

**558.** *Mechanism of Benzidine and Semidine Rearrangements. Part XIII.\* Products of the Non-catalytic Rearrangement of several Aromatic Hydrazo-compounds.*

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The products of the non-catalytic rearrangement of 2,2'-hydrazonaphthalene, *N*-1-naphthyl-*N'*-phenylhydrazine, *N*-2-naphthyl-*N'*-phenylhydrazine, and hydrazobenzene in ethanol, acetonitrile, acetone, and benzene, and in the absence of a solvent, have been investigated, the simpler analyses being made quantitative, and the others being left semi-quantitative or qualitative. Suggestive comparisons between the product-patterns of the acid-catalysed and uncatalysed rearrangements of the same hydrazo-compound, and among the product-patterns of uncatalysed rearrangements of the same hydrazo-compound in different solvents, are pointed out.

IN the work of Part XII<sup>1</sup> on the rates and products of the non-catalytic rearrangement of 1,1'-hydrazonaphthalene, the product compositions on their own account, and especially when considered against the background of those applying to the acid-catalysed rearrangement, seemed to suggest important conclusions. In order better to judge the value of these indications, it was necessary to secure a wider range of data. The work on the products, though not on the kinetics, of the non-catalytic reaction has therefore been extended to a range of aromatic hydrazo-compounds, covering most of those of which the acid-catalysed rearrangement is described in Parts I—XI of this series.<sup>1</sup>

In the non-catalytic decomposition of 1,1'-hydrazonaphthalene, five products are formed in substantial amount, and a fully quantitative analysis proved impracticable. Thus the analyses became semi-quantitative; however they contained a piece of quantitative information, that for many theoretical purposes is more important than to be able to give a precise figure for the percentage of each substance, namely, the information that nothing of significance had been overlooked, everything formed being recovered in recognisable products. The use of chromatography was responsible for this feature, and a combination of chromatography and absorptiometry provided the semi-quantitative classification, as major, minor, and trace products, of those materials which were not determined gravimetrically. When, in the present work, only a small number of products, *e.g.*, two, were formed in more than trace amounts, these were determined gravimetrically. But when a larger number, *e.g.*, four or five, were produced in more than trace amounts, recourse was had to the semi-quantitative technique described. Four further hydrazo-compounds have been thus studied.

*2,2'-Hydrazonaphthalene.*—The non-catalytic rearrangement of this substance was first reported by Krolik and Lukashevich,<sup>2</sup> who used ethanol and benzene as solvents and

\* The comparative discussion, referred to as Part XIII in several of the previous Parts of this series,<sup>1</sup> is now renumbered Part XV.

<sup>1</sup> Parts I—VII, *J.*, 1962, 2386—2444; Parts VIII—XI, 3294—3318. Part XII, preceding Paper.

<sup>2</sup> Krolik and Lukashevich, *Doklady Akad. Nauk, S.S.S.R.*, 1949, **65**, 37.

obtained 2,2'-diamino-1,1'-binaphthyl as the main product. Shine<sup>3</sup> examined the rate of decomposition of this hydrazo-compound in ethanol, acetone, and other solvents, as also did Shine and Trisler;<sup>4</sup> the latter authors examined the products formed in ethanol, acetone, and tetrahydrofuran at 80°. They obtained, besides the diamine, smaller but appreciable proportions of 3,4:5,6-dibenzocarbazole. However, the main product (70—77%) in acetone and tetrahydrofuran was 2,2'-azonaphthalene, even though these solvents are described as degassed. The authors showed that degassing has significance, for they studied the products formed in ethanol with and without degassing, and found that pre-treatment of the solvent reduced the proportion of formed azo-compound from 7 to 0.4%.

In the present work, 2,2'-hydrazonaphthalene was allowed to decompose in ethanol, acetonitrile, and acetone at 80, and at 110°, in benzene at 110°, and without a solvent at 110°, always with careful exclusion of oxygen, as described in Part XII.<sup>1</sup> 2,2'-Azonaphthalene was determined spectrophotometrically, and the other products gravimetrically. The formation of 2-naphthylamine was shown qualitatively in all the reactions, as was the formation of some tar (estimated by difference as about 4% by weight) in the reaction in benzene. The analytical results are given in Table I.

TABLE I.

Proportions (mole %) of products formed in non-catalytic decompositions of 2,2'-hydrazonaphthalene.

Solvent	EtOH		MeCN		Acetone		C <sub>6</sub> H <sub>6</sub>	None
	80°	110°	80°	110°	80°	110°		
Temperature							110°	110°
2,2'-Diamino-1,1'-binaphthyl	81.2	78.0	76.2	75.0	72.0	70.9	80.1	74.8
3,4:5,6-Dibenzocarbazole ...	18.3	20.1	21.2	20.3	21.2	22.0	10.0	23.6
2,2'-Azonaphthalene .....	0.1	0.2	1.2	1.8	4.0	3.9	3.1	0.5
Total * .....	99.7	98.5	99.8	98.9	101.2	100.7	96.3	99.4
Other products † .....	—	—	—	—	—	—	tar	—

\* Calculated assuming that 2 mols. of 2-naphthylamine are formed along with 1 mol. of 2,2'-azonaphthalene. † 2-Naphthylamine was found qualitatively in all experiments.

Shine and Tresler obtained 86% of diamine and 13% of the carbazole from the decomposition in degassed ethanol at 80°, a result which compares moderately well with our proportions, 81 and 18%, respectively. The main discrepancy between their results and those now recorded relates to the azo-product in aprotic solvents; they never obtained less than 70% of this product, and we never find more than 4% of it. There is evidence, however, in their rate data that, despite their degassing technique, oxygen was still affecting their reactions. Shine and Trisler<sup>4</sup> repeated Shine's rate measurements<sup>3</sup> in acetone at 80°, and produced rate constants about 3—4 times smaller. They attributed this effect, no doubt correctly, to their degassing procedure. However, even the revised rates showed an internal scatter amounting to 60%, as if the disturbance, reduced by degassing, had not been fully eliminated. In many examples, we have found that traces of oxygen greatly accelerate the processes of disproportionation, and, in particular, the formation of azo-products.

Table I shows that, for the protic or aprotic polar solvents at 80 or 110°, about 80% of the total rearrangement products consists of 2,2'-diamino-1,1'-binaphthyl, and about 20% the related carbazole; for benzene at 110°, about 90% of the identified rearrangement products appears as the diamine, and about 10% as the carbazole. These results show a close qualitative similarity to those recorded in Part III<sup>1</sup> for the products of the acid-catalysed rearrangement of 2,2'-hydrazonaphthalene in "60%" aqueous dioxan at 0°. In these conditions, there is formed 94% of the same diamine, traces of a second, but unidentified, amine, and 5% of the carbazole. The qualitative correspondence

<sup>3</sup> Shine, *J. Amer. Chem. Soc.*, 1956, **78**, 4807.

<sup>4</sup> Shine and Trisler, *J. Amer. Chem. Soc.*, 1960, **82**, 4054.

illustrated here between the products of rearrangement of the same hydrazo-compound, without and with acid catalysis, seems to be general among the cases examined.

As to the variation, in non-catalytic conditions, of the product proportions with the solvent, we may note three points. First, the formation of more azo-compound in aprotic solvents than in ethanol appears to be general among the hydrazo-compounds studied. Recalling that, in acid-catalysed hydrazo-rearrangements generally, disproportionation, often undetectably small, is appreciably enhanced as the acid catalysis is weakened (cf. Parts I, V, and VII<sup>1</sup>), this distinction agrees with Shine's idea<sup>3,4</sup> that solvent ethanol acts analogously to an acid catalyst.

Secondly, the formation of less carbazole in benzene than in the polar solvents, protic or aprotic, also seems by comparison with other cases to illustrate the general direction of the difference, at least when the difference is considerable. The relevant common property of the polar solvents may be that they are all proton-accepting, and may be able, as benzene would not be, to participate in, and assist, the proton migrations that must precede the carbazole ring-closure.

The remaining point to be noted is that the decomposition of 2,2'-hydrazonaphthalene in the absence of a solvent leads to products more closely resembling those obtained in polar solvents than in benzene. It would be reasonable to assume that the substrate and its products provide a polar medium. But it would be equally reasonable to expect intermolecular mechanisms to play some part in benzene, and in the absence of a solvent, and to lead to products different from those formed in polar solvents. The comparative situation among the hydrazo-compounds examined is that the correlation illustrated by 2,2'-hydrazonaphthalene does reappear elsewhere, but is not universal.

*N-1-Naphthyl-N'-phenylhydrazine*.—The non-catalytic rearrangement of this hydrazo-compound yielded mixtures which were more complex than those just described, and were analysed by combined chromatography and absorptiometry. The reactions in ethanol, acetonitrile, acetone, and benzene, and the decomposition in the absence of a solvent, were carried out at the same temperature as before. The work of Part V,<sup>1</sup> on the acid-catalysed rearrangement of this hydrazo-compound, had made available reference specimens to aid identification of all the major and minor products of these non-catalytic decompositions, except for some amines formed in certain conditions and in mere traces only. The results are summarised in Table 2, where the abundance classification is the same as that used in Part XII.<sup>1</sup>

TABLE 2.

Qualitative abundances of products formed in non-catalytic decompositions of *N-1-naphthyl-N'-phenylhydrazine*.

Solvent Temperature	EtOH		MeCN		Acetone		C <sub>6</sub> H <sub>6</sub>	None
	80°	110°	80°	110°	80°	110°	110°	110°
4- <i>p</i> -Aminophenyl-1-naphthyl-amine .....	++	++	+++	+++	++	++	++	+++
2- <i>o</i> -Aminophenyl-1-naphthyl-amine .....	+++	+++	+	+	+++	+++	+++	+++
1,2-Benzocarbazole .....	+	+	+	+	+	+	+(?)	+(?)
1-Phenylazonaphthalene .....	—	—	—	—	—	—	+++	+++
1-Naphthylamine .....	* —	—	—	—	—	—	++	++
Aniline .....								
" <i>ortho</i> -Semidine" † .....	—	—	—	+	—	—	+	++
Other products ‡ .....	—	+	—	—	—	—	+	—

\* The entries ++ refer to the sum of these products, and — dash means that neither could be detected. † Tentative classification (see text). ‡ The entries + signify four unidentified diazotisable amines, each in trace amounts (see text).

The classification "*ortho*-semidine" is given in Table 2 to a trace product which is a diazotisable amine, and on paper chromatograms in formamide developed with cyclohexane, gave an  $R_F$  value of 0.75. The only basis for the classification given is that Večera,

Petraneč, and Gasparič's chromatographic data<sup>5</sup> for the various types of rearrangement product from a number of aromatic hydrazo-compounds suggest that this particular substance has an *ortho*-semidine type of structure. It could not be identified with anything we knew, and it was certainly not the same as the trace amine which was found among the products of the acid-catalysed rearrangement of *N*-1-naphthyl-*N'*-phenylhydrazine and was provisionally assigned a diphenylene type of constitution (formula V of Part V<sup>1</sup>).

Among the products formed in ethanol at 110°, and in benzene at 110°, four additional diazotisable amines, the "other products" noted in Table 2, were detected in trace amounts. They could not be identified, and it seemed unsafe on the available evidence even to attempt assigning them to constitutional classes. It was shown that none was identical with any of the main products of non-catalytic rearrangement, in the same solvents, of either 1,1'-hydrazonaphthalene or hydrazobenzene. However, this result belongs more to the subject of Part XIV (following Paper).

In the acid-catalysed rearrangement of *N*-1-naphthyl-*N'*-phenylhydrazine in "60%" aqueous dioxan at 0° (Part V<sup>1</sup>), the products consisted of nearly equal proportions (43—44%) of the 4-*p*-diamine and the 2-*o*-diamine, together with a smaller proportion (11—12%) of the carbazole related to the latter, and quite small amounts (1% in 0.08N-acid) of an unidentified amine. The most general feature of the present results on the non-catalytic decomposition of *N*-1-naphthyl-*N'*-phenylhydrazine is that they disclose the same two major, and the secondary, rearrangement products, with qualitatively the same sort of average distribution, though with some striking detailed differences of distribution as we move from one solvent to another. Here is a further indication, the third so far, of a broad analogy between the acid-catalysed and the non-catalytic rearrangements.

As to the detailed differences in the products formed in different solvents, a notable one is that solvent acetonitrile gives an abnormally high proportion of 4,4'-biaryl-linked diamine. No similar effect appears with the other substrates examined, and so some specific matter of solvation must be involved. Another remarkable result is that disproportionation does not become appreciable in any of the polar solvents, but only in benzene, in which it is marked. It arises just as markedly in the decomposition of the hydrazo-compound in the absence of a solvent. In this respect, the reaction without a solvent resembles the reaction in benzene, rather than the reactions in polar solvents.

*N*-2-Naphthyl-*N'*-phenylhydrazine.—The products of the non-catalytic decomposition of this substance were simple enough to allow the analyses to be essentially gravimetric. 2-Phenylazonaphthalene was determined spectrophotometrically, and then the two main products, 1-*o*-aminophenyl-2-naphthylamine and 3,4-benzocarbazole, were determined gravimetrically. All residues were put through paper-chromatographic separations, and this resulted in the detection and partial identification of several trace products, as well as the finding of the expected 2-naphthylamine and aniline, formed in correlation with the azo-compound. The solvents and temperatures were as before. The analytical results are given in Table 3. Some notes on the trace products may be appropriate. The one classified as "semidine" gave the reactions of both primary and secondary amino-groups. On paper chromatography with the formamide-cyclohexane solvent-pair, it had an  $R_F$  value of 0.58. Judged in the light of the  $R_F$  values of Večera *et al.* for other products of hydrazo-rearrangements,<sup>5</sup> this figure suggests that the compound may be a *para*-semidine. However, no confirmatory evidence is available to support this more particular classification. In the three sets of conditions in which the compound appeared, its quantity was estimated as approaching 1%.

The "other products" mentioned in Table 3 were both diazotisable amines in which no secondary amino-group was detected. They were identified by their chromatographic behaviour, and by the absorption spectra of their coupling products, as the two trace amines which accompany the main and secondary products of the acid-catalysed rearrangement of *N*-2-naphthyl-*N'*-phenylhydrazine (Part VI<sup>1</sup>). In Table 3, these products are

<sup>5</sup> Večera, Petraneč, and Gasparič, *Coll. Czech. Chem. Comm.*, 1957, **22**, 1603.

TABLE 3.

Proportions (mole %) of products formed in non-catalytic decompositions of *N*-2-naphthyl-*N'*-phenylhydrazine.

Solvent	EtOH		MeCN		Acetone		C <sub>6</sub> H <sub>6</sub>	None
	80°	110°	80°	110°	80°	110°		
1- <i>o</i> -Aminophenyl-2-naphthyl-amine .....	95.3	90.7	89.2	89.0	93.2	90.0	92.3	68.3
3,4-Benzocarbazole .....	7.1	6.7	8.1	9.1	4.7	5.1	9.0	7.4
2-Phenylazonaphthalene .....	0.2	0.2	1.0	1.5	2.0	2.5	0.8	12.1
Total * .....	102.8	97.8	99.3	101.1	101.9	100.1	102.9	99.9
"Semidine" † .....	—	—	—	+	—	—	+	+

Other products (+) Two, identical with those formed by acid catalysis. ‡

\* Calculated assuming that 1 mol. of 2-naphthylamine and 1 mol. of aniline are formed for each mol. of 2-phenylazonaphthalene. † Tentative classification (see text). ‡ 2-Naphthylamine and aniline were found qualitatively in all experiments. As to the products marked +, see text.

not assigned to specific conditions, because the amounts formed were so much less than 1% that residues from several experiments, not all in identical conditions, had to be combined in order to provide a concentration of them sufficient for detection and investigation.

In the rearrangement of *N*-2-naphthyl-*N'*-phenylhydrazine under acid catalysis in "60%" aqueous dioxan at 0°, no disproportionation occurs, and 99% of 1-*o*-aminophenyl-2-naphthylamine may be recovered, together with 0.5% of 3,4-benzocarbazole, and traces, of the order of 0.1%, of two other primary diamines, which were not specifically identified. As Table 3 shows, the non-catalytic decompositions of the hydrazo-compound involve disproportionation in small, or very small, amounts. But the main, and the secondary, rearrangement products, and even the trace primary diamines, were the same as the products formed under acid catalysis. The differences are only that in non-catalytic conditions the secondary rearrangement product has gained in relative importance, and that in some conditions an additional trace product, one of semidine type, appears. Here we have yet another example of the general correspondence between the products formed from the same hydrazo-compound, with and without acid-catalysis.

The main feature of detail in Table 3 is that the decomposition of *N*-2-naphthyl-*N'*-phenylhydrazine without a solvent uniquely involves somewhat extensive disproportionation. However, in its products of rearrangement, this decomposition is closely similar to any of those occurring in solvents. For this hydrazo-compound, there is no clear difference of properties between polar solvents and benzene, with respect to the products of non-catalytic rearrangement.

*Hydrazobenzene*.—The non-catalytic decomposition of this substance has been examined in ethanol, acetonitrile, acetone, and benzene, at 110°, and in the absence of a solvent at 130°. The products were analysed semi-quantitatively by means of combined chromatography and absorptiometry, with the results in the notation explained already, shown in Table 4.

The decomposition of hydrazobenzene without a solvent at 150° was investigated by

TABLE 4.

Qualitative abundances of products formed in non-catalytic decompositions of hydrazobenzene.

Solvent	EtOH	MeCN	Acetone	C <sub>6</sub> H <sub>6</sub>	None
	110°	110°	110°	110°	130°
4,4'-Diaminobiphenyl .....	+	+	+	+	+
2,4'-Diaminobiphenyl .....	+++	+++	++	+	+
<i>o</i> -Aminodiphenylamine .....	—	+	+++	+++	+++
<i>p</i> -Aminodiphenylamine .....	—	—	—	++	++
Azobenzene .....	+	++	++	+	+
Aniline .....	+	++	++	+	+

similar methods by Večera, Gasparič, and Petranek,<sup>6</sup> whose results agree with those now recorded for 130°.

The acid-catalysed rearrangement of hydrazobenzene gives, as is well known, only benzidine and diphenylene, which appears in comparable amounts, the former preponderating. Table 4 shows that, in the non-catalytic decompositions of hydrazobenzene, a little disproportionation occurs. However, the rearrangement products are still benzidine and diphenylene, though with a shift of weight towards the latter, together with *ortho*-semidine, which is an important product in some solvents. Also, a little *para*-semidine becomes formed in the reactions in benzene, and without a solvent. We see here more contrast than before between the reactions with and without acid catalysis, even though the products arising in the former conditions reappear with others in the latter. However, larger differences might be expected in a comparison of the two types of decomposition of hydrazobenzene, than of the other hydrazo-compounds examined, because, in the reactions of hydrazobenzene, two protons, and not one only, have to be dispensed with in the non-catalytic as compared with the catalytic reaction.

The reaction without a solvent evidently resembles the non-catalytic reaction in benzene more closely than that in polar solvents. Taking a general oversight of hydrazo-decompositions, this does seem to be the commoner form of resemblance. It may indicate the incursion of some intermolecular process in benzene.

An interesting solvent effect on the proportion of *ortho*-semidine appears in Table 4. The semidine is a main product in benzene, and even in acetone, though it is largely suppressed in acetonitrile, and is completely suppressed in ethanol. These again are matters which are better discussed on comparative lines, as will be done in Part XV.

#### EXPERIMENTAL

*2,2'-Hydrazonaphthalene*.—The sample (0.2 g.) was dissolved in the solvent (20 ml.), and degassed and sealed, as described in Part XII.<sup>1</sup> The periods of heating were: 14 hr. for ethanol, 7 days for acetonitrile, and 14 days for acetone, at 80°; 1 hr., 12 hr., and 1 day, for the same solvents, respectively, at 110°; 15 days for benzene at 110°; and 15 days for the reaction without solvent at 110°. The completeness of the conversion was in all cases checked by titration with Bindschedler's Green.

The analyses were made by the gravimetric scheme described in Part I,<sup>1</sup> with omission of the first stage. At the second stage, the carbazole was precipitated, together with the azo-compound. The latter was determined by light-absorption at 400 m $\mu$  ( $\epsilon$ ,  $1.12 \times 10^4$  in benzene). (This is not a band maximum, but it is a wavelength at which interference from other substances is unimportant.) At the third stage of the separation, the diaminobinaphthyl appeared, together with the 2-naphthylamine, which was difficult to determine quantitatively, and was identified qualitatively, and removed. In the decomposition in benzene, some tar was formed (see Table I), which was removed by passage of the product mixture through a short column of activated alumina, followed by very thorough elution of the remaining products with methanol, prior to application of the gravimetric method.

It was verified that the diaminobinaphthyl is not converted into the dibenzocarbazole in any of the conditions used to decompose the hydrazo-compound.

*N-1-Naphthyl-N'-phenylhydrazine*.—The periods of heating were as follows: in ethanol, acetonitrile, and acetone at 80°, 3 days, and at 110°, 1 day; in benzene at 110°, 10 days; and in the absence of a solvent at 110°, 15 days. The methods were those of chromatography and absorptiometry, basically due to Večera *et al.*,<sup>5</sup> and described for applications similar to this in Parts I, IV, V, and VI of this series.<sup>1</sup> The method of direct comparison was used wherever possible (cf. Part IV). The commonly used solvent-system was formamide-cyclohexane, but it was supplemented by others in which formamide was still the stationary phase, whilst the moving phase was light petroleum, chloroform-ethanol (9:1), chloroform, or benzene, and by yet others in which silicone oil was the stationary phase, whilst the moving phase was either cyclohexane or benzene. Absorptiometric measurements on coupling products were usually made in the wavelength region 600–630 m $\mu$ . Control experiments with weighed amounts

<sup>6</sup> Večera, Gasparič, and Petranek, *Chem. and Ind.*, 1957, 299.

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of authentic amines showed a two-fold scatter in quantity estimates from the optical densities of their coupling products, a scatter due probably to non-quantitative diazotisation and coupling; this seems to be one of the main factors which prevents the chromatographic method from achieving full quantitative status. The completeness of the conversions of hydrazo-compound to products in the conditions specified was checked by titration with Bindschedler's Green, and was confirmed by the absence of the easily recognised hydrazo-compound from the chromatograms.

*N-2-Naphthyl-N'-phenylhydrazine.*—The periods of heating were exactly as for the *N-1-naphthyl* isomer in like conditions. Titration with Bindschedler's Green established that decomposition of the hydrazo-compound was complete in these conditions. The analytical methods were gravimetric, as described for the reactions of 2,2'-hydrazonaphthalene, combined with spectrophotometric determination of the 2-phenylazonaphthalene at 400 m $\mu$  ( $\epsilon$ ,  $2.93 \times 10^3$  in benzene). It was shown that 2,2'-diamino-1,1'-binaphthyl is not converted into 3,4:5,6-dibenzocarbazole under any of the non-catalytic conditions in which, in the present experiments, both were formed by rearrangement of the hydrazo-compound.

*Hydrazobenzene.*—The periods of heating were uniformly 15 days in the four solvents at 110°, and in the absence of a solvent at 130°. The analytical methods were as described above for *N-1-naphthyl-N'-phenylhydrazine*. It was shown by titration with Bindschedler's Green, and also chromatographically, that no hydrazobenzene remained after the specified periods of heating.

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