XXVIII.—*An Explanation of the Laws which govern Substitution in the case of Benzenoid Compounds.*

By Henry E. Armstrong.

It is well known that certain mono-derivatives of benzene yield a mixture of *para-* and *ortho-*di-derivative in proportions which apparently are much affected by the conditions under which substitution takes place, the *meta-*di-derivative being formed in relatively very small proportion, if at all; whereas other mono-derivatives chiefly yield the *meta-*di-derivative. A very noteworthy illustration of the manner in which the radicle first introduced exercises a specific influence on the subsequent displacement of a second hydrogen-atom is afforded by the production of a mixture of *ortho-* and *para-*nitrobromobenzene on nitrating bromobenzene, but of *meta*bromonitrobenzene on bromination of nitrobenzene in presence of ferric chloride (*Annalen*, **231**, 158). I am not aware that up to the present time any explanation of the remarkable difference in behaviour of mono-derivatives of benzene here referred to has been even hinted at.

To afford an opportunity of contrasting the behaviour of the various mono-derivatives of benzene, the accompanying tables (I and II) have been arranged, showing the nature of the radicle R' contained in the mono-derivative and the position which the radicle X' assumes relatively to R'. Whenever possible, the position of X' in the chief product is indicated by printing the figure in thick type; the position which it assumes in the product which is obtained in very small amount is indicated by underlining the figure; where no distinction is made, it is either because the proportions vary with the

conditions, or more often because exact information on this point is wanting. Table I illustrates what may be termed the para-ortho-law; Table II the meta-law.

TABLE I.—*Illustrating Para-ortho-law.*

R′.	Position of X′ relatively to R′.				
	Cl.	Br.	I.	NO_2.	SO_3H.
CH_3	2, 4	2, 4, 3	—	2, 4, 3	2, 4
CH_2Cl	4	—	—	4	—
$CHCl_2$	4	—	—	3	—
CCl_3	4	—	—	3	—
Cl....................	2, 4	2, 4	—	2, 4	4
Br	—	2, 4	—	2, 4	4
I	—	—	4	2, 4	4
OH	2, 4	2, 4, 3 (?)	2, 4, 3 (?)	2, 4	2, 4
NH·Ac	2, 4	2, 4	4	2, 4	—
$NH_2·SO_4H_2$	—	—	—	2, 4 3	4
$CH_2·COOH$	2, 4	4	—	2, 4	—
CH·CH·COOH	—	—	—	2, 4	---

TABLE II.—*Illustrating Meta-law.*

R′.	Position of X′ relatively to R′.				
	Cl	Br	I.	NO_2.	SO_3H.
NO_2.................	3	3	—	3, 2, 4	3, 2, 4
CN	—	---	—	3	—
COH	—	—	—	3	---
$CO·CH_3$	—	—	—	3, 2	—
$CO·CH_2Br$...........	—	—	—	3	—
$CO·C_6H_5$.............	—	—	—	—	4
CO·OH	3	3	3	3, 2, 4	3, 2, 4
$SO_2·OH$	---	3	—	3, 2, 4	3, 4
$SO_2·C_6H_5$	—	---	—	3	3

Now, on careful study of the examples collected in these tables, it will be noted that R′ in all compounds which obey the para-ortho-law is either a monad simple radicle or a compound radicle in which the grouping element of the radicle is combined with one or more monad radicles; whereas in compounds subservient to the meta-law the grouping element of the radicle R′ is associated with one or more polyad atoms—with N in CN, with O in NO_2, COH, $CO·CH_3$ and

CO·OH. The double influence exercised by $CHCl_2$ and CCl_3 is remarkable.

Before attempting to make use of these facts, it will be desirable to consider what conception is to be attached to the term "substitution"; in what way is substitution effected? Obviously, equations such as are commonly used—for example: $C_6H_6 + Br_2 = C_6H_5Br + HBr$—afford no information regarding the course of change, but serve merely to indicate the relative quantities concerned in the interaction; and text-books are all but silent on such matters. There would appear, however, to be floating in the minds of most of those who have been at the pains to consider this question at all a more or less clearly defined idea that in some way or other dissociation precedes substitution; that simplification is the antecedent of complication. Williamson, as far back as 1851, in his celebrated paper on the "Theory of Etherification," clearly expresses this view in words which leave no doubt (*Quart. Journ. Chem. Soc.*, **4**, 110). To quote but a few of his sentences, he says: "We are thus forced to admit that in an aggregate of molecules of any compound there is an exchange constantly going on between the elements which are contained in it. For instance, a drop of hydrochloric acid being supposed to be made up of a great number of molecules of the composition ClH, the proposition at which we have just arrived would lead us to believe that each atom of hydrogen does not remain quietly in juxtaposition with the atom of chlorine with which it first united; but, on the contrary, is constantly changing places with other atoms of hydrogen, or, what is the same thing, changing chlorine. Of course, this change is not directly sensible to us, because one atom of hydrochloric acid is like another; but suppose we mix with the hydrochloric acid some sulphate of copper (of which the component atoms are undergoing a similar change of place) . . . . . . the hydrogen does not merely move from one atom of chlorine to another, but in its turn also replaces an atom of copper . . . . . . Thus it is that at any moment of time in which we examine the mixture, the bases are divided between the acids . . . . . . Such is the general process of chemical decomposition."

These views necessarily derived much support from the researches of Deville and his pupils on dissociation; and it can scarcely be doubted that their acceptance at the present day is mainly attributable to Deville's discoveries. The classical research which led to their conception cannot now be said to afford any very cogent argument either for or against them.

I have elsewhere ventured to express my doubts concerning the universal occurrence of dissociation in the case of "atomic" compounds, and will here only add that the more I consider the evidence

the more I am led to think that our views on this subject need modification in not unimportant particulars. Be this as it may, my object now is to advocate the view that in the formation of substitution-products—in reactions of so-called double decomposition—an additive compound is first formed by the union of the interacting substances. The conviction that this is the case has grown upon me during several years past, although I cannot say in what it originated; looking up the question recently, however, I find that Kekulé in his *Lehrbuch der organischen Chemie* (Erlangen, 1867) takes this view in the most decided manner possible, speaking of it, in fact, as "Die einfachste und auf alle Fälle anwendbare Vorstellung;" he even goes so far as to express the idea graphically in the following manner:—

Before decomposition.   During decomposition.   After decomposition.
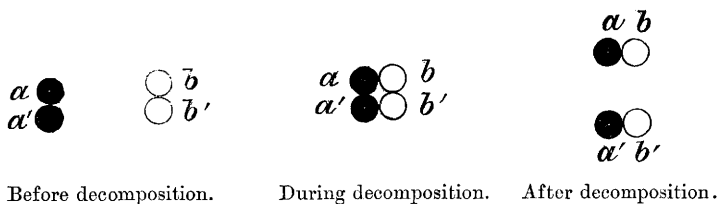
The two quotations serve to show that even authorities differ as to the interpretation which is to be given of the course of chemical change.

The formation of additive compounds has been observed in so many cases, that the possibility of their being formed from carbon compounds generally, excepting the paraffins, will scarcely be questioned, I imagine;* it is therefore permissible at once to pass to the consideration of the process involved in the production of the additive compound and its subsequent resolution into the substitution derivative.

To take the simplest case possible afforded by a benzenoid compound—the conversion of benzene into bromobenzene: according to the view advocated in this communication, the initial stage would be the addition of a molecule of bromine to *one* of the *six carbon-atoms;* the hydrogen-atom attached to this carbon-atom would thus find itself in the immediate presence of an element for which it has a strong affinity, and a very slight disturbance would lead to its separation with one of the atoms of bromine, whereupon the other bromine-atom would assume the place of the hydrogen-atom thus removed. A precisely similar explanation of the formation of mono-

* I may, perhaps, with advantage direct attention to Schramm's observations on the bromination of benzene (*Ber.*, **18**, 607) ; to an important investigation on the chlorination of toluene by Seelig (*Annalen*, **237**, 169) ; and to a paper by Istrati (*Ann. Chim. Phys.* [6], **6**, 367).

derivatives generally may be given. It is here supposed that the formation of the additive compound does not involve the separation and distribution of the bromine-atoms; this is not a necessary assumption, however: indeed it is well known that the first visible product of the action of bromine on anthracene and also on phenanthrene is a comparatively stable dibromide in which apparently the bromine-atoms are distributed, and it is therefore possible that similar compounds are formed in other cases but escape detection owing to their instability. But in the case of anthracene and phenanthrene it is easy to account for the formation of dibromides; the compound bearing a corresponding relation to the hydrocarbon is in the case of naphthalene a tetrabromide, and in the case of benzene a hexabromide: a tetrachloride, but not a tetrabromide, is actually producible from naphthalene, and a hexabromide and hexachloride of benzene are known, but there is no evidence of the production of intermediate compounds similar to these: so that it does not appear improbable that distribution only occurs when opportunity is given for complete saturation of the elements of the carbon ring. In connexion with this question, the experiments of Ador and Rilliet are of special interest (*Ber.*, **8**, 1286). These chemists added a relatively small quantity of bromine to very carefully cooled benzene, and after well washing and drying the solution, submitted it to the action of zinc ethyl. The product was then oxidised; and they obtained benzoic, meta- and para-bromobenzoic, meta- and para-phthalic acids, but not a trace either of orthobromobenzoic or of phthalic acid. Unfortunately the oxidation was effected by means of chromic mixture by which ortho-compounds are known to be destroyed; otherwise these results would serve to place it beyond doubt that in the formation of the additive compound the bromine-atoms do not become separated and attached to contiguous carbon-atoms.*

Frequently it is advantageous, if not essential, to add a so-called carrier in order to effect the production of haloid derivatives; the use of iodine for this purpose was first made known by Hugo Müller, in 1862, but of late years many metallic chlorides have been found to possess the property of facilitating the displacement of hydrogen by chlorine and bromine to a much greater extent than iodine. According to a recent statement by Seelig (*Annalen*, **237**, 169), if toluene

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* It may be suggested in explanation of Ador and Rilliet's results, that an additive compound of 2 mols. of benzene with 2 mols. of bromine is formed; and that the carbon-atoms affected are relatively in para-position; that the zinc ethyl acts initially by inducing the withdrawal of HBr, the place of the H atom withdrawn being at once taken by ethyl; and that by a repetition of this process either a para- or a meta-derivative is formed according as the second hydrogen-atom withdrawn as HBr is para- or meta- relatively to that first displaced.

cooled to 0° be saturated with chlorine and anhydrous ferric chloride
be then added, a vigorous effervescence will at once take place owing
to the escape of hydrogen chloride. It would therefore seem that the
function of such "carriers" is to induce the separation of haloid
hydride from the additive compound. This explanation of the action
of "carriers" appears the more probable as it is now well known that
metallic chlorides such as are used for the purpose combine more or
less readily with hydrogen chloride, forming unstable chlorhydrides.*

Passing now to the consideration of the formation of di-derivatives,
I may at once point out that the difference under discussion in the
behaviour of the two classes of mono-derivatives is, in my opinion,
attributable to the different manner in which they form additive
compounds. In the case of those which furnish the ortho- and para-
derivative, it may be held that the additive compound results from
the union of the reacting molecule with the carbon-atom to which the
radicle R' is attached.

The formation of an ortho-di-derivative from an additive compound
thus constituted would appear to follow as a matter of course,
involving as it does merely the separation and displacement of the
hydrogen-atom attached to the carbon-atom contiguous to that with
which the radicle R' is associated ; but as a matter of fact, although
in some cases the ortho-derivative preponderates—Seelig states that
about twice as much ortho- as para-chlorotoluene is formed on
chlorinating toluene—in the majority of cases the para-derivative is
the chief product. In order to account for the preponderating
influence which apparently is exercised upon the para-position, more
than one attempt has been made to devise a symbol for benzene in
which the carbon-atoms relatively in para-positions are exhibited as
in direct connexion (see especially Körner, this Journal) ; but
these cannot be regarded as successful. Moreover if the influence
which certain radicles exercise upon the para-position were held to
necessitate the assumption of a direct connexion between carbon-
atoms which are relatively in para-positions, the influence which
certain other radicles exercise in causing the production of meta-
derivatives must consistently be held in like manner to afford evidence
of the existence of a direct connexion between carbon-atoms which
are relatively in meta-positions. My own opinion is that there is no
such connexion,† and that the production of para-derivatives must

* The influence of iodine is probably ascribable to the readiness with which
iodine chloride and bromide unite with other bodies.

† I may be allowed to quote here the following passage from a recent paper of
mine on the "determination of the constitution of carbon compounds from thermo-
chemical data" (*Phil. Mag.*, February, 1887 :)—

"Thomsen . . . . maintains that the six atoms of carbon in this (benzene)

be regarded as the result of a kind of isomeric or intramolecular
change, which probably takes place owing to the existence in closed
chain compounds of a tendency to form symmetrical di-derivatives.
An even simpler explanation of the formation of para-derivatives
would be afforded by the assumption that the additive compound
results from the union of the reacting molecule not with the carbon-
atom to which the radicle R′ is attached but with that which
occupies the para-position relatively to R′.   For example, the

hydrocarbon are linked together by nine ' single bonds,' and not, in the manner
indicated by Kekulé's well-known formula, by three single and three double bonds.
Although of opinion that we cannot at present accept so absolute an interpretation
of the thermochemical data, I yet think that Thomsen's results, taken together with
all that is known of benzene, must be held to prove that benzene is in no sense a
compound of the same order as an olefine ; and that Kekulé's formula, if used at all,
must be literally interpreted as indicating that the carbon-atoms are held together
by nine affinities, there being abundant evidence to show that in the olefines the
carbon-atoms are not held together by double bonds.   In other words, if we employ
Kekulé's benzene formula, we are bound to abandon the use of the conventional
formula for olefines. From this point of view I see little difference between Kekulé's
symbol and the prism formula or the modification of the latter quite recently advo-
cated by Thomsen (*Ber.*, **19**, 2944). Objections have, however, been urged against
the prism formula which appear to be justified ; the symbol advocated by Thomsen
can scarcely be regarded as marking any particular advance ; and Kekulé's symbol
is open to the oft-raised objection that it indicates the existence of four distinct di-
derivatives. I venture to think that a symbol free from all objections may be based
on the assumption that of the twenty-four affinities of the six carbon-atoms twelve
are engaged in the formation of the six-carbon ring and six in retaining the six
hydrogen-atoms, in the manner ordinarily supposed ; while the remaining six react
upon each other,—acting towards a centre as it were, so that the 'affinity' may be
said to be uniformly and symmetrically distributed.   I would, in fact, make use of
the following symbol :—
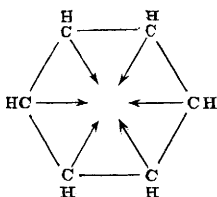
The only difference between this symbol and those employed hitherto arises from
the fact that I do not consider that, apart from its connexion with the other carbon-
atoms owing to their association in a ring, any one carbon-atom is directly connected
with any other atom not contiguous to it in the ring ; my opinion being that each
individual carbon-atom exercises an influence upon each and every other carbon-
atom."   It should be added that this symbol is not directly applicable to benzene-
derivatives.   The introduction of a radicle doubtless involves an altered distribution
of the "affinity," much as the distribution of the electric charge in a body is altered
by bringing it near to another body.

observation that potassium phenyl *sulphate*, on heating, becomes potassium phenol *parasulphonate* (Baumann), or that the nitrosamine $C_6H_5 \cdot NMe(NO)$ is converted by digestion with an alcoholic solution of hydrogen chloride into *paranitroso*methylaniline (*Ber.*, **19**, 2991), is sufficient to show that such an assumption is not necessary, however.

It remains but to add that there is abundant evidence to show that the proportions in which the para- and ortho-derivative are formed depend both on the nature of the reacting substances and the conditions at the time of change. Thus on heating *sodium* phenyl carbonate, sodium salicylate is formed, but *potassium* phenyl carbonate yields potassium parhydroxybenzoate; and whereas, according to Rosenstiehl, paranitrotoluene is the main product when a large excess of acid is used to nitrate toluene and the temperature is relatively high, orthonitrotoluene is chiefly formed if a small proportion of acid be used at a low temperature. In the case of phenol, however, Körner states that paranitrophenol is the chief product of nitration at a low temperature, and that orthonitrophenol is formed in larger quantity if the action takes place at higher temperatures.

Attention has already been directed to the difference between the radicle R′ in compounds which obey the para-ortho-law and in those which obey the meta-law. Now it is to be noted that radicles such as CN, NO_2, CO, SO_2, the presence of which favours the production of meta-derivatives, are admittedly capable of uniting with a variety of compounds, the explanation usually given being that combination takes place owing to the conversion, by the addition of the elements of the molecule X′ Y′, of the radicle AB—in which both constituents are polyad atoms—into the group $A\left\{\begin{array}{l} X' \\ (BY) \end{array}\right.$. Be this as it may, the radicles in questions are essentially different both in constitution and function from those whose presence favours the formation of ortho- and para-derivatives. Herein, I would suggest, lies the explanation of the meta-law, my opinion being that the additive compound which generates the meta-derivative is formed by the combination of the reacting molecule *with the radicle R′* of the mono-derivative, and not with the carbon-atom which carries that radicle.

Why an additive compound thus constituted should yield a meta- instead of an ortho- or para-derivative is a question to which no sufficient answer can be given at present; and we cannot hope to solve such a problem until the dynamics of the changes involved in the production of isomers have been thoroughly investigated. It is conceivable that the side-chain produced by the addition of the reacting molecule to the radicle R′ extends outwards sufficiently far to bring the added molecule into intimate connection with the

carbon-atom and its associated hydrogen-atom in the meta-position; the conception is a purely mechanical one, but I do not think this a sufficient reason to reject it altogether from consideration, the tendency of modern investigation being to show that the occurrence of a particular change more often than not depends on the formation of a system of a particular configuration, as in the production of the lactones, for example. The formation of a *parachloro-*, but of a *metanitro-derivative* from benzal chloride and benzotrichloride would appear to favour this explanation.

The production of a small proportion of meta-di-derivative from mono-derivatives which in the main obey the para-ortho-law may be accounted for by the assumption that the radicle R' in these has also the power of combining with the reacting molecule; and it is noteworthy that the production of the meta-derivative appears to take place especially in those cases in which R' contains a polyad atom; thus chloro- and bromo-benzene do not appear to furnish any meta-derivative, but a small proportion of meta-nitrotoluene is formed on nitrating toluene, and phenol is said to yield meta-bromo- and metiodo-phenol; and it is to be remarked that whereas acetanilide furnishes only the ortho- and para-derivative on nitration, aniline sulphate yields a small amount of meta-nitraniline also (Hübner).

In addition to the examples of compounds which obey the para-ortho- and meta-laws respectively given in Tables I and II, there are many others which are in complete agreement with them. So far as I am aware, there are only two apparent exceptions to be noted: the production of metaxylene from toluene and methyl chloride in presence of aluminium chloride, and the formation of a *para*sulphonic acid from benzophenone (Staedel). With regard to the former, although metaxylene is the chief product of the reaction in question according to Ador and Rilliet, it has since been stated by Jacobsen that orthoxylene is produced in by far the largest proportion; with regard to the latter, the exception is an interesting one, and it will be important to inquire into it, and to further study the behaviour of benzophenone.

The foregoing remarks have direct reference to benzene-derivatives proper; but it is desirable also to briefly point out that the consideration of the behaviour of benzenoid hydrocarbons generally is of the highest importance in any attempt to solve the problem involved even in the case of benzene itself. In a recent report to the British Association (comp. *Chem. News*, **54**, 326), I have summarised the results hitherto obtained by investigators of naphthalene-derivatives, and have especially dwelt on the fact that the preponderating tendency is to form α-derivatives; now this meets with an explanation

on the assumption that an additive compound is first formed. According to my view, the carbon-atoms common to the two nuclei are centres of attraction, and the additive compounds result from the attachment of the reacting molecule to one or other of these; the formation of an α-derivative from an additive compound thus constituted would appear to be almost a matter of necessity. In the conversion of the mono-derivative into a di-derivative, according to the nature of the radicle R' and also of the reacting molecule, the additive compound will be formed by the attachment of the reacting molecule either to the central carbon-atom contiguous to the radicle R' or to that which is uninfluenced by a contiguous radicle; or a mixture of the two possible additive compounds may result: and on subsequent decomposition of the additive compound, either a homonucleal or heteronucleal derivative will be formed according to circumstances. The behaviour of β-derivatives of naphthalene is in many respects noteworthy, and I would point to the conversion of betanaphthyl sulphate into Schaefer's betanaphtholsulphonic acid by mere warming (*Ber.*, 1882, 203) as being a most interesting case of isomeric change, especially if considered in connexion with the suggestion previously advanced in explanation of the production of para-di-derivatives of benzene; Schaefer's acid is most probably a $\beta^2\beta^{3'}$-derivative, and its relation to the isomeric sulphate is accordingly represented by the symbols—

Betanaphthyl sulphate.   Schaefer's betanaphtholsulphonic acid.

Even those who are of opinion that para-carbon-atoms in benzene are to be regarded as directly connected will scarcely be willing to admit the existence of any direct connexion between the $\beta^2\beta^{3'}$ carbon-atoms in naphthalene.

The production of haloid derivatives from paraffins may be held to negative the hypothesis advocated in this paper that the formation of additive compounds precedes that of substitution derivatives. I am of opinion, however, that this is not the case, and that even the paraffins are to a certain extent unsaturated bodies: it is because they are so nearly saturated, I believe, that the lowest terms especially are so slowly acted upon, and it is perhaps noteworthy that nitric and sulphuric acids, which appear to manifest less tendency than do the halogens to form additive compounds, act less readily on paraffins than do chlorine or bromine. But the view here advocated finds its chief support in the behaviour of the mono-haloid-derivatives of paraffins: these, it is well known, are far more readily attacked by halogens than

are the paraffins, and thus afford a strong argument in favour of my assumption that negative elements especially tend to attract each other. Without here entering into a full discussion of the subject, I may point out that the laws of addition and substitution generally are for the most part capable of explanation by means of this principle : for example, it is an established rule that in the formation of additive compounds from compounds of the olefine type, the negative radicle of the reacting molecule usually attached itself to the least hydrogenised carbon-atom, propylene, for instance, $CH_3 \cdot CH \cdot CH_2$, forming isopropyl iodide, $CH_3 \cdot CHI \cdot CH_3$, not propyl iodide, $CH_3 \cdot CH_2 \cdot CH_2I$: but the less hydrogenised is of necessity the more negative carbon-atom. Again, it is well known that negative radicles tend to accumulate : ethyl chloride, for example, yielding on chlorination as chief product not ethylene but ethylidene chloride, $CH_3 \cdot CHCl_2$; alcohol yielding on oxidation aldehydrol, $CH_3 \cdot CH(OH)_2$, not glycol, $CH_2(OH) \cdot CH_2(OH)$.

I have thought it advisable thus to direct attention to a possible explanation of the laws of substitution, because it appears to me that of late years the subject has not received that amount of consideration which from its importance it deserves—perhaps for want of a guiding principle. As yet but a mere rough survey of this field of inquiry has been effected ; true it is that this has enabled us to outline its characteristic features, but the accurate measurement of details which will enable us to draw the finished picture has yet to be accomplished, and will involve patient and prolonged investigation. It is more than probable that I may exaggerate its importance, but it appears to me that the doctrine of " Residual Affinity " of which I have ventured to become the exponent (*Proc. Roy. Soc.*, 1886, **40,** 268), will be of service as a guide in these inquiries.

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