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XXII.—*Notes on the recent papers by A. von Baeyer and Julius Thomsen : " On the Constitution of Benzene."*

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To determine the constitution of benzene it is necessary according to Baeyer (*Ber.*, **19**, 1797) to establish—

I. That hexahydrobenzene and hexamethylene are identical.

II. That ortho-, meta-, and para-substitution-derivatives of benzene furnish on reduction respectively 1 : 2, 1 : 3, and 1 : 4 substitution-derivatives of hexamethylene.

III. The symbols for benzene which II renders possible.

IV. The positions of the separable affinities.

I. Baeyer considers that the conversion of ethylic dihydroxyterephthalate—a benzene-derivative—into ethylic succinosuccinate—a hexamethylene-derivative—by the action of nascent hydrogen, establishes the identity of hexahydrobenzene with hexamethylene. Using Kekulé's symbol, the reaction is expressed thus :—
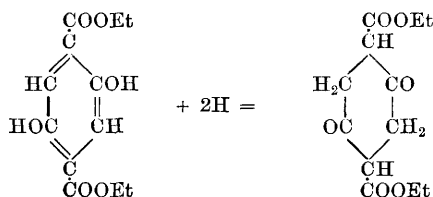

II. In support of the second point, namely, that ortho-, meta-, and para-substitution derivatives of benzene yield corresponding derivatives of hexamethylene on reduction, Baeyer cites the formation and behaviour (*a*) of ethylic succinosuccinate and (*b*) of ethylic phloroglucoltricarboxylate.

Baeyer's argument is that in the formation (*a*) of ethylic succinosuccinate, both the COOEt groups and the O atoms retain the para-position (for reaction see above) ; and that (*b*) in the case of phloroglucol-derivatives, the O atoms preserve the meta-position during the change of the so-called secondary into a tertiary ring, thus :—
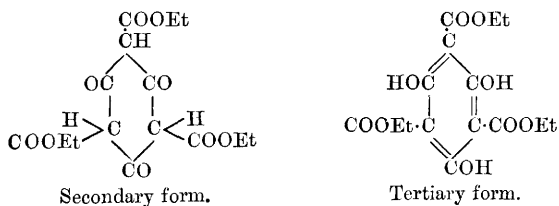
Now, on looking at the equation representing the first of these two changes, it will be noticed that in the conversion of the benzene-derivative into the *hexahydrobenzene*-derivative, not six but only two hydrogen-atoms are taken up. The reaction is therefore not a case of reduction or addition pure and simple, but is accompanied by an intramolecular change, according to Baeyer's own equation: yet Baeyer brings this forward as an argument in support of the proposition that ortho-, meta-, and para-substitution products of benzene yield, on *reduction*, $1:2$, $1:3$, and $1:4$ derivatives of hexamethylene.
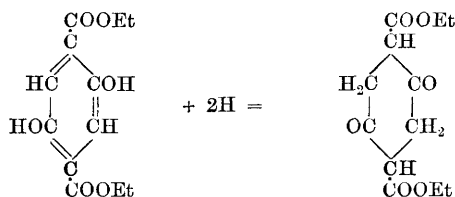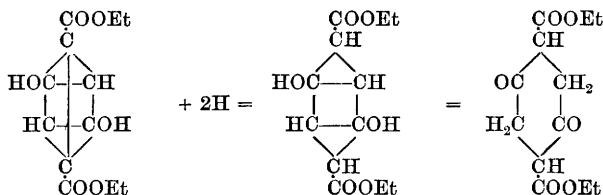

The second reaction upon which he bases his argument is not a case of reduction at all in the ordinary sense of the word, but involves an intramolecular change pure and simple :—
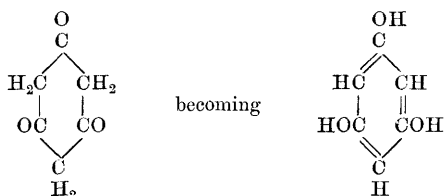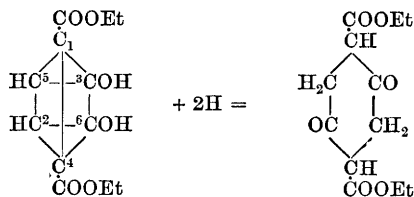

Reactions admittedly involving such intramolecular changes can scarcely be accepted as evidence either for or against any particular benzene formula, especially as we are altogether ignorant of the precise manner in which the isomeric change is brought about. If Baeyer's equation be accepted, the change may no doubt be regarded as involving merely a *migration* of hydrogen-atoms, but is not migration merely one of the many convenient terms in use for expressing changes we do not understand ?

Baeyer does not attempt to discuss the two reactions in question with reference to any other symbol than Kekulé's; Ladenburg (*Ber.*, **19**, 973), however, has shown how the first may be represented by means of the prism formula; in his opinion, it is possible to express the reduction of ethylic dihydroxyterephthalate to ethylic succino-succinate by the following symbols :—

$$
\begin{array}{c}
\text{COOEt} \\
\text{C} \\
\text{HOC—|—CH} \\
| \quad | \\
\text{HC—|—COH} \\
\text{C} \\
\text{COOEt}
\end{array}
\; + 2\text{H} = \;
\begin{array}{c}
\text{COOEt} \\
\text{CH} \\
\text{HOC——CH} \\
| \quad | \\
\text{HC——COH} \\
\text{CH} \\
\text{COOEt}
\end{array}
\; = \;
\begin{array}{c}
\text{COOEt} \\
\text{CH} \\
\text{OC} \quad \text{CH}_2 \\
| \quad | \\
\text{H}_2\text{C} \quad \text{CO} \\
\text{CH} \\
\text{COOEt}
\end{array}
$$

Here, however, Ladenburg himself has fallen into a curious mistake in using his own symbol: if the six carbon-atoms of the prism be numbered so that each shall correspond with the carbon-atom bearing the same number in Kekulé's symbol, it will be evident that the above formula represents the *ortho*-dihydroxy-derivative of ethylic terephthalate, whereas it is the *para*-dihydroxy-compound which yields ethylic succinosuccinate.

If the attempt be made to represent the change from a para-dihydroxy-derivative of ethylic terephthalate into ethylic succinosuccinate, employing the prism formula, an isomeric change must be assumed to occur.

$$
\begin{array}{c}
\text{COOEt} \\
\text{C}_1 \\
\text{HC}^5\text{—|—}^3\text{COH} \\
| \quad | \\
\text{HC}^2\text{—|—}^6\text{COH} \\
\text{C}^4 \\
\text{COOEt}
\end{array}
\; + 2\text{H} = \;
\begin{array}{c}
\text{COOEt} \\
\text{CH} \\
\text{H}_2\text{C} \quad \text{CO} \\
| \quad | \\
\text{OC} \quad \text{CH}_2 \\
\text{CH} \\
\text{COOEt}
\end{array}
$$

This change appears at first sight somewhat complicated, and therefore perhaps improbable ; but on closer examination it will be found to be no more complicated than that involved in the reaction as represented by Baeyer, the most important difference being that Baeyer's equation indicates a migration of hydrogen-atoms, whilst according to the above an atom of oxygen migrates from position 6 to position 2. But it must be borne in mind that in the prism formula the carbon-atoms 6 and 2 are directly united, and that this migration of oxygen is simply from one carbon-atom to an adjacent carbon-atom ; and, further, that since the molecule must be assumed to be changing form, that is, from a prism to a closed chain, this migration is necessary if the figure (originally symmetrical) is to retain its symmetry.*

* In connection with the question of symmetry, it may be pointed out that nearly all synthetical reactions involving the formation of benzene-derivatives from non-aromatic substances yield symmetrical products ; the following examples may be mentioned in illustration of this : synthesis of mesitylene from acetone or from allylene ; uvitic acid from pyruvic acid ; 1 : 3 : 5 tribromobenzene by the action of

The change which Baeyer assumes to take place in the case of phloroglucol-derivatives in passing from the secondary to the tertiary form, may be represented in the same way :—
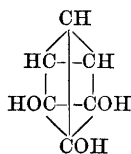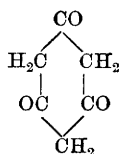
I do not offer this explanation in defence of the prism formula, but merely as one which might perhaps be brought forward as a last resource by the defenders of this symbol.*

III. In the third section of his paper, Baeyer brings forward his *one* argument against the prism formula. As the prism consists of two triangles united as in Fig. 1, it is evident that if in the forma-
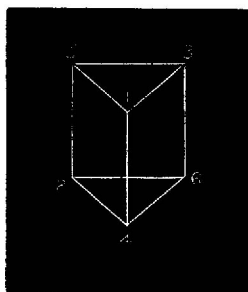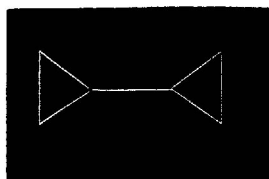
FIG. 1.

FIG. 2.

tion of additive compounds two of the three *para*-lines of union— $5 : 2, 1 : 4, 3 : 6$—can be severed, a derivative of ditrimethylene will be obtained, which on further reduction cannot possibly yield a derivative of hexamethylene.

If two elements present in the prism in the para-position to one another are also to occupy the positions $1 : 4$ in the corresponding hexamethylene-derivative, the $1 : 4$ union must vanish. If the same argument be applied to a second pair of para-atoms, a second para-union must go, and the product will no longer be capable of yielding a hexamethylene-derivative, Fig. 2. This is Baeyer's argument; and

light on bromacetylene; trimesic acid from propargylic acid; quinol or hydroquinone by the distillation of succinates; and lastly the syntheses of ethylic succinosuccinate and of ethylic phloroglucoltricarboxylate. Reactions involving the employment of high temperatures or of very powerful reagents cannot of course be included.

* In the number of the *Berichte* (**20**, p. 62) which has come to hand since this paper was read, this argument has actually been brought forward by Ladenburg.

if he could cite a single case in which two atoms of hydrogen (or of any other monad radicle) could be introduced into a benzene compound, so that they take up the positions 1 : 4, and then repeat the process so that the second pair should take up the positions 2 : 5 or 3 : 6, he

Fig. 3.
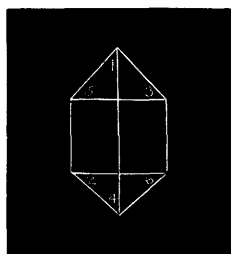
would be able to clearly disprove the prism formula. The only reaction, however, which he mentions in support of his argument, is the reduction of ethylic dihydroxyterephthalate to ethylic succino-succinate, and this certainly does not fulfil the conditions mentioned. Only one pair of hydrogen-atoms is added, the rest of the reaction being a molecular change, which can scarcely be regarded as supporting either view, throwing no light whatever on the positions of the " latent bonds."

IV. Undoubtedly the most valuable section of the paper under discussion is the fourth, as it contains many new and interesting facts; but these for the most part cannot be regarded as throwing any light on the constitution of benzene. There is, however, one experiment to be noticed, which, according to Baeyer, proves the existence of at least *one* pair of double bonds in benzene. Commencing with terephthalic acid, he converts this by the action of nascent hydrogen into tetrahydroterephthalic acid, which readily takes up two atoms of bromine, yielding dibromohexahydrotere-phthalic acid. The problem is then to determine the positions of the two bromine-atoms; if it can be proved that these occupy the ortho-position to one another, it will also be proved that the two carbon-atoms to which the bromine-atoms are attached were doubly linked before the addition of the bromine, thus proving the presence of at least one pair of double bonds in benzene. This is Baeyer's argument, and it evidently takes for granted the non-existence of free affinities. In order to determine the position of the bromine-atoms, the compound was treated with silver oxide, and hydroxyl substituted for the bromine-atoms. On concentrating the solution, a syrup was left which would not crystallise, and his attempts to obtain a crystalline

salt were equally unsuccessful.   Having failed to get any results
with the compound supposed to be dihydroxyhexahydroterephthalic
acid, he tried the action of bromine on it; this gave a substance, the
aqueous solution of which yielded a blue coloration with ferric
chloride.   He does not mention any other property of the substance,
neither does he say whether he analysed it, but apparently he did
not.   He simply states that it was tetrabromocatechol, and concludes
from this that there is at least one double union in benzene.

Even granting that the product in question is tetrabromocatechol,
and granting also the non-existence of free affinities, the production
of such a compound is only an argument in favour of, and no *proof* of,
the existence of the double bond.   Baeyer simply states that he
treated the dihydroxy-acid with bromine, but does not say how he did
this, or at what temperature; the reaction can scarcely be regarded
as a normal one, and if this be admitted the reaction proves nothing.

It may also be pointed out that the same reactions are brought
forward as proofs of propositions Nos. I, II, and III, and that they
are only two in number, so that unless it is perfectly clear how the
reactions take place, a single error in the explanation of either may
upset three arguments out of four.

The last part of the research, that is, the examination of the addi-
tive compounds of benzene and its derivatives, can scarcely fail to
yield results of considerable theoretical interest, but it is difficult to
avoid the conclusion that the research leaves the question of the con-
stitution of benzene just where it was before.

Julius Thomsen (*Ber.*, **19**, 2944) has also recently contributed to
the discussion on the constitution of benzene.   In the symbol which
he proposes, the six carbon-atoms represent the points of a regular
octahedron.   The arrangement of the bonds is best seen from the
figure, in which the white lines indicate the way in which the carbon-

FIG. 4.
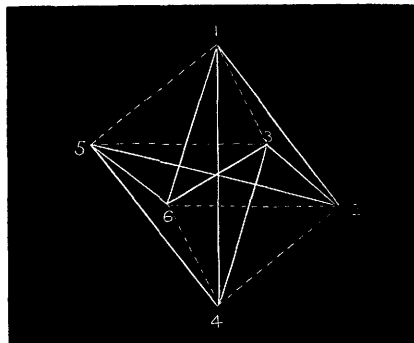
atoms are united, the dotted lines being added to complete the octa-
hedron.   The projection of this figure is a hexagon with diagonals,
but Thomsen points out that his symbol differs from the ordinary
diagonal formula, in that it is the projection of a solid figure, the
essentials of which are the diagonal bonds, and these cannot be
severed without the destruction of the molecule.   The formation of
additive compounds is explained by the severance of one, two, or
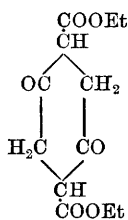three of the peripheral bonds, so that the nucleus of hexamethylene
will be—

FIG. 5.
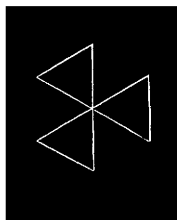
Thomsen's benzene symbol is, as he states, a symmetrical figure,
which renders possible three and only three isomeric disubstitution-
derivatives, namely, $1:2$, $1:3$, and $1:4$, the positions 2 and 6, also
3 and 5, being identical in their relation to 1.   These are the chief
points which Thomsen brings forward in recommendation of his
formula.*   There are, however, some other points of interest in
connection with this symbol, and which I think are of importance in
connection with the subject of the constitution of benzene.   Thomsen's
formula differs from Kekulé's formula and from the prism formula,
in that it renders possible four disubstitution-derivatives of hexa-
methylene, whilst three only are possible according to the other two
symbols, assuming in each case that the substituents are attached to
different carbon-atoms.   Another difference is that quinone cannot
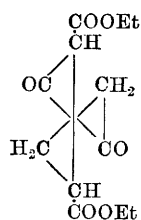be represented as a diketone, the formulæ—
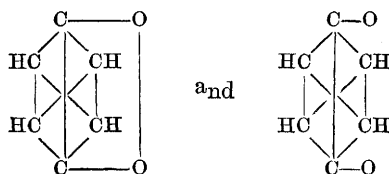
being alone possible.   The greatest difficulty, however, is perhaps the

* It may be mentioned that the representation of the diagonal symbol as a
regular octahedron is not new, and will be found in Laubenheimer's text-book
(1884), where the above symbol for the hexamethylene nucleus is also given.

representation of certain synthetical reactions, as for example, the synthesis of ethylic succinosuccinate, which is so readily shown by the symbols at present in use.

$$
\begin{array}{cc}
\underset{\displaystyle\text{Symbol generally employed.}}{
\begin{array}{c}
\text{COOEt} \\
\text{CH} \\
\text{OC} \quad \text{CH}_2 \\
\text{H}_2\text{C} \quad \text{CO} \\
\text{CH} \\
\text{COOEt}
\end{array}}
&
\underset{\displaystyle\text{Thomsen's symbol.}}{
\begin{array}{c}
\text{COOEt} \\
\text{CH} \\
\text{OC} \quad \text{CH}_2 \\
\text{H}_2\text{C} \quad \text{CO} \\
\text{CH} \\
\text{COOEt}
\end{array}}
\end{array}
$$

Indeed the difficulties presented by this formula outweigh the advantages claimed for it by its author, and on this account it may be doubted whether it will commend itself to chemists.

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