

EVIDENCE FOR A CATION RADICAL MECHANISM IN A BENZIDINE REARRANGEMENT

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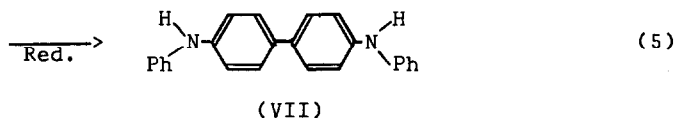
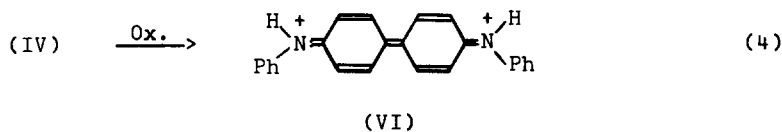
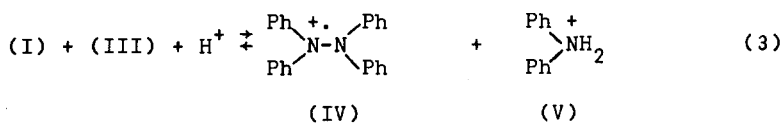
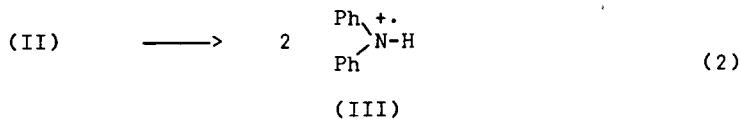
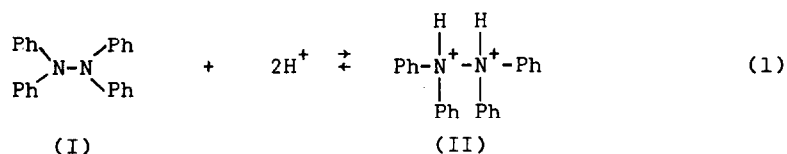
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Recent discussions in the literature have argued against the cation radical mechanism for the benzidine rearrangement.¹ It is well known that cation radicals generated by electro-oxidation of aromatic amines dimerize to benzidines,² yet no convincing evidence has been presented for the involvement of these intermediates during the rearrangement of arylhydrazines to benzidines. We now report unequivocal evidence for the involvement of cation radicals during formation of N,N'-diphenylbenzidine from tetraphenylhydrazine, a reaction which takes place by a mechanism not previously considered.

When tetraphenylhydrazine dissolves in trifluoroacetic acid (TFA) or in mixtures of TFA and dichloromethane at room temperature, a very rapid reaction ensues which is accompanied by the formation of equimolar amounts of the tetraphenylhydrazine radical ion (IV) and the conjugate acid of diphenylamine (V). The cation radical further reacts giving first the dication (VI) and after work-up, N,N'-diphenylbenzidine (VII). The reactions are illustrated in the Scheme.

The Scheme only takes into account the two proton mechanism, the intermediate of which has been recently demonstrated,³ but an analogous scheme may be written for a one proton mechanism. The fact that the oxidized form (VI) of the benzidine is formed clearly implicates an oxidized species as the rearranging intermediate since the reduced form (VII) is not converted to VI on dissolving in this medium. On addition of base, the dication is deprotonated to N,N'-diphenylquinonimine, which is unstable and undergoes reduction to the benzidine (VII). Neither the reductant in going from the quinonimine to (VII) nor the oxidant in going from (IV) to (VI) are known at the present although a most

likely intermediate in going from (IV) to (VI) is the cation radical of (VII).



Scheme

The rearrangement of (IV) could conveniently be followed by changes in the visible spectrum. A dichloromethane solution of (IV) (10^{-4} M), prepared by electro-oxidation of (I) showed an absorption band at 465 nm ($\epsilon = 5.6 \times 10^3$) on treatment of the dichloromethane solution with TFA (5% by volume) at 20° , (IV) underwent first order rearrangement ($t_{1/2} = 48.5$ min) to (VI) ($\lambda_{\text{max}} = 580$ nm).

The quantitative nature of the reactions producing (IV) from (I) in TFA was demonstrated by the observation that the magnitude of the visible absorption band at 465 nm exactly matched that of a solution of the calculated concentration

prepared by electro-oxidation of (I), as well as the fact that the peak current for voltammetric reduction of (IV) was identical to that calculated for the stoichiometric formation of (IV) according to the Scheme. The esr spectrum of (IV) generated by addition of TFA (33% by volume to a dichloromethane solution of (I) was identical to that of (IV) produced by 1e electro-oxidation of (I) in dichloromethane followed by dilution with TFA. Thus the identity of (IV) was established by three independent techniques; visible and esr spectra and voltammetric analysis. The amounts of the benzidine (VII) and diphenylamine present in the reaction mixture could be accurately estimated from ^1H n.m.r. spectra. The low field doublet of the AB patterns due to the biphenyl grouping is cleanly separated from the remainder of the aromatic protons. The spectrum of the reaction mixtures was compared to a series of standard mixtures of the benzidine and the amine and was found to be nearly identical to the spectrum of the 1-1 mixture of the components. Diphenylamine and (VII) were obtained in high yield upon work-up of the reaction mixtures.

Cation radical mechanisms have previously been considered for the benzidine rearrangement.^{1,4} Hammond and coworkers studied the reaction of (I) in sulfuric acid and concluded that (VII) was produced by dimerization of diphenylamine cation radical (III).⁴ Hammond and Clovis⁵ also concluded that radicals are involved in the disproportionation of hydrazotoluene. However, later attempts to detect radicals by two groups of workers^{6,7} all failed.

Electron transfer between initially formed cation radicals and substrate to give a new cation radical has not previously been considered. The reaction of (III) with (I) (eqn 3) is apparently very rapid, taking place so rapidly as to preclude other reactions of (III). The rapidity of the second order electron transfer reaction (eqn 3) accounts for the failure to detect the diphenylamine cation radical (III) which has recently been observed during lead tetraacetate oxidation of diphenyl amine.⁸ The rate of reaction (3) must be large compared to the preceding step (eqn 2) since the stoichiometry of equations (1)-(3) is rigidly followed.

Thus our results show that the benzidine rearrangement can take place by a cation radical mechanism. However, at this point we can only suggest that the

mechanism is also plausible and should be considered in cases other than TPH. It should be pointed out that the product composition, one mole of amine per mole of rearrangement product, is not generally observed in the benzidine rearrangement of hydrazobenzenes. The difference in stoichiometry observed for I as compared to diarylhydrazines could be due to the enhanced stability of III which allows the bimolecular reaction between III and I to take place in preference to recombination of III to give VII directly. Thus, in the case of less stable amine cation radicals, it is conceivable that recombination occurs before the radical ions can escape their "solvent cage". In this respect, we should emphasize that the mechanism observed for the benzidine rearrangement of I, involving intermediate formation of IV, differs from the previously considered caged cation radical mechanism.

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