The Benzidine Rearrangement: *p*-Hydrazobiphenyl

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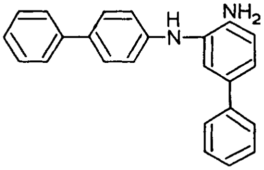
FRIEBEL and RASSOW[1] reported that when *p*-hydrazobiphenyl was heated with concentrated hydrochloric acid, or when *p*-azobiphenyl was heated in alcohol with stannous chloride and hydrochloric acid, only the disproportionation products, *p*-azobiphenyl and 4-aminobiphenyl, were obtained. Therefore, with the assumption that *p*-hydrazobiphenyl would not undergo a benzidine rearrangement, we chose that compound for for use in part of our study of the mechanisms of rearrangement and disproportionation in substituted hydrazobenzenes. We have now found that three products are obtained at 0° from *p*-hydrazobiphenyl in aqueous ethyl alcohol which is 0·01—0·5M in hydrogen chloride. Two of the products are those of disproportionation, and occur in approximately equal amounts of about 37—40%. We believe that the third product (20—25%) is the *o*-semidine (I). The presence of (I) in the reaction products was first detected by ultraviolet spectroscopy and next by thin-layer chromatography. Separation on a scale large enough for analytical work was achieved as follows. Ethanolic solutions of *p*-hydrazobiphenyl and aqueous hydrochloric acid were mixed at 0° to give final concentrations of 5×10^{-4}M in *p*-hydrazobiphenyl and 0·5M in acid. Reaction was complete within a few minutes. Azobiphenyl precipitated and was filtered off. The filtrate was evaporated to dryness under vacuum at room temperature. The dried residue was stirred with sodium hydroxide solution and extracted several times with ligroin; 4-aminobiphenyl was recovered from the dried ligroin solution. The ligroin-insoluble material was crystallized several times from 95% ethyl alcohol giving almost colourless plates, $C_{24}H_{20}N_2$, m.p. 201—203°; λ_{max} (95% ethyl alcohol) 336 mμ; ϵ, $4{\cdot}32 \times 10^4$. Acetic anhydride in benzene gave a monoacetyl derivative, $C_{26}H_{22}N_2O$, m.p. 271—272° (ethyl alcohol). Benzoyl chloride in benzene gave a monobenzoyl derivative, $C_{31}H_{24}N_2O$, m.p. 265—267° (ethyl alcohol). The equivalent weight of (I), determined by potentiometric titration with perchloric acid in anhydrous acetic acid, was 326. A sharp end-point was obtained. The analytical results exclude the possibility that (I) is the *o*-benzidine type of product. The possibility that it is the 4,4‴-diaminoquaterphenyl is also excluded by the physical properties of the latter (m.p. 154—155°[2]; 211—214°[3]; m.p. of the diacetyl derivative, 204—205°[2]; 385°[3]), and on theoretical grounds.[4]



(I)

The behaviour of *p*-hydrazobiphenyl in acidic

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solution has an important bearing on the mechanism of the benzidine rearrangement. Dewar has used Friebel and Rassow's report as a justification of his π-complex theory of the rearrangement, the argument being that protonated *p*-hydrazobiphenyl cannot rearrange because π-cloud repulsions of the terminal phenyl groups prevent the formation of a π-complex. The π-complex theory has been seriously criticized.[5] It is known to be invalid in kinetic form and in its predictions of the steric effects of *para*-substituents.[6] Our result with *p*-hydrazobiphenyl now shows that the work of Friebel and Rassow cannot be used to justify Dewar's interpretation of the way in which π-complexes participate in the benzidine rearrangement.

In the present work the major reaction is disproportionation. Our kinetic data show the overall disappearance of *p*-hydrazobiphenyl to be of first-order in hydrazo-compound and of second order in acid. The rate constants, obtained over a range of acidities (0·0122—0·514N) and *p*-hydrazobiphenyl concentrations ($0{\cdot}74$—$2{\cdot}9 \times 10^{-4}$M) limited by solubility and rates of reaction in 95% ethyl alcohol at 0°, ranged from 0·0034 to 5·8 min.$^{-1}$. Carlin's extensive data give a similar kinetic description of the reactions of *p*-hydrazotoluene.[7]

Because of these data, we feel that we cannot dismiss from considerations of the mechanism of the benzidine rearrangement the possibility that an intermediate exists, which is formed in a rate-controlling process and in which final carbon–carbon or carbon–nitrogen bonding has not occurred. A rapid one-step, two-electron oxidation of a hydrazo-molecule by the intermediate, much in the same way that hydrazo-compounds are oxidized by Bindschedler's Green, would account for the disproportionation reaction. It may be that the intermediate is a π-complex and the polar transition state describes the path of its formation.

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