

THE p-SEMIDINE REARRANGEMENT. 4-ETHOXY- AND 4-METHOXYHYDRAZOBENZENE.

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(Received in USA 29 September 1967)

For the most part the acid-catalyzed benzidine rearrangements have been accepted as embracing five types of intramolecular reorganization of an aromatic hydrazo compound. These lead, after scission of the N,N'-bond, to benzidines (4,4'-bonding), o-benzidines (2,2'-bonding), diphenylines (2,4'-bonding), o-semidines (2,N'-bonding), and p-semidines (4,N'-bonding).

Some years ago Hammick and Mason (1) proposed a theory for the mechanism of the benzidine rearrangements in which N-N'-bond scission was concerted with the formation of the new bond of the rearrangement product. Hammick and Munro noted the difficulty of fitting the p-semidine rearrangement to this theory, because the concerted bond breaking and making over the large distances required made the transition-state geometry unacceptable (2). Hammick and Munro observed also (erroneously, it is now known) that in all the reported cases of p-semidine formation an azoaromatic had been treated with a heavy-metal reducing agent, such as stannous chloride, and an acid. They proposed therefore that p-semidine formation was not a genuine acid-catalyzed benzidine rearrangement but instead involved in some way the participation of a heavy-metal ion. To test this proposal they studied the acid-catalyzed rearrangement of 4-ethoxyhydrazobenzene, since by treatment of the corresponding 4-ethoxyazobenzene with stannous chloride and hydrochloric acid, Jacobson (3) had obtained the p-semidine (4-amino-4'-ethoxydiphenylamine) in 14% yield. In contrast to Jacobson's result Hammick and Munro obtained only intractable products, and concluded that this result was in harmony with their view that p-semidines could not be produced from hydrazobenzenes by the action of acids alone. We have pointed out earlier (4) that Hammick and Munro's work

with 4-ethoxyhydrazobenzene is experimentally unsatisfactory, and we have now also investigated the reaction.

4-Ethoxyhydrazobenzene (I) was prepared under heavy-metal-ion-free conditions by the reduction of 4-ethoxyazobenzene with potassium azodicarboxylate in aqueous ethanol. Precipitation by the addition of water gave completely colorless I, m. p. 87-88°. Authentic 4-amino-4'-ethoxydiphenylamine (II) was prepared from 4-ethoxy-N-nitrosodiphenylamine by a Fischer-Hepp rearrangement and reduction of the resulting 4-ethoxy-4'-nitrosodiphenylamine. II was very sensitive to air oxidation, and, indeed, is likely to be an efficient redox indicator (5). Therefore, it was isolated as the acetyl derivative (III), m. p. 136.5-137°. Lit. value: 134° (6). Elemental analysis was satisfactory.

Rearrangement of I was carried out with hydrochloric acid in aqueous ethanol. The products were acetylated in the ethanolic solution with acetic anhydride without prior isolation, because attempts at isolation were troubled with extensive air oxidation. The acetylated products were extracted with benzene and separated by preparative TLC, using silica gel (Brinkmann's GF254) and a solvent mixture of 10 ml. of acetone, 0.5 ml. of absolute ethanol made up to 50 ml. with benzene. Authentic III was used to monitor the chromatography, and showed that III was present in the rearrangement products. The other compounds present and separated from the TLC plates were the acetyl derivatives of the two scission amines and another rearrangement product (the o-semidine), and 4-ethoxyazobenzene.

III was removed from the TLC plates with ethanol and assayed by ultraviolet spectroscopy. The yields from four separate experiments were 7.3, 9.5, 4.7 and 7.3%.

Thus there is no doubt that 4-ethoxyhydrazobenzene undergoes the p-semidine rearrangement under heavy-metal-ion-free conditions. The result obtained by Hammick and Munro is attributable probably to oxidation of not only the p-semidine but also the anticipated o-semidine.

Similar work with 4-methoxyhydrazobenzene has been carried out, using the commercially available 4-amino-4'-methoxydiphenylamine as a guide, and similar

results have been obtained.

Reports of acid-catalyzed *p*-semidine formation are to be found in the recent literature, although they deal mainly with rearrangements carried out in immiscible solvents or with solid hydrazo compounds (7). Contrary to Hammick and Munro's report that there was no recorded case of a *p*-semidine rearrangement's being brought about by the action of acid alone, Jacobson obtained 4-amino-4'-chlorodiphenylamine from 4-chlorohydrazobenzene in methanol containing hydrogen chloride (8). It is necessary to straighten the record on this point.

Chromatographic detection of *p*-semidines, obtained from rearrangements in ethanol-hydrochloric acid, in quantities too small for isolation has been reported (9). The isolation of *p*-semidines has also been accomplished in more recent work (10).

The *p*-semidine rearrangement has a particularly important part in benzidine rearrangements. We have put forward the view (4) that if the *p*-semidine rearrangement was found to be a genuine acid-catalyzed one, schemes for the mechanisms of the benzidine rearrangement should be modified to provide for the rate-determining formation of an intermediate in which the problem of the concerted-type transition-state geometry can be avoided. We shall emphasize this point of view further and give complete experimental results for the 4-alkoxyhydrazobenzenes in a subsequent publication.

This paper is considered to be Part XI in a series of articles on the Benzidine Rearrangement. Support by the Robert A. Welch Foundation (Grant No. D-028) is gratefully acknowledged.

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