466. *Mechanism of Benzidine and Semidine Rearrangements. Part VI.* Transitional Kinetics and Solvent-isotope Effect in Acid Rearrangement of* N-2-*Naphthyl*-N'-*phenylhydrazine.*

By D. V. BANTHORPE.

The rearrangement of *N*-2-naphthyl-*N'*-phenylhydrazine in the presence of acid in " 60% " or " 70% " aqueous dioxan has been followed over a 600-fold range of hydrogen-ion concentration. Throughout a broad central part of the range, the reaction has a non-integral kinetic order in acid which rises with increasing acidity. Thus in the " 70% " solvent at constant total electrolyte concentration, and at acidities from 0·02N to 0·30N in perchloric acid, the order in acid rose from 1·15 to 1·85. At lower hydrogen-ion concentrations to 0·001N, mostly maintained by buffers, the order in hydrogen ions was close to unity. At higher acidities to 0·6N perchloric acid in the " 60% " solvent, the rates were so related to Hammett's H_0 function as to show that the order in acid was substantially equal to two. The manner in which the order in acid changes with acidity is in quantitative accord with a suggestion by Hinshelwood concerning hydrazo-rearrangements generally.

When the water in the " 60% " dioxan solvent was replaced by deuterium oxide, the rearrangement was accelerated, but by different factors according to the acidity, and hence according to the kinetic order in acid. In 0·02N-acid, when, in the " 60% " solvent, the order in acid was 1·15, the factor of acceleration was 2·6. In 0·30N-acid, when the order was 1·75, the factor was 3·8. On comparison with data for other hydrazo-compounds, it appears that the solvent isotope effect is nearly the same for these substrates when the kinetic order is the same, and is essentially correlated with kinetic order. It is concluded that the protons, whether one or two, which catalyse hydrazo-rearrangements are in these examples transferred to their transition states to a similar extent, and are therefore probably completely so transferred.

The rearrangement gives one main product, 1-*o*-aminophenyl-2-naphthylamine (I), which was recovered in yields up to 99%. The chief by-product was 3,4-benzocarbazole (0·5%). Disproportionation to fission amines and azo-compound was not detected in the conditions of the rearrangements.

THE remaining previously uninvestigated example of acid-catalysed hydrazo-rearrangement in the series which starts with 1,1'-hydrazonaphthalene and ends with hydrazobenzene is that of *N*-2-naphthyl-*N'*-phenylhydrazine. This rearrangement is slower by about a power of ten than that of *N*-1-naphthyl-*N'*-phenylhydrazine (Part V *), but faster by a similar factor than that of hydrazobenzene. The somewhat severe analytical conditions, and the high rates at the higher acidities, which tended to limit the quantitative study in Part V of transitional kinetics in the example of the *N*-1-naphthyl compound are both ameliorated in the reaction of its *N*-2-naphthyl isomer, which has thus proved to be an example of transitional kinetics particularly amenable to quantitative investigation. It has provided an opportunity to correlate kinetic form with the solvent hydrogen-isotope effect on the rates of rearrangement of one and the same substrate.

(1) *Kinetics of the Acid Rearrangement of* N-2-*Naphthyl*-N'-*phenylhydrazine*

(1.1) *Kinetic Order in Hydrazo-compound.*—By one method or another, this rearrangement has been followed kinetically in aqueous dioxan over a 600-fold range of hydrogen-ion concentration. Throughout this range, except at its extremes, the kinetic form is changing. The total range was covered in four overlapping sub-ranges, 0·001—0·012, 0·01—0·10,

---

* Parts I—V, preceding papers.

0·02—0·30, and 0·10—0·60N in hydrogen ions. But for all four sets of conditions, it was shown, first, from the common first-order forms of the individual runs and, secondly, from the identity of first-order rate constants derived from different runs in conditions identical except for differences in the initial concentration of substrate, that the kinetics, though they may vary otherwise, are uniformly of first order in substrate. That point settled, we have compared rearrangement rates in various conditions, and, in particular, at different acidities, on the basis of first-order rate-constants in substrate.

(1.2) *Order in Perchloric Acid at Constant Electrolyte Concentration.*—The central 30-fold portion of the overall range of hydrogen-ion concentration was studied in runs at 0° in " 60% " or " 70% " aqueous dioxan (for definitions, see Part I, Section 2.2 and Part II, Section 2), with perchloric acid as the source of hydrogen ions and with made-up formal ionic strengths. This portion of the total acidity range was itself covered in two overlapping sub-ranges, the first (A) in " 60% " aqueous dioxan, with acid 0·01—1·0N, and enough lithium perchlorate to make up the total electrolyte to 0·10M throughout, and the second (B) in " 70% " aqueous dioxan, a somewhat slower solvent, with acid 0·02—0·30N, and the total electrolyte made up with lithium perchlorate to 0·3M throughout. The results of these two series of runs are in Table 1.

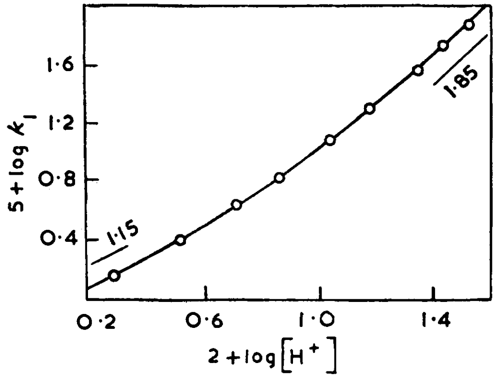


FIG. 1.

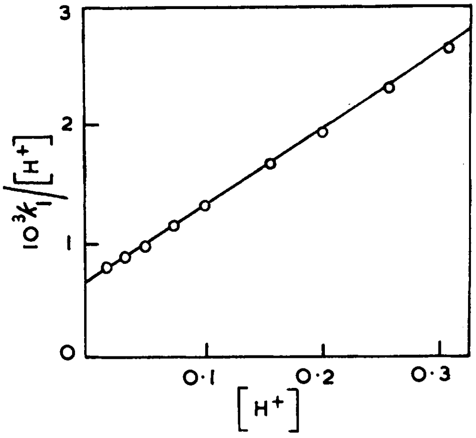


FIG. 2.

FIG. 1. Plot of the logarithm of the first-order rate-constant of rearrangement of *N*-2-naphthyl-*N'*-phenylhydrazine against the logarithm of the hydrogen-ion concentration, as supplied by perchloric acid in " 70% " aqueous dioxan at 0°, with a constant formal ionic strength, 0·3, made up with lithium perchlorate. (The slope rises from 1·15 at 0·02N-acid to 1·85 at 0·30N-acid. The short straight lines show these slopes.)

FIG. 2. Test for additivity of integral-order rates in the mixed-order rearrangement of *N*-2-naphthyl-*N'*-phenylhydrazine in " 70% " aqueous dioxan containing perchloric acid at 0°, and at a formal ionic strength of 0·3M made up with lithium perchlorate: plot of $k_1[H^+]^{-1}$ against $[H^+]$.

When the logarithms of the rates of Series A are plotted against the logarithms of the hydrogen-ion concentrations, points are obtained which define a smooth curve rising in gradient from about 1·1 to about 1·4. A similar result is obtained by a corresponding treatment of the results of Series B; but this is a longer series in a somewhat higher acid range, and now the gradient rises from about 1·15 to about 1·85, *i.e.*, most of the way between the expected integral limits of 1 and 2. This curve is shown in Fig. 1.

This work confirms the finding reported in Part V, that, as acidity rises, the order in acid of a hydrazo-rearrangement of non-integral order rises, contrary to two current explanations (Carlin's and Dewar's) of non-integral orders in such rearrangements, which both require that the order falls, but consistently with another suggestion (Hinshelwood's), which requires that it rises—according to a certain law. This law is that of equation (3) in Part V, and the present kinetic results, in which accuracy is more easily achieved than in those of Part V, provide a good opportunity to test its quantitative application. When we plot $k_1[H^+]^{-1}$ against $[H^+]$, the result should be a straight line. As can be seen from Fig. 2, that is so with a very satisfactory accuracy.

TABLE 1.

First-order rate-constants, k_1 in sec.$^{-1}$, of rearrangement of *N*-2-naphthyl-*N′*-phenylhydrazine, initially 0·004M, in aqueous dioxan at 0·0° in the presence of perchloric acid and lithium perchlorate.

(A) In " 60% " aqueous dioxan: $\mu = ([HClO_4] + [LiClO_4]) = 0{\cdot}1$M.

$10^3[HClO_4]$	10	25	50	75	100
10^3k_1	0·0112	0·0316	0·0728	0·116	0·178

(B) In " 70% " aqueous dioxan: $\mu = ([HClO_4] + [LiClO_4]) = 0{\cdot}3$M.

$10^3[HClO_4]$	20	33	50	70	100	150	200	250	300
10^3k_1	0·0164	0·0287	0·0505	0·0796	0·133	0·257	0·404	0·601	0·800

The slope and intercept of the line in Fig. 2 give the rate coefficients of the integral-order component reactions. The second-order coefficient of the reaction linear in hydrogen-ions is $k_2 = 0{\cdot}00067$ sec.$^{-1}$ mole^{-1} l. The third-order coefficient of the rearrangement quadratic in hydrogen ions is $k_3 = 0{\cdot}0066$ sec.$^{-1}$ mole^{-2} l.^{2}. These figures apply to the conditions of Series B in Table 1.

(1.3) *Order in Buffered Hydrogen Ion.*—This sub-section records the carrying of the hydrogen-ion concentrations downward, in an attempt to follow more closely the approach of the order in acid to the expected lower limit of one. As has been explained before, buffers must be used at the lower acidities, because the primary amines formed by rearrangement tend to neutralise the catalysing acid; and yet the use of buffers cannot be pressed below a certain threshold of acidity, because at higher pH values, as also at higher buffer concentrations, the basic anions selectively catalyse disproportionation of the hydrazo-compounds, a reaction from which we want their rearrangements to be free. In the present experiments another limit began to be felt still earlier. This was that, at low hydrogen-ion concentrations, the reaction is inconveniently slow (at an apparent pH of 2·9, the half-life is about 100 hr.); and it is inadvisable to raise the temperature, because that, as in the study recorded in Part I, selectively increases disproportionation. Mainly for this reason, we went only as far as pH 3, and not to beyond pH 4 as was done with the much faster-reacting 1,1′-hydrazonaphthalene treated in Part I.

The results obtained with an acetate buffer of ionic strength 0·08M, in " 60% " aqueous dioxan at 0°, are in Table 2. As usual, the rates are correlated with the pH measurements less accurately than with stoicheiometrically set acidities, essentially because of the indifferent performance of the glass electrode in the presence of a large proportion of a

TABLE 2.

First-order rate-constants, k_1 in sec.$^{-1}$, of rearrangement of *N*-2-naphthyl-*N′*-phenylhydrazine, initially 0·004M in the presence of acetate buffers at ionic strength 0·08M in " 60% " aqueous dioxan at 0·0° (Series C).

Apparent pH at 20°	1·81	2·95	2·15	2·45	2·90
$10^3[H^+]$	10·2	5·9	4·7	2·34	0·83
10^3k_1 at 0°	0·0201	0·0112	0·0063	0·0042	0·00112

non-aqueous co-solvent. We dealt with these difficulties as described in Part I (Section 2.5), and again converted the apparent pH values, on the basis of an empirical calibration, into terms of hydrogen-ion concentration as supplied by measured perchloric acid.

The logarithmic plot, shown in Fig. 3, of these rate-constants and hydrogen-ion concentrations defines a straight line of slope 1·1 ± 0·1. Thus the order in hydrogen-ion is indistinguishable from unity, having regard to the experimental error.

(1.4) *Order in Acid at High Acidities: Correlation with Hammett's Acidity Function.*—We have now to record the kinetic effect of taking the concentration of perchloric acid up to the limit beyond which the high rates rendered kinetic measurements too difficult. At the acidities involved, Hammett's function H_0 departs from the stoicheiometric acidity, and one must therefore be prepared to consider correlations of rate with Hammett functions.

The kinetics of rearrangement of *N*-2-naphthyl-*N'*-phenylhydrazine have been followed in " 60% " aqueous dioxan at 0·0° with various concentrations of perchloric acid up to 0·6N. The " 60% " solvent was chosen because it is one of those aqueous-dioxan solvents for which Bunton, Ley, Rhind-Tutt, and Vernon determined the acidity function H_0 of perchloric acid.[1] As is usual in determinations of an acidity scale, no salt was added: the recorded acidities were those of the acid present as the only electrolyte in the medium (apart from the indicator). Accordingly, in our Series D of kinetic experiments, intended for correlation with this acidity scale, we added no lithium perchlorate, as in other kinetic series we had done for the purpose of standardising the ionic strength. In this particular Series, then, kinetic salt effects had to go unstandardised; and this meant that a derived apparent order in acid would inevitably contain a fictitious increment of order arising from the considerable positive ionic-strength effect.

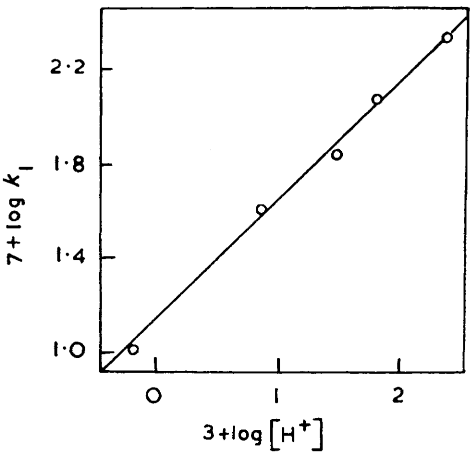


FIG. 3.

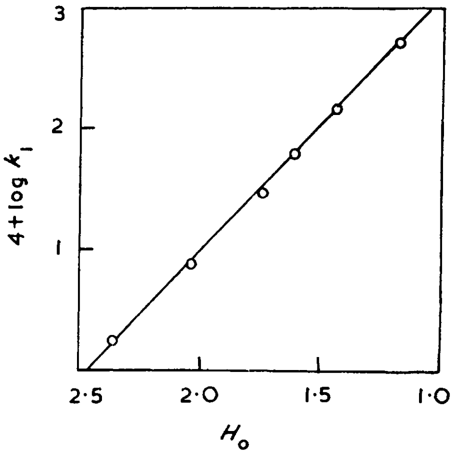


FIG. 4.

FIG. 3. Plot of the logarithm of the first-order rate-constant of rearrangement of *N*-2-naphthyl-*N'*-phenylhydrazine against the logarithm of the hydrogen-ion concentration in acetate buffer in " 60% " aqueous dioxan at μ = 0·08 and at 0°. (The line has slope 1·1.)

FIG. 4. Plot of the logarithm of the first-order rate-constant of rearrangement of *N*-2-naphthyl-*N'*-phenylhydrazine at 0° in " 60% " aqueous dioxan containing perchloric acid against the acidity function H_0 of that system. (The line has a slope of 2·13.)

---

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

Some time after these kinetic measurements were completed, it was realised that the acidity scale for perchloric acid in " 60% " aqueous dioxan, as given by Bunton, Ley, Rhind-Tutt, and Vernon, was not well defined in the acidity region of concern to us, because that region lay around the low-acid extremity of those authors' range. Some further acidity measurements in supplementation of theirs, and in extension towards lower acidities, were therefore undertaken, as will be described later (Part VIII); and it is with this revised and extended acidity scale that we now compare our rate measurements. The rate and acidity data are in Table 3.

When the logarithms of the specific rate are plotted against the H_0 values a straight line is obtained, as Fig. 4 shows, having a slope of about 2·1. As this slope must contain a small, but finite and positive, contribution from the kinetic effect of the rise of ionic strength with rising acidity in this Series, the indication is that the order in hydrogen ion is close to two in the range represented.

TABLE 3.

First-order rate-constants, k_1 in sec.$^{-1}$, of rearrangement of *N*-2-naphthyl-*N'*-phenylhydrazine, initially 0·004M, in the presence of perchloric acid in " 60% " aqueous dioxan at 0·0°, and the Hammett acidity values H_0 of the solutions (Series D).

$[HClO_4]$	0·10	0·20	0·30	0·40	0·48	0·60
H_0 (Part VIII)	2·37	2·03	1·78	1·37	1·41	1·22
10^3k_1	0·178	0·834	2·65	8·75	18·1	48·1

(2) *The Kinetic Isotope Effect of Solvent Deuterium in the Rearrangement of* N-2-*Naphthyl*-N'-*phenylhydrazine*

It was shown by Bunton, Ingold, and Mhala,[2] and confirmed in Part I (preceding), that replacing the water in " 60% " aqueous dioxan by deuterium oxide increases the rates of acid-catalysed benzidine rearrangements. It was also shown in Part I that the factor of acceleration was very different for two substrates which rearranged with different kinetic orders in acid: for 1,1'-hydrazonaphthalene, for which the order in acid is accurately 1, the ratio k_D/k_H was 2·3; whereas for hydrazobenzene, for which the order is accurately 2, the corrected ratio was 4·8. In this comparison one is changing two variables at once, the constitution of the substrate, and the kinetics of catalysis. And it was for reasons other than the internal logic of the case that we took the kinetics of catalysis to be the more direct correlative of the isotope effect.

In *N*-2-naphthyl-*N'*-phenylhydrazine we have a substrate which rearranges with various kinetic orders in acid, between 1 and 2, according to the acidity. It thus provides an opportunity to test the presumed correlation between the solvent deuterium-isotope effect and the kinetics of acid catalysts, without having to change the substrate. We have therefore measured the rate of this rearrangement at 0° in " 60% " aqueous dioxan, made up with either ordinary water or with deuterium oxide, and in each solvent at two concentrations of perchloric acid, a smaller one calculated to produce a kinetic order in acid of 1·15, and a larger one calculated to lead to an order of 1·75. According to the former work, and the interpretation given to it, we should expect the deuterium-solvent acceleration ratio, k_D/k_H, to rise from a figure somewhat above 2·3 at the lower acidity to one somewhat below 4·8 at the upper one. As Table 4 shows, the corrected ratio is 2·6 in the more dilute acid and 3·8 in the more concentrated.

There is remarkable consistency between these results for a substrate rearranging with a variable kinetic order, and the previous ones on substrates which rearrange with different fixed orders in acid. For any of the substrates, at any of the acidities, the

---

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

acceleration ratio, k_D/k_H, of the rearrangement is 2·2—2·4 times its kinetic order in hydrogen ions. This surely means that, when two protons are involed in reaction, they are transferred to its transition states to common extents, which moreover are the same as the extent to which one proton is so transferred when only one is involved. This would be difficult to understand unless all the proton transfers, even the second one when there are two, are complete in these examples.

TABLE 4.

Comparison of first-order rate-constants, k_1 in sec.$^{-1}$, of rearrangement of *N*-2-naphthyl-*N'*-phenylhydrazine in the presence of perchloric acid in mixtures of 60 vol. of dioxan with 40 vol. of either water or deuterium oxide at 0·0°.

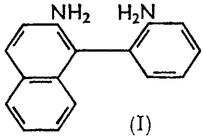
$[HClO_4]$ or $[DClO_4]$	System	Order in acid	10^3k_1	k_D/k_H Found	Corr. 1 [e]	Corr. 2 [f]
0·020	H	1·15 [c]	0·0144	2·5	2·5	2·6
0·020	D [a]	1·15 [c]	0·0365			
0·31	H	1·75 [d]	3·05	3·5	3·7	3·8
0·30	D [b]	1·75 [d]	10·6			

[a] The D_2O used contained 98·9 atoms % of D in its hydrogen. [b] The D_2O contained 96·9 atoms % of D in its hydrogen. [c] From Series A of Table 1. [d] Extrapolated from Series A of Table 1 by means of equation (3) in Part V. [e] Corrected to identical acidities. [f] Corrected to isotopically pure D_2O.

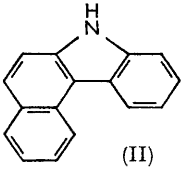
(3) *Products of the Acid Rearrangement of* N-2-*Naphthyl*-N'-*phenylhydrazine*

This rearrangement gave almost entirely one product, *viz.*, the *ortho*-benzidine-type diamine (I). After rearrangement in " 60% " aqueous dioxan at 0° or 20°, and at acidities in perchloric acid from 0·05 to 0·50N, some 96—99% of this diamine was recovered. It is a well-known compound,[3-5] and its constitution was confirmed by its conversion in boiling 5N-sulphuric acid into the benzocarbazole (II), which is also well-known and thoroughly characterised.[3-6]

The same carbazole (II) was also formed in the rearrangement, but in small quantities, probably diminishing with increasing acidity. In an experiment with 0·08N-perchloric acid in " 60% " aqueous dioxan at 20°, the recovery of the carbazole was 0·5%. Its production by rearrangement was certainly direct, and not by way of initially formed diamine (I), because cyclisation of this does not occur at the acidities and temperatures of our rearrangements.



(I)



(II)

Compounds (I) and (II) were obtained by Shine and his collaborators [5] as the only isolable products of the uncatalysed " thermal " rearrangement of *N*-2-naphthyl-*N'*-phenylhydrazine.

In our search for trace-products by paper chromatography we found two other diazotisable amines, both in insufficient amount for identification. We were unable spectroscopically to detect the formation of 2-phenylazonaphthalene, and thus we have no evidence of any disproportionation of the hydrazo-compound under the conditions employed for its rearrangement.

---

[3] Bucherer and Seyde, *J. prakt. Chem.*, 1908, **77**, 403.
[4] Fuchs and Nigel, *Ber.*, 1927, **60**, 209.
[5] Shine, Huang, and Snell, *J. Org. Chem.*, 1961, **26**, 380.
[6] Japp and Maitland, *J.*, 1903, **83**, 267.

EXPERIMENTAL

Preparations.—2-Phenylazonaphthalene was prepared as described by Ramart-Lucas and her collaborators[7] by alkaline condensation of 2-naphthylamine with nitrobenzene. The acidified product was steam-distilled, and the benzene extract of the residue was passed through alumina to remove tar, and evaporated. The orange azo-compound so obtained, crystallised from ethanol, had m. p. 83° (lit.,[5,8] 83—84°) (Found: C, 82·9; H, 5·5. Calc. for $C_{16}H_{12}N_2$: C, 82·7; H, 5·2%). It was reduced as usual with zinc and ammonium chloride, and the resulting *N*-2-naphthyl-*N'*-phenylhydrazine was purified by repeated precipitation from cold benzene with light petroleum. It was colourless and had m. p. 90°, showing no immediate signs of decomposition on melting (Shine *et al.*[5] record m. p. 104°). It was homogeneous by paper chromatography and had the theoretical reducing power towards Bindschedler's Green. Kept for some months it appeared to deteriorate, and there was a rise of m. p. An old specimen of m. p. 97°, on being re-purified, reverted to m. p. 91°.

Kinetics.—The methods were as described in Parts I and II. In this study, as in those of Parts II and III, and in contrast to those of Parts I and V, the products of rearrangement did not form coloured titanium complexes. Hence the end-points of titration of excess of Bindschedler's Green with titanous chloride could be determined visually, and had not to be located electrometrically. Moreover, in these experiments, in contrast to those described in Part V, the excess of Bindschedler's Green remained stable in the conditions, thus allowing sampling techniques to be used fairly freely.

Products.—The procedure of separation described in Part I yielded no insoluble sulphate in the first step, but in the second gave small amounts of 3,4-benzocarbazole (II), and in the third gave 1-*o*-aminophenyl-2-naphthylamine (I), along with chromatographically observed traces of two other amines. The benzocarbazole, crystallised from ethanol, had m. p. 135° (lit.,[3,5,6] 135°; the other two benzocarbazoles have m. p.s 225° and 333°) (Found: C, 88·1; H, 5·3. Calc. for $C_{16}H_{11}N$: C, 88·5; H, 5·1%). The 1-*o*-aminophenyl-2-naphthylamine, on being crystallised from ethanol, had m. p. 152° (lit.,[3-5] 154°). Its homogeneity was shown by paper chromatography with several solvent systems, *viz.*, formamide–cyclohexane, silicone oil–cyclohexane, dimethylformamide–cyclohexane, and formamide–benzene. The two trace-amines were found on the chromatogram of final mother-liquors from crystallisation of 1-*o*-aminophenyl-2-naphthylamine. On a paper on which this last had an R_F value of 0·77, they had R_F values of 0·37 and 0·10. They were not isolated, and all that is known of them is that both are diazotisable.

When 1-*o*-aminophenyl-2-naphthylamine was boiled with 5N-sulphuric acid for 15 hr., a 50% yield of 3,4-benzocarbazole was obtained. When the period of boiling was extended to 40 hr., the recovery of carbazole amounted to 75%. The carbazole so produced, and that obtained from *N*-2-naphthyl-*N'*-phenylhydrazine by rearrangement, were shown to be identical by their infrared spectra.

In searching for evidence of disproportionation among the products of rearrangement, we relied on spectroscopic detection of 2-phenylazonaphthalene, if formed, by means of its absorption at 400 mμ. This is not at a band maximum of the azo-compound, but the wavelength is one at which there is a minimum of interference by the other substances present. The extinction coefficient of 2-phenylazonaphthalene at 400 mμ is $2{\cdot}94 \times 10^3$.

WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, GOWER STREET,
LONDON, W.C.1.

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

---

[7] Ramart-Lucas, Guilmart, and Martynoff, *Bull. Soc. chim. France*, 1947, 415.
[8] Fierz-David, Blangley, and Merian, *Helv. Chim. Acta*, 1951, **34**, 846.