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NEW INFORMATION ABOUT ACID CATALYSIS IN FRIEDEL-CRAFTS TYPE REACTIONS

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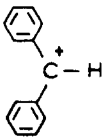
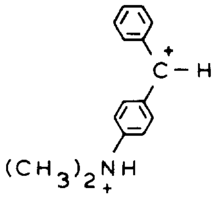
It is generally accepted that in Friedel-Crafts reactions the catalytic action of acids (Lewis acids as well as proton acids) consists in the formation of positive ions. However, we have found evidence that this is not the only contribution of acids to the course of the reaction.

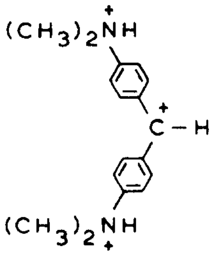
In a previous letter[1] on the pentamethylbenzyl cation (PMB^+) it has been reported that the reactivity of this ion towards e.g. hydrogen, alkanes and aromatic compounds is drastically enhanced by increasing the acidity of the medium. In order to study this effect more quantitatively in dependence of acid strengths the rate of conversion of carbonium ions of the diphenylmethyl ion type (I, II, III) in acid media has been measured.



I



II



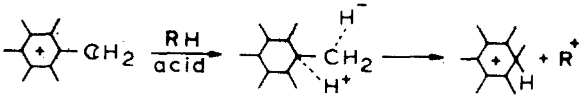
III

Since these ions react much more slowly than PMB^+ they are better suited for a kinetic investigation. Otherwise they react similarly towards aromatics as well as alkanes in forming substitution compounds or abstracting H^- ions.

The present letter describes kinetic investigations of reactions between diphenylmethyl ions and p-phenylbenzylamine in acid solutions. The latter compound being chosen for its solubility. The rate of decrease of the diphenylmethyl ion concentrations was measured by means of UV absorption spectroscopy. Solutions of these ions display an absorption maximum at about 25000 cm^{-1}. The experiments were carried out at room temperature in a mixture of sulphuric acid and phosphoric acid with a Hammett acidity function (H_o) varying from -6 to -10. It could be established that the logarithm of the measured rate constant (k) depends linearly on H_o:

$$\log k = \log k_o - 2H_o$$

where k_o depends on the carbonium ion under investigation. This equation suggests that the complex in the transition state contains in addition to the reacting molecules two protons. In discussing the role of these protons one may try to relate their influence to the basicity of the end product as in the case of PMB^+. There the course of the reaction may be visualized as:



The basicity of hexamethylbenzene is responsible for the formation of the carbonium ion as the end product of the reaction. This leads to the idea that in the transition state the adjacency of a proton is helpful in vacating the carbon atom which takes up the H^- ion. In the case of the diphenylmethyl ions the basicity of the leuco form of the dye which now is the end product is not sufficient to take up a proton. Nevertheless the participation of the two protons in the transition state may perhaps be interpreted according to the same mechanism as in the former case. An other possibility is that one or both protons contribute to the stability of the transition state by escorting the electron pair that has to be localized on a carbon atom - if an aromatic is the attacking agent - or as an H^- ion - in the case of an alkane - to form a sigma bond. It may also be that both mechanisms contribute simultaneously to the rate determining step.

The rate constants rise sharply with introduction of protonated dimethylamino groups in the para positions of the diphenylmethyl ion:

$$k_{II} > k_{III} \gg k_I; \quad {}^{k_{II}}/_{k_{III}} = 30$$

For a tentative explanation of these relations two consequences of a positively charged para dimethylammonium group could be envisaged. In the first place it has an inductive effect resulting in an increased positive character of the central carbon atom. At the same time it lowers the basicity of the nucleus to which it is attached. If only one para dimethylammonium group is introduced a strong influence on the positive character of the methyl carbon atom appears, whereas the basicity of the unsubstituted benzene nucleus remains practically unaltered. On substituting a second para ammonium group the positive character of the methyl carbon is still more increased, but the basicity drops to a much lower value.

The relative weight of these two factors may differ considerably dependent on the type of carbonium ion (e.g. benzyl ion, diphenylmethyl ion). This is illustrated by the striking disparity in the influence of an ammonium group substituted in the diphenylmethyl ion or in a PMB^+ ion. In the latter case it lowers the reactivity drastically (cf. 1).

[1] H.M. Buck, Mrs M.J. v.d. Sluys-v.d. Vlugt, H.P.J.M. Dekkers, H.H. Brongersma and L.J. Oosterhoff, Tetrahedron Letters, No. **40** , 2987 (1964).