Tetrahedron Letters No. 27, pp 2707 - 2710, 1972. Pergamon Press. Printed in Great Britain.

ON THE QUESTION OF RING-PROTONATION IN THE BENZIDINE REARRANGEMENT

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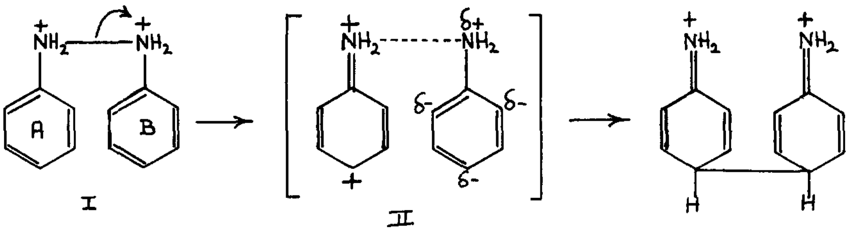
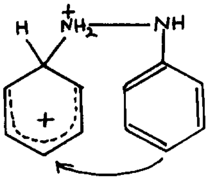
(Received in UK 27 March 1972; accepted for publication 25 May 1972)

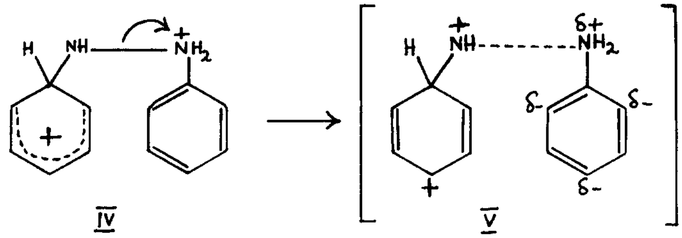
The available kinetic and product data for the acid-catalysed rearrangements of hydrazoarenes have been rationalised on the basis of a "polar transition state" mechanism.[1,2] This applies to both one and two-proton catalysed reactions, and in the latter case posits cleavage of a diprotonated substrate (I) to form a transition state (II) comprising an incipient dication (in which the ring charge is mainly located on C-4 to minimise charge repulsion) and an anilino moiety which couple to give quinonoid intermediates that in turn form p-p'-linked benzidines or other products.



Recently, Allan has restated[3] an earlier proposal[4] that relaxation of the bending force constants at C-1 (I; ring A) could enable close approach of C-4 (ring A) to C-4' (ring B); and he has considered the possibility of ring A in addition adopting a boat conformation. The former proposal had, in fact, been explicitly accepted and incorporated into the polar transition state mechanism,[1,2] whereas the latter suggestion had previously been discussed[5] and severely criticised.[5,6] More interestingly, Allan has proposed that the two-proton reaction generally involves ring-protonation and coupling as in III. However, the electronic migrations involved in heterolysis in either direction of the N,N' bond of III cannot smoothly lead to incipient moieties that could couple to give quinonoid intermediates and if ring-protonation does occur the formation of IV, which could rearrange through a transition state V, seems more probable.



III



IV V

Most of the available experimental data can be accommodated by either the polar transition state mechanism or by Allan's proposal if in the latter IV rather than III is an intermediate: however in some cases; (a) to (f) below; the two theories do lead to different predictions. Data on products and kinetics and interpretations of the polar transition state theory that are cited below are documented in reference 2.

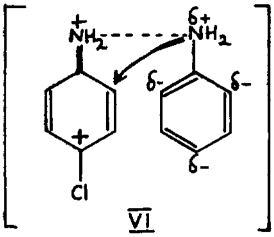
(a) Two catalytic protons are necessary to initiate rearrangement of most substrates that have been studied and the one-proton route is unobservably slow in comparison. This situation is understandable for the intermediate I, as N,N' fission is facilitated by adjacent-charge repulsion; but such repulsion would be small in IV and the function of a ring-bonded catalytic proton is obscure, save that it slightly modifies (cf. reference 4) the geometry at C-1. Electron release from the protonated ring to aid N,N' scission would also be small.

(b) The polar transition state theory can rationalise[1,2] the experimental situation that the one-proton catalysed mechanism can occur either if the unprotonated anilino moiety contains an electron-releasing substituent that can aid N,N-bond-breakage or if the substrate contains a substituent at C-2 that weakens the basicity of the amino nitrogen with respect to the situation in aniline.[1,2] In the absence of these conditions, the second catalytic proton is necessary to induce rearrangement. The kinetic form found for various substrates, however, does not fit ring-protonation. For example, hydrazobenzene reacts exclusively by the two-proton mechanism. Its 2,2'-dimethyl homologue should form a species similar to IV some 10^2-10^3 fold more readily than its parent (as judged from partial rate factors), and as the methyl substituent in the left-hand ring of IV would not appreciably facilitate N,N' scission, this compound should thus follow the two-proton route _a fortiori_. In fact the one and two-proton mechanisms co-occur in accessible ranges of acidity for the 2,2-dimethyl substituted compound. Similar kinetic forms that are unexpected if ring-protonation occurs are found for other C-2 substituted hydrazobenzenes and for hydrazonaphthalenes.

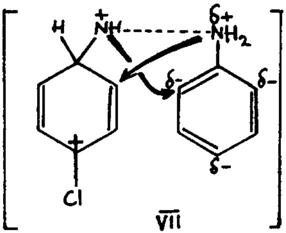
(c) On Allan's mechanism in its original or modified form the rate-limiting step would probably be transfer of the second catalytic proton to the ring. However, pre-equilibrium transfer of both protons has been demonstrated in several typical examples. If the opposite assumption is made, i.e. that IV is formed in pre-equilibrium, the implication would be that hydrogen exchange at C-2, C-4 and C-6 in the ring would occur over the period of rearrangement. Experiments using deuteriated substrates have found no such effect.

(d) IV leads to a transition state in which each moiety possesses an electrophilic nitrogen, whereas in II the nitrogen of ring A is quaternary and does not have this property. Consequently, the former intermediate should generally lead to significant amounts of o-semidine (N,2 linkage): however this product is not recorded in the dozens of examples that have been examined unless substituents at C-4 or C-4' are present.

(e) Unsymmetrical substitution of the rings introduces the possibility of formation of two o-semidines, two p-semidines, and two diphenylines: e.g., o-semidines (when they occur) could be linked 2,N' or N,2'. Nevertheless in all the available examples only one orientation of linkage is found. This situation is readily explained[1,2] on the polar transition state mechanism, cf. VI, but the ring-protonation mechanism would predict the formation of both products, cf. VII, sometimes (depending on the substituents) in comparable proportions.



VI



VII

(f) The thermal (or "no—proton") rearrangement of hydrazoarenes gives products that are similar to those from typical acid-catalysed processes in the same solvents and the details of the reactions can be well explained within the framework of the polar transition state mechanism.[1,2] Disproportionation of substrate to azo compound and fission amines, which frequently accompanies rearrangement, can also be similarly rationalised.[7] No convincing correlation of either type of reaction with the analogous or accompanying acid-catalysed rearrangements can be made if the latter involve protonation on the ring rather than on the nitrogens.

In summary, neither direct nor indirect evidence has been presented or inferred for the occurrence of ring-protonation in this class of rearrangements, and the new mechanistic proposal should be regarded with reserve.

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