Letters to the Editor

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NOTES ON POINTS IN SOME OF THIS WEEK'S LETTERS APPEAR ON P. 854.]

Direct Introduction of Deuterium into Benzene

THE interchange of hydrogen between benzene and 90 per cent sulphuric acid reported by Ingold, Raisin and Wilson¹ appears to us to be a special case of the following general principle, by which interchange with the hydrogen of unsaturated compounds may be effected.

The equilibrium between an ethylene derivative and the alcohol resulting by addition of water to the double bond has been studied recently by Stanley, Youell and Dymock². The dehydration is endothermic (by approximately 9,000 cal.), and hence, whenever the ethenoid compound and water are both present in appreciable concentrations, an equilibrium will be established with the formation of a finite quantity of alcohol.

Remembering that catalysts of dehydration must also accelerate the reverse process, we conclude that when a system consisting of an ethenoid compound and D₂O is brought into contact with a dehydrating catalyst, a trace of alcohol will be formed, which will, in its turn, immediately decompose with the reformation of the unsaturated compound. Owing to the approximate chemical equivalence of H and D, the water molecule eliminated during the course of this decomposition would appear to have an equal chance of being either HDO or D₂O. In the former case, an interchange of one of the original H atoms attached to an unsaturated carbon atom has occurred. The mechanism of the process can be depicted as follows:

After such a process of transitory addition of water, the ethenoid bond would necessarily be left in the more stable (*cis* or *trans*) steric form. If it had originally been in an unstable form, it would be converted into the stable one.

Furthermore, the process might result in a migration of the double bond as in the following scheme:

The same considerations would apply to the transitory addition of hydrogen halides to an ethylene linkage. Again, the occurrence of such transitory additions can be predicted, if catalysts by which the *splitting off* of the hydrogen halide with concomitant formation of a double bond is effected are present. Hence, in the presence of such catalysts, a hydrogen halide will act on an ethenoid double bond in three different ways: (a) hydrogen replacement; (b) *cis-trans*-inversion; (c) wandering of the double bond.

The interchange reported by Ingold and his co-workers comes under the principle enunciated here, if we make the probable assumption that the com-

pound is readily dehydrated by 90 per cent sulphuric acid to form benzene.

The strictness of the above conclusions depends on the condition that the splitting off of water or hydrogen halide from the alcohol or alkyl halide should not be affected by the presence of the reaction products in those concentrations in which they are to be applied in the interchange reaction. In this case—and assuming again equivalence of H and D—we can calculate the velocity constant *k* of exchange reaction from the equilibrium constant *K*, and the first order velocity constant *k'* of decomposition in the usual way: $k = k'/K$.

We consider the following two observations of an interchange of hydrogen atoms between ethylene and 96 per cent H₂SO₄ as a confirmation of our principle:

96 per cent H ₂ SO ₄		Quantity of C ₂ H ₄ absorbed	Ethylene recovered	
Quantity	per cent D		Quantity	per cent D
5.1 gm.	9.1	69 c.c.	28 c.c.	5.2
4.9 gm.	9.4	69 c.c.	27 c.c.	5.0

In the first case, the ethylene absorbed was left overnight in solution; in the second case it was removed, by heating the solution *in vacuo*, immediately after absorption had been completed.

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¹ NATURE, 134, 734, Nov. 10, 1934.
² J. Soc. Chem. Ind., 53, 625; 1934.

PROF. POLANYI and Dr. Horiuti have kindly shown us the manuscript of their letter referring to our observation of hydrogen exchange between aqueous sulphuric acid and benzene. We should like to indicate our point of view in the matter.

Whilst we concur in the suggestion that hydrogen exchange in unsaturated compounds through the action of reagents such as aqueous sulphuric acid would often be caused by the addition and elimination of some simple molecule such as water,

we would not apply this type of theory to exchange in benzene or in aromatic compounds generally. In its application to the aromatic case, this theory seems to us to be a special case of the two-point addition theories of aromatic substitution; these have now been abandoned as they give but a poor account of orientation and are inconsistent with the non-parallel relation between orientation and velocity¹.

We regard hydrogen exchange in benzene derivatives as a special application of our views on aromatic substitution by electrophilic reagents², and we expect to prove that the exchange obeys the ordinary orientation laws. Our theory involves one-point addition: aromatic substitution differs from substitution in saturated compounds mainly in the circumstance that the polarisability of the aromatic system is available to assist the formation of the