XXX.—*A Rule for determining whether a given Benzene Mono-derivative shall give a Meta-di-derivative or a mixture of Ortho- and Para-di-derivatives.*

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WHEN a monobenzene derivative C_6H_5X is so treated as to give a dibenzene derivative C_6H_4XY, it is well known that, as a rule, this dibenzene derivative is either (*a*) exclusively, or nearly so, a *meta*-compound, or (*b*) a mixture of *ortho*- and *para*- with none or very little

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meta- ; and that whether the case shall fall under (*a*) or (*b*) depends on the nature of the radicle X, and not at all, or only very slightly, on the nature of Y.

The first attempt at generalisation on this matter was made by Nölting, who attempted to classify radicles, so that one class should include those the compounds of which, with C_6H_5, give *meta*-di-derivatives, and the other class those the compounds of which, with C_6H_5, give *ortho*- and *para*-di-derivatives. But Nölting's classification, and all the rules derived from it, fail in precision. We cannot apply the rule so as to be quite sure of its meaning. When the rule seems to fail, it is always possible to find an excuse for it. Rules of such a kind are of little use practically or theoretically ; they are not really rules, but only indications of regularity.

We have gone over all the cases known to us, and have formulated a rule which holds in all these cases, and is always capable of rigorous application, so that, if in any case it should be found to fail, no excuse could be found for it. We shall best explain our rule by showing how we apply it. We shall write in column A a number of benzene mono-derivatives, in column B the radicles replacing one H of C_6H_6, in column C the hydrogen compounds of these radicles, in column D the hydroxy-compounds of the same radicles, and in column E the letters *m* or *o-p*, according as the mono-derivatives give *meta*- or a mixture of *ortho*- and *para*-di-derivatives.

In column C, we mark with an asterisk those substances which are *not* capable, by direct oxidation, of being converted into the corresponding hydroxy-compounds in the next column, and in column D we mark with an asterisk those substances which can be formed by direct oxidation from the corresponding hydrogen compounds, so that in each horizontal line there is one asterisk and, one only, either in column C or in column D. By direct oxidation we mean oxidation by one step. Thus, no doubt $H \cdot CH_3$ can be converted into $HO \cdot CH_3$, but not by one step of oxidation ; whereas $H \cdot CO \cdot CH_3$ can, by one step of oxidation, be converted into $HO \cdot CO \cdot CH_3$. Now it will be seen that wherever the H compound is asterisked, we find *o-p* in column E, and whenever the HO compound is asterisked we find *m* in column E. In other words, when X is naturally to be regarded as a derivative of HX, C_6H_5X gives *ortho*- and *para*-di-derivatives, and when X is naturally to be regarded as a derivative of HOX, C_6H_5X gives *meta*-di-derivatives. Our test by which we determine whether X is to be regarded as derived from HX or HOX is, can HX be directly, by a single oxidising step, converted into HOX or not? If it cannot, then X is to be looked on as derived from HX ; if it can, then X is to be looked on as derived from HOX.

A.	B.	C.	D.	E.
C_6H_5Cl	$\cdot Cl$	HCl^*	$HOCl$	$o\text{-}p.$
C_6H_5Br	$\cdot Br$	HBr^*	$HOBr$	$o\text{-}p.$
$C_6H_5CH_3$	$\cdot CH_3$	HCH_3^*	$HOCH_3$	$o\text{-}p.$
$C_6H_5NH_2$	$\cdot NH_2$	HNH_2^*	$HONH_2$	$o\text{-}p.$
C_6H_5OH	$\cdot OH$	HOH^*	$HO\cdot OH$	$o\text{-}p.$
$C_6H_5NO_2$	$\cdot NO_2$	HNO_2	$HO\cdot NO_2^*$	$m.$
$C_6H_5CCl_3$	$\cdot CCl_3$	$HCCl_3^*$	$HO\cdot CCl_3$	$o\text{-}p.$
$C_6H_5CO\cdot H$	$\cdot CO\cdot H$	$HCO\cdot H$	$HO\cdot CO\cdot H^*$	$m.$
$C_6H_5CO\cdot OH$	$\cdot CO\cdot OH$	$H\cdot CO\cdot OH$	$HO\cdot CO\cdot OH^*$	$m.$
$C_6H_5SO_2\cdot OH$	$\cdot SO_2\cdot OH$	$HSO_2\cdot OH$	$HO\cdot SO_2\cdot OH^*$	$m.$
$C_6H_5CO\cdot CH_3$	$\cdot CO\cdot CH_3$	$HCO\cdot CH_3$	$H\cdot CO\cdot CH_3^*$	$m.$
$C_6H_5CH_2\cdot CO\cdot OH$	$\cdot CH_2\cdot CO\cdot OH$	$H\cdot CH_2\cdot CO\cdot OH^*$	$HO\cdot CH_2\cdot CO\cdot OH$	$o\text{-}p.$

The table might have been further extended, but these examples are sufficient to show how we apply the rule.

It may be said that $C_6H_5\cdot CCl_3$ gives $mC_6H_5(NO_2)\cdot COOH$. But this is a case in which the experiment cannot be applied, because we have no means of knowing whether the conversion of $\cdot CCl_3$ into $CO\cdot OH$ takes place before or after the replacement of $\cdot H$ by $\cdot NO_2$; and when the experiment can be applied, as in the chlorination of $C_6H_5\cdot CCl_3$, we find that we obtain o and p $C_6H_4Cl\cdot CCl_3$.

The rule given above is not a *law*, because it has no visible relation to any mechanism by which the substitution is carried out in one way rather than in another way, but, if it is found to be rigorously applicable it must be related in some way to a law, and may be of use, both as grouping phenomena together and in guiding us to the cause of the formation of meta-compounds in certain cases, and of ortho- and para- in others.