465. *Mechanism of Benzidine and Semidine Rearrangements. Part V.* Transitional Kinetics and Products of Acid Rearrangement of* N-1-*Naphthyl*-N′-*phenylhydrazine.*

By D. V. BANTHORPE, E. D. HUGHES, and Sir CHRISTOPHER INGOLD.

The rearrangement of *N*-1-naphthyl-*N*′-phenylhydrazine in acidified "60%" aqueous dioxan has been followed over a 6000-fold range of hydrogen-ion concentration. In the lower part of that range, *i.e.*, from 10^{-4} to 10^{-3}N-hydrogen-ion, a sub-range mainly covered with the aid of buffers, the kinetic order in hydrogen-ion was 1·0. In the upper part, *viz.*, from 10^{-3} to 0·4N-acid, a sub-range in which the acidity was set with perchloric acid, often with lithium perchlorate added to provide more comparable conditions of ionic strength, the kinetic order in acid rose with increasing acidity, from 1·0 at the lower end of the sub-range to near 2 at the upper end, the observed upper limits being 1·9 with acidities in concentration units, and 2·1 or 2·2 when they were reckoned on the basis of Hammett scales. The form in which the order in acid changes with acidity is in good agreement with a theoretical suggestion by Blackadder and Hinshelwood concerning non-integral orders in benzidine-type rearrangements.

The main products of rearrangement are the diamine (I) involving 4,4′-biaryl coupling, and the diamine (II) involving 2,2′-coupling; and these along with a smaller amount of the carbazole (III), also 2,2′-coupled, accounted for the total material, in which no 2,4′-coupled compound was found. Thus, a single naphthalene residue in an aromatic hydrazo-compound suffices to exclude 2,4′-coupling. With increasing acidity, the proportions of products shift in favour of 4,4′-coupling, and against carbazole formation. Disproportionation to fission amines and azo-product was absent or unimportant.

CONTINUING the study of acid rearrangements in the series which started with the three hydrazonaphthalenes, in which the kinetic order in acid was found to be one or close to one, we deal in this paper and the next with the two *N*-naphthyl-*N*′-phenylhydrazines, whose rearrangement rates are generally 2—3 powers of ten smaller, though they are still 1—2 powers larger than for hydrazobenzene, for which the kinetic order in acid is known to be two. It is in the rearrangements of these naphthyl-phenyl-hydrazines that we expect to find the best examples in this series of transitional kinetics, with orders in acid between

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* Parts I—IV, preceding papers.

one and two. We have concerned ourselves with the detailed forms of the transitional kinetics which are in fact exhibited in these cases, particularly with the mode of variation with acidity of the non-integral order in acid, which is not, of course, in itself a kinetic constant. This is a matter on which there have already been various speculations; but it is experimentally determinable, and significant for mechanism.

In this paper we deal with the kinetics and products of the acid rearrangement of *N*-1-naphthyl-*N*′-phenylhydrazine. As to the kinetics, our study of the variation of order in acid with acidity has involved the use of acidities low enough to require maintenance by buffers, and high enough to necessitate employment of the Hammett function. The work at high acidities has in turn entailed remeasurement of part of the Hammett scale for perchloric acid in " 60% " aqueous dioxan in order to have covered more fully than heretofore the acid range of concern to us, and in order also to provide for the salt conditions that we employ in the kinetic studies. The description of this auxiliary work is included in a forthcoming paper (Part VIII), but its results are used in Section 1 below.

The products of the acid rearrangement of *N*-1-naphthyl-*N*′-phenylhydrazine have a special interest, because of the well-known difference in the pattern of internuclear coupling in rearrangements of the hydrazobenzene and hydrazonaphthalene series. The former are characterised mainly by 4,4′- and 2,4′-biaryl linkings when the relevant nuclear positions are free, and the latter by 4,4′- and 2,2′-linkings, with an exclusion of the intermediate 2,4′-mode of coupling. It has been tacitly assumed, and the assumption then taken as support for a mechanistic speculation, that *two* interacting naphthalene nuclei are needed thus to secure an exclusion of 2,4′-coupling. But do we need two naphthyl groups, or would one along with a phenyl group suffice? This again is a determinable point; and *N*-1-nathphyl-*N*′-phenylhydrazine, which has all the necessary free positions, is the best possible example in which to test it.

(1) *Kinetics of the Acid Rearrangement of* N-1-*Naphthyl*-N′-*phenylhydrazine*

(1.1) *Kinetic Order in Hydrazo-compound.*—We have followed the kinetics of rearrangement of this hydrazo-compound in " 60% " aqueous dioxan (cf. Part I, Section 2.2) at 0·0° over a 6000-fold range of hydrogen-ion concentration, covered in several overlapping sub-ranges. Concentrations from 10^{-4} to 10^{-3}N were maintained by buffers. Above that sub-range buffers were not used, but the acidity was set with perchloric acid, often with lithium perchlorate added to produce a fixed total electrolyte concentration. A series was run with perchloric acid ranging from 10^{-3} to 10^{-1}N, the total electrolyte being 0·1M throughout. Another series, with perchloric acid running from 10^{-2} to 4×10^{-1}N, the total electrolyte being adjusted to 0·4M, completed the overall acidity range, the upper part of which was duplicated in yet another series in which the lithium perchlorate was omitted, the object being now to correlate the rate with an acidity function, determined without an added salt. For all these sets of conditions, it was shown, first, from the first-order forms of the individual runs, and secondly, from the proportionality between initial rate and initial substrate concentration in different runs in common conditions apart from substrate concentration, that this reaction, however its order in acid may vary, is always of first order in substrate. In the following sub-sections, we have accordingly compared rearrangement rates in various conditions, in particular at various acidities, in terms of the first-order rate constants in the substrate.

(1.2) *Order in Perchloric Acid at Constant Electrolyte Concentration.*—Our main evidence concerning transitional kinetics in this rearrangement comes from the middle and the upper part of our total acid range. This stretch, amounting to a 320-fold range in acid concentration, was covered in two sets of runs, one over an 80-fold and the other a 40-fold range in acid, but with a 10-fold range of overlap. In both series the hydrogen ions were supplied as perchloric acid, and the formal ionic strength was kept constant with added lithium perchlorate. The first-order rate constants obtained in these two series of experiments are set down in Table 1.

TABLE 1.

First-order rate-constants, k_1 in sec.$^{-1}$, of rearrangement of *N*-1-naphthyl-*N'*-phenylhydrazine, initially 0·004M, in " 60% " aqueous dioxan at 0·0° in the presence of perchloric acid and lithium perchlorate.

(A) $\mu = ([HClO_4] + [LiClO_4]) = 0{\cdot}10$M.

$10^3[HClO_4]$	1·25	2·5	5·0	10·0	50·0	100·0
10^3k_1	0·0252 [a]	0·0528 [b]	0·105	0·223	1·32	3·34

(B) $\mu = ([HClO_4] + [LiClO_4]) = 0{\cdot}40$M.

$10^3[HClO_4]$	10	100	151	200	401
10^3k_1	0·447	7·77	14·1	22·2	77·3

[a] Initial specific rate. [b] Value over the first 15% of reaction.

In explanation of the notes below Table 1, it may be remarked that, at the two lowest acidities of Series A, a significant part of the catalysing acid is destroyed by the basic rearrangement products, wherefore only specific rates observed initially or early in the run can be compared with the acidities as originally set. Buffers are required to maintain these and lower acidities throughout reaction, as is illustrated in Section 2.3.

When the logarithms of the specific rates of the runs of Series A and B are plotted against the logarithms of the hydrogen-ion concentrations, points are obtained, which, as Fig. 1 shows, cannot be accommodated by straight lines, but are well picked up by smooth curves steepening towards higher acidities. For the generally less acidic series A, the slope of the curve rises towards higher acidities from 1·0 to 1·4, and for the overlapped but generally more acidic series B, the slope rises from 1·1 to 1·9. In the region of overlapping hydrogen-ion concentrations, the curves run nearly parallel, with a relative displacement which shows that the increased ionic strength in series B as compared with series A increases the reaction rate by a factor of rather more than 2, without significantly changing the kinetic form, in particular, the order in acid. This kinetic order evidently runs from a limiting value of one at low acidities, and closely approaches a value of two at the highest acidities of the overall range.

It is a significant result, to be discussed in more detail in Part XIII (forthcoming), that the non-integral order in acid rises, and does not fall, as the acidity rises. For two current explanations of non-integral orders in benzidine rearrangements (Carlin's and Dewar's) both require that it falls. It will be shown that, although the chemical assumptions in these theories are very different indeed, both theories lead to the same law of combination of limiting integral-order rates to give a mixed-order rate; and that this law is that the limiting rates combine by addition of their reciprocals to give the reciprocal of the mixed-order rate. In other words, reaction *times*, not rates, are additive; and thus the *slower* integral-order component will dominate a mixed-order rate. At low acidities, the reaction-component quadratic in hydrogen ions will be the slower, and therefore kinetically dominant, whilst at higher acidities the component linear in hydrogen ions will be the slower, and hence the dominant component. Thus, as the acidity rises the kinetic order in acid should fall. This is qualitatively contrary to the observations here described, and indeed to all our observations that bear on the point (cf. especially Parts VI and VII).

On the other hand, before the results reported in these papers were obtained, Blackadder and Hinshelwood had suggested [1] that a benzidine-rearrangement process linear in hydrogen ions might have the independent existence which we have since established, and that in favourable cases it might show itself alongside the well-known process quadratic in hydrogen ions, so to give an overall reaction of mixed kinetic order. In this case, the law of combination of the rates of the integral-order component reactions

[1] Blackadder and Hinshelwood, *J.*, 1957, 2898.

would be that their *rates* (not times) are directly additive. It would then follow that, in mixed-order reactions, the *faster* component will be kinetically dominant, so that at low acidities the principal rate term will be that linear, and at high acidities that quadratic in hydrogen ions. Thus, as the acidity rises the order in acid should rise—a conclusion with which our observations are at least in qualitative agreement.

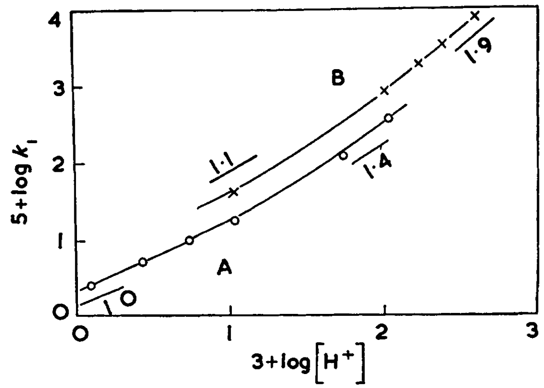

FIG. 1.

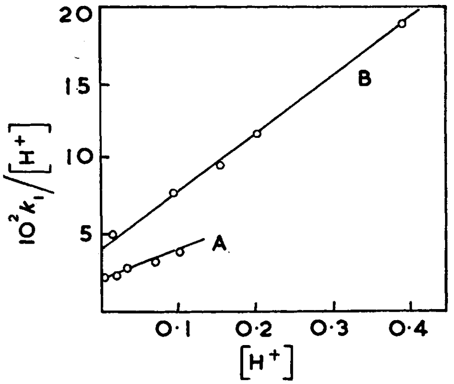

FIG. 2.

FIG. 1. Plot of the logarithm of the first-order rate-constant (k_1 in sec.$^{-1}$) of rearrangement of *N*-1-naphthyl-*N'*-phenylhydrazine against the logarithm of the concentration of hydrogen ions supplied by perchloric acid in " 60% " aqueous dioxan at 0°, the formal ionic strength (μ) being made up to a constant value in each series with added lithium perchlorate. (In Series A, $\mu = 0{\cdot}1$; in Series B, $\mu = 0{\cdot}4$. The slopes for curve A rise from 1·0 to 1·4, and for curve B from 1·1 to 1·9. The short straight lines show these slopes.)

FIG. 2. Test for simple additivity of integral-order component rates in the mixed-order rearrangements of *N*-1-naphthyl-*N'*-phenylhydrazine in 60% aqueous dioxan at 0° with perchloric acid. (Linear plots of $k_1[H^+]^{-1}$ against $[H^+]$. Series A is at $\mu = 0{\cdot}1$, and Series B at $\mu = 0{\cdot}4$, the ionic strengths in each Series being made up with lithium perchlorate.)

In order to apply a quantitative test, we combine equations (1) and (2) of Part I (preceding) in the Blackadder–Hinshelwood manner go give

$$k_1 = -\frac{d[\mathrm{Hydz}]}{dt}\Big/[\mathrm{Hydz}] = k_2[H^+] + k_3[H^+]^2 \qquad (3)$$

(where Hydz = hydrazo-compound) and note the consequence that the plot of $k_1[H^+]^{-1}$ against $[H^+]$ should be linear. Such plots for the runs of series A and B are shown in Fig. 2. They are indeed linear to within the accuracy of the measurements. We show in following papers (Parts VI and VII) that this is a general result.

From the intercepts and slopes of the plots of Fig. 2, it can be read that k_2 is 0·020 sec.$^{-1}$ mole^{-1} l. at $\mu = 0{\cdot}1$, and 0·038 sec.$^{-1}$ mole^{-1} l. at $\mu = 0{\cdot}4$, whilst k_3 is 0·13 sec.$^{-1}$ mole^{-2} l.^{2} at $\mu = 0{\cdot}1$, and 0·38 sec.$^{-1}$ mole^{-2} l.^{2} at $\mu = 0{\cdot}4$. The factors of increase in rate on account of the increase in salt concentration are thus about 2 and 3, the reaction of higher kinetic order in acid being the more salt-sensitive.

(1.3) *Rates with Buffered Hydrogen-ion: Correlation with* pH. The results of the preceding sub-section, extending in acidity as they do, down almost to 10^{-3}N, already make it fairly clear that a stable lower limit of unit order in acid is attained when the acidity is progressively reduced. For the purpose of establishing this limiting order more firmly, we have employed an acetate buffer in order to continue the rate measurements to still

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[2] Bunton, Ley, Rhind-Tutt, and Vernon, *J.*, 1957, 2327.

lower acidities. We have thus carried them to somewhat below 10^{-4}N in hydrogen ions. As was explained in Part I, buffers have to be employed in and below the millinormal region of acidity, because the basic rearrangement products destroy the catalysing acid. But, as is also there explained, a limit exists to the reduction of acidity thus made possible, because the basic anions in buffer solutions selectively catalyse disproportionation of the hydrazo-compounds to azo-compounds and fission amines, a side-reaction from which we want our rearrangements to be free. In the present case, already at 10^{-4}N-hydrogen ions, a few units per cent of disproportionation accompany rearrangement, and we therefore deemed it pointless to carry the acidity any lower.

The results are in Table 2. As will be clear from the fuller description of such measurements given in Part I (section 2.5), they are expected to be less accurate than measurements based on stoicheiometrically determined acidities, because of the indifferent performance of the glass electrode in the presence of a non-aqueous co-solvent. Nevertheless, it is worth while to convert the pH readings, on the basis of an empirical calibration, into terms of hydrogen-ion concentration as it would be provided by perchloric acid. The acetate buffer was made from sodium acetate and hydrogen chloride, and, as is our usual practice, a constant formal ionic strength, in this case 0·16M, built up by added lithium perchlorate, was maintained throughout the series.

TABLE 2.

First-order rate-constants, k_1 in sec.$^{-1}$, of rearrangement of *N*-1-naphthyl-*N'*-phenylhydrazine, initially 0·004M, in the presence of acetate buffers at ionic strength 0·16M in " 60% " aqueous dioxan at 0·0° (Series C).

Apparent pH at 20°	3·21	3·65	4·00	4·00
$-\log [H^+]$	3·38	3·83	4·18	4·18
$10^3 k_1$ at 0°	0·0103	0·0040	0·0015	0·0016

When the logarithm of the rate-constant is plotted against the logarithm of the hydrogen-ion concentration, a straight line is defined of slope 1·05 ± 0·05. Thus the order in hydrogen ion is unity to within the experimental error.

(2.4) *Rates with More Concentrated Acid: Correlation with Hammett's* H_0.—In this sub-section we examine further the approach of the order in acid to the expected upper integral limit of two towards the highest acidities at which the reaction rate allowed us to work (0·4N). For correlation with the logarithm of the specific rate, we now employ the Hammett function H_0. Past experience suggests this method. For the function has been determined for perchloric acid in " 60% " aqueous dioxan by Bunton, Ley, Rhind-Tutt, and Vernon;[2] and, using their scale, Bunton, Ingold, and Mhala showed,[3] for the rearrangement of hydrazobenzene, that, when, with increasing acidity, the $-H_0$ function fails to parallel the logarithm of the stoicheiometric acidity, then the logarithm of the specific rate of the rearrangement also fails to correlate with the latter in any simple way, but still continues linearly to follow the $-H_0$ function. However, a quantitative discrepancy arose, inasmuch as the slope of the linear correlation with $-H_0$ was 2·6, rather than 2·0, the well-established order in acid at lower acidities for the rearrangement of hydrazobenzene.

As will be pointed out in Part VIII (forthcoming), where this work is revised, we think that the quantitative discrepancy has several contributory causes, some of which we can do nothing about; but there are two which we can eliminate with considerably improved results. The most important is that Bunton, Ingold, and Mhala were concerned, as we now are, with acidities near, and even beyond, the low-acid extremity of the range covered by Bunton, Ley, Rhind-Tutt, and Vernon, whose scale is therefore least well-defined where we most need it. This scale has accordingly been redetermined in extension of their work towards the lower acidities that we require. These results are given in Part VIII, but are used below.

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[3] Bunton, Ingold, and Mhala, *J.*, 1957, 1906.

The second point is that acidity functions are commonly determined with the strong acid concerned as the only electrolyte apart from the indicator. When we determine the rate of an acid-catalysed reaction, having a positive ionic-strength effect, with the acid as the only electrolyte, we include in the apparent kinetic order in acid a fictitious increment of order arising from the increase in ionic strength along with the increase in acidity. In most of our kinetic experiments, we overcome this difficulty by measuring rates in Series of runs, the runs of any one Series having different acidities, but an ionic strength made constant for the whole Series with an added neutral salt. For correlation with such rate measurements, we evidently need an acidity function determined at an identically made-up, constant, ionic strength; and because an added neutral salt is likely (by sequestering water) to increase hydrogen-ion activity, such an acidity function is not expected to be the same as one determined in the absence of an added salt. The H_0 function of perchloric acid in " 60% " aqueous dioxan has therefore been determined over the acid range of present concern, not only in the absence of an added salt, but also at two levels of constant formal ionic strength, as made up with added lithium perchlorate (which is the salt we usually employ for such purposes in our kinetic experiments). These results also are recorded in Part VIII, but we make use of them below.

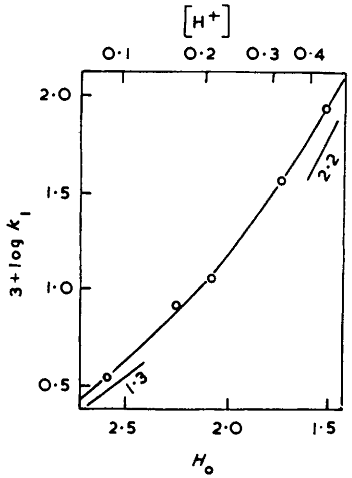

FIG. 3.

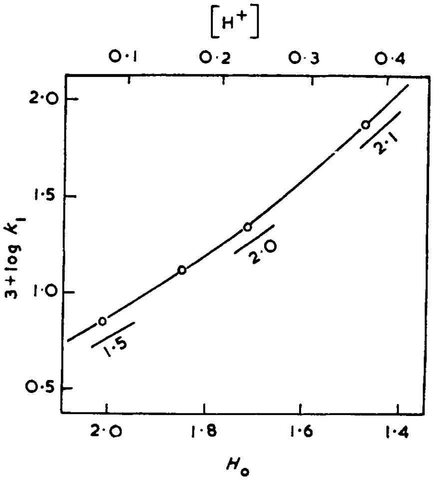

FIG. 4.

FIG. 3. Plot of the logarithm of the first-order rate-constant (k_1 in sec.$^{-1}$) of *N*-1-naphthyl-*N'*-phenylhydrazine against the acidity function H_0 of perchloric acid in " 60% " aqueous dioxan at 0°, without added salts.

FIG. 4. As for Fig. 3, except that lithium perchlorate was added in the rate and in the indicator measurement in order to maintain a uniform concentration of total electrolyte in each series of measurements (k_1 values are at $\mu = 0{\cdot}4$, and H_0 values at $\mu = 0{\cdot}5$).

The upper part of Table 3 records some specific rates of rearrangement of *N*-1-naphthyl-*N'*-phenylhydrazine in " 60% " aqueous dioxan at 0°, at increasing acidities supplied by perchloric acid, but without added lithium perchlorate. These rates are compared in the Table with the revised acidity scale for perchloric acid in this medium in the absence of added salts. In the plot, shown in Fig. 3, of the logarithms of these rates against the relevant H_0 values, the slope of the curve rises from 1·3 at 0·1M-acid to 2·2 at 0·4M-acid, indicating again an order in acid which rises with acidity, though the apparent orders now include a salt effect.

The lower part of Table 3 gives some specific rearrangement-rates, as measured in the presence of sufficient lithium perchlorate to make up the total electrolyte concentration

TABLE 3.

First-order rate-constants, k_1 in sec.$^{-1}$, of rearrangement of *N*-1-naphthyl-*N*′-phenylhydrazine, initially 0·004M in " 60% " aqueous dioxan at 0·0°, in the presence of higher concentrations of perchloric acid without or with added lithium perchlorate.

(D) $\mu = [\text{HClO}_4]$; no added salt.

$[\text{HClO}_4]$	0·100	0·200	0·300	0·401
H_0	2·38	2·03	1·73	1·56
$10^5 k_1$	3·34	10·0	53·0	77·3

(B) $\mu = ([\text{HClO}_4] + [\text{LiClO}_4]) = 0{\cdot}4$ in measurements of k_1, but 0·5 in measurements of H_0.

$[\text{HClO}_4]$	0·100	0·151	0·200	0·401
H_0	2·0	1·83	1·74	1·47
$10^4 k_1$	7·77	14·1	22·2	77·3

to 0·4M throughout. Of the various H_0 scales described in Part VIII, the one most nearly appropriate to these conditions is that in which the total electrolyte is held by added lithium perchlorate at 0·5M. We have consulted this scale, and the values relevant to the kinetic runs are in the Table. As shown in Fig. 4, the plot of the logarithm of the specific rate against these H_0 values is somewhat flatter than before, rising from about 1·5 at 0·1N-acid, to 2·0—2·1 in the region approaching the limit of our range at 0·4N-acid. There are, as is well known, causes other than those we have discussed here why Hammett slopes may not be exactly integral in reactions of integral order.

(2) *Products of the Acid Rearrangement of* N-1-*Naphthyl*-N′-*phenylhydrazine*

(2.1) *Identity of the Products.*—Nietzki and Zehntner obtained a rearrangement product of this hydrazo-compound, and assumed it to be a 4,4′-linked diamine, analogous to benzidine.[4] Bucherer and Sonnenberg also obtained it, and made the same assumption.[5] No proof of constitution was offered by these authors, and Jacobson may have doubted their assignment, because he omits the compound from his otherwise comprehensive list [6] of the hydrazo-rearrangement products known up to 1922.

We found two primary diamines, formed in comparable amounts, which, together with a smaller amount of a carbazole, accounted for practically the whole of the material.

One diamine had m. p. 70°, and was almost certainly identical with that obtained by Nietzki and by Bucherer and their co-workers. We thought that it was likely to be, as the earlier authors had assumed, the diamine (I), formed from the diarylhydrazine by 4,4′-internuclear linking. This opinion was based on the relatively low solublity of its sulphate,* on its low R_F values in paper chromatography, and particularly on its absorption spectrum, which, characterised by a strong and broad band at 270 mμ, indicated a larger degree of internuclear biaryl conjugation than the presence of a 2-amino-group in either ring of the biaryl system, as in (IV) or (V), would be expected to permit. We therefore undertook a rational synthesis of the diamine (I). A mixed Ullmann condensation of *p*-iodonitrobenzene with 4-iodonitronaphthalene led to a nitrophenylnitronaphthalene, which was reduced. The resulting diamine, necessarily of the constitution (I), was identical with the diamine of m. p. 70° obtained by rearrangement.

The other diamine, formed as a main product of rearrangement, had m. p. 128°. Because of the easy solubility of its sulphate, and its high R_F values in paper chromatography, we thought it likely to be the diamine (II), formed from the diaryl hydrazine

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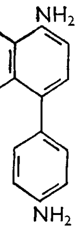
* Diaminobiaryls with 4,4′-amino-groups form less soluble sulphates than when the amino-groups are closer. Presumably, stronger crystals are formed when sulphate units must intermolecularly link the organic units, than when they may intramolecularly bridge them.

[4] Nietzki and Zehntner, *Ber.*, 1893, **26**, 143.
[5] Bucherer and Sonnenberg, *J. prakt. Chem.*, 1910, **81**, 19.
[6] Jacobson, *Annalen*, 1922, **428**, 76.

by 2,2′-internuclear coupling. This diamine has been described once before,[7] as a material obtained by way of a mixed Ullmann synthesis, but as of m. p. 119°. However, we were able to prove that our substance of m. p. 128° had indeed the structure (II), because we could convert it, by boiling aqueous sulphuric acid, into 1,2-benzocarbazole (III), a well-characterised compound.[8-11]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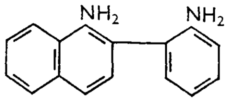
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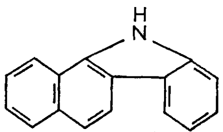
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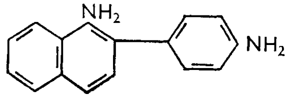
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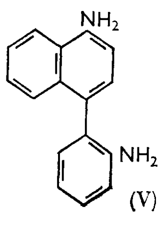
(V)

The third rearrangement product, and the only other one formed in substantial amount, was the same benzocarbazole (III). We showed that it was not formed from the diamine (II) under the conditions of the rearrangement, and therefore must be a primary product of rearrangement in those conditions.

(2.2) *Proportions of Products.*—For reasons explained in the Experimental section, quantitative separation of the products of this rearrangement is more difficult, generally wanting more material, and a much stricter adjustment of conditions, than is that of any of the other rearrangements similarly treated in this group of papers. However, we have quantitatively separated the products formed in " 60% " aqueous dioxan at 0°, in the presence of 0·08N-perchloric acid, which happens to be an especially convenient acidity for this purpose and is within the kinetically covered range of acidities: at this acidity, the order in acid is about 1·3. We have also conducted separations of the products of experiments supplied with 1N- and 2N-perchloric acid, acidities which are well above the kinetic range, and, indeed are to be correlated only qualitatively with the analytical results, because the rearrangements at these acidities are so fast that they will partly have occurred before the added acid is fully mixed in, and hence will have occurred at lower acidities than the ultimately supplied ones. The results of these analyses are collected in Table 4.

TABLE 4.

Proportions of products formed by rearrangement of *N*-1-naphthyl-*N*′-phenylhydrazine in 60% aqueous dioxan at 0° and at various acidities in perchloric acid.

[$HClO_4$]	Diamine (I)	Diamine (II)	Carbazole (III)	Total
0·08	44·4	41·4	11·6	97·4
,,	44·7	41·6	11·2	97·5
,,	44·2	43·3	11·4	98·9
1·0	57·6	32·1	6·2	95·9
2·0	62·3	30·0	4·0	96·3

An additional diazotisable amine could be separated from residues by paper chromatography. On papers on which the amines (I) and (II) had R_F values of 0·05 and 0·65, respectively, in formamide–cyclohexane, the additional amine had the value 0·35. Its structure is unknown, but we think it might be (V). The amount of it is not closely known, though we think that, in the experiments in 0·08N-acid, somewhat less than 1% was formed. However, in the experiments in 1—2N-acid, considerably more was produced—3 or 4 times as much, to judge from colour intensities.

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[7] Whally, Meadow, and Robinson, *J. Org. Chem.*, 1954, **19**, 977.
[8] Kym, *Ber.*, 1890, **23**, 2458.
[9] Japp and Maitland, *J.*, 1903, **83**, 262.
[10] Borsche, *Annalen*, 1908, **359**, 19.
[11] Oakeshott and Plant, *J.*, 1928, 1840.

As to the main products, several points emerge. The first is that with 0·08N-acid, conditions of known kinetics, *N*-1-naphthyl-*N*′-phenylhydrazine rearranges with 44% of 4,4′-internuclear coupling to give product (I), and 54% of 2,2′-internuclear coupling to give the products (II) + (III), these processes accounting for nearly all the material. It is of theoretical significance that no considerable amount of any product, such as (IV) or (V), appears which would result from the intermediate 2,4′-type of internuclear coupling. Herein *N*-1-naphthyl-*N*′-phenylhydrazine resembles 1,1′-hydrazonaphthalene; and it differs from hydrazobenzene, in the rearrangement product of which the 4,4′-ring-coupled benzidine is accompanied by a smaller but comparable amount of 2,4′-coupled diphenyline, but by practically no 2,2′-coupled *ortho*-benzidine. Evidently a single naphthalene nucleus in the hydrazine is sufficient to exclude unsymmetrical internuclear coupling.

The results in the Table also show that, when the acidity is so raised that the kinetic order in acid, although beyond the range of direct determination, must be close to 2·0, the proportion of rearrangement that proceeds by 4,4′-internuclear coupling is raised (as from 44% to 62%), whilst the proportion which involves 2,2′-internuclear coupling is reduced (as from 54% to 34%), though these two types of rearrangement still account for nearly all the material. The shift towards 4,4′-linking with increased protonation is reminiscent of cationic orienting effects on the *ortho-para*-ratio in electrophilic aromatic substitution of an ordinary kind. The shift also helps to explain why Nietzki and Zehntner recovered only one amine from the rearrangement, inasmuch as they used conditions of high acidity.

The other notable finding is that the proportion of the total of 2,2′-coupled products that appears in the form of a carbazole becomes reduced with increasing acidity (as from 25% to 12% in the range explored). This type of effect has already been illustrated in Parts I, II, and III. It is evidently general.

We have been able to discuss products of rearrangement apart from those of disproportionation, because, at acidities above 10^{-3}N no detectable disproportionation to form fission amines and azo-compounds accompanied rearrangement of the hydrazo-compound. But in buffers, in the hydrogen-ion range 10^{-3}—10^{-4}N, disproportionation did occur in amounts up to a few units per cent—always less than 5% as deduced from spectrophotometric determinations of the azo-product.

EXPERIMENTAL

Materials.—1-Phenylazonaphthalene was at first prepared by coupling diozotised aniline with 1-naphthylamine,[12] and deaminating the formed mixture of 2- and 4-phenylazo-1-naphthylamine by diazotising it, and reducing the diazonium salts with ethanol.[13] The azo-compound finally isolated was the pure 1-isomer. The same compound was later made by the method, which we prefer, developed by Ramart-Lucas and her collaborators for the preparation of 2-phenylazonaphthalene.[14] For the present purpose, nitrobenzene and 1-naphthylamine were condensed by alkali at 180°, as those authors described in their example, and then uncondensed materials were removed by distillation in steam. The benzene extract of the residue was passed through a column of alumina to remove tar, and then evaporated. The residual azo-compound, crystallised from ethanol, had m. p. 70° (lit.,[1,15] 70°) (Found: C, 82·9; H, 5·5. Calc. for $C_{16}H_{12}N_2$: C, 82·7; H, 5·2%). This azo-compound was reduced to *N*-1-naphthyl-*N*′-phenylhydrazine by means of zinc and ammonium chloride in the usual way, and the hydrazo-compound was purified by precipitation from benzene solution with light petroleum (Found: C, 82·3; H, 6·2. Calc. for $C_{16}H_{14}N_2$: C, 82·1; H, 6·0%). The decomposition point of this material seems remarkably sensitive, not only to heating rate (which we try to standardise to 1° per min.), but also to some adventitious factor that has no concern with analytical purity. We have observed various decomposition points from 120° to 139° (lit.,[1] 125°) in samples which were all chromatographically homogeneous, all had the theoretical reducing power towards

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[12] Turner, *J.*, 1949, 2282.

[13] Badger and Lewis, *J.*, 1953, 2154.

[14] Ramart-Lucas, Guilmart, and Martynoff, *Bull. Soc. chim. France*, 1947, 415.

[15] Michaelis and Petou, *Ber.*, 1898, **31**, 984.

Bindschedler's Green, and all gave consistent rearrangement rates in so far as these were checked by duplication. It is known that accidental rearrangement during preparation, purification, or subsequent keeping often raises the decomposition points of hydrazo-compounds, but the sample of this compound that had the highest decomposition point that we observed (137—139°) certainly contained no rearrangement products, nor any impurity that could be detected by analysis or chromatography. Similar properties have been observed in *o*-hydrazotoluene (Part VII, following paper).

Kinetics.—A number of runs were performed by quenching timed samples, withdrawn from a reaction flask, in small excesses of alkali, and then titrating the still unrearranged hydrazo-compound with Bindschedler's Green, this dye acting as its own indicator. However, the end-points were not very good, and it was difficult to make the excesses of quenching alkali small enough to ensure a complete avoidance of disproportionation, with premature destruction of some of the surviving hydrazo-compound. We have not here reported any results obtained by this method, though they are of tolerable accuracy; but we mention the method because it is practicable and because no method that we have tried is completely convenient.

The results reported in this paper were all obtained by quenching the rearrangement with Bindschedler's Green and titrating the excess of that material with titanous chloride. The end-point could not be detected visually, because one at least of the rearrangement products (the benzocarbazole) forms a blue complex in the titanous solution. However, the end-point was satisfactorily located electrometrically (cf. Part I), by the dead-stop technique. The difficulty still remained that, for some unelucidated reason, the excess of Bindschedler's Green was not completely stable in the presence of the rearrangement products and the products of its own reaction with this particular hydrazo-compound: after being kept for about 15 min. under nitrogen, the quenched solutions began quickly to lose Bindschedler's Green, as was found by subsequent titration with titanous chloride. The only other hydrazo-rearrangement in dealing with which we have noticed this type of side-reaction is the rearrangement of 1,1'-hydrazonaphthalene (Part I), where it was detectable but not fast enough to interfere with the analytical procedure. In the present case, it was sufficiently fast to determine that we could not, except at acidities below 0·005N, follow the reaction by sampling from a flask, or, indeed, by any method in which all the timed samples in a run had the same time-zero; for then, some samples, quenched at short intervals of time, had to be kept waiting to be titrated. Therefore, in all runs at acidities from 0·005N upwards, we used the inverted-Y-tube method. The hydrazo-solution being put into one limb, and the acid solution into the other, both mixing and quenching could be rapidly performed, and each analytical sample, having its own conveniently chosen time-zero, could receive undivided attention from the moment of its quenching.

Products.—The method of separation of the products of rearrangement of *N*-1-naphthyl-*N'*-phenylhydrazine was in principle the same as that developed in Part I (preceding) for the products from 1,1'-hydrazonaphthalene: diaminobiaryls with 4,4'-amino-groups form less soluble sulphates than when the amino-groups are closer; and carbazoles are non-basic. However, some less soluble sulphates become soluble in " 60% " aqueous dioxan above a certain threshold of acidity in perchloric acid: in the present case this acidity is highly critical. Among our rearrangement products, 4-*p*-aminophenyl-1-naphthylamine (I) had the less soluble sulphate. But that sulphate was not precipitated from " 60% " aqueous dioxan at 0° by a four-fold excess of sulphuric acid if the acidity in perchloric acid was above 0·2N. It was incompletely precipitated if the concentration of perchloric acid lay between 0·1N and 0·2N. And if the acidity in perchloric acid fell much below 0·1N, then 2-*o*-aminophenyl-1-naphthylamine (II), which had the more soluble sulphate, became nevertheless co-precipitated with the sulphate of the amine (I). Thus the band of acidities in perchloric acid which permits a clean separation of the two amines by the sulphate method is very narrow. Our practice was to adjust the concentration of perchloric acid, before commencing the separation, to 0·08N, if the rearrangement itself had been conducted at any other acidity. For this purpose, some moderate addition of perchloric acid or " 60% " aqueous dioxan might suffice; but if not, the solution after rearrangement was neutralised, and the organic material was extracted with ether, and, after evaporation of the ether, was re-dissolved in " 60% " aqueous dioxan, which was made 0·08N in perchloric acid. In these conditions, the amine (I) was precipitated as sulphate, and the amine (II) was left in solution, to be recovered in a subsequent step, after the carbazole (III) had been removed. Paper chromatography showed that the separated amine (I) was pure, whilst separated amine (II) contained amounts of the order of 1% of two impurities. One consisted of 0·7—1·0% of (I). The other was the additional amine mentioned in Section 2.2.

The amine (I) had m. p. 70° (lit.,[4,5] 64°, 69°), gave a diacetyl derivative of m. p. 281° (lit., 285°),[4] a sulphate of m. p. 280° (decomp.), and a dihydrochloride of m. p. 170° (decomp.). The amine titrated correctly as a diacid base with perchloric acid in acetic acid. It did not reduce Bindschedler's Green. Boiled for 3 hr. with 5N-sulphuric acid, it did not give a carbazole. It gave low R_F values (under 0·1) on paper chromatography in our solvents. Its ultraviolet spectrum showed the strong biaryl conjugation band at 270 mμ.

The amine (I) was synthesised as follows. 1-Iodo-4-nitronaphthalene was prepared by diazotising 4-nitro-1-naphthylamine in a mixture of sulphuric and acetic acid, according to Hodgson and Walker's general method for nitroarylamines,[16] and then decomposing the diazonium solution with aqueous potassium iodide and iodine. An equimolecular mixture of this iodo-compound and *p*-iodonitrobenzene was heated for 1 hr. at 150—170° with an equal weight of copper bronze, as described for an analogous preparation by Ward and Pearson.[17] The benzene extract of the product was passed through alumina to remove tar, and was then reduced with hydrogen at 70°/1 atm. for 24 hr. in 9 : 1 ethyl acetate–ethanol solution, in the presence of Raney nickel (B.D.H., stabilised). The filtered solution was evaporated, and the residue was dissolved in " 60% " aqueous dioxan. When this solution was made 0·2N in sulphuric acid, a mixture of benzidine and naphthidine sulphates was precipitated. This mixture was identified as such by its infrared spectrum. The amine which had remained in solution was recovered after basification, and dissolved in a much smaller volume of " 60% " aqueous dioxan, which was again made 0·2N in sulphuric acid. In this way a further small amount of a mixture of the same two sulphates was obtained. The base which remained unprecipitated at this acidity was isolated after basification, crystallised (yield 8%) and shown by its m. p., mixed m. p., and infrared spectrum to be identical with the amine (I) obtained by rearrangement from *N*-1-naphthyl-*N'*-phenylhydrazine.

Continuing the account of the separation of the products of rearrangement, the solution in " 60% " aqueous dioxan, from which the sulphate of the amine (I) had been precipitated and removed, was diluted with a large volume of aqueous N-sulphuric acid. This precipitated 1,2-dibenzocarbazole (III), the extra acid now serving to prevent co-precipitation of the amine (II). The benzocarbazole (III), crystallised from ethanol, had m. p. 225° (lit.,[8–11] 225°) (Found: C, 89·0; H, 5·2. Calc. for $C_{16}H_{11}N$: C, 88·5; H, 5·1%).

After separation of the carbazole, 2-*o*-aminophenyl-1-naphthylamine (II) was precipitated by basifying the solution and was extracted with ether. It was then precipitated from the dried ethereal solution as its dihydrochloride, m. p. 155° (decomp.). The free amine, crystallised from ethanol, had m. p. 128° (lit.,[7] 119°).

The constitution of this amine follows from its conversion into the above benzocarbazole (III) of m. p. 225°. When the amine was boiled with 5N-sulphuric acid, the carbazole was slowly deposited, and a 50% yield of it was collected after 4 hours' boiling. Its identity with the rearrangement product was proved by m. p. and infrared spectrum.

Disproportionation of the hydrazo-compound to fission amines and azo-compound was estimated, when it occurred, by spectroscopic assay of 1-phenylazonaphthalene, the extinction coefficient, ε (400 mμ) = $8·08 \times 10^3$ (solvent benzene), being used. This wavelength was not that of an absorption peak, but was chosen to minimise interference with the measurement by other substances. It was assumed in calculating these estimates of disproportionation, but was not established experimentally, that fission amines are produced in equivalence with the azo-product.

No spectroscopically detectable disproportionation accompanied any rearrangement conducted in " 60% " aqueous dioxan at 0° and at acidities above 10^{-3}N. Rearrangements at lower acidities down to 10^{-4}N, as maintained by acetate buffers, were accompanied by disproportionation, to an extent which rose as the acidity was reduced, but which remained under 5% in the range of acidities stated.

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[*Received, October* 30*th*, 1961.]

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[16] Hodgson and Walker, *J.*, 1933, 1620.

[17] Ward and Pearson, *J.*, 1959, 3378.