LIII.—*Note on Substitution in the Benzene Nucleus.*

By Dr. H. F. MORLEY.

DR. ARMSTRONG has recently drawn renewed attention to the regularities that may be observed in the conversion of the mono-derivatives of benzene into di-derivatives. As may be seen from the tables that he gives (this vol., p. 259), when one atom of hydrogen in benzene has been displaced by CH_3 , CH_2Cl , Cl , Br , I , OH , NH_2 , NHAc , $\text{CH}_2\text{CO}_2\text{H}$, or $\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$, the resulting compound gives, when a second substitution takes place, a para- or an ortho-derivative; whereas when an atom of hydrogen in benzene has been displaced by one of the radicles NO_2 , CN , CO_2H , COH , SO_3H , $\text{SO}_2\cdot\text{C}_6\text{H}_5$, or $\text{CO}\cdot\text{CH}_3$, a new element or radicle entering the benzene nucleus takes up a meta-position with regard to the radicle already present (see also Nölting, *Berichte*, **9**, 1797). The radicles producing para- or ortho-derivatives are more basylous than those producing meta-derivatives; this will readily be admitted in the case of amidogen, methyl, and side-chains beginning with CH_2 or CH , but it might be disputed in the case of the halogens. The halogens are of course "chlorous," but they are less chlorous than nitroxyl, carbonyl, carboxyl, or sulphonyl. This is apparent when we compare ethyl malonate, $\text{EtO}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{OEt}$, and nitro-ethane, $\text{CH}_3\cdot\text{CH}_2\cdot\text{NO}_2$, on the one hand, with methylene chloride, $\text{Cl}\cdot\text{CH}_2\cdot\text{Cl}$, and ethyl chloride, $\text{CH}_3\cdot\text{CH}_2\text{Cl}$, on the other, for the former yield sodium-derivatives,

$\text{EtO}\cdot\text{CO}\cdot\text{CHNa}\cdot\text{CO}\cdot\text{OEt}$, and $\text{CH}_3\cdot\text{CHNa}\cdot\text{NO}_2$, whilst the latter do not. It will be noticed that all the radicles under discussion are attached to benzene by a chlorous element (N, C, S, or a halogen), and that where this element stands alone (the halogens) or is attached also to one or more basylous elements (as in OH, NH_2 , CH_3) the radicle induces para- or ortho-substitution, whilst radicles in which the chlorous "grouping" element is attached to other chlorous elements (as in NO_2 , CO_2H , or SO_3H) induce meta-substitution. Accordingly we find that CCl_3 and CHCl_2 are capable of giving rise to meta-derivatives, whilst CH_2Cl resembles CH_3 in its characters, the two atoms of hydrogen preponderating over the single atom of chlorine. The formation of meta-nitro-benzylidene chloride by the nitration of benzylidene chloride can hardly be explained by the "molecular-addition" theory, which will shortly be referred to.

It appears, therefore, that the more basylous a radicle is, the less does it induce meta-substitution, but the view adopted by Dr. Armstrong, in a note which he read at a recent meeting of the Society, appears to take an exactly opposite view.

I drew attention to this at the time, but was assured by the author that this was not the case, as would be found on careful study of his paper. Accordingly I postponed further criticism until I could make myself thoroughly familiar with Dr. Armstrong's point of view. The result of this study has been to confirm my original objections, and as it appears very desirable that points of such theoretical importance should be fully discussed, I venture again to draw the attention of the Society to this matter.

Dr. Armstrong says (Proc., 2, 44): "Having in my mind the fact that the 'basic' powers of nitrogen become enhanced by introduction of hydrocarbon radicles in place of hydrogen, it appeared not improbable that the behaviour of a compound such as dimethylaniline, for example, would not in all cases be strictly in accordance with the para-ortho law." This sentence seems to me to mean that the more basylous a radicle becomes, the less is its behaviour in accordance with the para-ortho law, a statement which is directly contrary to the views I have just been advocating. Whether dimethylaniline is or is not more basic than aniline is a question which does not affect the interpretation I have given to the sentence.*

In studying Dr. Armstrong's original paper, I believe I have found the explanation of the statement in question. The author does not consider that the chlorous or basylous character of the radicle has anything to do with the laws of substitution, but that *unsaturated*

* If a mixture of equivalent quantities of aniline and dimethylaniline be more than half neutralised with aqueous hydrogen chloride in the cold, the greater part of the uncombined base is dimethylaniline.

radicles, which can combine directly with a molecule of the reacting substance (HNO_3 or Br_2) produce meta-derivatives, whilst saturated radicles which cannot so combine produce para- or ortho-derivatives. In the latter case, it is assumed that molecular combination nevertheless takes place, this time, however, between the reacting substance and one of the atoms of carbon in the benzene nucleus.

It is obvious that, if this view be accepted, such an unsaturated radicle as amidogen, which can of course combine with HNO_3 , ought to produce a meta-derivative. Unfortunately for the theory in question, the chief product, when aniline is nitrated in presence of not too large an excess of sulphuric acid, is paranitraniline. In order to avert the conclusions that may naturally be drawn from this experiment, Dr. Armstrong draws attention to some experiments on the nitration of benzene-derivatives containing the radicles NMe_2 and NHEt , which, however, may receive a very different interpretation from that which he gives.

In order to prove that alkyl-amidogen groups give rise to meta-substitution products, Dr. Armstrong relies on the following facts:—

That dimethylaniline sulphate, diethylaniline sulphate, ethylaniline sulphate, and ethylparatoluidine sulphate all produce meta-nitro compounds when nitrated, whereas aniline, bromodimethylaniline, and paracetyltoluidine give rise to para- or ortho-nitro compounds, the terms *ortho*, *meta*, and *para* being applied to the position taken up by the nitroxyl relatively to amidogen or alkylamidogen.

In the discussion which followed the note in question, I remarked that the effects observed were not due so much to the character of the original substance as to the manner in which the nitration was performed. It has been shown by Nölting and Collin (*Berichte*, **17**, 261), that when aromatic bases are nitrated in presence of a very large excess of sulphuric acid, cooled with ice and salt, meta-nitro compounds are produced, and that the amount of meta-compound so obtained is increased by increasing the quantity and strength of the sulphuric acid used.

Thus paracetyltoluidine, when nitrated by means of fuming nitric acid, in absence of sulphuric acid, gives an ortho-nitro-derivative, and the same result follows if only 4 parts of sulphuric acid are mixed with it; if 10 parts of sulphuric acid are used, a mixture of meta- and ortho-nitro-derivatives is formed, and on increasing the amount of sulphuric acid the proportion of the meta-derivative formed rises at the expense of the ortho-derivative. Paratoluidine itself, when nitrated in presence of 10 parts of sulphuric acid, gives both ortho- and meta-nitro derivatives, but when 20 parts of sulphuric acid are used, the meta-derivative is the only one formed. This shows that the presence of Me or Et in the amidogen is in

no sense necessary to the formation of meta-derivatives. Ortho-toluidine and its acetyl-derivative, when nitrated without the use of sulphuric acid, produce *para*-nitro derivatives, but when 20 parts of sulphuric acid are used the *meta*-nitro derivatives are the only ones formed. The same remarks apply to metaxylidine and to parabrom-aniline. Indeed the only case which appears at all doubtful is that of aniline itself. Nölting and Collin state, however, that by using 50 parts of sulphuric acid they succeeded in greatly reducing the amount of paranitraniline formed, and a patent for preparing meta-nitraniline by projecting aniline nitrate into cold sulphuric acid has been taken out (*Berichte*, 18, Ref., 203).

There is therefore no proof that alkylated amidogen has a greater tendency to produce meta-compounds than amidogen itself; in presence of a large excess of sulphuric acid, both produce meta-compounds; in the absence of sulphuric acid, neither produce meta-compounds.

The explanation of this phenomenon given by Hübner seems to me to be still tenable. We are dealing with sulphates. The group $\text{N}(\text{SO}_4\text{H})\text{H}_3$ is more chlorous than NH_2 , and hence gives rise to meta-derivatives. It remains to explain why the *quantity* of sulphuric acid can exert any influence on the result. I imagine that when but little sulphuric acid is present we have in the liquid not only molecules of the sulphate of the base but also free base, and that when nitric acid is added some of it attacks the base and some the sulphate, hence we get a mixed product; but by increasing the amount of sulphuric acid we can diminish the relative number of molecules of the free base until there are practically none left, and then we get a pure meta-derivative.

It is well known that aniline sulphate dissolved in water, when treated with bromine, gives a precipitate of tribromaniline, sulphuric acid remaining in solution; but I have observed that bromine is without action on aniline dissolved in cold strong sulphuric acid; even on raising the temperature, the greater part of the bromine is expelled in the free state. From this we may perhaps conclude that a solution of aniline sulphate contains free aniline which is precipitated by bromine, the equilibrium of the solution being thereby destroyed, more aniline being formed and precipitated, &c.

Be this as it may, the mechanism suggested by Dr. Armstrong to explain the formation of di-derivatives of benzene requires us to assume that when dimethylaniline is converted into paranitro-dimethylaniline by nitration in acetic acid solution, the nitric acid begins by combining, not with the nitrogen, but with an atom of carbon in the benzene nucleus, an assumption which is surely in the very highest degree improbable.