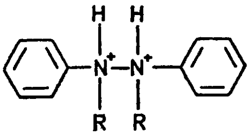
The Protonation and Benzidine Rearrangement of Tetraphenylhydrazine

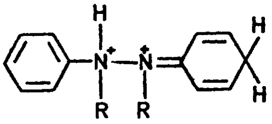
By ULLA SVANHOLM and VERNON D. PARKER*

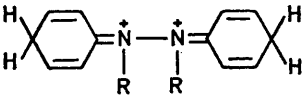
(*Department of General and Organic Chemistry, The H. C. Ørsted Institute, University of Copenhagen, Universitetsparken* 5, DK-2100 *Copenhagen, Denmark*)

Summary Tetraphenylhydrazine is stable at 0 °C in trifluoroacetic acid–antimony pentafluoride and can be recovered by caustic quench at low temperature but rapidly rearranges to *NN'*-diphenylbenzidine at room temperature.

ALTHOUGH the mechanism of the benzidine rearrangement has been the object of intensive study over the past century,[1] proposed intermediates have not been detected and mechanistic formulations have relied on kinetic data. The kinetic data observed is first order with respect to the substrate and second order with respect to hydrogen ions. Two different interpretations have been suggested, one involves a diprotonated substrate[2] and other involves the quick conversion of monoprotonated substrate to a π-complex[3] which then undergoes a rate-determining reaction with a second proton. Recent protonation studies of hetero-atom substituted aromatic compounds have shown that protonation may occur on either the hetero-atom or carbon or both.[4] Thus the structure of a diprotonated hydrazobenzene is not immediately obvious and three plausible structures, (I), (II), and (III) must be considered. We have now observed the second conjugate acid of tetraphenylhydrazine (TPH) and present conclusive evidence that it is of type (I).


(I)

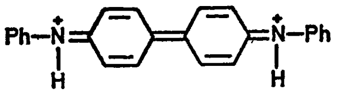

(II)


(III)

The ^{1}H n.m.r. spectrum of a solution prepared by dissolving TPH in trifluoroacetic acid–antimony pentafluoride[5] (TFA:SbF$_5$ 2:1) at 0 °C showed a single signal (W = 8 Hz) at 2·17 τ† for the aromatic protons and no other signals which could be due to carbon protonation. Protonation on carbon was rejected when ^{1}H n.m.r. studies in [^{2}H$_1$]trifluoroacetric acid–antimony pentafluoride failed to show any exchange of aromatic protons by deuterium. Diphenylamine conjugate acid in TFA–SbF$_5$ showed a single signal at nearly the same chemical shift as that observed for TPH and did not undergo exchange of aromatic protons in the deuteriated solvent. The narrow signal for TPH as well as the similarity to the spectrum of diphenylamine conjugate acid is only consistent with structure (I; R = Ph). In the same system at room temperature, exchange of protons on nitrogen of a related compound, the conjugate acid of *NN*-dimethyl-*p*-toluidine, was observed to be slow in that the signal for the methyl protons appeared as a doublet by virtue of coupling with the $\geqslant$N–H proton. Mono-protonation would result in a more complicated spectrum while carbon protonation is clearly ruled out by the above arguments as well as by the fact that structures such as (II) or (III) would give distinctive ^{1}H n.m.r. spectra showing several non-equivalent types of protons.

The diprotonated species is reasonably stable at 0 °C, no changes being observed in the spectra measured over 1 h. Quenching a solution of (I; R = Ph) prepared at 0 °C in MeOH–NaOMe at −78 °C resulted in the formation of TPH which was isolated with a recovery of about 60%. On warming to room temperature signals due to the second conjugate acid of *NN'*-diphenylbenzidine could be observed in the spectrum. The low temperature quenching of a solution which had been allowed to stand at room temperature for 2 h gave *NN'*-diphenylbenzidine in high yield. When a similar solution was quenched after 15 min at room temperature, a mixture of the substrate and the benzidine was obtained.

On dissolving TPH in TFA–SbF$_5$ at room temperature the solution immediately assumed an intense purple colour. The visible spectrum showed a single band at 535 nm‡ but on allowing the solution to stand this band faded and a new one with a maximum at 580 nm appeared. The species giving rise to the 580 band was identified as the dication (IV) by comparison with the visible spectrum of the authentic species prepared independently by anodic oxidation of *NN'*-diphenylbenzidine in methylene chloride. The amount of (IV) present accounted for less than 10% of the TPH used in the experiment.


(IV)

Hammond *et al.*[6] have pointed out that the mechanism of rearrangement involving decomposition of the second

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† It was not possible to include TMS in the solvent mixture, however this value refers to TMS assuming that the signal for the latter appears at the same position as in TFA.

‡ We have thus far been unable to determine the identity of the species giving rise to the 535 nm absorption band.

conjugate acid of TPH is arbitrary as far as direct experimental evidence is concerned because the rearrangement only takes place in very strongly acidic solutions where the reactions are immeasureably fast. Thus, our finding that the second conjugate acid of TPH is stable in the very strong acid system TFA–SbF_5 is quite unexpected and is evidence for the two proton mechanism of the benzidine rearrangement of TPH and against the π-complex mechanism.

Studies are in progress to determine whether (I) passes through the "polar-transition-state"[7] in going to rearranged product or forms other intermediates such as cation radicals which ultimately give the benzidine.

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[1] For a review see: H. J. Shine, 'Aromatic Rearrangements,' Elsevier, New York, **1967**.

[2] For extensive kinetic studies see D. V. Banthorpe, and M. O'Sullivan, *J. Chem. Soc.* (*B*), 1968, 627 and references therein.

[3] M. J. S. Dewar, 'Molecular Rearrangements,' ed. P. De Mayo, vol. I, Interscience, New York, 1963, p. 323.

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[5] M. G. Harriss and J. B. Milne, *Canad. J. Chem.*, 1971, **49**, 2937.

[6] G. S. Hammond, B. Seidel, and R. E. Pincock, *J. Org. Chem.*, 1963, **28**, 3275.

[7] D. V. Banthorpe, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 1964, 2864.