

CXXXVII.—*The Structure of the Benzene Nucleus.*
Part I. Intra-nuclear Tautomerism.

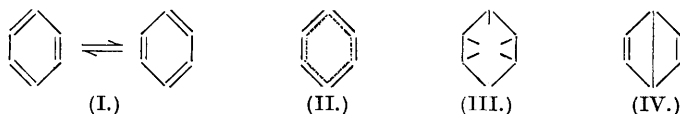
By CHRISTOPHER KELK INGOLD.

IN approaching the question of the constitution of the benzene nucleus it is essential to recognise that the best criterion of the truth of any suggested structure is its bearing on the problem of the

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unification of the essential reactions and basic general principles of the two main branches of organic chemistry. This attitude is fundamental to the argument outlined below.

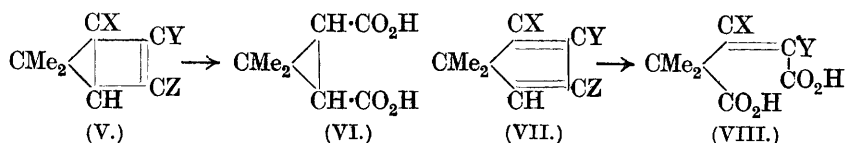
Hitherto the aliphatic and aromatic branches of organic chemistry have remained virtually distinct, each the field of operation of its own general laws, and the older conceptions embodied in Kekulé's dynamic formula (I), Thiele's half-valency formula (II), and Armstrong and Baeyer's centric formula (III) leave the problem of collation practically untouched; indeed, the centric formula definitely places benzene beyond the reach of any conceptions which could be evolved solely by the study of aliphatic compounds.



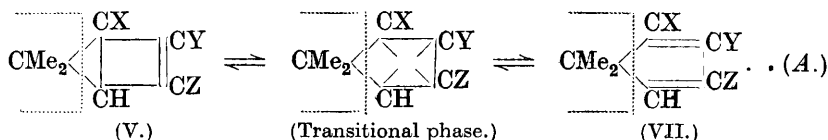
Considerable historical interest attaches to formula IV, which was first suggested by Dewar (*Proc. Roy. Soc. Edin.*, 1866—1867, 84) as one of seven possible formulæ for benzene. Another of the seven was the ordinary Kekulé formula, proposed by Kekulé in 1865 and reported on to the British Association by Dewar in 1868 (*Rep. Brit. Assoc.*, 1868, 34), after Dewar himself had become acquainted with Körner's position theory. It is perhaps remarkable that Dewar's bridged formula (IV) has never gained any considerable measure of acceptance; indeed, it seems never to have been seriously considered in relation to the chemistry of aromatic compounds, although Kauffmann has employed it in the development of his theory of fluorescence (*Ahrens's Vortrage*, 1908, **12**, 35). Baeyer did not regard the bridged formula as a possibility worth examining at any period during his experimental researches, and in Richter's "Organische Chemie" (edition 1909—1913) no mention is made of it even in connexion with obsolete formulæ such as those of Claus and Ladenburg. Yet it is the purpose of this paper to show that Dewar's formula, considered in relation to present-day conceptions of carbon tautomerism, is the clue to the constitution of the aromatic nucleus.

In the first place, it is necessary to refer to certain aliphatic bridged-ring compounds which appear to occupy a position in the systematic description of organic compounds intermediate between the aliphatic and the aromatic series. It has been shown (Farmer and Ingold, T., 1920, **117**, 1362) that certain acids containing a bridged *cyclopentane* ring behave under the influence of particular reagents as though they possessed, not a bridge, but an endocyclic double bond; or, as it is equally correct to say, certain monocyclic

unsaturated compounds behave towards some reagents as though they contained a bridge-bond similar in many respects to the para-bond in formula (IV). The same compound may be oxidised (as though its constitution were represented by formula V) to a *cyclo*-propane derivative (VI), and also (as if its structure were expressed by formula VII) to an unsaturated open-chain acid (VIII) :



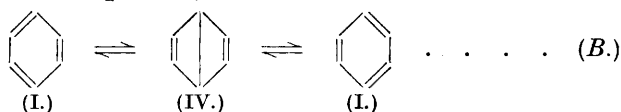
Now the investigation of these bridge-bonded compounds is obviously of great importance for the understanding of aromatic character, and the significant fact in this connexion is that *both* formulæ (V) and (VII) are necessary to explain the reactions of the substance ; for recent investigation has shown (Farmer, Ingold, and Thorpe, this vol., p. 128) that all these compounds have a dual set of properties. The view which has been adopted, and which appears to be the only one capable of explaining the facts, is that the types (V) and (VII) are merely phases of a state of tautomerism involving valency exchange across and within the *cyclopentane* ring. The two individuals, it will be observed, are valency isomerides and no transmigration of a hydrogen atom occurs. The process is represented thus :



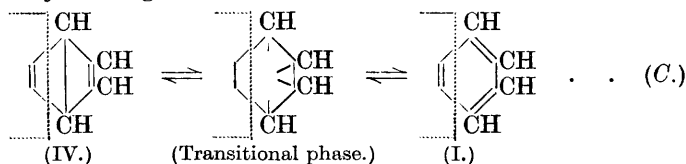
the "centric" phase, for which no direct chemical evidence exists, being inserted to aid visualisation of this intra-annular valency-exchange and to represent some uncomprehended intermediate condition which must occur, however transiently, at some moment during the transformation.

It is obvious that this phenomenon, which has been termed "intra-annular tautomerism," and has been strikingly confirmed by more recent experiments, must, if it is true, permeate every field of organic chemistry in which cyclic compounds are met with, and, in particular, must be fundamentally concerned in the production of aromatic character. Now for several years past, and on quite other grounds (below), the author has held the view that the true conception of the benzene molecule is a dynamic one, in which the

bridged phase (IV) occupies a position intermediate between the two double-bonded phases (I) :



We know that a bridge-bond, equally with a double bond, is invariably a point of unsaturation, so that each of these three phases consists of an endless (or closed) chain of unsaturated elements. Let us isolate from this double equation the right-hand member only, and expand it by introducing a formula for the transitional state; we obtain in this way equation (C), in which the analogy (confining attention for the moment to the right-hand sides of the dotted lines) with the tautomerism of the five-carbon rings (equation A) is very striking :

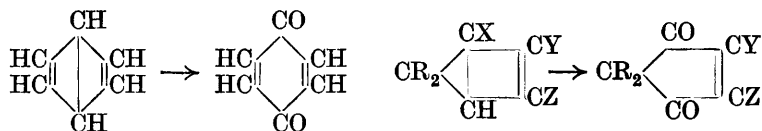


The complementary transformation involving the portion of the ring to the left of the dotted lines is that corresponding with the left-hand member of equation (B) and is exactly similar. In short, the five-carbon intra-annular transformation constitutes a simple model illustrating the rearrangement of half the benzene ring.

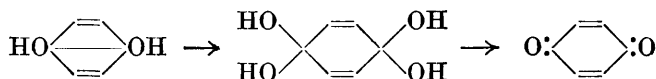
However, such an analogy, although striking and valuable as confirmation, proves nothing, and the contention which has been made clearly requires the strongest possible supporting evidence. In the following parts of this series it is proposed to submit new experimental evidence bearing on the question; the purpose of the present communication is to indicate by some typical illustrations the manner in which certain classes of known fact confirm the view which has been adopted.

Probably the most characteristic, unique, and most extensively observed type of change which aromatic compounds undergo is the benzenoid-quinonoid transformation. None of the formulæ I, II, III, possesses as part of its face value any feature which clearly suggests the remarkable prevalence and the uniqueness of this change. Plainly, however, the introduction of the bridged phase brings this transformation exactly into line with those reactions which result in the formation and fission of bridge-bonds in the aliphatic series; no other formula can do so. Many reactions of benzene and its substitution products are reactions of the bridged form; many are

reactions of the double-bonded form. For instance, the electrolytic oxidation of benzene to *p*-benzoquinone is a reaction of the bridged phase, and is exactly analogous to the oxidation, recently accomplished, of a bridged tautomeric individual of type V to a cyclic 1 : 4 diketone :

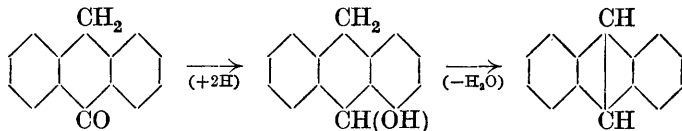


The oxidation of quinol to benzoquinone is caused by the addition of two hydroxyl groups at the bridge :



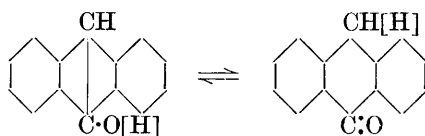
These instances are typical of a very large family of reactions in which para-quinonoid structures are produced by oxidation or by additive reactions. It seems scarcely necessary to add that the changes which result in the formation of ortho-quinonoid structures are reactions of one or other of the double-bonded (Kekulé) phases of the aromatic complex (*B*).

With regard to the formation of benzenoid compounds from quinonoid, it is to be remarked that whenever the elements of water, hydrogen bromide, etc., can be eliminated from the 1 : 4-positions of a para-quinonoid substance a benzenoid structure is produced, usually with quite remarkable ease ; in fact, it is generally impossible to isolate substances capable of undergoing this reaction owing to the facility with which it occurs. An illuminating instance is the reduction of anthrone to anthracene ; here the primary reduction product, although very unstable, can be isolated, and, on loss of water, passes into anthracene :

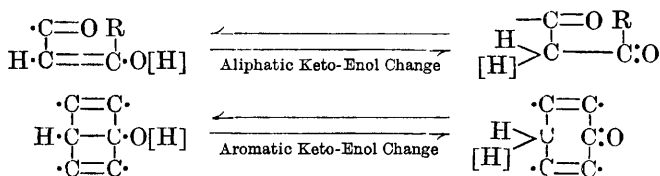


The establishment of para-linkings by this means, and the extraordinary ease with which the changes take place, find exact parallels in a number of instances of the formation of bridge-linkings across a cyclopentane ring. These cases are discussed in the paper previously referred to (Farmer, Ingold, and Thorpe, *loc. cit.*), and it is only necessary to notice here that none of the substances undergoing the reaction could be isolated owing to the facility with which it took place.

Interchange between benzenoid and para-quinonoid systems can take place, however, not only by addition and by elimination of groups, but even by tautomeric interchange, and this circumstance constitutes one of the strongest reasons why the recognition of this bridged phase of the benzene nucleus is essential for the collation of the properties of aromatic compounds with known facts relating to the aliphatic series. For instance, the tautomerism of anthrone with anthranol (K. H. Meyer, *Annalen*, 1911, **379**, 39, 43) remains inexplicable and uncollated by the general theory of keto-enol tautomerism as developed by the study of aliphatic substances unless a bridged phase for anthranol be assumed. If, however, we may suppose that anthranol reacts in its bridged form, then the change can be expressed as follows : *



(the mobile hydrogen atom being shown in brackets), and the analogy of aromatic keto-enol change in general with ordinary aliphatic keto-enol tautomerism becomes complete. The formal identity of the types depends solely on the similarity of a bridge-bond and double bond as elements of unsaturation (Farmer and Ingold, *loc. cit.*). In each case the mobile hydrogen atom (shown in brackets) crosses the keto-enol system C—C—O :

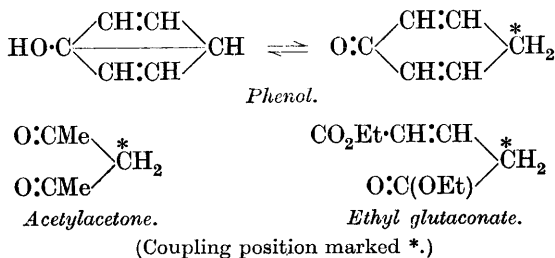


In the same way, the formation of quinonoid structures from aromatic amines by reversible isomeric change falls within the category of imino-ename tautomerism, since here the mobile hydrogen atom passes across the system C—C—N.

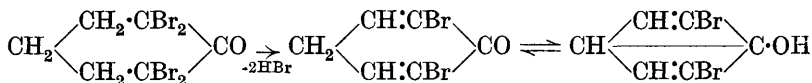
“Coupling” reactions are evidently bound up with the phenomenon of tautomerism in a very intimate manner, and form another striking illustration of collation with the aliphatic series on the basis of a bridged phase of the benzene nucleus. Phenol, for instance, condenses with diazonium salts through its bridged form, the ketonic (or anthrone-like) modification of which (related to the bridged

* A paper on tautomerism which involves the opening and closing of *simple* four-carbon rings will shortly be published.

individual much as ethyl acetoacetate is to ethyl β -hydroxyacrylate) is constituted absolutely analogously to those compounds of the aliphatic series which show corresponding properties :†



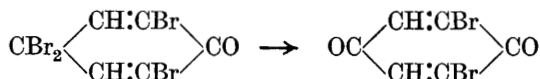
Baly and Ewbank supposed, in order to account for the absorption spectrum of phenol, that this substance exhibits tautomerism and contains a mobile hydrogen atom (T., 1905, **87**, 1347). The analogy with anthranol (p. 1138) suggests that phenol, although, of course, it is practically completely enolic, should be capable of exhibiting mobility of the kind shown in the equation above, and, indeed, there is much chemical evidence available which proves that the para-interchange postulated can and does occur in phenol itself and its derivatives. For instance, Wallach found (*Annalen*, 1905, **343**, 42) that tetrabromocyclohexanone, when warmed alone, lost two molecules of hydrogen bromide. The product should be an unsaturated ketone, which, according to the view under discussion, is the ketonic modification of the bridged phase of 2 : 6-dibromophenol :



As a matter of fact, the product was ordinary 2 : 6-dibromophenol, showing that conversion from the keto to the enol form by the movement of a hydrogen atom across the six-carbon ring actually does occur. This is but one of many instances which might be cited. Tautomerism, however, is reversible isomeric change, and it is necessary, therefore, to show that the retrograde transformation, that is, from the enol form to the keto-form, can also take place. One instance of the occurrence of this change is furnished by the formation of 2 : 4 : 6-tribromophenol bromide from phenol

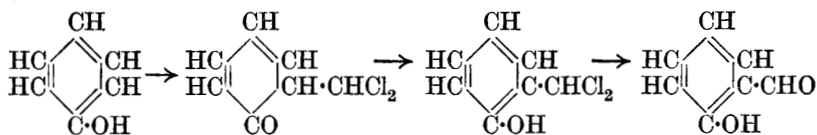
† Without doubt it is the enolic (or phenolic) form which actually undergoes the condensation (compare K. H. Meyer, *Ber.*, 1921, **54**, [B], 2265); nevertheless the substituted phenol thus formed can pass into its ketonic modification, which accounts for its apparent identity with the quinone-phenylhydrazone. Similar considerations apply to the reaction between phenol and nitrous acid.

and bromine water. The constitution of this bromide has been established by Thiele and Eichwede (*Ber.*, 1900, **33**, 673), who have converted it into 2:6-dibromobenzoquinone by warming with aqueous lead acetate :

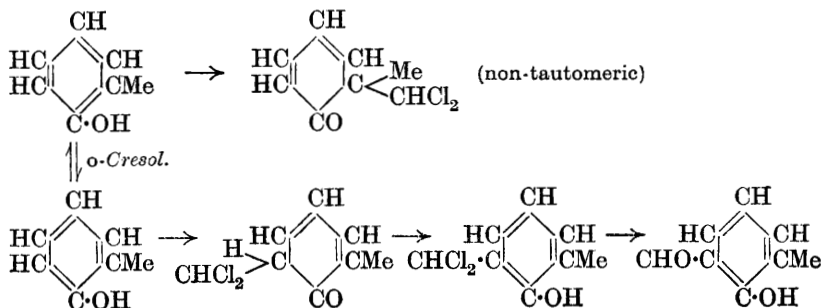


The bromide, therefore, is the tetrabromo-derivative of the ketonic modification of phenol, and its production must at some stage have involved tautomeric conversion of the (bridged) enol form into the keto-form.

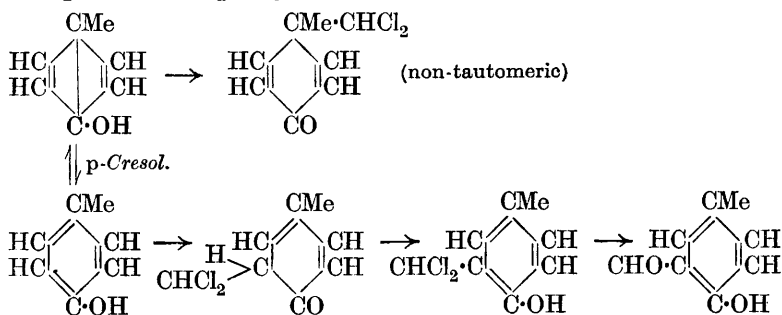
Phenol, however, may also exhibit the kind of keto-enol tautomerism which corresponds with the ordinary double-bonded formula for that substance, and it is this property which doubtless determines the course pursued by the Reimer-Tiemann reaction. Alkylation occurs on carbon as follows :



That this is so is proved by the fact that *o*-cresol, which, like all orthodisubstituted benzenes, has two double-bonded forms, gives, when condensed with chloroform, two products, one corresponding with each of the Kekulé forms of *o*-cresol. One of these products is a homologue of salicylaldehyde, but the other is a ketone, which, owing to the position of the methyl group, contains no mobile hydrogen atom and cannot revert to an enolic (phenolic) condition. Therefore, the general course of the series of reactions which would have taken place in other circumstances is, in this instance, arrested with the formation of a substance the constitution of which clearly reveals the mechanism of the change :



In the case of *p*-cresol, there are two forms only which are capable of undergoing tautomeric change of the keto-enol type: one is double-bonded and the other is bridged. If these two forms be examined in relation to their ability to enter into condensation with chloroform, it is at once observed that in this instance it is the condensation of the bridged modification which must be arrested after the initial stage owing to the absence from the initial condensation product of capacity for tautomerism:



Actually this is what occurs (Auwers and others, *Ber.*, 1905, **38**, 1693, and earlier) and it is difficult to imagine a satisfactory alternative explanation.

A large class of reactions in which the properties of the bridged phase of the aromatic nucleus are manifested is that group of irreversible isomeric changes which lead ultimately to substitution in the para-position. A well-known instance is the conversion of methylaniline into *p*-toluidine. The simplest assumption which one can make as to the mechanism of this change, indeed of all reactions of this type, is that they take place through the bridged phases of the initial and final products.

Many conflicting views have been expressed regarding the mechanism by which substituents in general enter the benzene nucleus, but that which seems to have gained the greatest measure of acceptance, and which is certainly the simplest and most rational, is that, in general, addition to one of the double bonds of a Kekulé phase is the first stage, and that the elimination of water, hydrogen bromide, etc., is a subsequent occurrence. Hollemann ("Die direkt Einführung von Substituenten in den Benzolkern") has stated this hypothesis in very clear terms, and has further supposed that the directive influence of groups is to be attributed to their increasing or decreasing the reactivity of the adjacent double bonds. Here, however, a difficulty is encountered in connexion with the necessity for bringing ortho- and para-substitution within the same scheme. This difficulty Hollemann endeavours to meet by introducing a

somewhat unsatisfactory assumption in which the Thiele hypothesis * is employed in a highly artificial manner, but from the preceding discussion it will be plain that the recognition of the bridged form of the aromatic nucleus as an essential phase of the complete tautomeric scheme obviates the necessity for any such supposition. One must indeed assume that those groups (the ortho- or para-directing groups) which enhance the reactivity of the adjacent double bond also favour that bridged phase in which the bridge is attached to the carbon atom carrying the group. This, however, seems probable on general grounds, for such groups would enhance the reactivity of an adjacent bridge-bond, and thus render the bridge phase more prone to yield evidence of its existence by entering into chemical reactions. It is well known, moreover, that groups, such as hydroxyl- and amino-groups, which favour conversion by oxidation or isomeric change into quinonoid structures invariably have ortho- and para-directing properties. Phenol, for instance, has two principal phases, one double-bonded and one bridged, and the nitration of phenol, therefore, yields a mixture of ortho- and para-isomerides because the first stage of the process consists in the addition of the groups $\text{HO}-\text{NO}_2$ to the activated double bond of one phase and to the bridge-bond of the other.

In the case of compounds containing substituent groups which decrease, or, at any rate, do not enhance, the reactivity of the adjacent double bond (or bridge-bond) it is probable that the most vulnerable of all the possible phases is the bridged form containing a bridge-bond between two carbon atoms other than that which bears the substituent. In certain cases, however, meta-substitution may proceed through the double-bonded phase in accordance with the mechanism suggested by Hollemann (*loc. cit.*).

These, however, are amongst the many matters which will have to be settled in the future by *experimental* investigation, for it is plain that once the broad principle outlined in this communication is accepted the whole field, not only of benzene derivatives, but also of naphthalene, anthracene, pyridine, and acridine derivatives, indeed of all aromatic compounds, lies before us, and much carefully planned experimental work is required. It has been stated, however, that quite apart from such new proof as can be obtained from specially devised experiments, the general hypothesis requires definite support from the mass of known facts relating to the aromatic series. Certain directions in which supporting evidence may be obtained have been indicated above, but it is not the purpose of the present paper to deal with this aspect of the subject even moderately completely. It is desired rather to adumbrate

* A paper dealing with this subject will shortly be published.

by means of a few chosen examples the manner in which some degree of preliminary justification of what appears to be a reasonable working hypothesis is to be sought, and in which the theoretical origin of the experiments described in the following series of papers was actually reached.

The author owes to the kindness of Sir James Dewar the information contained on p. 1134 regarding the early history of the benzene formula.

THE IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON, S.W. 7.

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