653. *Mechanism of Benzidine and Semidine Rearrangements. Part IX.*[1] *Substrate-isotope Effects on Kinetics and Products of Acid Rearrangement of* 1,1′-*Hydrazonaphthalene.*

By D. V. BANTHORPE, E. D. HUGHES, Sir CHRISTOPHER INGOLD,
and (in part) R. HUMBERLIN.

1,1′-Hydrazonaphthalene, as well sa its 2,2′- and 4,4′-dideutero-derivatives, the preparation of which is described, have been rearranged with acid in " 60% " aqueous dioxan, and comparisons have been made of rearrangement rates and product proportions. The same hydrazo-compounds have been rearranged with acid in 95% aqueous ether–ethanol, and comparisons have been made of product proportions. In the conditions of these comparisons, three products alone are formed, the single 4,4′-ring-coupled product, naphthidine, and the pair of 2,2′-ring-coupled products, dinaphthyline, and its cyclised relative, dibenzocarbazole, all in substantial, easily measurable, amounts. In the dioxan solvent, neither 2-deuteration nor 4-deuteration affects the overall rate of rearrangement. In both solvents, neither 2- nor 4-deuteration affects the ratio of 4,4′- to total 2,2′-ring-coupled products. In both solvents, 2-deuteration, but not 4-deuteration, does change the internal ratio of the two 2,2′-ring-coupled products, the shift being large, and in favour of the carbazole. Conclusions are drawn concerning the activation of the aromatic proton losses, and their disposition among the product-forming steps of rearrangement.

IN the preceding papers,[1] we have been concerned to determine the degree of proton uptake by aromatic hydrazo-compounds that is required to secure the nitrogen-bond rupture

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[1] Parts I—VIII, *J.*, 1962, 2386—2444, and preceding paper.

involved in their acid-catalysed rearrangements. There is another point at which the question of the mechanism of rearrangement can be attacked, and that is by studying the proton loss needed to permit the intranuclear bonding or nuclear substitution involved in the formation of the products of rearrangement. By replacing selected aromatic hydrogen atoms in the hydrazo-compound with deuterium, and then examining rates of rearrangements and product ratios, we can in principle tell whether or not the loss of the proton so substituted is rate-controlling for the rearrangement; or, if it is not, whether, after the reaction-path splits into branches leading severally to individual products, a proton-loss belongs to the rate-controlling step of any one branch-path, between its origin in a bifurcation and termination in its particular product.

One investigation based on this principle has already appeared,[2] and we shall refer to it more particularly in Part X (following paper). All that need be said now is that it confirmed the preconception, with which we started this work, that proton-loss was unlikely to be found rate-controlling for overall rearrangement. We were, however, open-minded as to whether it might not be rate-controlling for one or another of the branches into which the reaction path might split after having passed over its main activation barrier. If it were rate-controlling in this more restricted sense, we should find no change in the rate of rearrangement, but the product ratio would be changed; for the balance of competition between the rates of reaction steps, which run in parallel after the reaction-path has bifurcated, must become altered when one such step kinetically depends on loss of the isotopically changed hydrogen.

(1) *Choice and Preparation of Deuterated Substrates.*—It was important to choose for study a rearrangement of which the kinetics were simple and known, and the products, or groups of products, involving substitution or coupling in alternative nuclear positions, were formed in ratios not too far from unity. The latter requirement was simply that we wanted any shift in such a ratio, caused by the introduction of deuterium into one position or another, to be sensitively reflected in measured percentage compositions of rearrangement products.

Among the acid-catalysed benzidine rearrangements of which we knew the kinetics and products, the one which best fulfilled these conditions was that of 1,1′-hydrazonaphthalene, described in Part I.[1] In "60%" aqueous dioxan over a wide range of acidities this rearrangement shows uniform kinetics. In these and generally similar conditions, it gives a little above 60% of a single 4,4′-ring-coupled product, naphthidine (4,4′-diamino-1,1′-binaphthyl), and just under 40% of a pair of 2,2′-ring-coupled products, namely, dinaphthyline (1,1′-diamino-2,2′-binaphthyl) and its cyclisation imine (1,2:7,8-dibenzocarbazole); and the last two products are themselves formed in approximate equivalence. Evidently the important ratios of competing rates should here be strongly reflected in the percentage compositions of rearrangement products.

Each of the equivalent aromatic nuclei in 1,1′-hydrazonaphthalene has only two coupling positions, and they are non-equivalent. Hence the proposed test for a rate- or product-controlling proton-loss involved filling the alternative pairs of equivalent active positions in the diarylhydrazine with pairs of deuterium atoms, so as to give 2,2′- and 4,4′-dideutero-1,1′-hydrazonaphthalene. The rates and products of rearrangement of these derivatives then had to be compared with those of their undeuterated parent.

Several synthetic schemes were tried (cf. the Experimental sub-section 4.7) for the preparation of these two dideutero-compounds, but the only ones which were developed usefully were the two corresponding ones outlined below. Even in these schemes, special conditions had to be observed in order to get the deuterium into place and keep it there. Some of the points involved in the establishment of these methods are of general chemical significance, and require more extensive comment than it is convenient to include in this paper: they are therefore dealt with in a companion paper (Part XI, following). Other

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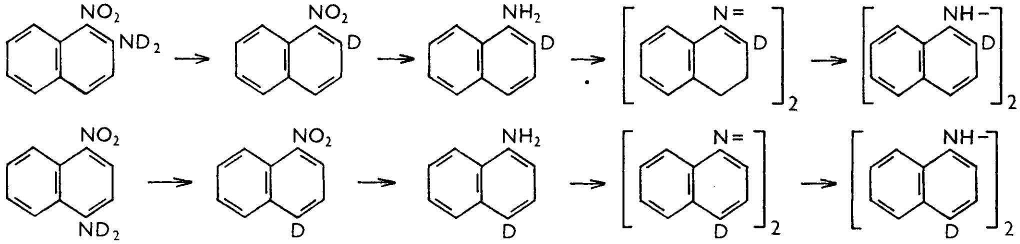
[2] Hammond and Grundemeier, *J. Amer. Chem. Soc.*, 1955, **77**, 2444.

points are touched upon in the Experimental section of this paper. Here we restrict our remarks to an outline of the synthetic routes employed, and to such notes on the products as are needed to clarify the ensuing account of their rearrangements.

The starting points were 1-nitro-2-naphthylamine and 4-nitro-1-naphthylamine, which were deuterated on amino-nitrogen by exchange with deuterium ethoxide, and then diazotised in deuterium oxide by dideuterosulphuric acid and sodium nitrite, the diazonium ion being reduced as formed by trideuterohypophosphorous acid. Despite precautions to exclude all ionising protium, indeed all protium except that bound in the naphthalene rings, the proportion of deuterium that could thus be introduced was only 85—90% of the theoretical. Reasons for this are indicated in the Experimental sub-section 4.2, and are more fully considered in Part XI. However, in each case, the deuterium that had been introduced was wholly in its intended positions. This also is proved in Part XI. The syntheses then continued as formulated below. The deuteronitronaphthalene had to be reduced to deuteronaphthylamines without loss of deuterium, and the diazonium ions derived from the amines had to be reduction-coupled to give dideutero-1,1′-azonaphthalenes, without loss of deuterium or any displacement of it relatively to nitrogen. Finally, the azo-compounds had to be reduced to hydrazonaphthalenes without other change. When this was done by the methods finally evolved, it was found that the requirement of deuterium conservation had been fulfilled, inasmuch as all the deuterium introduced in the first diazonium reduction was still in the final product, and wholly in its intended positions. The evidence for the above statements concerning the content and position of introduced deuterium will be found in Experimental sub-sections 4.2 and 4.3, and in Part XI. The overall yields of 2,2′- and 4,4′-dideutero-1,1′-hydrazonaphthalene obtained from 1-nitro-2- and 4-nitro-1-naphthylamine, respectively, were both 12%.



(2) *Rates of Rearrangement of* 1,1′-*Hydrazonaphthalene and its* 2,2′- *and* 4,4′-*Dideutero-derivatives.*—The first point to be determined was whether the introduction of 2,2′- or 4,4′-deuterium into 1,1′-hydrazonaphthalene changed its rate of acid-catalysed rearrangement. This has been tested for " 60% " and " 70% " aqueous dioxan at 0°, and at various acidities either maintained by buffers or set with perchloric acid. The results are in Table 1. For each Series A—D, *i.e.*, each medium and setting of acidity, the conditions were strictly comparable over the substrates, inasmuch as all reaction solutions of any one Series were made up in the same way from the same main stocks of mixed solvent and aqueous perchloric acid or buffer mixture. The three substrates examined were the " parent " 1,1′-hydrazonaphthalene, its 2,2′-dideutero-derivative in a sample having 85 atoms % of deuterium in its 2,2′-positions, and the 4,4′-dideutero-derivative with 90 atoms % of deuterium in its 4,4′-positions.

It has been explained in Part I[1] that, even with as low an initial concentration of substrate as is analytically convenient, only the initial parts of some runs at low acidities may be available for the computation of first-order rate-constants, because at a certain stage of such a run the rearranged bases will begin appreciably to destroy the catalysing acid. This is chiefly true of unbuffered runs, but it may arise also under buffering, which can only be mild, because buffer anions catalyse the disproportionation of hydrazo-compounds, a side-reaction which we have to exclude. Table 1 contains an indication of the approximate proportions of these runs that were in fact followed, and shown to obey the first-order rate-equation, and, accordingly, were used in order to compute the first-order rate-constants quoted. The reason for including these figures in the record is that our 2,2′- and 4,4′-dideutero-substrates contained only 85% and 90% respectively of the theoretical content of deuterium. It is therefore necessary to establish that we are not here recording specific rates so narrowly initial that they might conceivably belong to relatively fast-reacting light-isotopic forms present in the substrates. That type of interpretation is clearly excluded, and we have to accept the result that neither 2,2′- nor 4,4′-dideuteration makes any difference to the rate of acid rearrangement of 1,1′-hydrazonaphthalene.

TABLE 1.

First-order rate-constants, k_1 in sec.$^{-1}$, of rearrangement of 1,1′-hydrazonaphthalene and of its 2,2′- and 4,4′-dideutero-derivatives, each initially 0·004M in " 60% " or " 70% " aqueous dioxan at various acidities and at 0°.

Series	A	B	C	D
Aqueous dioxan	" 60% "	" 70% "	" 60% "	" 60% "
[$HClO_4$] (M)	0·011	0·040	—	—
Buffer	—	—	Acetate	Phthalate
Apparent pH at 20°	—	—	3·3	3·1
μ (M)	0·05	0·04	0·08	0·025
Percentage of run used	50	80	50	75
10^3k_1 All-H Parent	18·0, 18·3	28·1	0·205, 0·210	0·175, 0·189
10^3k_1 85% 2,2′-D	17·2, 18·6	28·9, 29·9	0·203	0·186, 0·182, 0·168
10^3k_1 90% 4,4′-D	18·2, 18·0	28·5	0·200	0·173, 0·180

(3) *Products of Rearrangement of* 1,1′-*Hydrazonaphthalene and of its* 2,2′- *and* 4,4′-*Dideutero-derivatives.*—Product compositions were investigated in two solvents, the first being the " 60% " aqueous dioxan, in which the kinetics of the rearrangement had been investigated. A definite effect of introduced deuterium on product composition was observed. We then wanted to confirm it—if possible, as a shift from a different basic product-composition given by the undeuterated " parent." This consideration led us to take, as our second solvent, what we call " 95% " ether–ethanol, *i.e.*, a mixture of 47·5 volumes each of ether and ethanol with 5 volumes of water. The kinetics of the rearrangement of 1,1′-hydrazonaphthalene in this solvent have not yet been studied; but it is shown in Part I[1] that the proportions of the products formed in it from 1,1′-hydrazonaphthalene are appreciably different from proportions formed in the aqueous dioxan.

The runs in either solvent were made strictly comparable over the substrates with respect to medium, which, for all runs, was prepared from the same main stocks of mixed solvent and standard perchloric acid. The substrates compared were the all-protium parent hydrazo-compound, two samples of the 2,2′-dideuterated material, one with 13 and the other with 85 atoms % of deuterium in the 2,2′-positions, and a sample of the 4,4′-dideuterated substance with 90 atoms % of deuterium in the 4,4′-positions. The analyses of the mixtures formed by rearrangement were made by gravimetric separation, as described in Part I. The determinations of the three components were independent, and so the deviations of their totals from 100% furnish some indication of the size of the errors. Table 2 collects these analytical results. The main classificatory division of the three products falls between the single 4,4′-ring-coupled naphthidine, and the pair of 2,2′-ring-coupled products, dinaphthyline and dibenzocarbazole. Therefore, beside the individual abundance of these 2,2′-coupled products, we list their sum, as well as the totals (which should be 100%) of all three products.

Table 2 discloses the same findings in both the solvents investigated. Neither 2,2′- nor 4,4′-deuteration measurably changes the ratio of 4,4′-ring-coupled to total 2,2′-ring-coupled products; but 2,2′-deuteration, though not 4,4′-, does markedly shift the ratio

TABLE 2.

Proportions of the products, naphthidine (I), dinaphthyline (II), and dibenzocarbazole (III), formed, by rearrangement in certain aqueous organic solvents at 0° in the presence of perchloric acid, from 1,1′-hydrazonaphthalene and from its 2,2′- and 4,4′-dideuterated derivatives having known atomic proportions of deuterium in these positions.

	Products (mol. %)				
	4,4′-Coupled	2,2′-Coupled			
Substrate	I	II	III	Sum	Total
Series E. In " 60% " dioxan with 0·08N-*perchloric acid.*					
All-H parent	63·8	16·4	17·1	33·5	97·3
,,	63·7	17·5	16·8	34·3	98·0
,,	63·2	16·6	17·0	33·6	96·8
,,	63·7	17·6	16·0	33·6	97·3
Mean	63·6	17·0	16·7	33·7	97·3
13% 2,2′-D	64·3	14·7	20·1	34·8	99·1
,,	63·8	13·5	20·8	34·3	98·1
,,	64·3	15·7	18·2	33·9	98·2
,,	64·6	14·8	18·8	33·6	98·2
,,	63·6	14·0	23·1	37·1	100·7
Mean	64·1	14·5	20·2	34·7	98·9
85% 2,2′-D	62·3	5·4	30·9	36·3	98·6
,,	63·6	7·0	29·0	36·0	99·6
,,	64·2	7·0	28·0	35·0	99·2
,,	62·2	5·7	30·0	35·7	97·9
,,	62·5	7·0	29·5	36·5	99·0
,,	63·5	6·9	29·3	36·2	99·7
Mean	63·1	6·5	29·5	36·0	99·1
90% 4,4′-D	63·2	18·1	18·8	36·9	100·1
,,	61·7	18·5	19·6	38·1	99·8
,,	62·7	17·8	17·1	34·9	97·6
Mean	62·5	18·1	18·5	36·6	99·1
Series F. 95% *Ether–ethanol with* 0·05N-*perchloric acid.*					
All-H parent	57·7	19·9	26·0	45·9	103·6
85% 2,2′-D	56·4	5·1	36·3	41·4	97·8
90% 4,4′-D	56·9	19·0	26·3	45·3	102·2

in which the two 2,2′-coupled substances are produced, the shift favouring the formation of the dibenzocarbazole at the expense of the dinaphthyline.*

We need not here do more than point out the most immediate conclusions. The first is that the aromatic proton-loss involved in the rearrangement is inherently able to produce

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* A preliminary experiment has shown that an isotope effect in the same direction and of similar magnitude arises in the rearrangement of 2,2′-hydrazonaphthalene, as a result of deuteration in the 1,1′-position. The ordinary 2,2′-hydrazo-compound (Part III [1]), on rearrangement in " 60% " aqueous dioxan containing perchloric acid at 0°, gives 95% of 2,2′-diamino-1,1′-binaphthyl, and 5% of 3,4 : 5,6-dibenzocarbazole, both 1,1′-ring-coupled products. A sample of largely 1,1′-deuterated 2,2′-hydrazo-compound, in identical conditions, gave 84% of the diamino-compound and 16% of the carbazole.

These figures will underestimate the shift in product composition resulting from 1,1′-deuteration, because, in the sample of hydrazo-compound prepared for this pilot experiment, the 1,1′-positions could not have been completely deuterated. 2-Naphthylamine hydrochloride was boiled with recovered deuterium oxide, calculated to contain about 95 atoms % of deuterium, until the infrared spectrum did not change any more. Theory teaches that hydrogen exchange would first occur in position 1. The deuterated 2-naphthylamine was then converted into 2,2′-azonaphthalene, and thence into 2,2′-hydrazonaphthalene, under the conditions of reduced acidity described in this paper (Section 4.2) for the conversion of deuterated forms of 1-naphthylamine into 1,1′-hydrazonaphthalene. without any loss or displacement of deuterium.

a primary deuterium isotope effect of considerable magnitude, when a suitably competing reaction-step is available against which the kinetic effect can be manifested: this implies an activated displacement of the proton. The fact that two protons have to be lost in order to establish any one biaryl bond, and that we have looked for two isotope effects on product-ratios, and have found one but not the other, points to a second conclusion. It is that the two protons are lost in different locations along the reaction co-ordinate, one unassociated, and the other associated with a competing reaction step. The results of Section 2 above allow the further conclusion to be drawn that both locations lie beyond the main transition state for rearrangement, indeed, further beyond in terms of reduced energy than the activation energy of either proton loss. These matters will be further discussed in Part XIII.

EXPERIMENTAL

(4.1) *Deuterium Reagents.*—It was important to obtain trideuterohypophosphorous acid substantially free from protium, because kinetic isotope effects leading to k_H/k_D ratios up to 6 have been observed in the hydrogenating reactions of hypophosphorous acid, and thus a little residual protium could be seriously detrimental to the products we were to prepare. Purchased 60% hypophosphorous acid was concentrated at 40°/0·1 mm. until, after 2 days, no more water could be removed. The residue (55 ml.) was then left to come to equilibrium with 99·8% deuterium oxide (50 ml.) at 45° for 24 hr., and then the deuterium oxide was pumped off at 25°/0·1 mm. This procedure of exchange was then repeated 9 times, with fresh deuterium oxide (25 ml.) each time. The final product was shown by nuclear magnetic resonance to be of isotopic purity well over 99% in deuterium, and closer to the theoretically possible 99·8% than the spectrometer could distinguish. It was " dry," *i.e.*, analytically free from deuterium oxide. As to oxidation state, titration to two end-points, those of Methyl Red and thymolphthalein, showed that it consisted of 92 mol. % of D_3PO_2 and 8 mol. % of D_3PO_3. The material was kept in a desiccator over phosphoric oxide.

There are several points of difference here from the description of this preparation given by Hammond and Grundemeier.[2] They carried out their evaporations " below 100°." Our much lower temperatures of evaporation were adopted, because we had found that the acid decomposes, especially easily when it is concentrated, to give red phosphorus and phosphine, besides oxidation acids, at temperatures approaching 100°. Our longer time and higher temperature of equilibration, than those of Hammond and Grundemeier, were determined in consequence of some rough knowledge we had of the rate of this somewhat slow exchange. Then, the infrared spectrum of our product bore no resemblance to the spectrum described by Hammond and Grundemeier for theirs. In particular, our spectrum did not show the band at 1720 cm.$^{-1}$, which those authors ascribed to a P–D stretching vibration and relied on for their measurements of deuterium content. That is why we went over to analysis by the proton magnetic resonance spectrum.

For the preparation of dideuterosulphuric acid, sulphuric oleum was refluxed for 10 hr. with chromium trioxide, and sulphur trioxide was distilled off in a special apparatus provided with sleeved joints.[3] It was then redistilled into 99·8% deuterium oxide, the quantities being so adjusted that the resulting acid contained 98% by weight of D_2SO_4 and 2% of D_2O. The isotopic purity of this material was shown by its nuclear magnetic resonance spectrum to be better than 99·5% in deuterium. The acid was kept in a desiccator over phosphoric oxide.

Deuterium ethoxide was prepared [4] by boiling diethyl sulphite with the theoretical amount of deuterium oxide, slightly acidified with dideuterosulphuric acid, until the sulphur dioxide had disappeared, and distilling the residual deuteroalcohol.

(4.2) *2,2'-Dideutero-*1,1'-*hydrazonaphthalene.*—*N*-Acetyl-2-naphthylamine was nitrated in acetic acid by Smith's method [5] to give *N*-acetyl-1-nitro-2-naphthylamine, which, crystallised 3 times from ethanol (yield 60%), had m. p. 127° (lit., 127°). This compound (300 g.), dissolved in ethanol (1800 ml.), was heated at 100° for 2 hr. with a mixture of equal parts by weight of sulphuric acid and water (1500 ml.). Hot water (500 ml.) was then added, and, after a further 2 hr., the precipitated 1-nitro-2-naphthylamine (yield 90%) was collected and crystallised from

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[3] E. A. Robinson, Thesis, University of London, 1958.
[4] Shine, *J. Amer. Chem. Soc.*, 1956, **78**, 4807.
[5] Smith, *Org. Synth.*, 1933, **13**, 72.

ethanol (m. p. 127—128°; lit., 123—124°). The amine-hydrogen in this amine was now completely exchanged for deuterium, in order that such exchangeable light hydrogen should not be introduced into the diazotisation of the amine, and hence into the succeeding reduction by trideuterohypophosphorous acid. To this end, the nitro-amine (10 g.) was dissolved in deuterium ethoxide (100 ml.), and the solvent was pumped off. This procedure was then repeated with fresh deuterium ethoxide.

Preliminary experiments with undeuterated materials showed that, when attempting reductive deamination of 1-nitro-2-naphthylamine by diazotisation followed by treatment of the diazonium ion with hypophosphorous acid, it was easy to obtain good yields of unwanted compounds, particularly, 1,1′-dinitro-2,2′-azonaphthalene, naphthalene-2,1-diazo-oxide, or, if hydrochloric acid was present, 1-chloronaphthalene. In the method evolved, sulphuric acid was used in the diazotisation, and the diazonium ion was produced in the presence of a fairly large excess concentration of the hypophosphorous acid that was to attack it. The remaining critical condition proved to be the ratio of water to sulphuric acid: without elucidating the underlying chemistry, we found empirically that the yield of 1-nitronaphthalene passed through a sharp maximum when this ratio was close to 1 : 1 v/v. On this information, the following procedure was established for the preparation of 2-deutero-1-nitronaphthalene.

The dideuteroaminonitro-compound (8 g.), 98% by weight D_2SO_4 (25 ml.), D_2O (16 ml.), and dry D_3PO_2 (16 ml.), all these materials being near to 99·8% in isotopic abundance of deuterium, were put into a well-dried flask fitted with a stirrer, and with drying-tubes (omission of which caused a loss of 5% in the deuterium content of the final product); and the solution was then diazotised at 0° with a solution of sodium nitrite (3·04 g.) in D_2O (8·0 ml.), added during 45 min. The mixture was stirred at 0° for 7 hr., and kept at 0° for a further 12 hr.; then the tarry product was extracted with ether, dried therein, and chromatographed with ether and light petroleum on alumina, to yield chemically (apart from isotopically) pure 2-deutero-1-nitronaphthalene (4·5 g., 62%). This had m. p. 61°. It was identified, *i.e.*, apart from isotopic substitution, by comparing, with respect to m. p. and mixed m. p., and also infrared spectrum, the similarly prepared undeuterated form (Found: N, 8·0. Calc. for $C_{10}H_7NO_2$: N, 8·0%) with authentic 1-nitronaphthalene. The deuterium content of the deuterated specimen, determined mass-spectrometrically, was 0·85 deuterium atom per molecule. The conclusion that the whole of the deuterium that is present occupies position 2 is based, as described in Part XI, on deuterium analyses of chemical transformation products of the material.

The deficiency in deuterium abundance is greater than could arise either from residual protium in the inorganic deuterium compounds employed in the preparation, or from the incompleteness of exclusion of atmospheric moisture. The only considerable source of protium consists in the six aromatic protium atoms of the dideuteroaminonitronaphthalene, protium which we had assumed to be non-exchangeable. It is known, however, that the *o*- and *p*-hydrogen atoms of aniline are somewhat slowly exchanged with acid, and therefore we tested for any similar exchange of aromatic hydrogen in 2-nitro-1-naphthylamine with acid in the conditions of our diazotisation and reduction. The undeuterated amine was put into a deutero-acid solution made up exactly as for reductive deamination, except for omission of the sodium nitrite. After being kept in this solution at 0° for the previous length of time, the amine was recovered, normalised with respect to amino-hydrogen by exchange with ethanol, and examined mass-spectrometrically. It was found that there had been no significant uptake of deuterium. A similar experiment was done with the deamination product, 1-nitronaphthalene. This also failed to take up any deuterium. In view of these results, we are of the opinion, though it is admittedly reached by exclusion, that most of the 15% of protium in our 2-deutero-1-nitronaphthalene did come from the aromatic protium in the 1-nitro-2-naphthylamine, but by way of the side-reactions which converted a substantial fraction of that material into tar. It is almost certain (cf. Part XI) that inorganic radicals are formed in the course of reduction by hypophosphorous acid; and an attack by such on an aromatic molecule would produce tar, and would concurrently convert some of the aromatic hydrogen into inorganic, and hence exchangeable, hydrogen.

We failed (cf. sub-section 4.7) to develop a satisfactory method for the reductive coupling of 1-nitronaphthalene to give 1,1′-azoxy- or 1,1′-azo-naphthalene, and therefore explored the method of reduction to 1-naphthylamine, followed by reductive coupling of the naphthalene-1-diazonium ion. The first problem was to reduce the nitro-compound to the amine without nuclear hydrogen exchange. We knew that too much acid had to be avoided. We avoided it in finding that 1-nitronaphthalene was reduced to 1-naphthylamine quantitatively at 100° in 2 hr. by iron dust and 1% aqueous ammonium chloride.[6] However, when the experiment was repeated with the ammonium chloride solution made up in deuterium water, and the amino-hydrogen was normalised in the recovered 1-naphthylamine by exchange with ethanol, very extensive exchange of nuclear hydrogen had occurred. Some light on this was thrown by another experiment, in which 1-naphthylamine hydrochloride was boiled for 13 hr. in deuterium water, and the amino-hydrogen in the recovered amine was normalised as before: only 35% of the hydrogen in positions 2 and 4 had now undergone exchange. It was concluded that, in the previous experiment, the iron must have catalysed exchange, and that, for the purpose of reducing the nitro-compound to the amine without exchange of nuclear hydrogen, not only acid, but also dissolving transition metals were to be avoided.

To keep within these limitations, the following process was developed. The nitronaphthalene (2·9 g.), anhydrous hydrazine hydrate (25 ml.), and palladised asbestos (0·75 g.), in methanol (150 ml.), were heated under reflux for 1 hr. The mixture was filtered, diluted with water, and extracted with ether, from which the hydrochloride of the amine was precipitated by passing in hydrogen chloride. The yield of pure 1-naphthylamine was quantitative. This process was next repeated with a deuterium methanol (containing 40% of $CH_3{\cdot}OD$) in place of the ordinary methanol, in order to test for any exchange of nuclear hydrogen. When the finally recovered 1-naphthylamine had had its amino-hydrogen normalised with ethanol as usual, it was found to contain no deuterium. The method, thus shown to be harmless to nuclear hydrogen, was now applied to the samples of 2-deutero-1-nitronaphthalene, which were thus reduced quantitatively to 2-deutero-1-naphthylamine, without, as was subsequently shown, any disturbance to their deuterium.

Similar difficulties arose with respect to the reductive coupling of the 1-naphthyldiazonium ion to give 1,1′-azonaphthalene. Bogoslavski's "reversed Sandmeyer" method[7] of decomposing the diazonium ion in mildly acid conditions with cuprous oxide, though claimed as an efficient general method, gave only tars, and no azo-compound, in the present instance. The problem was solved by adapting the reduction by sulphite, developed as a preparative method by Cohen and Oesper,[8] and so used in Part I, to conditions of minimum acidity, as follows. 1-Naphthylamine hydrochloride (4·30 g.) in water (70 ml.) containing concentrated hydrochloric acid (5 ml.) was diazotised during 1·5 hr. at 0°, with sodium nitrite (1·72 g.) in water (25 ml.). The mixture was then buffered by addition of sodium acetate (9 g.) in water (38 ml.), and sodium sulphite (4·2 g.) in water (30 ml.) was next added. The reduction was completed according to the directions of Cohen and Oesper, and the product was purified as described in Part I (yield, 2·24 g., 44%). When this preparation was repeated with the use of deuterium water in place of ordinary water, the resulting 1,1′-azonaphthalene was free from deuterium. The method, thus vindicated for application to deutero-derivatives, was now applied to our samples of 2-deutero-1-naphthylamine, which were thereby converted into 2,2′-dideutero-1,1′-azonaphthalene, without, as was subsequently confirmed, any disturbance to the deuterium.

The method of the final step, due essentially to Krolik and Lukashevich,[9] and used in Part I for converting 1,1′-azo- into 1,1′-hydrazo-naphthalene, consists in shaking a solution of the azo-compound in moist methanol–benzene with zinc dust and ammonium chloride. This process had to be shown innocuous to nuclear hydrogen isotopes, and it was accordingly applied to ordinary 1,1′-azonaphthalene, but with the use of deuteromethanol (50% $CH_3{\cdot}OD$), in place of ordinary methanol, in the methanol–benzene solvent. The resulting 1,1′-hydrazonaphthalene, after isotopic normalisation of its hydrazo-hydrogen by dissolution in, and recovery from, ordinary methanol, proved to be free from deuterium. This vindicated the method, which was therefore applied to our samples of 2,2′-dideutero-1,1′-azonaphthalene. They were thus reduced to 2,2′-dideutero-1,1′-hydrazonaphthalene, without loss of or disturbance to the deuterium. The absence of loss is succinctly illustrated by the result that our sample of 2-deutero-1-nitronaphthalene, which contained 0·85 atom of deuterium per molecule,

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[6] Cf. Lukashevich and Voroshilova, *Org. Chem. Ind. U.S.S.R.*, 1937, **4**, 253.

[7] Bogoslavski, *J. Gen. Chem. U.S.S.R.*, 1946, **16**, 193.

[8] Cohen and Oesper, *Ind. Eng. Chem. Analyt.*, 1936, **8**, 306.

[9] Krolik and Lukashevich, *Doklady Akad. Nauk S.S.S.R.*, 1949, **65**, 37.

passed through all the subsequent reaction steps to give finally 2,2′-dideutero-1,1′-hydrazonaphthalene having 1·70 atoms of deuterium per molecule, *i.e.*, still 0·85 per naphthalene residue. To prove the absence of any disturbance to the position of this deuterium was a more complicated matter, which is explained in Part XI.

(4.3) *4,4′-Dideutero-1,1′-hydrazonaphthalene.*—The starting substance, 4-nitro-1-naphthylamine, was prepared by a standard method.[10] Crystallised twice from ethanol, it had m. p. 194°.

Exploratory work on the reduction of its diazonium ion with hypophosphorous acid disclosed restrictive conditions similar to those found for the 1,2-isomer, though the critical water–acid optimum was slightly different, as is reflected in the following procedure for the introduction of deuterium. For this purpose, the amine was first deuterated in its amino-group by exchange with deuterium ethoxide, as described for the 1,2-isomer. A solution of the dideuteroamine (10 g.) in a mixture of D_2SO_4 (35 ml.) and D_2O (25 ml.), to which D_3PO_2 (20 ml.) had been added, was diazotised with sodium nitrite (3·80 g.) in D_2O (20 ml.), and the eventual reduction product was worked up as in the similar reaction of sub-section 4.2. The extracted solid was chromatographed on alumina with ether, with 9 : 1 ether–light petroleum, and with 3 : 2 light petroleum–benzene. Tar and other impurities were thus removed, and chemically pure 4-deutero-1-nitronaphthalene, m. p. 61°, was obtained (4·6 g., 48%). Mass-spectroscopic examination showed that it contained 90% of the theoretical content of deuterium. We explain the deficiency as for the 1,2-isomer (sub-section 4.2).

For the ensuing preparation of 4-deutero-1-naphthylamine, its diazotisation, and the subsequent reduction of the diazonium ion to 4,4′-dideutero-1,1′-azonaphthalene, and the reduction of this to the deutero-hydrazo-derivative, the details are practically identical with those described in sub-section 4.2 for the 1,2-isomers. As before, no deuterium was lost in this chain of processes, the final 4,4′-dideutero-1,1′-hydrazonaphthalene having 1·8 atoms of deuterium per molecule, *i.e.*, still 90% of the theoretical. Furthermore, as is shown in Part XI, this deuterium was wholly in the 4,4′-positions.

(4.4) *Deuterium Analyses.*—Inorganic deuterium compounds to be used as reagents were checked for isotopic purity by their nuclear magnetic resonance spectra. This was kindly done for us by Dr. B. N. Figgis.

The important organic deuterium analyses were made in the mass-spectrometer, and we are much indebted to Dr. C. A. Bunton for them. His procedure was to burn the substances in copper oxide and lead dioxide, and convert the formed water with zinc into hydrogen, which was isotopically analysed. The method was calibrated with hydrogen from artificial mixtures of H_2O and D_2O.

Analyses by infrared band-intensity was used for routine control, where we knew the spectra of " light " and " heavy " forms, and could calibrate for intensity against isotopic composition.

(4.5) *Kinetics of Rearrangement.*—They were followed, as in Part I, by quenching with Bindschedler's Green, and titrating the excess with titanous chloride, end-points being located electrometrically.

(4.6) *Analyses of Rearrangement Products.*—The gravimetric methods, described in Part I, were used.

(4.7) *Abandoned Synthetic Schemes* (*with* R. HUMBERLIN).—The common consideration underlying the first three below was that this work might have been much less costly had we been able to introduce deuterium near the end of the reaction sequence, rather than at the beginning. The fourth scheme below accepted the early introduction of deuterium, and sought a " short-cut " thereafter.

(i) In the course of the work on 1,2-derivatives of naphthalene, the attempt was made to reduce *N*-acetyl-1-nitro-2-naphthylamine with zinc to 2,2′-di(acetamido)-1,1′-azonaphthalene, with the idea that this could be deacetylated and then diazotised, in order to introduce deuterium only one step before the final one. However, the reduction could not be satisfactorily stopped at the azo-stage: some azoxy-compound could be obtained, but further reduction led directly to 2-acetamido-1-naphthylamine.

(ii) An attempt was made to convert this last compound, by diazotising it, and reducing the diazonium ion with sulphite, into 2,2′-di(acetamido)-1,1′-azonaphthalene. However, the acetyl substituent failed to protect its amino-group, and naphtho-1,2-triazole was formed.

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[10] Price and Woong, *Org. Synth.*, 1948, **28**, 81.

(iii) The analogous reaction in the 1,4-series could not fail for that reason. But it did fail, inasmuch as, under several variations of conditions, the intended diazo-reduction led to 1,4-naphthaquinone.

(iv) The object was to establish reductive coupling of 1-nitronaphthalene to 1,1′-azonaphthalene by a method that could be applied to 2- or 4-deutero-1-nitronaphthalene without loss of deuterium. Treatment of the nitro-compound with zinc and alkali under various conditions, with glucose and alkali, and with lithium aluminium hydride, gave red oils and black solids, difficult to purify. Reduction by electrolytic means, by zinc and ammonium chloride, by ethanolic sodium ethoxide, by sodium amalgam and by sodium and ethanol, gave impure mixtures containing azo- and azoxy-products. Further reduction of these by electrolysis, by zinc and alkali, by lithium aluminium hydride, by hydrogen and a platinum catalyst, by magnesium and magnesium iodide,[11] and by phenylmagnesium bromide,[12] gave intractable tars, with very little, if any, separable azo-compound.

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

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[11] Bachmann, *J. Amer. Chem. Soc.*, 1931, **53**, 1524.

[12] Kursanov, *J. Gen. Chem. U.S.S.R.*, 1938, **8**, 1786.