464. *Mechanism of Benzidine and Semidine Rearrangements. Part IV.* Crossing Tests on Products of Acid Rearrangements of Mixtures of Hydrazonaphthalenes.*

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The newly disclosed kinetic dichotomy of acid-catalysed benzidine rearrangements has led us to re-open the question of their inter- or intramolecularity by extending to the hydrazonaphthalene series the non-crossing tests which formed the basis of an earlier conclusion favouring intramolecularity in the hydrazobenzene series, in conditions of undetermined kinetics. We have examined the rearrangement in " 60—70% " aqueous dioxan at 0°, conditions in which the relevant kinetics are fully known, of mixtures of pairs of the three isomeric hydrazonaphthalenes. The product of each such mixed rearrangement was a mixture in the expected proportions of the products of the two individual rearrangements, which had thus been made to run concurrently, with none of any product of the individual rearrangement of the third hydrazo-isomer, or, indeed, of any product foreign to the component rearrangements. Matters of accuracy and significance are discussed, and a conditional conclusion in favour of intramolecularity for the linear-acid-dependent rearrangements is drawn.

THE first theories of the acid rearrangements of the hydrazobenzenes assumed either homolytic,[1] or the pre-electronic equivalent of heterolytic [2] dissociation at the N-N bond, to give fragments, in either or both of which the point of unsaturation migrated into the ring before the fragments recombined. Then Wieland showed [3] that the demonstrable

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* Parts I—III, preceding papers.

[1] Tichwinsky, *J. Russ. Phys. Chem. Soc.*, 1903, **35**, 667.

[2] Stieglitz, *Amer. Chem. J.*, 1903, **29**, 62.

[3] Wieland, *Annalen*, 1912, **392**, 127; *Ber.*, 1915, **48**, 1095.

homolysis of tetra-arylhydrazines is not necessarily associated with benzidine-type rearrangement, and Jacobson[4] that AB-type hydrazobenzene derivatives gave AB-type, and not AA- or BB-type benzidines, a point which has since been established more quantitatively by Wheland and Schwartz,[5] by Bloink and Pausacker,[6] and by Večera Petranek, and Gasparič.[7] These demonstrations have been held to exclude the theory of homolytic dissociation. The heterolytic dissociation theory is not thus excluded, because the AB-type hydrazo-compound could split into parts whose distinctions of charge would ensure that the same species recombined. However, Ingold and Kidd showed[8] that two similar AA- and BB-type hydrazobenzenes (actually 2,2′-dimethoxy- and 2,2′-diethoxy-), when rearranged in the same acid solution, gave only AA- and BB-type benzidines, and no AB-benzidine, as far as was disclosed by the fusion phase-diagram. And Smith, Wheland, and Schwartz made an equivalent point with much increased precision by showing[9] that two similar AA- and *AB-type hydrazobenzenes, the asterisk denoting a label of radioactivity (they were 2,2′-dimethyl-, and 2-^{14}C-methyl-), when rearranged in the same acid solution, gave an AA-benzidine containing none of the radioactive *AA-form. These observations have been held to exclude the theory of heterolytic dissociation. All subsequent discussion of the mechanism of the acid rearrangement of hydrazobenzenes has proceeded on the premise that it is intramolecular.

Shine and his co-workers[10] have recently drawn the same conclusion for the non-acidic, so-called "thermal," rearrangements of hydrazo-compounds, their evidence being that, when AB-type factors were heated alone or in neutral solvents, the only recoverable rearrangement products were of AB-type. The difficulty is present here that recoveries are not quantitative because of the complexity of the products.

We have now to re-open the question of the inter- or intra-molecular nature of the acid rearrangement of hydrazo-compounds. The main reason is that all the above-mentioned demonstrations of non-crossing in this reaction apply to hydrazobenzenes, and we have been concerned with the rearrangements of hydrazonaphthalenes, which pursue kinetics different from those of the acid rearrangement of hydrazobenzene itself, and of a number of its simpler derivatives, including one of those used in the non-crossing tests. Obviously, conclusions supposed to be established for the acid rearrangements of hydrazobenzenes must be independently tested in the hydrazonaphthalene field. We shall want later to relate the two limiting forms of kinetics now known in a single theory of the rearrangements of hydrazo-compounds; and, for this purpose, we must ascertain whether the kinetically distinct reactions are alike or not in other ways.

When the work showing non-crossing in rearrangements in the hydrazobenzene series was done, the now-known kinetic dichotomy of benzidine rearrangements in general was, of course, unsuspected. It was therefore an excusable weakness in those earlier demonstrations that the kinetics were never determined in the conditions used to check cross-product formation. Now that that weakness is disclosed, we hope to repair it.

In the meantime, we here record our extension of these crossing tests to the hydrazonaphthalene series; and in this extension we have used conditions in which the kinetics, including the absolute rates, are known. The absolute rates are material, because, when seeking cross-products from mixed factors, it is important that one rearrangement should not be almost over before the other has sensibly begun. Indeed, the rates of the separate rearrangements ought not to differ by more than some small multiple, such as 5 or 10, depending on the analytical accuracy attained in the examination of the product.

The available substrates are 1,1′-, 1,2′-, and 2,2′-hydrazonaphthalene, and the products

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[4] Jacobson, *Annalen*, 1922, **428**, 76.

[5] Wheland and Schwartz, *J. Chem. Phys.*, 1949, **17**, 425.

[6] Bloink and Pausacker, *J.*, 1950, 450.

[7] Večera, Petranek, and Gasparič, *Coll. Czech. Chem. Comm.*, 1957, **22**, 1603.

[8] Ingold and Kidd, *J.*, 1933, 984.

[9] Smith, Wheland, and Schwartz, *J. Amer. Chem. Soc.*, 1952, **74**, 2282.

[10] Shine, Huang, and Snell, *J. Org. Chem.*, 1961, **26**, 380.

of their independent rearrangements, as determined in Parts I—III (preceding), are set out in Table 1, for the solvents of present concern, *viz.*, " 60—70% " aqueous dioxan. The Table is restricted to products arising in amounts of 1% or more. The proportions of the products are given in approximate form, because they may vary a very little with solvent composition in the range stated, and with temperature in the overall range of the determinations, 0—25°; and for the 1,2′-hydrazo-compound, and probably for its 2,2′-isomer, they do vary a little with the acidity in the broad decinormal range used in the present work with mixtures. One of the products from the 1,2′-hydrazo-compound is called " 2,4′-diamino-1,1′-binaphthyl (?)," because our evidence of its structure is not complete; but we do know what is important for the present work, namely, that it is not identical with any of the other diamines in the Table, in particular, not with any derived from the 1,1′- or 2,2′-hydrazo-compounds.

TABLE 1.

Products of independent rearrangement of isomeric hydrazonaphthalenes in " 60—70% " aqueous dioxan at 0—25° in the presence of 0·05—0·20N-perchloric acid.

Hydrazo-naphthalene	Aqueous dioxan	Temp.	Binaphthyl (B) or carbazole (C)	Approx. (%)
1,1′-	" 60% "	0°	4,4′-Diamino-1,1′-B	61
			1,1′-Diamino-2,2′-B	20
			1,2 : 7,8-Dibenzo-C	19
1,2′-	" 70% "	20—25	2,1′-Diamino-1,2′-B	58
			2,4′-Diamino-1,1′-B(?)	1
			1,2 : 5,6-Dibenzo-C	41
2,2′-	" 60% "	25	2,2′-Diamino-1,1′-B	95
			3,4 : 5,6-Dibenzo-C	5

Table 1 already records one experiment of what may be called the Jacobson type. For the 1,2′-hydrazo-compound is an AB-type factor, and its products, if we accept the proposed structure of the minimal one, are all constituted by combining an A with a B residue in various ways; in any case, none is identical with any of the products obtained from the AA- and BB-type factors.

For the analysis of products of rearrangements of mixed hydrazonaphthalenes, we have used gravimetric separation, as developed for the products of independent rearrangements and described in Part I, but now backed by chromatography of the separated materials, including the paper-chromatographic detection of trace-products. We have tested these methods with artificial mixtures, and believe that we can detect less than 1% of a minor isomer: we have detected as little as 0·1%. The sensitivity of the procedure for the detection of cross-products is therefore intermediate between that of Ingold and Kidd's fusion-diagram method (about 3%), and that of the radio-tracer method (0·03%) of Wheland *et al.*; but it is enough to establish the point of substance * for rearrangements so structurally and kinetically similar as ours.

We have carried through rearrangements of two mixtures of two of the hydrazo-isomers, separating the products, and searching them particularly for products of rearrangement of the third isomer, and for any products foreign to the independent rearrangements of the substrates used. The conditions of the mixed rearrangements, and the rates of the independent rearrangements, thus caused to run concurrently, are in Table 2.

In runs 1—3 on the 1,2′- and 2,2′-hydrazo-isomers, the rates of the individual rearrangements are only 20% apart, and hence the case is exceptionally favourable for the detection of cross-products, if formed. The actual products were those to be deduced from Table 1,

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* A special product formed in very minute amount might always be the result of some minute, normally insignificant, side-reaction. Hence, to detect, or even to measure, such a trace-product would justify no conclusion about the reaction of main interest.

TABLE 2.

Conditions of rearrangements of mixtures of hydrazonaphthalenes and first-order rate-constants (k_1 in sec.$^{-1}$) under like conditions of the independent rearrangements.

Runs	Aqueous dioxan	Temp.	[$HClO_4$] (N)	Hydrazo-naphthalenes	Proportions (%)	Individual 10^3k_1
1 2,3 *	" 70% "	0·0°	0·15	1,2′-	50	43·6
				2,2′-	50	37·0
4 5,6,7 *	" 60% "	0·0°	0·06	1,1′-	50	100·8 †
				2,2′-	50	28·6

* Control: successive rearrangements in the same solution. † Extrapolated.

in the correct ratios for concurrent individual rearrangements of 1,2′- and 2,2′-hydrazonaphthalene. No products of rearrangement of 1,1′-hydrazonaphthalene were detected.

Runs 2 and 3 illustrate a method by which the proportions of products in the mixed and individual rearrangements can be compared, often with greater accuracy than that with which their absolute values can separately be measured. In run 2, equal weights of the isomeric hydrazo-compounds were put into a solution, and, by adding the acid last, were rearranged together. In the control run 3, weights accurately identical with the previous ones of the same substances were rearranged in a common solution, but one after the other, the rearrangement of one substrate being run to completion before addition of the second substrate. The products of runs 2 and 3 were then worked up in parallel, and weights and other analytical measures (*e.g.*, photometric) were compared at every stage. In the final chromatograms, accurately identical test-samples were taken, and corresponding separated products were eluted and directly compared in the absorptiometer. Except for trace-products, the accuracy of the comparison was 2%, reckoned on the percentage, whether that was large or small; and it was thus shown that every non-trace-product was formed in quantities identical to within these limits in runs 2 and 3, and, furthermore, that no additional trace-product arose in run 2.

Runs 4—7, dealing with the 1,1′- and 2,2′-hydrazo-isomers, are more strictly on the lines of the work of Ingold and Kidd, and of Smith, Wheland, and Schwartz: two symmetrical factors AA and BB are rearranged together, and the mixed products are searched for AB-type components. Here, the rates of the individual rearrangements are in the ratio 3·5 : 1, but the " Mendelian " proportion of crossed products is still 35%, and hence our methods, with their 1% accuracy or better, are quite sensitive enough to deal with the case. Once again, we found the actual products to be those listed for the two substrates in Table 1, in the proportions to be expected from independent rearrangements of the substrates. No trace was detected of any other product, in particular, none of either of the two dominating rearrangement products of 1,2′-hydrazonaphthalene.

Runs 5 and 6 were duplicate simultaneous rearrangements of mixed 1,1′- and 2,2′-hydrazonaphthalenes, whilst the control run 7 was a run of their consecutive rearrangements in a common solution under otherwise identical conditions, the quantities of each substrate taken being strictly the same in all the three runs 5—7. The absolute proportion of 4,4′-diamino-1,1′-binaphthyl, the main rearrangement product of the 1,1′-hydrazo-compound, is particularly easily determined: in the simultaneous rearrangement of run 5, this proportion was 62·0%, in that of run 6, it was 61·8%, and in the product of the consecutive rearrangements of run 7, it was 62·2% of the 1,1′-hydrazonaphthalene taken. The remaining products obtained in these runs of concurrent or successive rearrangements were treated by the method of comparison, based on chromatographic separation and absorptiometry, as described above. Corresponding products were formed in the same proportions, to within about 2% of those proportions, in all the three experiments. No additional product, above the sensitivity limit of 1% arose in runs 5 and 6, that was not produced in run 7.

We conclude that neither homolytic nor heterolytic dissociation at the N–N bond is involved in those acid rearrangements of hydrazo-compounds, which proceed according to the linear-hydrogen-ion rate-law of equation (1) in Part I. In terms of the usual two-fold classification of mechanism, these reactions are intramolecular.

EXPERIMENTAL

Equimolecular quantities (*e.g.*, 0·15 g. each) of the hydrazo-compounds to be rearranged together were dissolved in a suitable dioxan–water mixture, and, after adjustment of the temperature, enough dilute perchloric acid was added to yield a solution (50 ml.) of the required solvent-composition and acidity (cf. Table 2). After rearrangement had occurred, the product was put through the procedure of gravimetric separation and chromatography described for the product of an individual rearrangement in Part I (preceding).

The individual hydrazo-compounds were separately rearranged in identical conditions, and their products of rearrangement were separated in the same manner. This was done in order to provide comparison material to aid the chromatographic and spectroscopic detection of crossed or foreign products, should they arise, in the mixed rearrangement, and also to help establish the sensitivity of these methods for the detection of minor isomers.

Crossed and foreign products were looked for primarily by chromatography of the chemically separated fractions, on Whatman's no. 4 paper, with the use of the following solvent systems, in each of which the first-mentioned component is the stationary phase: (1) formamide + cyclohexane; (2) formamide + benzene; (3) dimethylformamide + cyclohexane; (4) silicone oil + cyclohexane; (5) formamide + ammoniacal propan-1-ol (a mixture of 6 vol. of propan-1-ol, 3 vol. of concentrated aqueous ammonia, and 1 vol. of water). Sometimes one- and sometimes two-dimensional chromatograms were made. Both the usual sprays, *N*-1-naphthylethylenediamine after diazotisation with nitrous gases, and *p*-dimethylaminobenzaldehyde, were employed for detection.

We could not obtain the required certainty and precision by relying on the separately measured R_F values of the formed substances. Even after prolonged soaking of the paper in a 10% solution of the stationary phase in ethanol, and subsequent thorough air-drying, these quantities differed a little from paper to paper, presumably owing to incomplete removal of water from the surfaces of the fibres. However, on each paper on which a test-spot of a particular gravimetric fraction of the product of a mixed rearrangement was planted, test-spots were planted beside it of the corresponding gravimetric fraction of the products of the two involved individual rearrangement, so that the three adjacent chromatograms could be developed concurrently. The identification of the products of the mixed rearrangement was thus direct, and the detection of any product other than those given by the separate rearrangements was made very simple. By similarly running the chromatogram of the gravimetric fraction of the product of rearrangement of two mixed hydrazonaphthalenes against one of a series of artificial mixtures of the same material with known small amounts of the corresponding fraction of the product of rearrangement of the third hydrazonaphthalene, it was shown that the sensitivity of the method for detecting the products of rearrangement of the third hydrazo-isomer, if they had been formed in the mixed rearrangement, was below 1%. The use of several solvent systems renders undetected inhomogeneity in the spots of the chromatograms most unlikely.

In the experiments on successive rearrangement (nos. 3 and 7) the 1,2′- or 1,1′-hydrazonaphthalene was rearranged first, and the 2,2′-isomer afterwards in the same solution. Comparative conditions were maintained in the chromatography as described above, and acetone–ether was used as eluant in preparing samples for absorptiometry.

Although, as explained already, R_F values are slightly variable from one chromatogram to another, these values are different enough, as illustrated by Table 3, and the pattern of their differences is uniform enough, as between corresponding gravimetric fractions of the products from different substrates, to leave no doubt that, if, for example, any product of rearrangement of the 1,2′-hydrazo-compound had appeared among the products found after the concurrent rearrangement of the 1,1′- and 2,2′-isomers, it would easily have been detected.

The infrared and ultraviolet spectra of the gravimetric fractions of the mixed and the individual rearrangements, and of artificial mixtures of the products of individual rearrangement, were measured. These methods were less useful for the detection of trace-products, but

TABLE 3.

Comparison of R_F values in identical conditions (solvent system no. 1) of the gravimetric fractions of the products of acid rearrangement of the hydrazonaphthalene isomers.

Fraction	1,1′-Hydrazo	1,2′-Hydrazo	2,2′-Hydrazo
(1) Amines with insol. sulphates	0·18	0·25	0·30 *
(2) Neutral carbazoles	0·73	0·62	0·83
(3) Amines with sol. sulphates	0·72	0·69	0·84

* Trace-product.

were valuable for confirmation and for furnishing supplementary quantitative information. In particular it was shown that the spectra of the products of a mixed rearrangement could always be matched by an artificial mixture of the correct proportions of the involved individual rearrangements.

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