462. *Mechanism of Benzidine and Semidine Rearrangements. Part II.* Kinetics and Products of Acid Rearrangement of 1,2′-Hydrazonaphthalene.*

By D. V. Banthorpe and E. D. Hughes.

1,2′-Hydrazonaphthalene rearranges somewhat more slowly than does the 1,1′-isomer in like conditions in aqueous dioxan at low acidities. However, in " 70% " aqueous dioxan in the presence of perchloric acid up to 0·15N, the 1,2′-compound rearranges according to the new rate law, *i.e.*, with linear, rather than a quadratic, rate-dependence on hydrogen-ion concentration. The products are the *ortho*-linked primary diamine (I) and the dibenzocarbazole (II). The latter was produced by cyclisation of the former, but could not be so produced under the conditions of the experiments in which the two compounds were formed together by rearrangement. The only other rearrangement product was about 1% of a second diamine. No concurrent disproportionation was observed. At somewhat higher acidities than those over which the kinetics were established, a shift in product composition towards diamine and away from carbazole was found. This is in contrast to the rearrangement of 1,1′-hydrazonaphthalene, which shows such a shift only in a much higher acidity range. A possible interpretation of these facts is suggested.

1,1′-Hydrazonaphthalene, the acid-catalysed rearrangement of which was treated in Part I,* is the most sensitive to that reaction of any of the hydrazo-compounds compared in this group of papers. In " 60% " dioxan at 0°, in the presence of 0·05N-hydrogen ions, it rearranges more than 20,000 times faster than hydrazobenzene. One may suspect that the mechanism involving the linear-hydrogen-ion kinetics of equation (1) in Part I is more exclusively entrenched in the rearrangement of that compound than in those of most other hydrazo-compounds. Our plan now was to study the effect of structure, in the first place hydrocarbon structure, on the kinetic form of the acid rearrangements of hydrazo-compounds, by replacing the two 1-naphthyl groups in this initial example, severally and successively, by 2-naphthyl and by phenyl. Somewhere along this progression one must encounter a change in kinetics, from the linear-hydrogen-ion form to the quadratic-hydrogen-ion form of equation (2) in Part I; for we already know that at the other end of the series, that is, in the acid rearrangement of hydrazobenzene, the latter kinetics are firmly in control. The first step along this progression was to 1,2′-hydrazonaphthalene.

(1) 1,2′-*Hydrazonaphthalene.*—This compound has not previously been prepared,† although, as noted in Section 3, a product of its rearrangement has been obtained from 1,2′-azonaphthalene by reduction and rearrangement in acid conditions. For the present work, the azo-compound was made, as has been described before,[1,2] by coupling diazotised 2-naphthylamine with 1-naphthylamine, and removing the amino-group from the 1-amino-4-azo-product by diazo-reduction in ethanol. In the first step of this process, the 1-amino-2-azo- and 1-amino-4-azo-products are formed together; but they were not separated, and need not be, though, if both acted similarly, we should end with a mixture of 1,2′- and 2,2′-azonaphthalene. But, as has been elucidated in analogous examples,[3] the 1-amino-2-azo-isomer gives a triazole in the second step, leaving, in the present case, 1,2′-azonaphthalene as the only final azo-product. On reduction, by essentially the method employed in

---

* Part I, preceding paper.

† Since this was written, it has been, twice, as described in papers to which reference is made on p. 2404.

[1] Nietzki and Gottig, *Ber.*, 1887, **20**, 612.

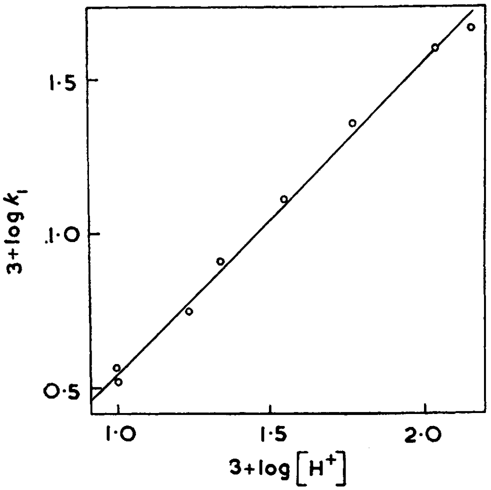
[2] Badger and Lewis, *J.*, 1953, 2154.

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

the preparation of 1,1′-hydrazonaphthalene, this azo-compound gave 1,2′-hydrazonaphthalene, m. p. 130°. It is formed by reduction more easily, and is reoxidised to the azo-compound less easily, than is the 1,1′-isomer.

(2) *Kinetics of Rearrangement of* 1,2′-*Hydrazonaphthalene.*—The kinetics of the acid-catalysed rearrangement of this substance were studied by the general kinetic and analytical techniques discussed in Part I. The solvent was " 70% " aqueous dioxan (a mixture of 70 vol. of dioxan with 30 vol. of water), and the temperature 0°. The acidities were set with added perchloric acid. For many of the runs lithium perchlorate was also added.

Over the range of acid concentrations specified below, the individual runs followed the first-order rate-law. Also, the initial rates of different runs, at the same acidity and ionic strength, were closely proportional to the initial concentrations of the substrate. The rearrangement was therefore concluded to be of first order in substrate, and the rates of runs were represented in terms of first-order rate-constants.



Plot of the logarithm of the first-order rate-constant of rearrangement of 1,2′-hydrazonaphthalene against the logarithm of the concentration of perchloric acid in " 70% " aqueous dioxan at 0·0° at constant total electrolytic concentration. The slope of the line is 1·00.

The acid-dependence of the rate was investigated over the range 0·01—0·15N-hydrogen ions, supplied as perchloric acid, which was taken as fully dissociated. This upper limit of acidity gave rates as fast as could be measured by the inverted-Y-tube method. The total electrolyte was always made up to 0·15M with added lithium perchlorate. In this way, salt effects were standardised as well as they could be. We call them salt effects, rather than ionic-strength effects, because in this medium, at these electrolytic concentrations, ionic association is sufficiently pronounced to render ionic strength a very formal concept. The rates observed in these conditions are recorded in Table 1.

TABLE 1.

First-order rate-constants, k_1, in sec.$^{-1}$, of rearrangement of 1,2′-hydrazonaphthalene, initially 0·004M, in " 70% " aqueous dioxan at 0·0°, in the presence of perchloric acid and lithium perchlorate.

([$HClO_4$] + [$LiClO_4$] = 0·15M.)

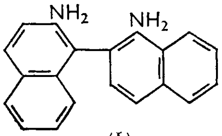
10^3[$HClO_4$]	10	10	16	20	30	50	100	150
10^3k_1	3·43	4·00	5·82	8·13	11·5	19·0	39·3	43·6

Their significance is made clear by the logarithmic plots of rate against hydrogen-ion concentration in the Figure, which shows that the formal reaction-order in hydrogen ions is unity, to within the experimental error. Thus the rearrangement of 1,2′-hydrazonaphthalene, though it is slower by several-fold than that of 1,1′-hydrazonaphthalene in like conditions, resembles it in obeying the new rate-law (equation 1) with some accuracy.

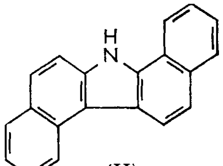
(3) *Products of Rearrangement of* 1,2′-*Hydrazonaphthalene.*—One of the rearrangement products of 1,2′-hydrazonaphthalene was first obtained by Cook, Hewett, and Kennaway from 1,2′-azonaphthalene by reduction and rearrangement in acid without isolation of the intervening hydrazo-compound.[4] Ward and Pearson improved the process as a preparative method, obtaining a high yield of the diamine, which they showed by synthesis was 2,1′-diamino-1,2′-binaphthyl (I);[5] they looked for other rearrangement products chromatographically, but detected none.

On rearranging pure 1,2′-hydrazonaphthalene with dilute perchloric acid in aqueous dioxan, using a variety of acidities and medium compositions, we always obtained two comparably important rearrangement products, which together accounted for almost the whole of the material. One was the above diamine (I). The other was 1,2:5,6-dibenzocarbazole (II).

The carbazole is well known,[6-9] though it has been obtained before by other routes. We have produced it by boiling the 2,1′-diamine (I) with 2N-sulphuric acid, a method which independently establishes its constitution. It was confirmed that the carbazole is not produced from the diamine under the conditions in which, in our experiments, both were produced together in the rearrangement of 1,2′-hydrazonaphthalene, *i.e.*, at a much lower temperature and at lower acidities.



(I)



(II)

There was one other product, a primary amine, which, on chromatographic evidence, was probably a primary diamine, and may be thought, on account of the insolubility of its sulphate, to have its amino-groups well separated in the molecule. It may have been the 2,4′-diamino-1,1′-binaphthyl. But there was only 1% of it, and the matter of its identity was not pursued. We could find no signs, either chromatographic or spectroscopic, either of another primary diamine, or of any semidines, or of any azo- or amino-products of disproportionation, in the rearranged materials produced in our experiments.

Ward and Pearson's paper appeared while this work was in progress, and we were surprised to note that they had neither isolated the carbazole nor detected it chromatographically in the reduction-rearrangement product from 1,2′-azonaphthalene. We therefore carried out the rearrangement of 1,2′-hydrazonaphthalene using their solvent, acetone, and 0·1N-perchloric acid as catalyst. We now obtained much less of the carbazole, less than 5%, consistently with their claimed yield of diamine. But the carbazole could be separated and also chromatographically detected. Probably the point of importance here is that it is not disclosed on the paper chromatogram by the otherwise generally applicable spray of *p*-dimethylaminobenzaldehyde.[10] But, on treatment of the paper with nitrous gases, it is revealed as a yellow spot, which does not couple, as the various primary amines do, on subsequent spraying with *N*-1-naphthylethylenediamine.

The rearrangement of 1,2′-hydrazonaphthalene on addition of acid to the solid substance has recently been described by Krolik and Lukashevich.[11] In these heterogeneous conditions, the main products were the diamine (I), and a *para*-semidine (of a type not found

---

[4] Cook, Hewett, and Kennaway, *Amer. J. Cancer*, 1940, **40**, 62.
[5] Ward and Pearson, *J.*, 1959, 3378.
[6] Japp and Maitland, *J.*, 1903, **83**, 267.
[7] Bucherer and Schmidt, *J. prakt. Chem.*, 1909, **79**, 369.
[8] Buu-Hoï, Hoan, and Khoi, *J. Org. Chem.*, 1949, **14**, 492.
[9] Felton, *J.*, 1952, 1668.
[10] Večera, Petranek, and Gasparič, *Coll. Czech. Chem. Comm.*, 1957, **22**, 1603.
[11] Krolik and Lukashevich, *Doklady Akad. Nauk S.S.S.R.*, 1960, **135**, 1139.

before in hydrazonaphthalene rearrangements), whilst small proportions of the carbazole and of 1,2′-azonaphthalene were sometimes found. Still more recently, the rearrangement of the hydrazo-compound by heating it in cyclohexane without acid has been described by Shine, Huang, and Snell,[12] who report the recovery of small amounts of diamine and carbazole from a complex mixture of products.

(4) *Proportions of the Rearrangement Products.*—Our quantitative study of product proportions was carried out, first, in the solvent and in the acidity range in which the kinetics of rearrangement had been measured, and then also in conditions broadened to include aqueous dioxan solvents of lower water content, and higher acid concentrations, then were employed in the kinetic investigations.

The gravimetric method described in Part I was employed. In the first step, about 1% of an insoluble amine sulphate was precipitated. The non-basic part of the residual material consisted only of the carbazole (II), and the basic part only of the diamine (I). The purity of the main products, and the absence of products other than the three mentioned, were checked by the chromatographic methods of Večera, Petranek, and Gasparič.[10] The results of these analyses are in Table 2.

TABLE 2.

Proportions of the products of rearrangement of 1,2′-hydrazonaphthalene in aqueous dioxan containing perchloric acid.

Dioxan (vol. %) in solvent	Temp.	[HClO$_4$]	Products * Diamine (I) (%)	Products * Carbazole (II) (%)	Dioxan (vol. %) in solvent	Temp.	[HClO$_4$]	Products * Diamine (I) (%)	Products * Carbazole (II) (%)
70	25°	0·08	56·3	40·5	70	20°	1·00	67·2	32·8
80	,,	,,	60·0	39·2	,,	25°	0·05	54·7	43·6
90	,,	,,	54·1	45·4	,,	,,	0·08	56·3	40·5
70	20°	0·12	53·7	42·3	,,	,,	0·16	61·3	36·8
,,	,,	0·24	56·2	40·3	,,	,,	0·40	67·2	31·7
,,	,,	0·48	64·1	34·8					

* Apart from about 1% of a second, but unidentified, diamine, throughout.

There is a suggestion in these figures, though it is less pronounced than in those relating to the rearrangement of 1,1′-hydrazonaphthalene (Part I), of a shift in product composition towards carbazole and away from diamines, as the solvent becomes less aqueous. However, the main contrast disclosed by Table 2 between the two rearrangements is in reference to the dependence of product composition on acidity. In the rearrangement of 1,1′-hydrazonaphthalene, no dependence was found at acidities such as are employed here, though at much higher acidities a fall in production of the carbazole was noticed. In the present experiments with the 1,2′-isomer, we see a marked drift in product composition towards more diamine and less carbazole as the acidity is increased. Naïvely, it seems the more remarkable that extra acid should cause a change of composition in this direction, inasmuch as acid is the reagent that converts pre-formed diamine into carbazole.

Our thought about this is that the beginnings of a change of mechanism may be causing the change in product proportions, though we cannot check the idea kinetically, because, at the acidities at which the change in products is undoubted, the rates are too rapid for measurement. However, various arguments make the suggestion plausible. First, it would be consistent with the effects of structure on mechanism, as disclosed in this series of papers, to assume that the mechanism involving linear-hydrogen-ion kinetics is more firmly in control of the rearrangement of 1,1′-hydrazonaphthalene than of its 1,2′-isomer; with the consequence that, whilst acidities below the molar range do not disturb that control over the former reaction, they permit in the latter some concurrent incursion of the mechanism involving quadratic-hydrogen-ion rate-dependence. Then, it would seem reasonable to assume that the latter mechanism would give little or no carbazole, because,

---

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

in the ring-closure, one amino-nitrogen, the one that makes this new bond, must be in basic form, whilst the other, the one eliminated, must be in cationic form, and hence a transition state containing one added proton would be in the right state of charge to produce such a situation, whereas another added proton would be an embarrassment. One might also thus partly understand the historical situation that none of the previous investigators of homogeneous acid-catalysed benzidine rearrangements in the naphthalene series has reported a carbazole, whereas we have never failed to find one, and in some cases have found large amounts. The significant difference might be that in the earlier procedures, especially those in which azo-compounds are reduced with rearrangement under acid conditions, higher acidities were used than those to which we have been limited by our need to correlate studies of products with those of rates.

EXPERIMENTAL

Preparations.—1,2′-Azonaphthalene was prepared by coupling diazotised 2-naphthylamine with 1-naphthylamine, and deaminating the mixed amino-azo-compounds.[1,2] The tarry product was chromatographed on alumina with ligroin (b. p. 60—80°), the first red band being rejected. The eluted azo-compound, crystallised 6 times from ethanol, had m. p. 145° (lit., 144°) (Found: C, 85·5; H, 5·5. Calc. for $C_{10}H_{14}N_2$: C, 85·1; H, 4·9%). A solution of this compound (2 g.) in 1 : 1 v/v methanol–benzene (120 ml.) at 5° was treated with ammonium chloride (2 g.), water (5 ml.), and zinc dust (5 g.). The solution was shaken for a few minutes, and, when colourless, was quickly filtered, and the filtrate was poured into ice-water (500 ml.). The benzene layer was separated, and, without drying, was evaporated at the water-pump to 10—15 ml. During this process a small amount of reconversion into azo-compound occurred, but on 15-fold dilution of the concentrate with light petroleum (b. p. 40—60°), colourless crystals of 1,2′-hydrazonaphthalene separated. It was purified by repeated partial precipitation from cold benzene with light petroleum. It had m. p. 131—133° (decomp.; heating 1° per min.), and about 140° (at 8° per min.), was chromatographically pure, and had more than 99·5% of the theoretical reducing power towards Bindschedler's Green (Found: C, 84·7; H, 6·0. Calc. for $C_{20}H_{16}N_2$: C, 84·5; H, 5·6%). Krolik and Lukashevich's preparation [11] had m. p. 141—143° (decomp.) and Shine, Huang, and Snell's [12] m. p. 149—153° (at 8° per min.). The presence of rearrangement products is a possible cause of a high m. p.

Kinetic Methods.—These were the same as in Part I (preceding), except that, as the products of this rearrangement did not form coloured titanium complexes, the end-point of the titration of the excess of Bindschedler's Green with titanous chloride was determined visually rather than electrometrically. Near the end-point the solutions were warmed to about 50°.

Product Analyses.—The gravimetric method of Part I was used. The first step gave a little unidentified amine sulphate. The second yielded 1,2:5,6-dibenzocarbazole, and the third 2,1′-diamino-1,2′-binaphthyl, each chromatographically pure. Crystallised from ethanol, the diamine had m. p. 149° (lit., 149—151°). Boiling 2N-sulphuric acid converted it into the dibenzocarbazole. The latter, crystallised from ethanol, had m. p. 230° (lit., 231—238°). The identity of the material, as obtained by rearrangement of the hydrazo-compound, and by cyclisation of the diamine, was checked by infrared spectra.

William Ramsay and Ralph Forster Laboratories,
University College, Gower Street,
London, W.C.1.

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