557. *Mechanism of Benzidine and Semidine Rearrangements. Part XII.[1] Kinetics, Products, and Isotope Effects in the Non-catalytic Rearrangement of 1,1'-Hydrazonaphthalene in Ethanol and in Aprotic Solvents.*

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2,2'-Dideuteration reduces the rate of decomposition of 1,1'-hydrazonaphthalene in neutral solvents, but 4,4'-dideuteration has not clearly been observed to do so. In aprotic solvents, no 4,4'-linked rearrangement products are formed, and the formation of 2,2'-linked products is strongly retarded by 2,2'-deuteration. In ethanol, both 4,4'-linked and 2,2'-linked products are formed, and the retardation of formation of the latter is, as a consequence of 2,2'-dideuteration, much weaker. On the basis of these findings, some general comparisons are made between the mechanism of rearrangement as previously investigated under conditions of acid catalysis and the mechanism operating in the absence of catalysis in ethanol, and also in aprotic solvents.

THE demonstration given in the preceding Parts of this series [1] of acid-catalysed benzidine rearrangements by two related mechanisms, one involving the preliminary uptake of two protons by the hydrazo-molecule, and the other of only one, aroused our interest in benzidine-type rearrangements without any added protons.

Shine and his co-workers have shown [2] that 2,2'-hydrazonaphthalene undergoes rearrangement at temperatures near 80°, in the absence of acid, in solution either in alcohols or aprotic solvents. The disappearance of hydrazo-compound was found to obey first-order kinetics. It was faster by about one power of ten in alcoholic than in aprotic solvents. In alcoholic solvents the main products were 2,2'-diamino-1,1'-binaphthyl (80—85%) and 3,4:5,6-dibenzocarbazole (15—20%), although redox or other non-rearranged products, notably 2,2'-azonaphthalene, were formed in small amounts. In aprotic solvents, the same substances were obtained, but the proportions of redox products, such as 2,2'-azonaphthalene, were larger. In all solvents, the rearrangement products were identical with those formed as the only products under acid-catalytic conditions. An examination was reported of the products, though not of the kinetics, of the decomposition of 1,2'-hydrazonaphthalene and of N-2-naphthyl-N'-phenylhydrazine in cyclohexane in the absence of acid. In these cases the products were more complex and less fully identified; however, those recognised were again the diamines formed by *ortho*-benzidine-type rearrangements, and the corresponding carbazoles. Again they were the same as the substances found by us to be the only products of the acid-catalysed rearrangements of these hydrazo-compounds. Reports have appeared [3-5] which refer to products of thermal decomposition of some other hydrazo-compounds, including 1,1'-hydrazonaphthalene, with which we deal below.

Shine's main conclusion [2] was that, in the reactions in alcoholic solvents, the alcohol acts as a catalysing acid. He offered no opinion on the mechanism of rearrangement in aprotic solvents. He did show that the specific rate of rearrangement of 2,2'-hydrazonaphthalene in ethanol at 80° is reduced from 7.7×10^{-5} to 4.5×10^{-5} sec.$^{-1}$ by an addition of 10% of pyridine to the ethanol. The smallness of this effect suggests to us that, if the alcohols act as proposed, they must be exerting only a general-acid catalysis, whose distinction of result from that of the general solvent effect of a polar solvent ought to be more completely illustrated, whilst the experimental characteristics of the mechanism

[1] Parts I—VII, *J.*, 1962, 2386—2444; Parts VIII—XI, 3294—3318.
[2] (a) Shine, *J. Amer. Chem. Soc.*, 1956, **78**, 4807; (b) Shine and Trisler, *ibid.*, 1960, **82**, 4054; (c) Shine, Huang, and Snell, *J. Org. Chem.*, 1961, **26**, 380.
[3] Večera, Gasparič, and Petranek, *Chem. and Ind.*, 1957, 299; Shine and Snell, *ibid.*, p. 706.
[4] Krolik and Lukashevich, *Doklady Akad. Nauk, S.S.S.R.*, 1949, **65**, 37.
[5] Holt and Hughes, *J.*, 1953, 1666; 1955, 98, 1320.

which operates in the presence only of the general solvent effect of aprotic solvents ought to be more fully specified.

At the conclusion of the work described in Part IX,[1] we found ourselves in a position to contribute to these problems, inasmuch as we had on hand small but useful stocks of 85% 2,2'-dideutero- and 90% 4,4'-dideutero-1,1'-hydrazonaphthalene. We knew that, in the presence of a catalysing acid, the deuterium in these compounds does not affect the rates of their rearrangement. We could check whether or not this property belongs also to the rearrangements which they undergo in the absence of acid in alcoholic and in aprotic solvents.

The kinetics of the decomposition of 1,1'-hydrazonaphthalene in organic solvents in the absence of acid have not been reported before. Shine [2a,b] did attempt to study the kinetics of this system, but was unable to devise a satisfactory titrimetric method for following the disappearance of hydrazo-compound. Perhaps because of the experience gained in the work reported in Parts I and IX,[1] and our resulting appreciation of the need to thoroughly de-gas the materials, we had no such difficulty, though our rate data are not quite as self-consistent as were those obtained for the acid-catalysed rearrangement of this hydrazo-compound. In the solvents that we have used, the reaction proceeds at convenient speeds at about 70—80°, following the first-order rate law. The rate constants thus obtained for 1,1'-hydrazonaphthalene and for its 2,2'- and 4,4'-dideutero-derivatives at 69·1° are given in Table 1.

TABLE 1.

Specific rates (k_1 in sec.$^{-1}$) of decomposition of 1,1'-hydrazonaphthalene and its 2,2'- and 4,4'-dideutero-derivatives in organic solvents in the absence of acids at 69·1°.

Substrate	Solvent	$10^5 k_1$	Mean k_1	Substrate	Solvent	$10^5 k_1$	Mean k_1
Parent	EtOH	82, 81	81·5	4,4'-Di-D ...	MeCN	8·4, 8·0	8·2
2,2'-Di-D...	EtOH	70, 68	69·0	Parent	Acetone	6·7, 6·5, 6·1	6·4
Parent	MeCN	8·6, 8·8, 8·3, 8·2	8·5	2,2'-Di-D ...	Acetone	4·0, 3·9	4·0
2,2'-Di-D...	MeCN	5·2, 5·6	5·4	4,4'-Di-D ...	Acetone	5·7, 6·0, 6·0	5·9

We see that, in partial contrast to the acid-catalysed rearrangement of 1,1'-hydrazonaphthalene, in which neither 2,2'- nor 4,4'-dideuteration affects the reaction rate, the non-catalytic decomposition of that hydrazo-compound in ethanol is appreciably retarded, and in either acetonitrile or acetone, is markedly retarded, by 2,2'-dideuteration, though, as far as examined, it is little if at all retarded by 4,4'-dideuteration. Evidently, there is a difference between the acid-catalysed and the uncatalysed reactions with respect to the stage at which the aromatic protons, displaced by rearrangement, are expelled.

In order further to judge the significance of these kinetic effects, it was necessary to examine products of the reaction in non-catalytic conditions. The analytical problem proved difficult. The solution from the rearrangement was red, owing to the presence of azo-compound, but in agreement with a report by Shine and his co-workers,[2c] in the course of the subsequent analytical procedure, in which we could not contrive to exclude air, some tarry material was generated and the solution darkened. At least five substances are formed in the rearrangement, too many, and some of them too much alike spectrally, to permit analysis by the theoretically general method of measuring optical absorption at a corresponding number of wavelengths. Moreover, the gravimetric scheme described in Part I [1] for quantitative analysis of mixtures of the three rearrangement products formed from 1,1'-hydrazonaphthalene in the presence of acids could not be so developed as to achieve a satisfactory material-balance of substances separated from the more complicated mixtures produced in the absence of acids. What the attempts made in these directions did show was that the mixtures owe their initial complexity almost wholly to the presence in comparable amounts of two groups of products, namely, rearrangement products and redox products, as seems not unnatural since the former dominate in acid conditions and the latter in basic. However, the redox reactions could not be assumed to have a simple stoicheiometry in terms of the substrate only. Carlin and Wich first

noted this [6] in the case of an acid-catalysed hydrazo-rearrangement, that of 4,4'-dimethyl-hydrazobenzene, in which diaminobiaryls are not formed and an *ortho*-semidine is the main rearrangement product, whilst redox by-products, strongly out of equivalence, assume very considerable importance. In our uncatalysed reactions, 1,1'-azonaphthalene and 1-naphthylamine were always formed, both in substantial quantities, but, as we could show despite the incompleteness of our analyses, in quantities far out of equivalence in some solvents at least. Thus every substance formed presented its additional analytical problem, and in the end we had to settle on a compromise between quantitative and qualitative analysis. Our procedure was as follows.

1,1'-Azonaphthalene was determined spectrophotometrically by use of the absorption band at 400 mμ. 4,4'-Diamino-1,1'-binaphthyl ("naphthidine") and 1,2:7,8-dibenzo-carbazole were each determined gravimetrically, using the appropriate parts of the method described in Part I.[1] Then, the 1,1'-diamino-2,2'-binaphthyl ("dinaphthyline"), the 1-naphthylamine, and various minor and trace products were qualitatively assayed by means of the paper-chromatographic methods of Večera, Petranek, and Gasparič.[7] In applying these, we distinguished broadly between main products (marked + + +, and believed to be present to the extent of not less than 10%), minor products (+ +, 1—10%), and trace products (+), as shown in Table 2. Our identification of the minor and trace products as the "*ortho*-semidine," *N*-(1-amino-2'-naphthyl)-1-naphthylamine, and the "diphenyline analogue," 4,1'-diamino-1,2'-binaphthyl, are based on the agreement of their R_F values with those assigned by Večera and his co-workers to those products, and are not confirmed by independent methods. It may be recalled that those investigators claim to have found these substances (and a "*para*-semidine") among the products of the acid-catalysed rearrangement of 1,1'-hydrazonaphthalene,[7a] but that we have never found any of them under such conditions, not even when we used their methods. Krolik and Lukashevich [4] made qualitative estimates of the diazotisable amines and of the carbazole formed in this non-catalysed rearrangement in ethanol and in benzene.*

* Since this was written, a new Paper [8] by Lukashevich and Krolik has come to hand, which reports gravimetric analyses of products of the "thermal" rearrangement of 1,1'-hydrazonaphthalene with a large number of solvents at 100°. Their figures are in rough accord with ours for solvent ethanol, but in no sort of accord for acetonitrile, acetone, and benzene. In these non-hydroxylic solvents, they found, for instance, substantial and comparable amounts of *ortho*- and *para*-semidines among the products, whereas we find only traces of the former and none of the latter; they also found the 4,4'-diamine (naphthidine) as a major product, whereas with us it only as a minor product, if we found any at all. We suggest two causes of these discrepancies.

First, the quantities of hydrazo-compound and solvents used by Lukashevich and Krolik were such that, in our non-hydroxylic solvents at least (and, as we have verified, for cyclohexane, which was another of theirs), much solid phase must have been present during the decompositions. These authors showed before [9] that, in the acid rearrangement of 1,1'-hydrazonaphthalene, a *para*-semidine results only when the amount of solvent is insufficient to dissolve all the hydrazo-compound. Hammick and Munro first showed [10] that, in benzidine rearrangements generally, *para*-semidines result from more-complex mechanisms than those from which the other rearrangement products normally arise.

Secondly, Lukashevich and Krolik's gravimetric separations appear to us unsatisfactory. They treated their mixtures with benzene and aqueous acid, and claimed that, under the prescribed conditions, naphthidine precipitates, whilst dinaphthyline and 1-naphthylamine go one into each liquid phase. However, they report no control experiments. We therefore repeated their described procedure with various synthetic mixtures of naphthidine, dinaphthyline, the dibenzocarbazole, naphthylamine, and azonaphthalene, mixtures which present a simpler analytical problem than faced them, inasmuch as, not having samples, we could not include additionally the *ortho*- and *para*-semidines. We found that the naphthidine was incompletely (*e.g.*, 70%) precipitated, and that some of it (*e.g.*, 15%) was recovered from the benzene layer by a procedure which should separate only the *ortho*-semidine when present. We also found that dinaphthyline and 1-naphthylamine were present in both liquid layers, the former being, indeed, comparably distributed between the two. On the other hand, we found that the carbazole could be determined accurately, and 1,1'-azonaphthalene fairly accurately, by Lukashevich and Krolik's method.

We were struck by the fact that these authors describe no de-gassing procedure such as we have found essential in all our attempted quantitative work on the rearrangement of 1,1'-hydrazonaphthalene.

[6] Carlin and Wich, *J. Amer. Chem. Soc.*, 1958, **80**, 4023.
[7] (*a*) Večera, Petranek, and Gasparič, *Coll. Czech. Chem. Comm.*, 1957, **22**, 1603; (*b*) *ibid.*, 1958, **23**, 249.
[8] Lukashevich and Krolik, *Doklady Akad. Nauk, S.S.S.R.*, 1962, **147**, 1090.
[9] Krolik and Lukashevich, *Doklady Akad. Nauk, S.S.S.R.*, 1960, **135**, 1139.
[10] Hammick and Munro, *J.*, 1950, 2049.

The most interesting feature of Table 2 is the absence of any major proportion of the *para*-linked rearrangement product, 4,4′-diamino-1,1′-binaphthyl, from the reaction products formed in aprotic solvents, *i.e.*, in solvents other than ethanol.* Under acid catalysis, which, according to our evidence, is of the specific hydrogen-ion type, involving the preliminary and complete transfer of one proton to the reacting system, this *para*-linked biaryl is the chief rearrangement product. In the absence of acids, but in solvent ethanol, it is still one of the main products, whilst it would seem that, in aprotic solvents, polar or non-polar, it is formed hardly at all. This finding gives strong support to Shine's view that in alcoholic solvents, in the absence of acids, a special mechanism is at work in which the alcoholic function is used in a specific way. If the reacting system is activated by presentation to it of the hydroxylic proton, such activation would amount to a general-acid catalysis, apart from the circumstance that the activating substance is the solvent, and would not normally be called a catalyst. Therefore such activation might be expected to create potentialities of rearrangement approaching, though not reaching, those conferred on the system by acid catalysis proper.

TABLE 2.

Quantitative (mole %) and qualitative analysis of the products of decomposition of 1,1′-hydrazonaphthalene in polar organic solvents at 80°, and in benzene solution and in the solid state at 110°.

Solvent	EtOH	MeCN	Acetone	C_6H_6	None
4,4′-Diamino-1,1′-binaphthyl	20	4	0	0	3
1,1′-Diamino-2,2′-binaphthyl	+++	+++	+++	+++	++
1,2:7,8-Dibenzocarbazole	30	10	10	30	0
1,1′-Azonaphthalene	17	30	60	25	60
1-Naphthylamine	+++	+++	+++	+++	+++
" *ortho*-Semidine "	+	+	+	+	+
" Diphenyline analogue "	+(?)	+(?)	+(?)	+(?)	+
" *para*-Semidine "	—	—	—	—	+
Other Products	—	—	—	—	tar

Technical difficulties have so far prevented determination of the kinetics of the reaction in benzene, but the products formed in this solvent are generally similar to those formed in polar aprotic solvents. The main new features of the decomposition of the solid are the formation of a small amount of the 4,4′-linked rearrangement product, and of a smaller amount of a " *para*-semidine," which has been found before by Večera and his co-workers.[7a] The mode of formation of this last substance is quite obscure. Provisionally, we picture it as intermolecular.

Comparison of Tables 1 and 2 allows further conclusions to be drawn. Table 1 shows that the total rate of decomposition of 1,1′-hydrazonaphthalene in the polar aprotic solvents is substantially unaffected by 4,4′-dideuteration. Since any marked kinetic effect could only be a primary isotopic effect on 4,4′-hydrogen loosening in the transition state of reaction, it is a sufficient explanation of the absence of such an effect that only small quantities at most of 4- or 4′-linked products are formed in aprotic solvents.

Table 1 shows also that, on the contrary, 2,2′-deuteration leads to a marked reduction of decomposition rate in aprotic solvents, and to a mild reduction in solvent ethanol. In all these solvents, two 2,2′-linked products are formed, namely, 1,1′-diamino-2,2′-binaphthyl and 1,2:7,8-dibenzocarbazole, though only the latter was quantitatively determined. However, the figures in Table 2 show that overall proportions of 2,2′-linked products in the

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* Krolik and Lukashevich [4] obtained the *para*-linked product from solvent ethanol, and concluded that Nietzki,[11] who had previously obtained it, though he had believed it to be the hydrazo-compound, by the alkaline reduction of the azo-compound in aqueous ethanol, had been observing a " thermal " rearrangement of first-formed hydrazo-compound. If so, this rearrangement, itself owing nothing to the alkali, must have been running concurrently with disproportionation (which is definitely alkali-catalysed) in the alkaline medium.

[11] Nietzki, *Ber.*, 1885, **18**, 3253.

various solvents are bracketed between minima of 10—30% according to the solvent, and maxima of 40—75%. (Thus for solvent ethanol, the proportion must be more than 30% and less than $100 - 20 - 17 = 63\%$.) Now the reductions of total rate caused by 2,2′-di-deuteration must arise from a primary isotope effect on the formation of these 2,2′-linked products. Thus the rate reductions of 30% or more found in the aprotic solvents imply strong reductions in the rates of formation of these products. Thus the median figure of 36% for 2,2′-linked products would imply a 6-fold reduction in their rate of formation when the 2,2′-hydrogen is replaced by deuterium. This shows that the loosening of 2,2′-hydrogen is an essential part of the rate-determining process in non-catalytic rearrangement. Here is a marked contrast with the acid-catalysed rearrangement, in which 2,2′-dideuteration makes no difference either to the total rate of reaction or to the total rate of formation of the 2,2′-linked products, thus showing that no loosening of 2,2′-hydrogen, just as no loosening of 4,4′-hydrogen, takes place in the transition state of that form of rearrangement.

The mild reduction of rate in solvent ethanol caused by 2,2′-deuteration may mean that the specific mechanism there in operation has analogies, not only, as we have already seen, in product formation with the acid-catalysed mechanism, but also in its kinetically important phase, with the non-catalytic mechanism as this reveals itself in aprotic solvents. It might, perhaps alternatively be argued that in alcohols a mixture of two mechanisms is at work, one of which has its closer analogies with the acid-catalysed mechanism, and the other with the aprotic mechanism.

EXPERIMENTAL

The tubes used in the kinetic experiments were cleaned, not, as usual, with chromic acid, but with a detergent, in order to avoid accidental inclusion of any trace of acid.

All solvents were purified by standard methods, and solutions were thoroughly degassed before use. For this purpose, each tube containing a sample which was to yield a point on the reaction–time curve was connected to a vacuum line, frozen in liquid oxygen, and pumped down to 0·5 mm. Hg. After the sample had been allowed to thaw, oxygen-free nitrogen was admitted, and then the sample was again frozen in liquid oxygen, and its containing tube again evacuated. After four such cycles, the tube was sealed so as to contain a nitrogen atmosphere, and was in this way separated from the vacuum manifold. Other materials were prepared as described in Part I.

The kinetic methods were those described in Part I.[1] A specimen run is recorded in Table 3.

TABLE 3.

Decomposition of 2,2′-dideutero-1,1′-hydrazonaphthalene in acetone at 69·1°. (Binschedler's Green solution was added to quench each aliquot sample of the reaction mixture, and the excess was back-titrated with *ca.* 0·01N-TiCl$_3$ solution; x is the amount of Binschedler's Green, expressed in terms of the TiCl$_3$ solution, that reacted with the residual substrate at each point.)

t (min.)	0	20	30	60	90	121	170	180	231
x (ml.)	8·46	8·12	7·81	7·40	6·76	6·41	5·62	5·36	4·91

A plot of $-\log_{10} x$ versus t was linear, and, from the slope, k_1 was calculated to be $(4{\cdot}0 \pm 0{\cdot}1) \times 10^{-5}$ sec.$^{-1}$.

The product analyses were made on solutions of 1,1′-hydrazonaphthalene which had been heated in ethanol, acetonitrile, or acetone in sealed tubes at 80° for 30 hr., or at 110° for 15 days in benzene or in the solid state. The product was first titrated with Bindschedler's Green, in order to ascertain the proportion in which the 1,1′-hydrazonaphthalene had been decomposed; in fact, the decomposition was nearly always quantitative. Next, the 1,1′-azonaphthalene was determined spectrophotometrically by the method outlined in Part I. The solution was then evaporated at room temperature, and the residue was dissolved in aqueous dioxan in preparation for the gravimetric procedure, which was applied, as described in Part I, to the

determination of 4,4′-diamino-1,1′-binaphthyl and 1,2:7,8-dibenzocarbazole. During this procedure, the solution darkened, owing to the formation of a tarry material. The application of the chromatographic methods of Večera *et al.*[7] was conducted as indicated in Part I.

It was ascertained that 1,1′-diamino-2,2′-binaphthyl is not converted into 1,2:7,8-dibenzo-carbazole under any of the conditions used for rearrangement or analysis in these experiments.

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