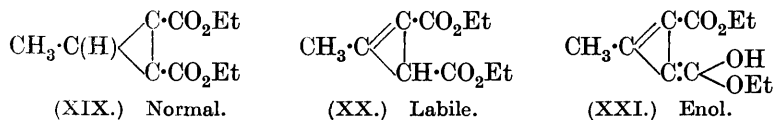
In this case the occurrence of stereoisomeric forms is not possible and the question arises, What are the structures of the two forms (XIX) and (XX)? It is still an open one, but it is evident that the work on this substance must be repeated and interpreted in the light of the large amount of data obtained recently by Kon in connexion with the mobility of the three-carbon system.

The only two facts which remain, therefore, to prevent a complete acceptance of the view that the glutaconic acids are examples of *cis-trans*-stereoisomerism, modified by the special conditions attaching to three-carbon tautomerism, are (1) the existence of the ester (XIX) and (2) the occurrence of 1 : 3-addition to the glutaconic system. The latter can doubtless be explained on the assumption that addition occurs to the " normal " ion, but the former cannot be explained on those lines.

APPENDIX.

(a) *Tautomeric Change and Electrolytic Dissociation.*

It was inevitable that some connexion should be sought between the phenomena of tautomeric change and electrolytic dissociation as soon as the great discovery of Arrhenius had received general acceptance and it seems desirable to show briefly the manner in which expression was given to those early views. It seems that

Goldschmidt in 1890 was the first to do this (*Ber.*, 1890, **23**, 257), for he says " Bei Reactionen tautomerer Verbindungen, welche sich unter dem Einfluss von Electrolyten vollziehen, werden die Atom-verschiebungen durch die freien Ionen veranlasst." Six years later four of the leading investigators in this field noted a connexion between the ease of isomerisation of tautomeric substances in solution and the dissociating power of the solvent. Claisen (*Annalen*, 1896, **291**, 86) noted that the change in acetyldibenzoylmethane was rapid in 50% aqueous alcohol, slow in absolute alcohol and in acetone, and inappreciable in benzene. In the same year W. Wislicenus (*ibid.*, p. 161) and Brühl (*ibid.*, p. 142, footnote) made the observations on which they were afterwards to base their theoretical views and commented on the apparent connexion between dissociation and tautomeric change. Finally, Knorr (*Annalen*, 1896, **293**, 70), from his investigations on ethyl dibenzoyl-succinate, noticed that the reversion of the unstable enol (α-) form of the ester occurred spontaneously in the liquid substance itself, and in absolute or dilute alcoholic solution, but not to any perceptible extent in solutions in benzene or ether. From this and from his investigations on antipyrine (*ibid.*, p. 1) he was led to the view that dissociation was the first step in the tautomeric process, and that after the separation of the ions had occurred the change in the mobile bonds in the anion became possible, being " unhindered by the hydrogen atom, now separated as kation " (*loc. cit.*, p. 38).

In his monograph " Ueber die Tautomerie " (1898) W. Wislicenus (Ahrens Sammlung, 1898, **2**, 230) foreshadows modern theory in such a remarkable way that his conclusions may perhaps be quoted at some length. " One cannot pass over these phenomena without coming to the conclusion that the interconversion of the forms is dependent on dissociation . . . dissociation is, therefore, to be assumed in these substances (certain keto-enol tautomerides) as a setting free of the mobile hydrogen atom—we may say at once as kation—but occurring only in a small number of the molecules. In the anion the movement of the bonds can occur more readily as a transport of a hydrogen atom is no longer necessary. The position of the bonds is changed as free valency in the molecule, and it is by this free valency that the reunion of the hydrogen to the anion can occur. On the attainment of a state of equilibrium the opposed reactions come into balance. The slowness of the reaction, the proportionately long time that elapses before the attainment of the state of equilibrium, is explained by the fact that in weak acids, such as are dealt with in this type of work, the dissociation in organic solvents is very small. Whether it is quite right directly to claim electrolytic dissociation, perhaps only

exhaustive quantitative measurements can show. It is possible that it is only a weak kind (abgeschwächte Art) of dissociation that occurs here, a loosening of the hydrogen atom to a definite degree. . . ."

Wislicenus also suggests that the considerably increased velocity of the change in aqueous solutions of sodium salts (for example, that of formylphenylacetic ester) is due to the greater facility with which the latter dissociates.

Support for these views came from the work of Brühl (*Ber.*, 1899, **32**, 2326), who studied the velocities of the keto-enol change *inter alia* in Claisen's ethyl mesityloxide oxalate. The change enol → keto took place most readily in alcoholic solution, less readily in carbon disulphide, α-bromonaphthalene, and benzene, and hardly at all in chloroform. Brühl suggested that the change was due to ionic dissociation of the enol, followed by reassociation of the ions in the keto-form, and further drew attention to the fact that the change was most readily effected in solvents of high dielectric constant. In another paper, dealing with the rôle of the medium in phenomena occurring in solution, Brühl (*Z. physikal. Chem.*, 1899, **30**, 35) pointed out that the connexion between the dissociating and the tautomerising power of a solvent would not necessarily be the same for all substances.

Similar ideas were being developed in England by Lapworth and Lowry. In 1898 Lapworth (J., 1898, **73**, 445) drew attention to the connexion between the apparently dissimilar reactions of tautomeric change and scission :

$$\underset{\underset{\text{M}}{|}}{\text{R}\alpha}\text{—R}\beta\text{=}\text{R}\gamma \;\rightleftharpoons\; \text{R}\alpha\text{=}\text{R}\beta\text{—}\underset{\underset{\text{M}}{|}}{\text{R}\gamma} \qquad . \quad . \quad . \quad (1)$$

and

$$\underset{\underset{\text{M}}{|}}{\text{R}\alpha}\text{—R}\beta\text{=}\text{R}\gamma \;\rightleftharpoons\; \text{R}\alpha\text{=}\text{R}\beta + \text{R}\gamma\text{M} \quad . \quad . \quad . \quad (2)$$
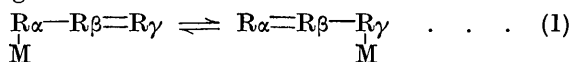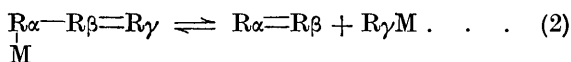
and discussing the general phenomenon of tautomerism wrote, " . . . It is not necessary . . . to imagine that the group M [in (1) above] ever becomes free, but rather that it is always under the influence of the attraction of Rα or Rγ, and possibly at the same instant of both simultaneously; thus the lability of the molecule may be imagined to depend on a species of dissociation. . . ." Three years later (J., 1901, **79**, 1265) this dissociation was compared to the dissociation of weak electrolytes and the suggestion was made that the majority of changes in organic compounds could most probably be assigned to electrolytic dissociation, often doubtless in extremely minute amount.

From a study of the mutarotation of nitrocamphor Lowry (J., 1899, **75**, 211) came to the conclusion that this was due essentially

to a reversible isomeric change, nitro-form $\rightleftharpoons$ ψ-nitro-form, which proceeded with the attainment of a definite equilibrium. The examination of the change in a large number of solvents showed that it was facilitated most in oxygen-containing solvents such as acetone, the alcohols, and the carboxylic acids, and least in hydro-carbons, chloroform, and carbon disulphide. It was noted that the change was enormously accelerated by the presence of bases and even to some extent by neutral salts. The important point was made that the change was only possible in the presence of a catalyst.

Although Lowry makes no mention of dissociation, the general trend of the paper can be gathered from the statement : " As these changes take place in all solvents which have been examined, they must be of the nature of isomeric change and are independent of any chemical interaction with the solvent," and also from the interpretation of the action of bases (p. 221) :

$$\text{nitro-form} + \text{NaOEt} \rightleftharpoons \text{sodium salt} + \text{EtOH}$$
$$\Updownarrow$$
$$\psi\text{-nitro-form} + \text{NaOEt}$$

The latter is an interesting link with the modern view that the essential change occurs in the anion, which is naturally more stable in the salt than in the free nitro-compound. Later Lowry (J., 1908, **93**, 119), as the outcome of his work on sugars, abandoned these views in favour of reversible catalyst addition.

Another worker whose results led him to similar conclusions was Stobbe (*Annalen*, 1903, **326**, 359), who divided solvents for keto-enol tautomerides into two classes :

Group 1 : The dissociating solvents : catalysers of the change.

Group 2 : Benzene, chloroform, etc., weakly dissociating solvents. These had little or no catalytic effect and might even conserve the transitory condition of a tautomeric substance and in this sense act anti-catalytically.

Later, Tiffeneau, as a result of his studies of molecular migrations of a less facile kind, came to conclusions similar to those of Wisli-cenus and Lapworth which he expressed in rather different terms. In 1907 he wrote, " . . . I have thought that, in all molecular transpositions, the migration is subsequent to the first action of the reagent. In place of this idea of saturated intermediates, conse-cutive to the migration, I have substituted the idea of *unsaturated* intermediate systems determining the migration. All interconver-sion reactions are composed of two phases, one of disorganisation or of desaturation, provoked by chemical and physical agents, and one of reorganisation in the course of which the molecular trans-position is produced. . . ." (*Rev. gén. Sci.*, 1907, 583).

It is evident, therefore, that at the beginning of this century most of the leading authorities on tautomerism had come to look upon the first stage of the process as being one of breaking down of the molecule from its fixed condition into a labile form in which the change could readily occur.

The above is, then, a brief account of the history of the application of the dissociation hypothesis to explain tautomeric change. Thereafter it was to be subjected to considerable criticism, notably through the work of Dimroth from 1904 to 1913, but 'the general view to-day is that ionisation precedes tautomeric change. Thus, in the three-carbon system, the change is interpreted (J., 1926, 1477) as a removal of the mobile hydrogen as a proton, followed by the movement of the change in the electromeric ion. Such movement may be confined to the α- and γ-carbon atoms (1) or may include the " activating group " (2). If the latter, the change may finally influence an atom (such as O or N) with tolerance for it, under the conditions present, greater than that of carbon.

$$(1) \quad C\text{=}C\text{--}CH \rightleftharpoons C\text{=}C\text{--}\bar{C}\}\overset{+}{H} \rightleftharpoons \bar{C}\text{--}C\text{=}C\}\overset{+}{H}$$

$$\Updownarrow$$

$$CH\text{--}C\text{=}C$$

$$(2) \quad C\text{=}C\text{--}CH\text{--}C\text{=}O \rightleftharpoons C\text{=}C\text{--}\bar{C}\text{--}C\text{=}O\}\overset{+}{H} \rightleftharpoons C\text{=}C\text{--}C\text{=}C\text{--}\bar{O}\}\overset{+}{H}$$

$$\Updownarrow$$

$$CH\text{--}C\text{=}C\text{--}C\text{=}O \rightleftharpoons \bar{C}\text{--}C\text{=}C\text{--}C\text{=}O\}\overset{+}{H}$$

There is a lack of direct experimental evidence in support of this view, but reference may be made to some recent experiments of Kon and Linstead (in the press) in which it has been found that in the promotion of a three-carbon change in certain ketones the order of effectiveness of catalysts is sodium *iso*propoxide> sodium *n*-propoxide>sodium ethoxide>sodium methoxide (compare Ingold and Shoppee, J., 1929, 447). In other words, the most " vigorous " reagent is the least effective. This is not intelligible on an " intramolecular " basis, but is readily understood on the dissociation theory, for the ease of change will depend upon the formation of the active anion and hence upon the availability of the sodium. This will in turn be greater, the weaker the acidity of the competing reagent, namely, the alcohol of the alkoxide.

The modern views on dissociation are notable for their simplicity and for the effective way in which tautomeric change is correlated with other apparently unrelated phenomena. In spite of this, the large differences between organic and inorganic chemistry and the fact that the former is so largely the " chemistry of the covalencies "
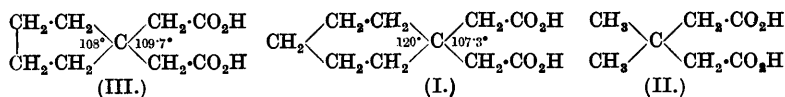
must always introduce an element of reserve into the reception of any theory postulating complete ionic reaction in virtually non-conducting media. Such considerations undoubtedly influenced the earlier supporters of the dissociation hypothesis and led them to qualify their views by such expressions as " a weak kind of dis-sociation," " a species of dissociation," " a phase of disorganis-ation " and so on.

I have to add that the above data have been collected by Dr. R. P. Linstéad and I have to thank him for the trouble he has taken in the matter.
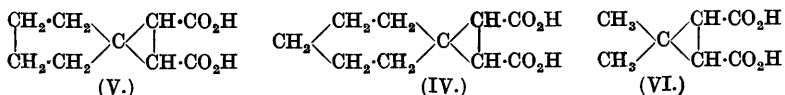
(b) *The Modified Strain Theory of Ring Formation.*

It may be said at once that the only problem which remains unsolved in this field is the uniplanar character or otherwise of the *cyclo*hexane structure, or, to put it probably more correctly, the problems remaining unsolved centre round this particular one. The multiplanar character of the rings beyond those containing six carbon atoms is now fairly generally accepted, as is also the uni-planar character of rings below those containing six carbon atoms. But the six-membered ring has still to rid itself of or adopt the Sachse–Mohr " arm-chair " and " boat " hypothesis which provides for the relief of the strain, due to the closing of the ring, by the " buckling " of the ends. The problem is one of fundamental importance owing, amongst other things, to the relationship between *cyclo*hexane and benzene, the latter being generally accepted as uniplanar owing to the non-existence of stereoisomeric forms of benzene derivatives and to recent strong evidence on the physical side. At present there is no evidence either chemical or physical which supports the Sachse–Mohr hypothesis, as regards simple cyclic types, although many attempts have been made to obtain such evidence. On the other hand there is a great deal of chemical evidence, as well as some of a physical character, which is in opposition to the hypothesis in its application to such types.

The chemical evidence is based on the hypothesis that when two valencies of a carbon atom are included in a six-membered carbon ring so as to make them conform to the angle of the hexagon, that is, 120°, the remaining two valencies of that carbon atom are deflected so as to occupy the remaining space equally. It has been calculated that in this case the remaining two valencies have the angle 107·3° between them as in (I).

$$\begin{array}{ccc}
\underset{\text{(III.)}}{\overset{\displaystyle CH_2 \cdot CH_2}{\underset{\displaystyle CH_2 \cdot CH_2}{\bigg|}} \overset{108°}{\diagdown} C \overset{109 \cdot 7°}{\diagup} \overset{\displaystyle CH_2 \cdot CO_2H}{\underset{\displaystyle CH_2 \cdot CO_2H}{\diagdown}}} &
\underset{\text{(I.)}}{CH_2 \overset{\displaystyle CH_2 \cdot CH_2}{\underset{\displaystyle CH_2 \cdot CH_2}{\diagdown}} \overset{120°}{\diagdown} C \overset{107 \cdot 3°}{\diagup} \overset{\displaystyle CH_2 \cdot CO_2H}{\underset{\displaystyle CH_2 \cdot CO_2H}{\diagdown}}} &
\underset{\text{(II.)}}{\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\diagdown}} C \overset{\displaystyle CH_2 \cdot CO_2H}{\underset{\displaystyle CH_2 \cdot CO_2H}{\diagup}}}
\end{array}$$

By a comparison between the corresponding diacetic acids (I), (II), and (III) it is possible to obtain definite evidence in support of the hypothesis. This evidence is based on (a) the ease of form-

$$\begin{matrix} CH_2 \cdot CH_2 \\ | \qquad\quad \\ CH_2 \cdot CH_2 \end{matrix} C \begin{matrix} CH \cdot CO_2H \\ | \\ CH \cdot CO_2H \end{matrix} \qquad CH_2 \begin{matrix} CH_2 \cdot CH_2 \\ \\ CH_2 \cdot CH_2 \end{matrix} C \begin{matrix} CH \cdot CO_2H \\ \\ CH \cdot CO_2H \end{matrix} \qquad \begin{matrix} CH_3 \\ \\ CH_3 \end{matrix} C \begin{matrix} CH \cdot CO_2H \\ | \\ CH \cdot CO_2H \end{matrix}$$

$$\qquad\qquad (V.) \qquad\qquad\qquad\qquad\qquad (IV.) \qquad\qquad\qquad\qquad (VI.)$$

ation and stability of the *spiro*-compounds (IV) and (V) as compared with those of the *cyclo*propane acid (VI) and (b) the recurrence of

$$\begin{matrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{matrix} C \begin{matrix} CO \cdot CO_2H \\ CH_2 \cdot CO_2H \end{matrix} \qquad CH_2 \begin{matrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{matrix} C \begin{matrix} CO \cdot CO_2H \\ CH_2 \cdot CO_2H \end{matrix}$$

$$\qquad (VII.) \qquad\qquad\qquad\qquad\qquad (VIII.)$$

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix} C \begin{matrix} CO \cdot CO_2H \\ CH_2 \cdot CO_2H \end{matrix} \quad (IX.)$$
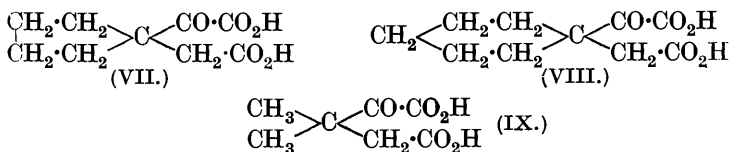
the keto-acids (VII), (VIII), and (IX) or the hydroxy-acids (X), (XI), and (XII) or equilibrium mixtures of the two.

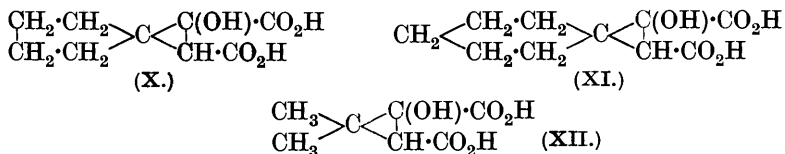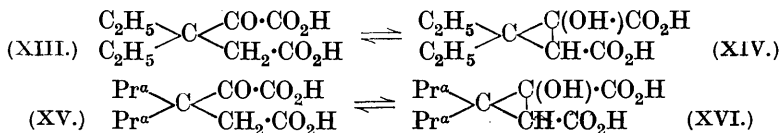$$\begin{matrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{matrix} C \begin{matrix} C(OH) \cdot CO_2H \\ CH \cdot CO_2H \end{matrix} \qquad CH_2 \begin{matrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{matrix} C \begin{matrix} C(OH) \cdot CO_2H \\ CH \cdot CO_2H \end{matrix}$$

$$\qquad (X.) \qquad\qquad\qquad\qquad\qquad\qquad (XI.)$$

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix} C \begin{matrix} C(OH) \cdot CO_2H \\ CH \cdot CO_2H \end{matrix} \quad (XII.)$$

It was found, for example, that the acid (IV) was more easily formed and, when formed, possessed greater stability than either of the acids (V) and (VI). The keto-acid (VIII) is, apparently, incapable of existence and passes at once into the ring acid (XI), whereas there is no ring acid of formula (XII), the keto-acid (IX) alone being capable of isolation. As regards acids (VII) and (X), the latter is a *cis*-form and readily gives an anhydride (Lanfear and Thorpe, J., 1923, **123**, 1683) and it has been clearly shown that it is only the *trans*-forms of those acids which undergo fusion to yield the keto-acids. Actually, in the case of the acids (XIII) and (XIV) and (XV) and (XVI) tautomerism has been shown to occur in concentrated alkaline solution.

$$(XIII.) \begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix} C \begin{matrix} CO \cdot CO_2H \\ CH_2 \cdot CO_2H \end{matrix} \rightleftharpoons \begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix} C \begin{matrix} C(OH \cdot) CO_2H \\ CH \cdot CO_2H \end{matrix} (XIV.)$$

$$(XV.) \begin{matrix} Pr^a \\ Pr^a \end{matrix} C \begin{matrix} CO \cdot CO_2H \\ CH_2 \cdot CO_2H \end{matrix} \rightleftharpoons \begin{matrix} Pr^a \\ Pr^a \end{matrix} C \begin{matrix} C(OH) \cdot CO_2H \\ CH \cdot CO_2H \end{matrix} (XVI.)$$

The physical evidence of the dissociation constants of the diacetic acids (Spiers and Thorpe, J., 1925, **127**, 538) is based on the assumption that the nearer two carboxyl groups are to one another the greater is the enhancement of the primary dissociation constant.

A table showing the results obtained, as well as the chemical evidence briefly summarised above, is given below.

SPIERS' TABLE.

	Substituent.	Calc. value of angle.	Equilibrium mixture.		$K_{25^\circ} \times 10^5$.
			% Keto.	% Enol.	
1	H,H	115·3°	100	0	4·69
2	Me,H	112·5	—	—	6·00
3	Et,H	?	—	—	5·29
4	(CH$_2$)$_4$ (*cyclo*pentane ring)	109·7	100	0	17·3
5	Me,Me	109·5	100	0	19·8
6	Me,Et	?	100	0	24·4
7	Et,Et	?	38	62	33·9
8	Pr,Pr	?	29	71	33·9
9	(CH$_2$)$_5$ (*cyclo*hexane ring)	107·2	0	100	33·4

There is then considerable evidence in favour of a strained *cyclo*-hexane structure both from the chemical and the physical side and none whatever in favour of the strainless multiplanar ring, and it would seem to follow that, when one carbon atom of a six-membered carbon ring is attached to two side-chains, the strain set up by the enlargement of the tetrahedral angle from 109·5° to 120° causes a deflexion of the normal angle made by the other two valencies, the six-membered ring remaining uniplanar. In other words, the strain set up in the ring is relieved by the deflexion of the other two valencies of the six carbon atoms involved.

When one of these carbon atoms is involved in a second ring to form a *spiro*-compound, it follows that the deflexion of the angle will enhance the ease of formation of a three-membered ring and will render it more stable when once formed—a result which has been confirmed by experiment, but in what manner the strain in a *spiro*-compound is shared by the two rings is not yet known, although the fact that the *spiro*-system always breaks down by rupture of the bond between the carbon atoms carrying the carboxyl groups seems to show that each ring retains its own angular values.

The work has recently been extended to include those compounds which have a six-membered ring locked in the 1 : 2-position by means of another ring, such as *cis*- and *trans*-decalone.

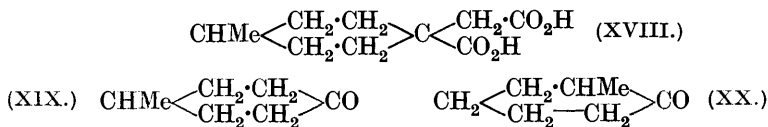(XVII.)   *cis*-   *trans*·

From a study of the diacetic acid (XVII) it has been found by Rao (J., 1930, 1162) that the *trans*-decalone ring structure is strainless and simulates the five-membered ring.   More recently A. Kandiah (in the press) has applied the same experimental tests to the diacetic acids from *cis*- and *trans*-hexahydro-β-hydrindone, with the result

cis-   *trans-*
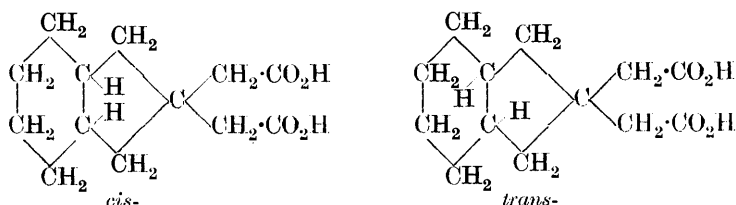
that both are found to be strainless.   We are therefore faced with the fact that when the six-membered ring is locked in this way all strain ceases or is so far diminished as to be incapable of detection by the methods we have applied.

It is also interesting to note that one of my former students, Dr. Qudrat-i-Khuda, has written recently to " Nature " stating that he has been able to isolate four forms of the succinic acid (XVIII).   If this is so, it represents the first example of the occurrence of monocyclic isomerides demanded by the Sachse–Mohr

$$CHMe{<}^{CH_2 \cdot CH_2}_{CH_2 \cdot CH_2}{>}C{<}^{CH_2 \cdot CO_2H}_{CO_2H} \quad \text{(XVIII.)}$$

$$\text{(XIX.)} \quad CHMe{<}^{CH_2 \cdot CH_2}_{CH_2 \cdot CH_2}{>}CO \qquad CH_2{<}^{CH_2 \cdot CHMe}_{CH_2{-}CH_2}{>}CO \quad \text{(XX.)}$$

hypothesis.   Judgment on this point must be reserved until further details are available showing without question that the four acids have the structures assigned to them.   It is always a difficult matter to obtain the ketone (XIX) unmixed with small quantities of the ketone (XX) and it is possible that one pair of acids may be derived from the ortho-ketone.