SOME RECENT ADVANCES IN THEORETICAL ORGANIC CHEMISTRY[1]

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I. INTRODUCTION

Theoretical organic chemistry appears at the present time to be in a transitional phase of development. It is becoming increasingly difficult to reconcile experimental developments with the classical theories, and as yet relatively few of the host of new theoretical ideas seem to have achieved any considerable success.

The present state of disorder is due chiefly to the influence of modern physics, and may be ascribed for the most part to two general underlying causes. One of these is the attempt to apply the electronic conception of valence to organic compounds. The replacement of the time-honored but meaningless line bond by an electron pair would seem to be certain to revolutionize our ideas of valence and hence most of our fundamental theories. The results in this direction thus far have indeed not been negative, but they have frequently brought confusion rather than clarity.

Most of the classical problems of the science, such as tautomerism, the structure of benzene, rearrangements, relation of physical properties to constitution, steric hindrance—all these and many others—have been translated into the new terms, and each has given rise not, as was to be hoped, to one clear and consistent version, but rather to a number of conflicting speculations. Thus, in going forward, theory has experienced that increased disorder which is characteristic of transitional phases in development.

The second factor contributing to the present state of theoreti-

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cal disarray comes from new and improved technical methods which have given us new types of data on such subjects as crystal structure, electrical moment, molecular volume and optical properties. These new data are often very difficult to explain in terms of our old theories.

In general, it is doubtful whether or not recent theoretical speculations and improved technical methods have in any very real sense consolidated the problems before us. Yet in view of these, it is hard to believe that the classical treatment of the chemistry of carbon compounds can survive without serious modification.

This state of affairs greatly enhances the difficulty of preparing an unbiased report of progress, for it is only here and there that we can single out a contribution which we can confidently label as a step forward. It is true, however, that these contributions present a certain unity in that they are chiefly concerned in some way with our notions of valence. Accordingly, for this review there have been selected from the mass of valuable material available, a few outstanding contributions in the general field of valence. No attempt has been made to select the material on the basis of relative merit but, rather, those studies have been included which, it is felt, best illustrate the general trends discernible in the development of the field.

For convenience of treatment the development of valence theory as applied to organic chemistry may be divided, following the chronological order, into four general phases.

1. The first of these is the concept of valence as made up of a definite number of discrete linkages—an idea which was first fully recognized in 1858 when Kekulé showed that carbon is tetravalent.

2. Next came the question of the spatial arrangement of the bonds. In 1874 van't Hoff proposed the tetrahedral form for the carbon atom, thus laying the foundation for modern stereochemistry.

3. As a sort of corollary of this, there arose the question of distortion of the tetrahedral form—a question which brought forward in 1885 the celebrated strain theory of Baeyer.

4. Finally, following the electron theory put forward simultaneously in 1916 by Lewis and by Kossel, we have the study of the physical nature of the bond.

Although these general problems are no longer new, each continues to stimulate a vast amount of research, and each has brought forth important developments within the period under consideration.[2] It will be convenient, therefore, to discuss the various contributions by reference to their relation to the foregoing outline.

II. CONSTANCY OF VALENCE NUMBER

The constancy of the valence numbers of carbon, hydrogen, oxygen, nitrogen and other elements commonly found in organic compounds long ago reached the stage of certainty which corresponds to that of a law rather than of a theory. Indeed, the interest in this connection has long since come to be centered rather about the exceptions to this law. Thus we have the development of the chemistry of divalent and trivalent carbon, of divalent nitrogen and of univalent oxygen in which these elements exhibit unusual valence numbers. The classification of free radicals as "odd molecules", i. e., molecules having an unpaired electron, has given a satisfactory explanation of their peculiar properties. In general, therefore, the behavior of these compounds has been such as to "prove the rules" of normal valence.

Of unusual interest is the announcement by Paneth and Hofeditz of the production of free methyl by thermal decomposition of lead tetramethyl (1). Subsequent work by Schultze and Müller (2) has shown, however, that Paneth's observations may be ascribed to the action of atomic hydrogen. The conclusions of Paneth are thus left open to question.

Among abnormal valence compounds those of divalent carbon have not yet been adequately fitted into our general picture. For this reason the work of Scheibler in this field commands first attention. Scheibler and Ziegner, in an investigation of the

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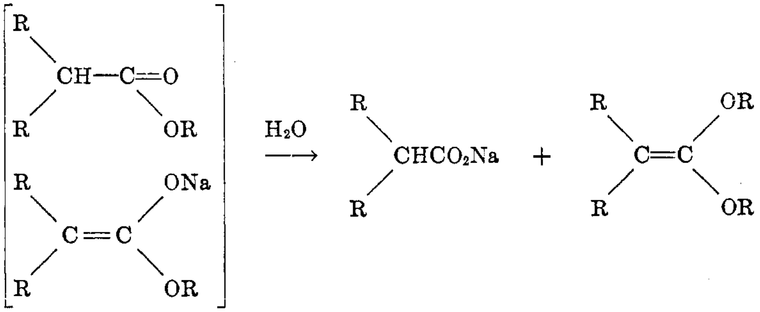
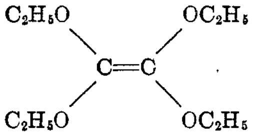
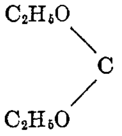
[2] An attempt has been made to restrict this review to the developments which have appeared during the period from 1924 to 1929, inclusive; but, as will be seen, the discussion has required frequent reference to earlier papers.

mechanism of the acetoacetic ester condensation (3), discovered a general method for the preparation of ketene acetals—a class of compounds hitherto practically unknown. The method consists in treating an ester with an equimolecular amount of the sodium derivative of the ester in cold dilute ether solution. The addition product when decomposed by water yields the ketene acetal:



The most interesting of the acetals is that obtained from ethyl diethoxyacetate:


I


II

This should lead to tetraethoxyethylene (I). The product obtained, however, has only half the calculated molecular weight and has been assigned the structure II—diethoxymethylene—in which there is a divalent carbon atom.

The physical and chemical properties are in good agreement with this formula. The compound, like ethers and ordinary acetals, is stable to alkali, and is readily hydrolyzed in the presence of acids to give carbon monoxide and alcohol:

$$(C_2H_5O)_2C + H_2O \longrightarrow 2\ C_2H_5OH + CO.$$

When heated the acetal yields carbon monoxide and diethyl ether:

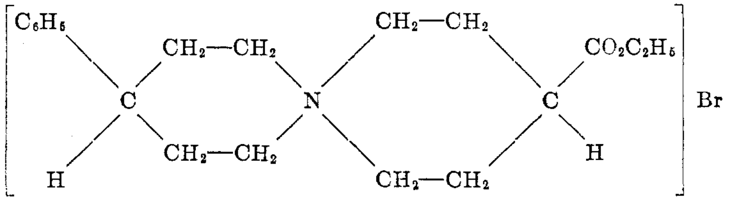
$$(C_2H_5O)_2C \longrightarrow C_2H_5\text{—}O\text{—}C_2H_5 + CO.$$

It is not attacked by bromine and only slowly by alkaline permanganate. There is a very marked exaltation of the molecular refractivity. Diethoxymethylene is of particular interest among divalent carbon compounds because it is the first example containing a divalent carbon atom attached to two univalent radicals (4).

Although the existence of diethoxymethylene appears to be consistent with the dissociation series of Staudinger and Engle (5), very recent work has shown that it nevertheless occupies a unique position. Scheibler and Baumann (6) have shown that unsymmetrical diethoxydiphenoxyethylene is stable to heat. It is interesting to note also that tetramethyltetrathioethylene and tetraethyltetrathioethylene have likewise been shown to be stable to heat (7).

III. SPATIAL ARRANGEMENT OF BONDS

The second phase of valence development, which concerns the spatial arrangement of the bonds, has produced an adequate theoretical explanation of the facts of stereochemistry by the assumption of a tetrahedral form for the carbon atom. Much dispute, however, exists over the question of a tetrahedral form for nitrogen. Of first interest in this field, therefore, is the work of Mills and his students with reference to the nitrogen atom in ammonium compounds. These investigators have continued to add to the evidence favoring the tetrahedral as opposed to the pyramidal form for the nitrogen atom in these compounds. In 1925 Mills and Warren (8) resolved 4-phenyl-4′-carbethoxybispiperidinium-1, 1′-spirane bromide.



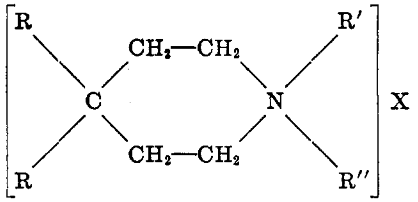
It had previously been shown that:

1. The four bonds of nitrogen are interequivalent.

2. Quarternary ammonium salts containing four dissimilar groups are resolvable into enantiomorphous forms.
3. Position isomerism does not occur in these compounds.

The pyramidal and the tetrahedral forms are, therefore, the only ones which explain the facts.

It is evident that if the nitrogen atom in the spirane bromide has the pyramidal form there will be a plane of symmetry and, therefore, no possibility of resolution into enantiomers. The tetrahedral form, on the other hand, is asymmetrical and should be resolvable. Mills, Parkin and Ward (9) have continued this study by investigating the isomerism of compounds of the type:



According to the tetrahedral formula these should exist in two geometrical non-resolvable isomers which become identical when R′ and R″ are the same. On the other hand, a pyramidal nitrogen atom would give rise to two resolvable compounds in each case; when R′ = R″ two geometrical isomers would occur. Each of the five different salts used was found to exist in two geometrically isomeric forms, thus proving that in these compounds also the nitrogen atom is tetrahedral rather than pyramidal.

A similar disposition has been made of the case of the dimethyltelluronium dihalides which were reported by Vernon (10) to exist in two stereoisomeric forms. This represents one of the very few instances in which the existence of isomerism in quadrivalent compounds has required the assumption of a planar arrangement of the bonds. In a recent paper, however, Drew (11) has shown that the supposed stereoisomers of Vernon are actually different structurally. A return to the tetrahedral arrangement is thus made possible in the case of the tellurium atom in telluronium compounds.

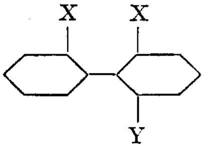
A decision in favor of the tetrahedral distribution of bonds has apparently been reached also in the case of the central carbon atom in pentaerythritol for which Mark and Weissenberg (12) had proposed the pyramidal form in order to explain certain crystallographic data. Resolution studies by Böeseken and Felix (13) and recent x-ray data by Knaggs (14) have thrown the balance of evidence in favor of the commonly accepted tetrahedral configuration.

IV. VALENCE DISTORTION

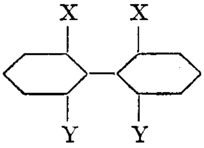
In connection with the third phase of development—the question of distortion of linkages—we find considerable disagreement and much progress within the past few years.

1. Stereoisomerism of diphenyl compounds

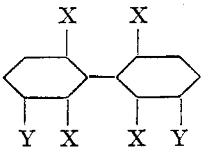
The conception of a valence bond as directional and possessed of a certain degree of rigidity finds support in the isomerism exhibited by certain derivatives of diphenyl. A large number of these have been found to be resolvable into pairs of mirror images. Christie and Kenner (15) have resolved compounds of types III and IV. Compounds of type IV have also been resolved by Meisenheimer and Höring (16) and by Kuhn and Albrecht (17). More recently Moyer and Adams (18) have effected the resolution of two compounds of type V.



III



IV



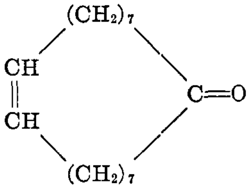
V

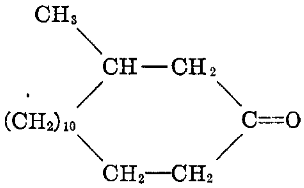
The most acceptable explanation of this type of isomerism is the purely mechanical one of Bell and Kenyon (19) and Mills (20), namely, that the groups in the *ortho* positions act as obstacles to free rotation. This view is supported by the fact that, in general, these compounds are difficult to racemize. A further confirmation of the correctness of this view has been furnished by Stanley and Adams (21) who find that when one of the restricting groups is fluorine, which has a very small atomic volume, racemization takes place rapidly. Thus active difluorodiphenic acid is readily racemized.

2. Strain theory

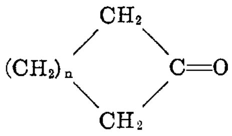
The idea that valence bonds possess a certain degree of rigidity is likewise involved in the new developments in strain theory.

Large rings. The discovery by Ruzicka (22) and his students that the stable, naturally occurring substances muscone and civetone are constituted of large carbon rings of 15 and 17 members, respectively, has at last set aside the Baeyer postulate regarding the instability of large rings. These investigators, following the lead of nature, have already achieved far-reaching synthetic results in the field of large carbon rings.

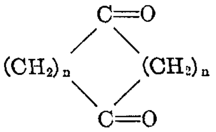

Civetone


Muscone

By the distillation of thorium and yttrium salts of suitable dibasic acids Ruzicka and his co-workers (22) have prepared cyclic ketones constituted of from 9 to 21 members; also those of 29 and 30 members:



Diketones of the type



are formed at the same time; of this series those of 16, 18, 20, 22 and 30 members have been isolated and studied. By reduction of the mono- and diketones the corresponding hydrocarbons are obtained, and of these those of 15, 16, 17, 18 and 30 members have been reported.

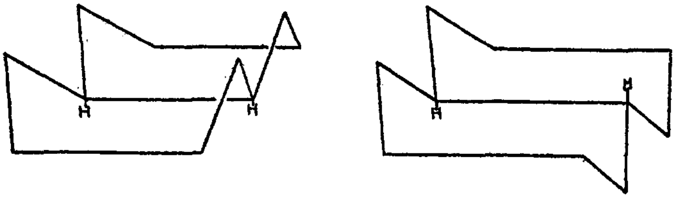
The outstanding feature of this work, at least from a theoretical point of view, is the fact that all of these compounds appear to be fully as stable as five- and six-membered rings or, for that matter, as their straight-chain analogues. Thus, cycloheptadecanone was passed over thoria at 400–420° and recovered unaltered. Cyclopentadecane and cycloheptadecane were recovered completely after treatment with phosphorus and hydrogen iodide at 250.° In other words, there is no positive evidence that these compounds involve "strain" in the Baeyerian sense. This is, of course, entirely in agreement with the Sachse-Mohr theory of strainless rings (24).

Strainless rings. That carbon rings constituted of more than six carbon atoms exist in strainless multiplanar configurations now seems certain. If one constructs a model of one of these rings, using tetrahedral atoms, he will find that the model will naturally assume a multiplanar unstrained form. That the ring should assume the strained uniplanar form when a strainless form is possible does not seem very likely, and now that we know that the large rings are stable there remains no reason to ascribe to them a structure postulated solely to explain their supposed instability.

This new point of view carries with it certain new possibilities of isomerism and of stable endocyclic bridges, and already much progress has been made along these new lines.

Hückel and his co-workers (25) have discovered a number of new cases of isomerism in bicyclic systems which are predicted by the strainless ring theory, and are exceedingly difficult to account for on the basis of uniplanar rings. One or two examples will suffice to show the general type of compound involved. Decahydronaphthalene has been found to exist in two forms. Hückel represents them as shown in figure 1. Similarly, Hückel (26) has isolated four β-hydroxydecahydronaphthalenes and four βaminodecahydronaphthalenes, the number in each case being that predicted by the theory. Many additional cases of isomerism of this type have since been reported.

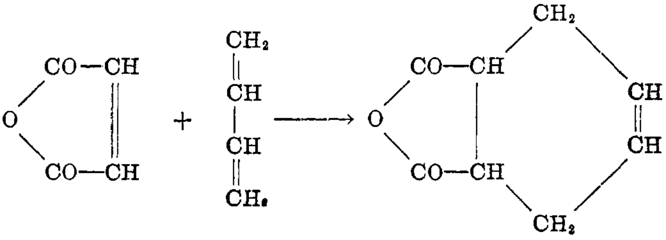
Endocyclic bridges. Another type of evidence in favor of the strainless ring theory is to be found in the existence of numerous types of endocyclic bridge structures which, to judge from their stability, are nearly, if not quite, without strain. It is not possible to give these compounds even moderately unstrained configurations on the basis of uniplanar rings. The Sachse-Mohr theory, on the other hand, gives to them multiplanar forms which would seem to be more nearly in accord with the facts.



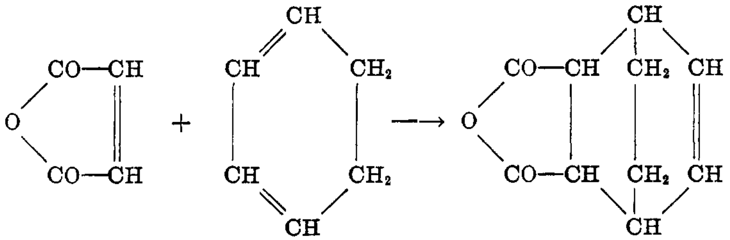
(cis) (trans)

FIG. 1. TWO FORMS OF DECAHYDRONAPHTHALENE

This is admirably illustrated by the important synthetic method of Diels and Alder (27), who have shown that the anhydrides of certain unsaturated acids react with compounds containing a system of conjugated double bonds to give 1, 4 addition products. Thus, maleic anhydride adds to butadiene as follows:



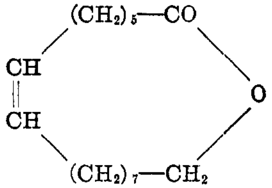
In this same manner maleic anhydride adds to cyclohexadiene:



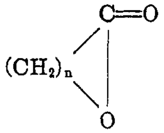
VI

Compound VI is a good example of a large class of compounds the stability of which can be accounted for more satisfactorily on the basis of strainless rings than on the basis of uniplanar rings.

High molecular weight polymers. It should be mentioned that large heterocyclic rings have also been studied. Kerschbaum (28) has shown the essential constituent of vegetable musk to be a lactone of 17 members:



By oxidation of the corresponding cyclic ketones with Caro's acid, Ruzicka and Stoll (29) have prepared lactones of the type



containing rings of 13, 14, 15, 16 and 17 members. Similar compounds have been prepared by Lycan and Adams (30) from ω-hydroxy acids. According to Staudinger, Carothers and others, large rings of this type probably also exist in high molecular weight polymers.

V. THE ELECTRON THEORY OF VALENCE

The chief value of the electron theory of valence has been in the explanation of the differences which exist between bonds. For, although previous to 1916 there was no clear idea as to the physical nature of bonds, the evidence showed that they were not all alike. They were of three distinctly different types and served to divide chemistry into as many apparently irreconcilable groups. How the advent of the electron theory has removed these barriers and given us a consistent picture of the whole will be best appreciated by a glance at the situation which existed in 1916 and the historical developments which led up to it.

At that time there were recognized three types of bonds, each more or less successful in its own domain but of little or no value outside of it. There was the ionizing type of bond, dating from 1812 when Berzelius put forth his celebrated theory of chemical union by electrostatic attraction. Although long in disrepute, the Berzelian theory in modified form still served to explain the properties of a large number of inorganic compounds.

The rise and development of organic chemistry is inseparably linked with the non-ionizing type of bond, which seemed to have nothing in common with the ionizing bond and, beginning about 1840, served to split the science of chemistry into the two major divisions which exist today.

About 1892 Werner put forth his theory of coördination and, in order to account for the properties of the compounds under consideration, invented a third type of valence—the coördinate. By 1911 the body of facts in support of Werner's ideas had shown that this new type of valence was as successful in its own domain as were the older types in theirs.

1. *The polar bond*

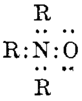
The ionizable or polar bond was given an adequate explanation in Kossel's early paper, in which he ascribed the electrostatic bonding force to the passage of an electron from one atom to the other. This gives one of the atoms an extra electron and, therefore, a negative charge. The other atom, having lost one electron, is positively charged, and what has been called the valence bond is the electrostatic attraction of these two oppositely charged ions.

2. *The non-polar bond*

In Lewis' paper, published in 1916, it is postulated that the non-ionizable or non-polar bond consists of a pair of electrons shared jointly by the two atoms, each contributing one electron to the pair. The idea that the bonding pair is often shared unequally and in the extreme case is taken over entirely by one of the atoms served to explain the observed differences in polarity.

3. *The semipolar bond*

The coördinate or semipolar linkage of Werner has not been so easy to explain. It turns out to be a bond consisting of a pair of electrons, both of which are contributed by one and the same atom. Actually this type of bond may be thought of as a double bond made up of one non-polar bond and one polar bond. For, since the electron pair is furnished solely by one of the uniting atoms, this atom effectually loses one electron (one half of the pair) and the other atom gains it. The donor, therefore, carries a positive charge and the acceptor a negative charge. The case of the amine oxides is a good example.



$$\begin{array}{ccccc} & \mathrm{R} & & & \\ & \cdot\cdot & & \cdot\cdot & \\ \mathrm{R}: & \mathrm{N} & : & \mathrm{O} & : \\ & \cdot\cdot & & \cdot\cdot & \\ & \mathrm{R} & & & \end{array}$$

Here the oxygen atom in sharing the lone pair of the nitrogen atom has seven electrons and is therefore negatively charged. The nitrogen atom having given up half of its lone pair of electrons is positively charged.

It is evidence in support of this explanation of coördination with which we have had to do in organic chemistry during the past few years. This work has indicated that (*1*) *there are two distinct types of double bonds* and (*2*) *one of these types is unsymmetrical.*

4. *The parachor*

The division of double bonds into non-polar and semipolar groups has been accomplished through Sugden's concept, the parachor (31). This quantity, which is a measure of molecular volume, is arrived at from Macleod's equation for the relationship between surface tension and density for normal liquids,

$$\gamma = C\,(D - d)^4$$

where γ = surface tension, D = density of the liquid and d = density of the vapor, all measured at the same temperature. For non-associated substances, C is a characteristic constant independent of temperature.

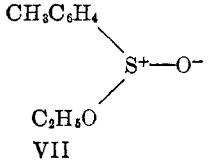
If the fourth root of C is multiplied by the molecular weight we get

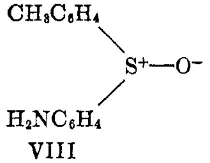
$$C^{1/4} M = P = \frac{M}{D - d}\,\gamma^{1/4}$$

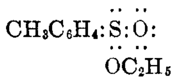
where P has the dimensions of volume and, for low temperatures where d is small, is in fact the molecular volume.

This quantity P, known as the parachor, has been found to be related to chemical composition and is an additive function of the atomic and structural units. The presence of a double bond, for example, has been found to increase the parachor by 23.2 units. This value holds for all double bonds involving carbon but in many cases of double bonds between other elements, such as sulfur and oxygen or nitrogen and sulfur, an entirely different value of −1.6 units is obtained. The remarkable thing about these results is that the values for the double bonds examined fall sharply into one or the other of these two classes. These results indicate that double bonds are of two classes.

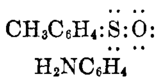
The final proof that the double bonds of parachor values of −1.6 correspond to the semipolar linkages came from certain studies which have shown these bonds to be unsymmetrical. In the sulfur compounds, for example, sulfoxides and sulfonic esters of the types VII (32) and VIII (33) should possess semipolar bonds. The plausibility of this assumption will be more apparent if we write the electronic structures for the compounds:


VII


VIII



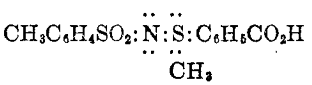
$$\mathrm{CH_3C_6H_4{:}\underset{\displaystyle OC_2H_5}{\overset{..}{\underset{..}{S}}}{:}\overset{..}{\underset{..}{O}}{:}}$$



$$\mathrm{CH_3C_6H_4{:}\underset{\displaystyle H_2NC_6H_4}{\overset{..}{\underset{..}{S}}}{:}\overset{..}{\underset{..}{O}}{:}}$$

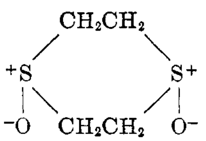
These predictions have been verified by Phillips and his students, who have been able to resolve these compounds into pairs of mirror images. The presence of the semipolar bond is thus proved, for otherwise the molecule would be symmetrical and unresolvable.

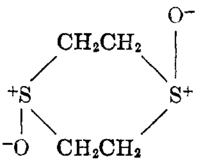
These authors have subsequently resolved the sulfilimine (34)



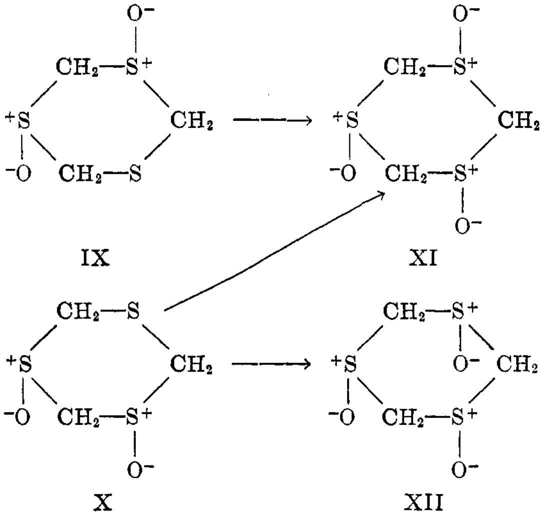
$$\mathrm{CH_3C_6H_4SO_2{:}\overset{..}{\underset{..}{N}}{:}\underset{\displaystyle CH_3}{\overset{..}{\underset{..}{S}}}{:}C_6H_5CO_2H}$$

in which the asymmetry is referred to a semipolar bond between a sulfur atom and a nitrogen atom. Bell and Bennett (35) have extended the work in this field by a study of the disulfoxides. 1,4-Dithiandisulfoxide has been shown to exist in two geometrically isomeric forms:





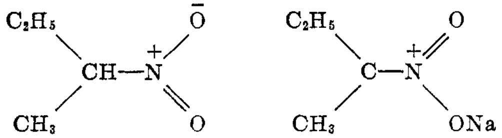
During the present year these authors have examined the dioxides and trioxides of trimethylene trisulfide (36). According to theory there should be two dioxides and two trioxides. Experiment has fully confirmed these predictions. Bell and Bennett have not only isolated two dioxides and two trioxides but have succeeded in determining the configuration in each case.



The structure of XI follows from the fact that it is obtained from both IX and X. XII can be obtained only from X. This establishes at once the structure of IX and X as well as that of XII.

5. *Optically active aci-β-nitrobutane*

A further contribution as to the nature of the semipolar bond has been made by Kuhn and Albrecht (37), who have isolated the sodium salt of active β-nitrobutane and have found that it is optically active. They represent the nitro compound and its active salt by the following formulas:

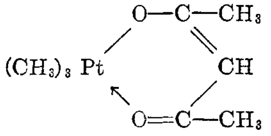


Thus, according to Kuhn and Albrecht, the reaction involves the intramolecular displacement of a semipolar double bond. It is noteworthy that this is the only instance in which a semipolar character has been suggested for a double bond involving a carbon atom.

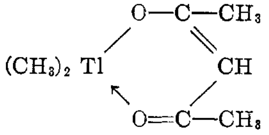
6. *Chelate derivatives of diketones*

It has long been known that many metal enolates of β-diketones exhibit anomalous physical properties in that they are not salt-like, but are very soluble in organic solvents and can be distilled or sublimed. Following the suggestion of Werner, these have generally been regarded as internal coördination compounds.

The nature of these derivatives is well illustrated by the trimethyl platinum acetylacetone (XIII) of Menzies (38), the dimethyl thallium acetylacetone (XIV) of Menzies, Sidgwick, Cutcliffe and Fox (39)

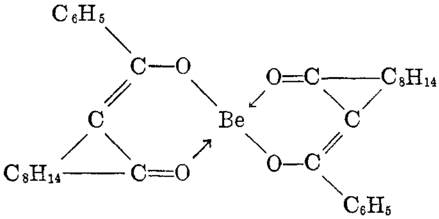


XIII



XIV

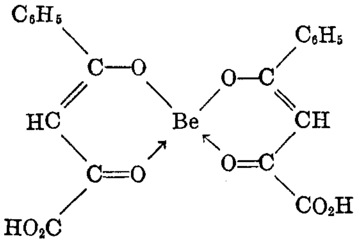
and the beryllium benzoyl camphor of Burgess and Lowry (XV) (40).



XV

In terms of the new valence theory the beryllium atom in XV is supposed to complete its octet by coördination with the two carbonyl oxygen atoms. Thus it is linked to two of the oxygen atoms by non-polar bonds and to the two remaining oxygens by semipolar bonds.

The nature of the valency of the metals in this type of compound has been put on a firm experimental basis by Mills and Gotts, who have studied the beryllium derivative of benzoylpyruvic acid. According to the theory, this compound should have the following structure:



It should be mentioned also that this formula is supported by the x-ray findings of Morgan and Bragg (41), who state that in this compound the beryllium atom is surrounded by four oxygen atoms in a tetrahedral arrangement.

This idea of a tetrahedral arrangement furnishes at once a tool whereby the correctness of the structure may be tested, for in that case the molecule as a whole will be asymmetrical and, therefore, capable of resolution into enantiomorphous forms. Experiment has fully supported these ideas. Mills and Gotts (42) prepared the active forms of the dimethylammonium salt of beryllio phenylpyruvic acid.

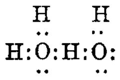
The resolution of this compound demonstrates at once that the beryllium is actually bound simultaneously to the four oxygen atoms and that these are arranged in the tetrahedral form. It is noteworthy that the active forms of the compound are racemized with the utmost ease—a result which is in entire agreement with the formula. Similar results were obtained with the zinc and copper derivatives of phenylpyruvic acid.

From these results emerges the conclusion that the bonds involved in coördination compounds have the directional properties of ordinary non-polar bonds—are, in a word, like the semipolar bonds which are found in such compounds as amine oxides and sulfoxides.

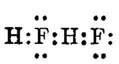
7. *Divalent hydrogen*

In view of the information now available with reference to coördination compounds in general, it seems probable that the driving force behind coördination reactions is the tendency of atoms to complete stable shells. In most instances the stable group is the octet, but in a few compounds the stable shell would appear to contain ten, twelve or even more electrons. It has been suggested by Huggins and by Latimer and Rodebush that hydrogen may become divalent by coördination in such a way as to complete a shell of four electrons. This theory, which has achieved signal success in inorganic chemistry, has been used by the organic chemist in explaining molecular association.

It is probable that the molecular association of water, hydrogen fluoride, alcohols and other hydroxyl-containing compounds is due to coördination through hydrogen:



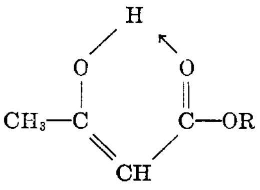
$$\mathrm{H{:}\underset{\cdot\cdot}{\overset{\overset{H}{\cdot\cdot}}{O}}{:}H{:}\underset{\cdot\cdot}{\overset{\overset{H}{\cdot\cdot}}{O}}{:}}$$



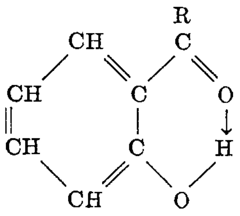
$$\mathrm{H{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}{:}H{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}{:}}$$

Evidence of a conclusive nature in favor of this has been brought forward by Sidgwick and his students in an investigation extending over the past fifteen years.

It has been shown, for example (43), that in β-diketones the enol form is less polar, i.e., more volatile, more soluble in organic solvents and less associated than the keto form. It cannot, therefore, have a hydroxyl group, but could exist in a chelated form (XVI) which would be expected to show the observed non-polar properties.



XVI



XVII

In a similar way certain *ortho*-substituted phenols (44) have been shown to be less associated, more volatile and in general less polar than their *meta* and *para* isomers. The assumption that these compounds are chelated through hydrogen (XVII) again gives a satisfactory explanation of their anomalous properties. For the anomalously non-polar character appears only when the substituent next to the hydroxyl group is NO_2, CHO, or CO_2H, i.e., a group which has a lone electron pair to conjugate with the hydrogen, and is absent when the substituent is an alkyl group, a group which can furnish no lone electron pair.

VI. CONCLUSION

In conclusion, it might be well to point out certain general trends which are apparent in the development of valence theory at the present time.

1. The so-called classical considerations, *viz.* the number of bonds, their spatial arrangement and the problem of bond distortion, still engage the attention of the majority of investigators. These problems continue to yield highly significant results, illustrative examples of which have been mentioned.
2. Certain rather surprising developments, notably the explanation of the isomerism of diphenyl compounds and the theory of strainless rings, seem to require the return to a more rigid type of model for the tetrahedral carbon atom.
3. The electron theory of valence has consolidated the various fields of chemistry by an explanation of the differences in the bonds characteristic of these fields.
4. Finally, it might be pointed out that the great importance of the problem of reaction mechanism has gained more general recognition. Nothing is more eloquent of this than the vast amount of work which has been done in an attempt to apply the new valence theory to the problem. Moreover, nothing shows more clearly than these attempts the real inadequacy of the theory in its present form. Reaction mechanism certainly calls for a dynamic theory of valence, and in this respect the new theory is open to essentially the same criticism as was the old—it is a static theory. It might be predicted, and it is certainly to be

hoped that the next great step ahead in the field of valence will be in this direction.

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