

559. *Mechanism of Benzidine and Semidine Rearrangements. Part XIV.*¹ *Crossing Tests on Products of the Uncatalysed Rearrangements of some Aromatic Hydrazo-compounds.*

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The non-catalytic rearrangements, in ethanol, acetonitrile, and acetone, at 80 and 110°, and in benzene at 110°, of the unsymmetrical hydrazo-compounds *N*-1- and *N*-2-naphthyl-*N'*-phenylhydrazine, give no symmetrical products. Rearrangements of these hydrazo-compounds in admixture, in the same range of conditions, give no products that could result from the crossings allowed by homolytic dissociation of the rearranging compounds. Rearrangements of mixtures of the symmetrical hydrazo-compounds 1,1'- and 2,2'-hydrazonaphthalene, again in the same range of conditions, gave no unsymmetrical products, such as would result from the crossings which would follow either homolytic or heterolytic dissociation of the rearranging compounds. The analytical sensitivity was 1% or better, and materials were accounted for quantitatively as separated products to this accuracy. It is concluded that neither homolytic nor heterolytic dissociation of the N-N bond plays any part in these non-catalytic hydrazo-rearrangements.

NOTWITHSTANDING the conclusions so far reached in our study (Parts I—XI¹) of the acid-catalysed rearrangement of aromatic hydrazo-compounds, the preconceptions with which we approached the non-catalytic (so-called "thermal") rearrangements of these substances required independent consideration of two basic questions in their regard. The first is that of whether the bond-changes in non-catalytic rearrangement are homolytic, leading to charge-symmetry between the two aromatic nuclei during rearrangement, or are heterolytic, with strong charge-transfers between the aromatic nuclei. The second question is that of whether the non-catalytic rearrangements are intramolecular, or

¹ Parts I—VII, *J.*, 1962, 2386—2444; Parts VIII—XI, 3294—3318; Parts XII and XIII, the two preceding Papers.

whether they proceed by some form of prior dissociation of the hydrazo-compound into fragments which can re-unite in various ways. As regards the acid-catalysed rearrangements, these are settled questions in our view. However, we should not be justified in carrying over conclusions on such fundamental matters to the non-catalytic case without first seeking specific evidence with respect to the latter. A main object of the work of Part XII, and particularly of Part XIII,¹ was to find some basis for a view as to whether the bond-changes in non-catalytic rearrangement are homolytic or heterolytic; the experimental findings were not discussed from that point of view in those Papers, because such a discussion is more conveniently included in Part XV (following Paper). The object of this Paper, to which Part XIII also contributes, is to present specific evidence on the question of whether or not some sort of dissociation plays a significant role in the non-catalytic rearrangements.

The long history of the same question in relation to the acid-catalysed rearrangements of aromatic hydrazo-compounds is summarised in the first paragraph of Part IV.² Comment on the question as it applies to non-catalytic rearrangements has previously been offered by two groups of workers. Večera, Gasparič, and Petranek³ heated some aromatic hydrazo-compounds at 150° without a solvent, and made a chromatographic examination of the products. One of their hydrazo-compounds was of the unsymmetrical AB-type, 4-methylhydrazobenzene, and from it they obtained an *ortho*-semidine and a *para*-semidine, which were both of AB-type. Nothing is said of other products, or of the recoveries of identified products, but the general conclusion is drawn that "rearrangements not involving protons take an intramolecular course, similar to rearrangements in an acid medium."

Shine, Huang, and Snell⁴ carried out studies of the products of non-catalytic rearrangement of two AB-type hydrazo-compounds in solvents at 90–95°. The more critical experiment, which they would like to have done, was non-catalytically to rearrange in homogeneous solution a mixture of two symmetrical hydrazo-compounds, AA and BB, which rearrange individually at comparable rates, and then to look for AB type cross-products. They contemplated the example of a mixture of 1,1'- and 2,2'-hydrazonaphthalene, Shine and Trisler having previously studied the kinetics and products of the individual non-catalytic rearrangement of the 2,2'-isomer.^{5,6} However, they were frustrated in attempting similar work with the 1,1'-isomer, and therefore in pursuing their intentions concerning the non-catalytic rearrangement of the mixture, by a difficulty which we think we identified as arising from the presence of oxygen, and certainly overcame, as described in Part XII.¹ Shine and his co-workers therefore fell back on the less critical rearrangement of AB-type hydrazo-compounds with a view to seeking AA- and BB-type products. They rearranged 1,2'-hydrazonaphthalene non-catalytically in cyclohexane at 95°. Only a small proportion of the material was recovered in identified products, but the two products recognised were of AB-type, and were, indeed, 2,1'-diamino-1,2'-binaphthyl and 1,2:5,6-dibenzocarbazole, the two substances which we have shown (Part II¹) to constitute 99% of the product of the acid-catalysed rearrangement of 1,2'-hydrazonaphthalene. The authors also rearranged *N*-2-naphthyl-*N'*-phenylhydrazine non-catalytically in 95% aqueous ethanol at 90°. The recoveries were much better in this case, though still somewhat far from complete; but again the two identified products were of AB-type, namely, 1-*o*-aminophenyl-2-naphthylamine and a little 3,4-benzocarbazole, the two substances which, in similarly uneven proportions, we have shown (Part VI¹) to constitute 99% of the product of the acid-catalysed rearrangement of the hydrazo-compound. The authors' conclusion was that "thermal rearrangement is intramolecular."

As comes out clearly in the history of the same problem in relation to acid-catalysed

² Banthorpe, *J.*, 1962, 2413.

³ Večera, Gasparič, and Petranek, *Chem. and Ind.*, 1957, 299.

⁴ Shine, Huang, and Snell, *J. Org. Chem.*, 1961, **26**, 380.

⁵ Shine, *J. Amer. Chem. Soc.*, 1956, **78**, 480.

⁶ Shine and Trisler, *J. Amer. Chem. Soc.*, 1960, **82**, 4054.

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benzdine rearrangements (Part IV ²), a stricter argument leads to more-open conclusions. The first is that results like the above on AB-type hydrazo-compounds would, *if all* the material formed could be identified, build up a cumulative case against homolytic dissociation; but that such results, even were this important condition fulfilled, would still say little or nothing about heterolytic splitting, because the AB-type hydrazo-compound would then split into parts whose distinctions of charge would ensure that the same species recombined. To cope with this case, we need the more crucial test, which equally covers both homolytic and heterolytic dissociation, of rearranging AA- and BB-type hydrazo-compounds concurrently in a common solution.

We have continued from the points reached by Shine at both these levels of criticality and cover. As regards work with AB-type hydrazo-compounds, the essential need was for quantitative recovery with total separation. As described in Parts XII and XIII,¹ we can fulfill this requirement by paper chromatography of all products not gravimetrically separated, and of all residues from such separations, the individual substances being eluted, and measured spectrophotometrically. As described in Parts IV ² and XIII,¹ these measurements were, wherever possible, made comparatively with like measurements on authentic samples of the same pure compounds, the chromatograms of the test samples and reference substances being concurrently developed on the same paper, for better correlation by position; also, the chromatograms were made with weighed amounts of the sample and of the reference compounds, in order to give meaning to the comparative absorptiometry of the eluted substances. The important quantitative aspect of these methods rests on their totality of detection. Trace products, formed in quantities between 0.1 and 1%, were usually detected with ease, and one could be confident that no product formed to the extent of, say, 1% could be overlooked.

The two AB-type hydrazo-compounds which we have thus examined, at first individually, are *N*-1- and *N*-2-naphthyl-*N'*-phenylhydrazine; the record of both of these groups of experiments is in Part XIII.¹ From the viewpoint of this Paper, the most important experiments with the *N*-1-naphthyl-compound were those in ethanol, acetonitrile, and acetone at 80 and 110°; this is because, in these polar solvents, the non-catalytic rearrangement of this hydrazo-compound is quantitative, and in particular, provided that oxygen is excluded, is unaccompanied by any detectable disproportionation. As recorded in Part XIII,¹ the three fully identified substances, which together constitute substantially the whole product, are all of AB-type; they are, indeed, 4-*p*-aminophenyl-1-naphthylamine, 2-*o*-aminophenyl-1-naphthylamine, and 1,2-benzocarbazole, the three substances which have been shown (Part V ¹) to constitute 99% of the product of rearrangement of the hydrazo-compound under catalysis by dilute acid in aqueous dioxan at 0°. In our non-catalytic conditions, there remained several trace amines, probably not amounting to more than 1% altogether, which were not specifically identified; however, it was shown by comparative chromatography that none of them was identical with any product formed by the non-catalytic rearrangement of either 1,1'-hydrazonaphthalene or hydrazobenzene, in like conditions.

The experiments with *N*-2-naphthyl-*N'*-phenylhydrazine in ethanol, acetonitrile, and acetone at 80 and 110°, and in benzene at 110°, are all relevant. As shown in Part XIII,¹ a little disproportionation does occur in all these conditions, only 0.5% in ethanol, but 1.5—5.0% in the other solvents. However, the 95—99% of material that has arisen by rearrangement consists, to the extent of at least 99%, of the two AB-products, 1-*o*-aminophenyl-2-naphthylamine and 3,4-benzocarbazole, which have been shown (Part VI ¹) to make up 99% of the product of the acid-catalysed rearrangement of the hydrazo-compound in aqueous dioxan at 0°. In all the non-catalytic conditions used, there remained two trace amines, in quantities of the order of 0.1%, which were not specifically identified, but were shown by means of comparative chromatography and spectrophotometry to be identical with the two unidentified trace amines which appeared (Part VI ¹) among the products of the acid-catalysed rearrangement of the hydrazo-compound. In two of the

sets of non-catalytic conditions, namely, in acetonitrile and in benzene at 110°, a third trace amine appeared, in quantities more nearly approaching 1%, which was shown to be a semidine, but was not more particularly identified. However, we have shown by comparative chromatography that none of these three trace products was identical with any product formed by the non-catalytic rearrangement of either 2,2'-hydrazonaphthalene or hydrazobenzene in like conditions.

A further series of experiments has been done with *N*-1- and *N*-2-naphthyl-*N'*-phenylhydrazine, which amounts to rearranging non-catalytically a mixture of AB- and BC-hydrazo-compounds, with the object of looking for any products identical with those given by the AC- and BB-hydrazo-compounds. This test is not of any wider scope in the diagnosis of mechanism than is that of rearranging either of the AB- and BC-hydrazo-compounds individually, but the mixed rearrangement does offer an opportunity for the application of comparative chromatography in a form sensitive for the purpose of detecting cross-products.

The non-catalytic rearrangement of an equimolar mixture of *N*-1- and *N*-2-naphthyl-*N'*-phenylhydrazine was examined in ethanol, acetonitrile, and acetone, at 80 and 110°; in each case, the analytical results were compared with those applying to the products of the individual rearrangements, carried out in parallel with the mixed rearrangement. The chromatogram of the products obtained from the mixture of hydrazo-compounds was a straightforward superposition of those given by the products from the separate hydrazo-compounds; this correspondence extended through the subsequent assay by absorptiometry of the individually eluted substances. There were no additional appearances on the chromatogram from the mixed rearrangement, and nothing that could have been a product given by either 1,2'-hydrazonaphthalene or hydrazobenzene under the conditions.

Particularly because all material is accounted for in separated products, these three groups of experiments with AB-type hydrazo-compounds appear collectively to build up a strong case against homolytic splittings in non-catalytic rearrangements, and, indeed, appear to go about as far as work with unsymmetrical hydrazo-compounds could go in de-limiting our ideas of dissociation in such rearrangements.

The more crucial test, more comprehensive in its allowed conclusions, which uses symmetrical hydrazo-compounds, was carried out for the case which Shine considered but abandoned for reasons already explained, namely, that of a mixture of 1,1'- and 2,2'-hydrazonaphthalene. The kinetics of the individual non-catalytic rearrangement of 1,1'-hydrazonaphthalene in ethanol, acetonitrile, and acetone, and the products formed in these solvents at 80 and at 110°, are reported in Part XII.¹ The kinetics and products of non-catalytic rearrangement of 2,2'-hydrazonaphthalene in ethanol and acetone at 80° have been reported by Shine and Trisler,⁶ and a more complete account of the products formed in ethanol, acetonitrile, and acetone at 80 and at 110°, and in benzene at 110°, is contained in Part XII.¹ The measured rates of rearrangement of the two isomers are not directly comparable, but, allowance being made for the difference in conditions, these rates can be seen to differ in like conditions by factors of the order of ten, the 1,1'-compound being the faster-reacting isomer. This kind of rate-ratio is within the range of comparability allowed by our analytical technique, with its sensitivity of 1% or better. Thus, assuming a rate-ratio of 15, which is about the figure for solvent ethanol, and assuming equal amounts of the mixed hydrazo-compounds, the statistical proportion of crossing during rearrangement by dissociation would be 12%; with twice as much of the less- than of the more-reactive isomer in the mixture, the proportion would be 20%.

Various mixtures of 1,1'- and 2,2'-hydrazonaphthalene were non-catalytically rearranged in the four solvents, and at the two temperatures, for which we know the products of the individual rearrangements, and the analytical results were compared as before with those obtained for the products of the separate rearrangements in like conditions. Once again, the chromatograms of the products given by the mixtures were superpositions of

those of the products of the separate rearrangements, weighted, as the subsequent absorptometric measurements showed, with respect to the abundances of the two groups of products, as would be expected if the rearrangements occurring in the mixture of hydrazo-compounds proceeded independently of each other, each pursuing the same course as when taking place alone. No additional substances appeared on the chromatograms of the mixed rearrangements; in particular, neither of the two dominating products, 2,1'-diamino-1,2'-binaphthyl and 1,2:5,6-dibenzocarbazole, given by 1,2'-hydrazonaphthalene could be recognised, though we consider that we could have detected the former in 0.5 and the latter in 1% abundance.

This very clear result allows us to conclude that neither homolytic nor heterolytic dissociation of the N-N bond of the aromatic hydrazo-compounds plays any part in their uncatalysed rearrangements in either polar or non-polar solvents at 80–110°. In terms of a common classification of mechanisms, these rearrangements are intramolecular.

EXPERIMENTAL

All essential points in the methods of conducting the rearrangements and analysing the products are covered in the experimental descriptions in Parts XII and XIII,¹ when supplemented with details given in certain earlier Papers, particularly Parts I¹ and IV.²

The mixed rearrangements of *N*-1- and *N*-2-naphthyl-*N'*-phenylhydrazine were, for each solvent and temperature, run over periods identical with those used in the rearrangements of these two hydrazo-compounds individually (Part XIII¹). For the mixed rearrangements of 1,1'- and 2,2'-hydrazonaphthalene, the periods of heating were as follows: for the solvents ethanol, acetonitrile, and acetone at 80°, 1, 7 and 15 days, respectively; and for ethanol, acetonitrile, acetone, and benzene at 110°, 3 hr., 12 hr., 1 day, and 15 days, respectively. In all cases, the completeness of reaction was checked with Bindschedler's Green.

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