THE FORMATION OF CYCLIC COMPOUNDS. PART I. THE RELATIVE EASE OF FORMATION AND THE RELATIVE STABILITY OF SIMPLE CARBON RINGS.

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Received November 20th, 1933. Published January 28th, 1934.

It has been shown by Ruzicka and his co-workers⁽¹⁾ that large carbon rings such as, for example, cyclopentadecane, cycloheptadecane and cyclooctanone, etc. are as stable as five or six membered rings, a fact which does not conform with Baeyer's strain theory. In order to account for this and also for other facts such as the existence of two forms of decahydronaphthalene⁽²⁾ it has been assumed that fully reduced alicyclic structure composed of 6 carbon atoms and more possesses, not uniplanar strained, but multiplanar unstrained configurations. With regard to rings of less than 5-membered, which are supposed to have the atoms lying in one plane, since general experience indicates that they are not as stable as larger rings,

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(1) *Helv. Chim. Acta*, **9** (1926), 499.

(2) Hückel and others, *Ann.*, **441** (1925), 1.

Baeyer's conception must still be regarded as correct in so far as the stability of small rings is concerned. On the other hand, it has repeatedly been observed that the strain hyphothesis fails completely when applied to explain the relative ease of formation of small strained rings, a fact for which, as far as the author is aware, no satisfactory explanation appears to have been suggested. It is the object of this paper to seek, in a more fundamental manner than has hitherto been done, the cause or causes which affect the ease of formation of simple carbon rings and to present at the same time a view which seems to afford a satisfactory explanation for the facts which the other theories so far put forward fail to explain.

Strictly speaking, in the formation of small rings in particular, it would seem that the comparison of capacity of ring formation simply on the basis of the number of carbon atoms composing rings as has been done by Baeyer and the other workers on this subject is not justified, for there are two cases (A) and (B) in ring formation which, for the reason which will become plain later in this article, must be considered separately:

(A) The formation of a ring from one molecule of an open chain substance.

(B) The formation of a ring from more than one molecule of an open chain substance or from more than one substance.

Let us examine, in the first place, the case (A). If a ring is to be formed from a carbon chain, the prime necessity is clearly that the terminal atoms of that chain are to come close together. It follows therefore that the easier the terminal atoms can approach one another, the easier ring formation can take place.

Thus, the fact that rings other than those constituted of 5 and 6 carbon atoms are formed with difficulty would imply that there is some cause or other which makes the coming close together of the terminal atoms of carbon chains other than those composed of 5 or 6 carbon atoms difficult. And since the strain theory of Baeyer fails to explain the facts satisfactorily, it is certain that there is some cause or causes affecting the ease of formation of rings to which no consideration had been given by him. It is one of the fundamental assumptions (or rather the foregone conclusion) in organic chemistry that any two carbon atoms contained in saturated carbon chains can have complete free rotation about the bond, an assumption which means that the relative position of the terminal atoms of all the fully reduced chains except those composed of 2 and 3 carbon atoms is not fixed but alterable in liquid states and in solutions. This is the point to which no attention was paid by Baeyer and Ingold(3) and it seems most probable that

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(3) *J. Chem. Soc.*, **119** (1921), 305.

the failure of their theories to account satisfactorily for the relative ease of formation of rings had its origin in this, for it would be difficult to suppose that such a nature possessed by carbon chains should not exert any influence on the relative ease of ring formation from them.

Assuming this supposition to be correct, the difficulty with which formation of large carbon rings is attended may be accounted for as follows: although the terminal atoms of carbon chains of upwards of 5-membered may be caused to approach one another by free rotation of the atoms, it would seem reasonable to assume that the larger the number of carbon atoms composing these carbon chains, the slighter there is probability of the terminal atoms coming close together.

The terminal atoms of carbon chains of 3- and 4-membered do not come close together when the angle between the carbon to carbon valencies is normal and the difficulty with which formation of the rings of 3- and 4-membered is attended must undoubtedly be attributed to this fact, although, in the comparison of the ease of formation of these two rings, it would seem that the influence of free rotation of the atoms about the bonds on the relative position of the terminal atoms of the two chains must be considered at the same time. Finally, the terminal atoms of a 2-chain are always in mutual contact, a condition which is unique in all the chains. Doubtless it must be due to this condition that, in spite of the production of the greatest strain which of necessity follows, a 2-ring (a double bond), as has always been observed, is produced with the greatest ease of all rings.

Accepting the views above stated, what has to be taken into account in the comparison of the ease of ring formation from fully reduced carbon chains is, in the case of chains composed of 5 carbon atoms and more, the influence of free rotation of the atoms on the relative position of the terminal atoms and, in the case of chains containing 4 carbon atoms and less, in addition to the above influence, the effect which originates in the production of strain. To make the matter clear, fully reduced open carbon chains may be arranged in four classes according to (i) whether, as a result of free rotation of the atoms, there is a probability of the terminal atoms coming close together (condition X) or not (condition X') and (ii) whether, by free rotation of the atoms, there is a possibility of the relative position of the terminal atoms being altered (condition Y) or not (condition Y'):

	conditions fulfilled
(1) chains of 5-membered and more	X and Y
(2) 4-chain	X' and Y
(3) 3-chain	X' and Y'
(4) 2-chain	(X) and Y'

By (X) is meant that a 2-chain possesses the unique condition that the terminal atoms are always in mutual contact. Accepting the assumption already stated, the relative ease of formation of rings from the chains belonging to the class (1), which fulfil conditions X and Y, would solely depend on the number of carbon atoms composing these chains. Thus, a 5-ring should be formed from a 5-chain more readily than a 6-ring from a 6-chain and a 6-ring from a 6-chain more readily than a 7-ring from a 7-chain, etc. An experimental evidence which favors this view was offered by Vogel⁽⁴⁾ who studied slow thermal distillation of adipic, pimeric, suberic, azelaic and sebacic acids, a reaction which satisfied the two conditions required for the comparison of capacity of ring formation, that is, (1) a main reaction involving the formation of the cyclic compound (in this reaction a cyclic ketone) and (2) an alternative side reaction leading to an open chain compound (in this case a saturated monobasic acid), the progress of ring formation in competition with the side reaction being taken as a measure of the ease of ring formation. It was shown that the yields of cyclopentanone and cyclohexanone were respectively 80% and 52% and moreover that the yield of monobasic acid was greater in the pimeric than in the adipic acid series. It was further found that suberic, azelaic and sebacic acids gave good yields of n. heptoic, n. octoic and n. nonoic acids and that the yields of ketone in the first two cases did not exceed 2%.

Experimental verification for the present hypothesis concerning rings composed of more than 7 carbon atoms is difficult to obtain owing to the lack of method of production of these large rings, the only method available at present being that which consists in the dry distillation of the salts of dibasic acids which however, as rightly pointed out by Vogel,⁽⁴⁾ can not be employed to compare ring forming capacity, as the yields of ketone vary with the metal employed.

A convincing evidence demonstrating the correctness of the view that free rotation of the atoms composing a saturated chain exercises a great influence on the ease of ring formation is forthcoming from the comparison of the ease of ring formation from the two different states assumed by a given chain, one saturated and the other unsaturated or any state in which free rotation of the atoms is partly inhibited by some means or other. It is to be expected that if the difficulty with which formation of a saturated carbon ring is attended is due to slight probability of the terminal carbon atoms of a chain coming close together as a result of free rotation of the atoms, then it should be possible to remove or to diminish that difficulty by the inhibition of free rotation between some of the atoms constituting that

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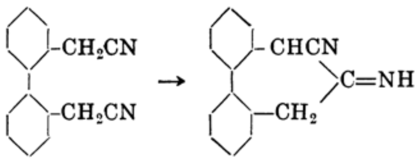
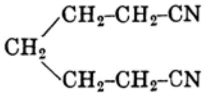
(4) *J. Chem. Soc.*, **1929**, 722.

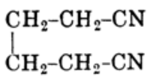
chain by such means as the introduction of a double linkage or linkages into the system or otherwise, although it is of course necessary that in the latter form also the terminal atoms can approach each other. As a matter of fact, we find that this is precisely what happens in a 7-chain, for, whilst 7-rings are generally produced from saturated 7-chains with great difficulty, it is a well-known fact that there is no difficulty encountered in obtaining 7-membered rings from certain 2.2′-substituted diphenyls. For example, whilst the compound (II) is readily formed from $\omega\omega'$-dicyano-2,2′-dimethyl diphenyl (I) under the influence of sodium ethoxide⁽⁵⁾ even derivatives of cyclohexanone can not be prepared from $\alpha\epsilon$-dicyanopentane (III) by this method⁽⁶⁾ although this condensation occurs readily when applied to $\alpha\delta$-dicyanobutane (IV), giving rise to the cyclopentane derivative.⁽⁷⁾



(I) (II)



(III)



$$\begin{array}{l} CH_2\text{-}CH_2\text{-}CN \\ | \\ CH_2\text{-}CH_2\text{-}CN \end{array}$$

(IV)

Similarly, the compound (VI) is produced in an 80% yield when ethyl 2,2′-dimethyl diphenyl-$\omega\omega'$-dicarboxylate (V) is treated with sodium,⁽⁸⁾ while under similar conditions ethyl cycloheptanone carboxylate (VIII) is obtained from ethyl suberate (VII) only in a 10% yield.⁽⁹⁾

(V) (VI)

(VII) (VIII)

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(5) Kenner, *J. Chem. Soc.*, **99** (1911), 2101.

(6) *J. Chem. Soc.*, **103** (1913), 614.

(7) Thorpe, *J. Chem. Soc.*, **95** (1909), 1901.

(8) Kenner, *J. Chem. Soc.*, **103** (1913), 615.

(9) Dieckmann, *Ann.*, **307** (1901), 50.

Although diphenic anhydride can easily be prepared from diphenic acid by the action of a dehydrating agent, only a very poor yield of adipic anhydride results when adipic acid is similarly treated.

In the formation of 5-rings also, there is evidence to show that a 5-ring is more readily formed from a 5-chain when free rotation of the atoms is partly inhibited than when otherwise. Thus, maleic and phtharic acids on distillation passes quantitatively into the anhydrides, while succinic acid is incompletely converted into the anhydride by the same treatment.(10) It follows therefore that it is not simply the presence, in 2,2′-substituted diphenyls, of four angles of 120° which is larger than the normal angle that is responsible for the ready formation of 7-rings from them, for, if so, succinic acid should give the 5-membered anhydride more readily than phtharic acid in which there are present two angles of 120° involved in the formation of the anhydride. As will again be discussed later in the case of formation of small rings, the fact would seem to be that the production of strain following ring formation is not a factor which affect the ease of ring formation to so great an extent as has hitherto been supposed.

With regard to the relative ease of formation of 2-, 3- and 4-rings, respectively, from 2-, 3- and 4-chains, it has repeatedly been observed that a 2-ring (double bond) is formed more readily than a 3-ring and a 3-ring more readily than a 4-ring, a fact which is not in agreement with the strain theory. On the other hand, general experience indicates that as required by Baeyer's conception a 4-ring is more stable than a 3-ring and a 3-ring more stable than a 2-ring. These observations that the relative ease of formation and the relative stability of the three rings are not parallel would naturally lead one to suppose that, since the relative stability of the rings can be satisfactorily accounted for, at any rate qualitatively, by the strain theory, there should be present in these short chains, in addition to the remoteness between the normal positions of the terminal atoms (2-chains excepted) as assumed in the simple conception of Baeyer and Ingold,(2) some factor or other which must be taken into account in comparing the ease of ring formation. It seems very probable that as already stated, this factor is one that is brought about by free rotation of the atoms which exercise different influences on the relative position of the terminal atoms of a 4- and a 3-chain belonging to the different classes (2) and (3). And if it is to be accepted that the possibility of free rotation of the atoms does at all affect the ease of formation of large rings from longer chains, there is no reason why the same effect should not play any part in the formation of rings from the short chains. If that is the case, it will be found easy to account for all the

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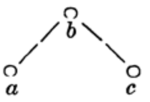
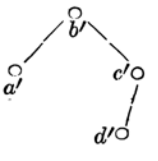
(10) Meyer and Jacobson, "Lehrb. d. Org. Chem." Bd. I. T. II, 362.

known facts concerning the relative ease of formation of strained rings for which no satisfactory explanation appears to have been suggested.

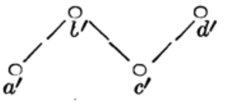
As above referred to, the fact that a 2-ring, which ought to be in the most strained state as required by the strain theory and as reflected by its greatest instability, is actually produced with the greatest ease of all the rings must undoubtedly be attributed to the unique condition, the most favorable to ring formation from the point of view of the present hypothesis, that the terminal atoms are always in mutual contact. At the same time, this fact may be regarded as indicating that the production of strain which follows ring formation cannot be the cause which affect the ease of ring formation to so great a degree as has hitherto been supposed, a matter of importance when considering the relative ease of formation of a 3- and 4-ring. There seems to be no difficulty now to account for the fact that a 3-ring is formed from a 3-chain more readily than a 4-ring from a 4-chain. Thus, whilst a 4-chain belongs to the class (2) fulfilling the conditions X′ and Y which both are unfavourable to ring formation, there is present in a 3-chain only one unfavourable condition X′. In the diagrams (IX), (X) and (XA), the carbon atoms a, b, c, a′, b′, c′ and d′ composing respectively a 3- and a 4-chain are supposed to be lying in the plane of the paper. In the formation of a 3-ring from a 3-chain (IX) the terminal atoms a and c cannot but come close together merely by the deflection of the angle between the carbon to carbon valencies, for in a 3-chain the relative position of the terminal atoms is not altered by free rotation of the atoms. On the other hand, in a 4-chain, as will be seen in the diagrams (X) and (XA) showing the two cases of arrangements assumable by a 4-chain, in which one is obtained from the other when the atom c′ rotates through an angle of 180°, there is a possibility of the relative position of the terminal atoms a′ and d′ being altered, a condition which is not present in the terminal atoms of a 3-chain. It would be only when a 4-chain assumes the arrangement (X) and also perhaps the arrangements close to (X) that there is any chance of the union of a′ and d′ taking place. In the arrangements other than those mentioned above it is evident that the mere deflection of the angle between the carbon to carbon valencies cannot bring the terminal atoms a′ and d′ near together.



(IX)



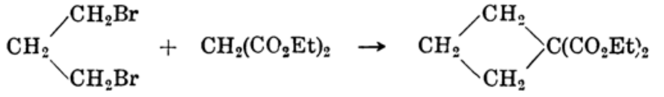
(X)

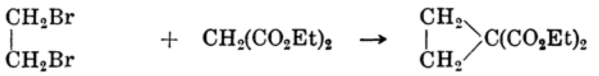


(XA)

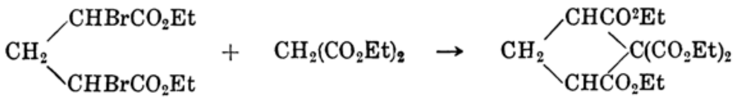
In other words, whilst in a 3-chain, there is at any moment a possibility of the closure of a 3-ring, in a 4-chain the arrangement in which there is a possibility of ring formation would on an average be of much shorter duration than that in which there is no possibility of ring formation. In this connection, it should be noted that, although a 4-chain may assume either the arrangements (X), or (XA) or any intermediate state between the two, it is probable that the zigzag arrangement (XA), especially when the terminal atoms a′ and d′ bear the same grouping (or indeed any two kinds of grouping which possess the same sign of electrical charge), is more stable than (X), since, as is well-known in the cis-trans isomerism, a trans form is more stable than a cis form. And if it is so, this effect may well play part to hinder the closure of a 4-ring. In these circumstances, it would seem that there is nothing strange in the fact that a 3-ring is formed from a 3-chain more readily than a 4-ring from a 4-chain.

Experimental support for the above view is furnished through the comparison of the ease of formation of a 4-ring and a 3-ring respectively from two substances. The examples described below are those which were cited by Vogel⁽⁴⁾ in order to show that the modified theory of Ingold fails to cover all the facts which have been discovered, but which, instead, provide evidence in favour of the present hypothesis. It was found that the cyclobutane compound (XI) was produced in a greater yield than the cyclopropane compound (XII) when trimethylene bromide and ethylene bromide was condensed, respectively, with ethyl sodiomalonate⁽¹¹⁾:


(XI)


(XII)

The cyclobutane (XIII) and the cyclopropane (XIV) compounds were obtained in the almost equal yields in the condensation of ethyl $\alpha\alpha'$-dibromoglutarate with ethyl sodiomalonate in alcoholic solution; condensation in benzene solution gave a 70-80% yield of (XIII)⁽¹²⁾:


(XIII)

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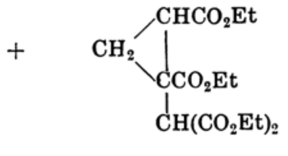
(11) Perkin, *J. Chem. Soc.*, **47** (1885), 801; **51** (1887), 1; Perkin and Prentice, *J. Chem. Soc.*, **59** (1891), 823.

(12) Ing and Perkin, *J. Chem. Soc.*, **127** (1925), 2387.

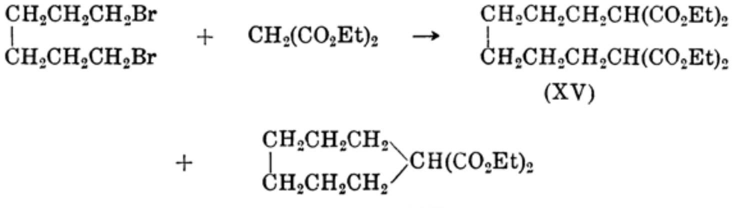


(XIV)

It will be noticed at once that, in each reaction, one molecule each of two substances, a 3-chain in one and an atom in the other, takes part in forming a 4-ring. There seems no doubt that it is due to this fact that, whilst in general a 4-ring is formed from a 4-chain with greater difficulty than a 3-ring from a 3-chain, the cyclobutane compounds (XI) and (XIII) are produced more readily than the cyclopropane compounds (XII) and (XIV) in these reactions.

According to the present hypothesis, no difficulty is encountered in giving a satisfactory explanation for the difference between the two cases. It is evident that, since in the above reactions the relative position of the terminal atoms of a 3-chain is not altered by free rotation of the atoms, the conditions under which the cyclobutane rings (XI) and (XIII) are produced by its combination with the carbon atom in the sodiomalonate are entirely different from those when a 4-ring is formed from a 4-chain, the relative position of the terminal atoms of which is alterable. Thus in the reaction by which the cyclobutane (XI) and cyclopropane (XII) compounds are formed, not only the relative position of the terminal atoms of each of the 3- and the 2-chains contained respectively in trimethylene bromide and ethylene bromide is unalterable, but also the terminal atoms in each chain are so close to one another that the carbon atom in the sodiomalonate is able to approach them simultaneously. The outcome would be that in this reaction the factor which affects the ease of formation of the cyclobutane (XI) as well as cyclopropane (XII) compounds is only the strain which is to be produced, and hence the greater yield of the former (XI). The better yield of the cyclobutane compound (XIII) than the cyclopropane compound (XIV) is also to be ascribed to the same cause.

In the formation of a large ring, however, it will be rare that it is formed from more than one substances without going through an intermediate stage, since in a long carbon chain, the relative position of the terminal atoms of which are alterable, there is slight probability of both terminal atoms of the chain approaching the terminal atoms of the other chain or chains at the same moment. Thus, for example, the condensation of hexamethylene bromide with ethyl sodiomalonate yielded mainly ethyl octane tetracarboxylate (XV), the cycloheptane compound (XVI) being obtained in a very poor yield.[13]



$$\begin{matrix}CH_2CH_2CH_2Br\\ |\\ CH_2CH_2CH_2Br\end{matrix} + CH_2(CO_2Et)_2 \rightarrow \begin{matrix}CH_2CH_2CH_2CH(CO_2Et)_2\\ |\\ CH_2CH_2CH_2CH(CO_2Et)_2\end{matrix}$$

(XV)

$$+ \begin{matrix}CH_2CH_2CH_2\\ |\\ CH_2CH_2CH_2\end{matrix}\!\!>CH(CO_2Et)_2$$

(XVI)

In this reaction, the cycloheptane compound (XVI) must have been produced mostly through the intermediate compound. In that case, the reaction is the same as that in which a 7-ring is formed from a 7-chain.

There seems to be no difficulty now to explain the fact that the relative ease of formation and the relative stability of small rings are not parallel, for, as already mentioned, there is present in the formation of strained rings a factor, other than that which originates in the production of strain, which greatly affect the ease of ring formation. Before ring formation, 4-, 3- and 2-chains belong, respectively, to the different classes (2), (3) and (4) which satisfy different conditions regarding the relative position of the terminal atoms, a fact which imply that the conditions under which the small rings are to be formed from these chains are not comparative. But with the union of the terminal atoms, such a difference as existed between the chains disappears, and 4-, 3- and 2-rings are now under comparative conditions as to their stability, the degree of strain indicating the degree of instability of the small rings.

The rather difficult case in which the closure of a 4-ring occurred very easily from a 4-chain and which is apparently in conflict with the present hypthesis is that when methyl $\alpha\beta\delta$-tribromobutane-$\beta\delta$-dicarboxylate (XVII) was treated with zinc, acetic acid and a little water at first in the cold and afterwards on the water bath the quantitative production of cis-cyclobutane-1,3-dicarboxylate (XVIII) and not the cyclopropane compound (XIX) resulted.[14] Perkin and Simonsen concluded from the result that the cyclobutane compound (XVIII) was more readily formed than the cyclopropane compound (XIX) in agreement with the strain theory. It appears however they have overlooked another alternative that there is strong reason to believe that the zinc first of all would attack the $\alpha\beta$-bromine atoms giving rise to the unsaturated compound (XX) as an intermediate product:

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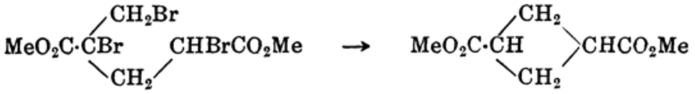
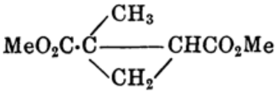
(13) Haworth and Perkin, *J. Chem. Soc.*, **65** (1894), 599.

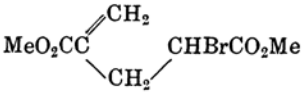
(14) Perkin and Simonsen, *J. Chem. Soc.*, **95** (1909), 1169.



(XVII) (XVIII)



(XIX)



(XX)

The compound (XVII) is therefore an interesting substance which, according to the ways of debromination, may yield different compounds containing either a double bond or a 3-ring or a 4-ring. Before considering the probable mechanism of the production of (XVIII) from (XX) some of the previous result on the debromination of various dibromo-compounds by the action of zinc must be given. In this case too, there is a mass of evidence which shows most convincingly that $\alpha\beta$-dibromo-compounds are very much more easily debrominated yielding unsaturated substances than $\alpha\gamma$- and $\alpha\delta$-dibromocompounds.

Thus, for instance, Petrenko-Kritschenko and Konschin⁽¹⁵⁾ studied the debromination velocity of various dibromo alkane. The method employed was to shake the dibromocompounds with zinc dust in alcohol at ordinary temperature. The results obtained after one hour and 6 hours are shown in the table below, the quantities of the dibromoalkane which reacted with zinc being given in percentages:

	1 hr.	6 hr.
ethylene bromide	19.87%	—
$\alpha\beta$-dibromopropane	20.87 ,,	53.58%
trimethylene bromide	2.02 ,,	2.68 ,,
$\alpha\delta$-dibromopentane	1.80 ,,	1.55 ,,
$\alpha\varepsilon$-dibromopentane	1.25 ,,	—

It will be seen from the table that (a) the $\alpha\beta$-dibromocompounds reacted with zinc very much more easily than the others, (b) whilst the quantity of $\alpha\beta$-dibromopropane which reacted increased greatly with the lapse of time, the quantities of the others after one hour, which are all so negligibly small, are practically the same as those after 6 hours, that is, the reaction stopped after a short time, and (c) with the increase of the number of carbon atoms existing between the bromine atoms, the reaction took place with more difficulty. Again, it was found by Zelinsky and Schlesinger⁽¹⁶⁾ that although on treatment of ethylene bromide with zinc dust and glacial acetic acid a violent reaction took place yielding ethylene, no reaction occurred when

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(15) *Ann.*, **342** (1905), 57.

(16) *Ber.*, **41** (1908), 2429.

trimethylene bromide was submitted to the same treatment. They found however that trimethylene bromide reacted with zinc in presence of 50% acetic acid giving rise to cyclopropane but the reaction velocity was very small at ordinary temperature. Hamonet(17) obtained butane on treatment of tetramethylene bromide with zinc and ethyl alcohol. As a matter of fact, the reaction which used to take place when dibromacompounds other than αβ-dibromocompounds are treated with zinc and acetic acid is, not debromination leading to ring formation, but reduction involving the production of saturated open chain substances.(18) To take a few more examples in which a carboethoxyl group is present, ethyl αβ-dibromobutyrate gave ethyl crotonate when its ethereal solution was treated with zinc,(19) whereas ethyl αγ-dibromobutyrate yielded on treatment with zinc and ethyl alcohol ethyl butyrate.(20)

These examples cited above are only a few of the numerous facts which have been discovered showing that debromination occurs most easily in the case of αβ-dibromocompounds. As described above, although trimethylene bromide gives under certain conditions cyclopropane, as far as the author is aware no example is recorded in which a cyclobutane compound is produced from an αδ-dibromo-compound by the action of zinc and acetic acid.

In view of these facts, there seems no reason why, notwithstanding the presence of the bromine atoms in the αβ-positions of (XVII), only in the production of (XVIII) from (XVII) the debromination of the αδ-bromine atoms leading to the formation of the cyclobutane ring should occur in the first phase of the reaction, and since the cyclopropane compound (XIX) was not actually produced, a result which is not surprising, one is forced to conclude that the zinc first of all must have attacked, most probably while cold, the αβ-bromine atoms of (XVII) giving (XX) as the intermediate product which then, probably when heated, would have passed into (XVIII) through the hypothetical intermediate state (XXI) produced by the elimination of the δ-bromine atom by the action of nascent hydrogen.

The fact that cinnamic acid (XXII), a derivative of acrylic acid, has a marked tendency to polymerise giving rise to the cyclobutane compound, α-truxillic acid (XXIII), may be taken as an example indicating that somewhat analogous change as the transformation of (XXI), also a derivative of acrylic acid, into the cyclobutane compound (XVIII), of which α-truxillic acid is a diphenyl derivative, is not altogether an unjustifiable supposition.

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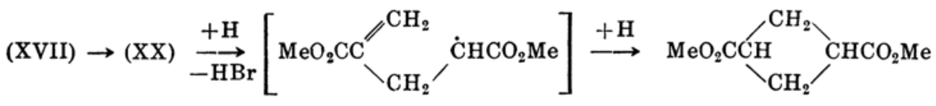
(17) *Compt. rend.*, **132**, 789.

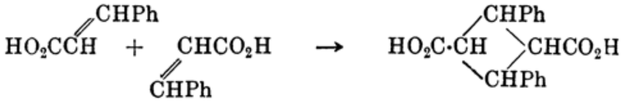
(18) Compare, Victor Meyer u. Jacobson's "Lehrbuch d. Org. Chem.", Bd. II, T. I, 770.

(19) Michael and Schulthess, *J. Pr. Chem.*, **43** (1891), ii, 590.

(20) Kishner, *J. Russ. Phys.-Chem. Ges.*, **41**, 660.



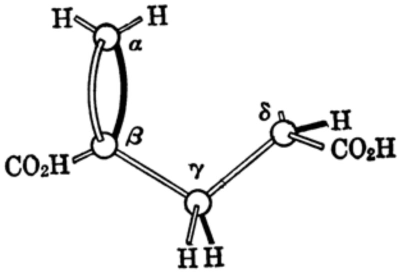
(XXI)		(XVIII)



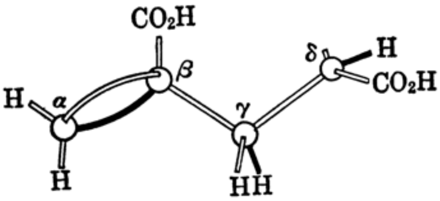
(XXII)		(XXIII)

It is also possible that the debromination of the $\alpha\beta$-bromine atoms by the action of zinc and the removal of the δ-bromine atom by the action of nascent hydrogen might have occurred at the same time, but Zelinsky and Schlesinger(16) stated that in absence of water zinc and acetic acid did not react at all with each other and that even when 50% acetic acid was used the reation took place with difficulty.

It is interesting to note that, if it is assumed that the production of the hypothetical intermediate state (XXI) is the case, then it follows that there is no possibility of the production of the cyclopropane compound (XIX) from it. In the diagrams (XXIA) and (XXIB) representing the two cases of arrangements which may be assumed by (XXI) (one is obtained from the other when the β-carbon atom rotates through 180°), the α-, β-, γ- and δ-carbon atoms are supposed to be lying at the angular points in the plane of the paper and therefore the plane of the double bond would lie in a plane perpendicular to the plane of the paper. Now, assuming that the production of the hypothetical product (XXI) precedes the formation of the cyclobutane (XVIII) or cyclopropane (XIX) compounds, in order that (XXI) is transformed into (XVIII) as well as (XIX), (XXI) must in the first place have the arrangement (XXIA), for in the other arrangement (XXIB) or in any arrangement representing the intermediate state between (XXIA) and (XXIB) the valencies linking the α- and β-carbon atoms, one of which is required to close the 4- or 3-rings, emanate in the direction where there is no possibility of ring formation. In other words, it is evident that in the arrangement (XXIB) the presence of the carboxyl group carried by the valency emanating in this derection from the β-carbon atom would render *the formation of a 3-ring through the $\beta\delta$-atoms impossible. Again, in the* arrangement (XXIA), if the attempt be made to approach the β-carbon atom to the δ-atom, it will be seen that it is, not the β-atom, but the α-atom which is the first to come close to the δ-atom, the formation of the cyclobutane compound (XVIII) by the union of the α- and δ-atoms being thus left as the only possibility.



(XXIA)



(XXIB)

In view of the large number of facts satisfactory correlated by the present hypothesis it seemed desirable to undertake a series of experiments with the object of examining the more essential points stated in this communication on the causes which seem to affect the ease of ring formation. It is intended to publish the results of the experiments in future papers.

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