655. *Mechanism of Benzidine and Semidine Rearrangements. Part XI.*[1] *Notes on Two Types of Diazo-reduction.*

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When the 1-nitronaphthalene-2-diazonium ion is reduced with protium-free D_3PO_2 in the presence of D_2SO_4 in dioxan, with exclusion of atmospheric moisture, most of the diazo-group is replaced by protium. This protium is derived from the dioxan, in which it becomes replaced by deuterium. A similar effect on deuteration through Grignard reagents and D_2O in ether is recalled, and an explanation is advanced which relates both effects to the autoxidation of ethers.

When naphthalene-1-diazonium ions containing deuterium in known positions are converted by reductive coupling with buffered sulphite into 1,1′-azonaphthalenes, the original orientations of deuterium relative to nitrogen are preserved in both aryl groups of the azo-derivative. The deuterium orientations were determined in the corresponding hydrazo-compounds, by rearranging them with acid, separating the products, and comparing the deuterium contents of the factors and separated products. The results delimit possible views of the mechanism of the reductive coupling. It is shown or confirmed that the various deuterated hydrazo-compounds, the preparation and reactions of which are described in Parts IX and X, have the constitutions there assigned to them.

The subjects now to be considered arose out of the syntheses, described in Part IX,[1] of hydrazonaphthalenes containing deuterium in specific orientations. The points here to be made have an interest outside the limited purposes of Part IX. However, the work to be mentioned not only guided in part the synthetic procedures of Part IX, but also provided the proof, necessary to give significance to Parts IX and X, that the synthetically introduced deuterium was indeed in its intended positions in the hydrazo-compounds with which those papers deal.

(1) *Arenediazonium Ions and Hypophosphorous Acid.*—As described in Parts IX and X, we have relied on this reaction in order to introduce deuterium, or, in one case, protium in the presence of deuterium in other positions, in the place of a diazotisable amino-group. When using the method for the introduction of deuterium, we aimed to avoid the presence of exchangeable protium: the amino-compound was first converted into an ND_2-compound, which was diazotised in D_2O; the diazonium solution was acidified with D_2SO_4 and reduced with protium-free D_3PO_2. But in our first experiments we were not as ruthless as we subsequently became in excluding all avoidable protium, whether presupposed to be exchangeable or not. Thus, in an experiment starting from 1-nitro-2-naphthylamine, a mixture was made up for diazotisation and reduction as follows: the ND_2-derivative (30 g.), D_2SO_4 (13 ml.), D_3PO_2 (25 ml.), and peroxide-free dioxan (500 ml.). The dioxan was here introduced in order to economise deuterium solvent. Our view then was that, as the bond-energies of P–H and methylene C–H bonds are given as 77 and 94 kcal./mole, respectively, the dioxan hydrogen would be secure against involvement in the reduction. However, the resulting 1-nitronaphthalene contained only 15% of the expected one atom of deuterium.

Thus the question was posed as to where the 85% of protium came from. We showed that none of it could have come from other nitronaphthalenediazonium ions, or nitronaphthalene molecules, or, indeed, from any entity which ended its career as recovered 1-nitronaphthalene. For some deuterium would then have entered where any such protium had been taken from, *i.e.*, into various naphthalene positions, particularly α-positions; and we could show (cf. Section 2, below) that all the deuterium which had entered was where the 2-amino-group had previously been. Furthermore, a parallel

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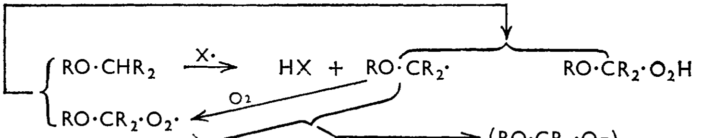
[1] Parts I—X, *J.*, 1962, 2386—2444, and the three preceding papers.

experiment with protium reactants, *i.e.*, with 1-nitro-2-naphthylamine, sulphuric acid, and hypophosphorous acid, in dioxan, to which, however, largely deuterated benzene had been added in an amount approximately equivalent to the hypophosphorous acid, resulted in deuterium-free 1-nitronaphthalene.

By argument of exclusion, these results pointed to dioxan as the source of the protium, an inference which would mean that, molecule for molecule in the experiment illustrated, the dioxan was supplying protium about half as fast as the deuterated hypophosphorous acid was supplying deuterium to the aromatic compound. Following up this idea, we showed that, when 1-nitro-2-naphthylamine was diazotised in dioxan, as before except for the omission of the hypophosphorous acid, the diazonium ion was slowly decomposed to give 15—20% of 1-nitronaphthalene after 36 hr. at 0°. When, at an early stage of such an experiment, a few drops of hypophosphorous acid were added, gas evolution at once became fairly brisk, and 50% of 1-nitronaphthalene could be recovered after a few hours at 0°. When the diazonium compound was decomposed in dioxan in the presence of trideuterohypophosphorous acid, the recovered dioxan solvent was found, by infrared and mass-spectrometric examination, to contain deuterium.

We were reminded by this finding of an early experience here in the preparation of aromatic deuterium compounds: when certain aromatic Grignard reagents were decomposed with deuterium oxide in diethyl ether, an appreciable proportion of protium became introduced, which could only have come from the ether.[2] Since Grignard compounds are reducing and diazonium ions are oxidising, the one common property that might account for both results would seem to be that both kinds of compound are easily susceptible of free-radical reactions. This was, indeed, the explanation originally given to the reactions of the Grignard compounds.[2] It has also been shown [3] that the reduction of diazonium ions by hypophosphorous acid is catalysed by oxidising agents and inhibited by benzoquinone, thus displaying radical-chain characteristics.

That such reactions would implicate ethers follows empirically from the ready autoxidation of ethers,[4] and can be rationalised on the basis that an oxygen unshared electron-pair easily becomes unpaired (dramatically in O_2), and that the sharing of one such electron with α-carbon would loosen α-hydrogen as an atom, just as the sharing of a pair will loosen α-chlorine as an anion.* Thus autoxidation may pursue a repetitive cyclic path, with input and off-take branches somewhat as follows:



The simple view of the diazo-reduction, *viz.*, that, whether initiation is thermal or by means of an adventitious oxidant, the propagation process is:

$$ArN_2^+ + (D_2PO_2)\cdot \longrightarrow Ar\cdot + N_2 + (D_2PO_2)^+ \ (\xrightarrow{OD^-} D_3PO_3)$$

$$Ar\cdot + D_3PO_2 \longrightarrow ArD + (D_2PO_2)\cdot$$

leads naturally to the assumption that, when an autoxidisable ether is present, the same radicals will participate in a second chain process, *viz.*,

$$Ar\cdot + RO\cdot CHR_2 \longrightarrow ArH + RO\cdot CR_2\cdot$$

$$RO\cdot CR_2\cdot + D_3PO_2 \longrightarrow RO\cdot CDR_2 + (D_2PO_2)\cdot$$

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* The radical would have a 3-electron CO bond, or, in molecular-orbital terms, four bonding and one antibonding CO electrons.

[2] Weldon and Wilson, *J.*, 1946, 235.

[3] Kornblum, Cooper, and Taylor, *J. Amer. Chem. Soc.*, 1950, **72**, 3013.

[4] Walling, " Free Radicals in Solution," Chapman and Hall, London, 1957, p. 412.

This would account for the entry of protium into the aromatic compound and deuterium into the ether.

(2) *Naphthalenediazonium Ions and Sulphurous Acid.*—The formation of 1,1′-azonaphthalene by reduction of naphthalene-1-diazonium ion with sulphite in an acetate buffer was first described by Lange.[5] The reaction has limited application among diazonium compounds, partly because stable diazosulphonates are often formed in the conditions. We used the method (Part IX [1]) to convert 2- and 4-deuterated 1-naphthylamines, by diazotisation and subsequent reductive coupling, into deuterated 1,1′-azonaphthalenes, in the hope that these azo-products would have their deuterium in a retained orientation relative to nitrogen in both aryl residues. However, nothing is known about the mechanism of the reductive coupling; and various suggestions have been made, some of which would imply that our hopes of retained orientations of deuterium might not be fulfilled.

All theories of the mechanism of the process assume the first two of the following steps; and it has been suggested that an aryl radical attacks the solvent, so bringing in the third step:

$$\mathrm{ArN_2^+} \longrightarrow \mathrm{ArN_2}\cdot \longrightarrow \mathrm{Ar}\cdot \longrightarrow \mathrm{ArH}$$

One theory suggests that the radicals $\mathrm{ArN_2}\cdot$ and $\mathrm{Ar}\cdot$ combine, which they might do either at the radical centres,[6] or at an *ortho*- or *para*-position with displacement of aromatic hydrogen. It would be possible for two radicals $\mathrm{ArN_2}\cdot$ to combine in similar ways with loss of a nitrogen molecule. Again the ion $\mathrm{ArN_2^+}$ might couple with the radical $\mathrm{Ar}\cdot$, either at the radical centre,[7] or at an *ortho*- or *para*-position with migration of the aromatic hydrogen displaced therefrom. Or, the ion $\mathrm{ArN_2^+}$ and the radical $\mathrm{ArN_2}\cdot$ might couple, either by reaction between the diazo-centres, or by attack on an *ortho*- or *para*-position, the hydrogen from which migrates to replace the lost $\mathrm{N_2}$-group.[8] Or again, the radical $\mathrm{ArN_2}\cdot$ might attack the molecule ArH in various positions.[7] Some of these suggestions have been made before, and we here fill in the remaining possibilities:

(1) $\mathrm{Ar}\cdot + \mathrm{ArN_2}\cdot$ at radical centres.[6]
(2) ,, ,, at *ortho* or *para*.
(3) $\mathrm{ArN_2}\cdot + \mathrm{ArN_2}\cdot$ at $\mathrm{N_2}$-centres.
(4) ,, ,, at *ortho* or *para*.
(5) $\mathrm{Ar}\cdot + \mathrm{ArN_2^+}$ at radical centre.[7]
(6) ,, ,, at *ortho* or *para*.
(7) $\mathrm{ArN_2}\cdot + \mathrm{ArN_2^+}$ at $\mathrm{N_2}$ centres.
(8) ,, ,, at *ortho* or *para*.[8]
(9) $\mathrm{ArN_2}\cdot + \mathrm{ArH}$, various positions.[8]

Mechanisms (1), (3), (5), and (7) would preserve the original orientation of deuterium relative to nitrogen in both aryl groups of the final azo-compound. Mechanisms (2), (4), (6), and (8) would not do so; and mechanism (9) would not necessarily do so. Thus the need arose to determine the orientation of the deuterium in our azo-products. The primary object was to check the suitability of these azo-products for the purposes for which they were prepared. An incidental result was to delimit possible views of the mechanism of the reductive coupling of diazonium ions, a reaction which it is intended further to investigate.

We were predisposed to favour mechanisms which preserve orientation, for the reason that no one has yet isolated an unsymmetrical azo-compound from the product of a diazo-reduction by Lange's method; though it must be admitted that the frequent low yields of identified products considerably reduce the strength of this argument.

For the particular diazo-reduction with which we are here concerned, *viz.*, that of the naphthalene-1-diazonium ion by sulphite, we were also predisposed to favour mechanisms that do not involve aryl radicals, *e.g.*, mechanisms (3) and (7) as against (1) and (5). This

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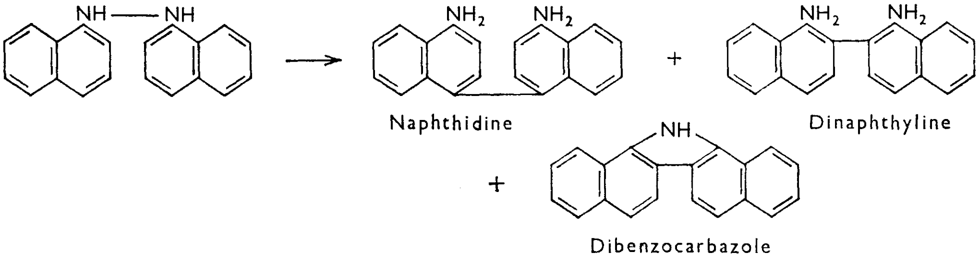
[5] Lange, D.R.-P., 78,225; " Friedlander," Vol. IV, p. 1016.
[6] Hodgson, Leigh, and Turner, *J.*, 1942, 744; Hodgson, *J.*, 1948, 348.
[7] Saunders and Waters, *J.*, 1946, 1154.
[8] Holt and Hopson-Hill, *J.*, 1952, 4251.

was because we could not detect any formation of 1,1′-binaphthyl, although biaryl formation is common in diazo-reductions generally, and is known within the field of reductions by Lange's sulphite method. Blank tests showed that 1,1′-binaphthyl could have been detected in traces by the methods of column chromatography we employed, because of the ease of its elution and its powerful fluorescence in solution.

Our method of determining the orientation of deuterium in the azo-compounds was to reduce them with zinc and ammonium chloride to the hydrazo-derivatives, then to rearrange these with perchloric acid in aqueous dioxan as usual, and to separate the three rearrangement products, formulated below, as in a gravimetric analysis to determine product composition (Part I [1]).



The content of deuterium in the separate rearrangement products, on comparison with that in the original hydrazo-compound, will determine the orientation of the deuterium in the latter. If the hydrazo-compound contains x% of 2 of its 16 atoms of hydrogen in the form of deuterium, the naphthidine contains y% of 2 atoms, and the dinaphthyline and dibenzocarbazole each contain z% of 2 atoms—2 in 16 in the one case, and 2 in 13 in the other—then $(x - y)$% will be the deuterium content of the 4- and 4′-positions in the original hydrazo-compound, and $(x - y)/x$ will be the fraction of the deuterium having that orientation. Similarly $(x - z)$% will be the deuterium content of the 2- and 2′-positions, and $(x - z)/x$ will be the fraction of deuterium with that orientation.

A series of results which establish deuterium orientation in this way in samples of 1,1′-hydrazonaphthalene prepared from 2- and from 4-deuterated 1-naphthylamine are given in the Table. They show that all the deuterium derived from 2-deuterated 1-naphthylamine is in positions 2 and 2′ in the hydrazo-product, and similarly that all deuterium deriving from 4-deuterated 1-naphthylamine appears in the 4,4′-positions in the hydrazo-compound.

Orientation of deuterium in 1,1′-hydrazonaphthalenes by comparisons of deuterium content between them and their rearrangement products.

		D-Content (% of 2 atoms per molecule)	
Sample		Mass-spec.	Infrared
From 2-deuterated 1-naphthylamine:			
1,1′-Hydrazonaphthalene		85	—
From this	naphthidine	82	—
	dinaphthyline	~4	<2
	dibenzocarbazole	~3	<2
From 4-deuterated 1-naphthylamine:			
1,1′-Hydrazonaphthalene		66	—
From this	naphthidine	~4	<2
	dinaphthyline	63	—
	dibenzocarbazole	66	—

The mass-spectrometric errors, when multiplied by 8 or 6·5 because of our interest in only 2 out of 16 or 13 hydrogen atoms, are about 3%, and are believed to be rather more at low than at high abundances of deuterium. When the deuterium content was expected to be zero, the mass-spectrometric figure was of about the magnitude of the error, but was always positive. We have tried to determine whether this is significant, with the result that we do not now think that it is. At low deuterium contents, we could secure a little more sensitivity in deuterium analyses by the infrared method: we could thus detect 2% of 2 atoms of deuterium with ease and certainty. We therefore checked in this way, as indicated in the Table, all samples which had given a mass-spectrometric figure doubtfully distinguishable from zero; and none of them contained a sufficient amount of deuterium to be detected by the infrared method. The conclusion thus seems firm that deuterium orientation is quantitatively retained in our reductions of the naphthalenediazonium ions by sulphite.

Experimental.—The hydrazo-compounds were prepared as described in Part IX.[1] Their rearrangements were effected in " 60% " aqueous dioxan by perchloric acid at 0°, as noted in Part IX. The rearrangement products were separated as described in Part I.[1]

The deuterium analyses by mass-spectrometer were made for us by Dr. C. A. Bunton, to whom we are most grateful. His general method of operation has been indicated in Part IX (Section 4.4).

Our infrared analyses for deuterium were based chiefly on the appearance, on deuteration of any of the substances here treated, of strong C–D bands in the deformation region, 10—14 μ. For example, the naphthidine derived from 2,2′-deuterated 1,1′-hydrazonaphthalene had strong C–D bands at 14·0 and 10·9 μ, whilst the dinaphthyline from the 4,4′-deuterated hydrazonaphthalene had a strong band at 13·2 μ.

Though it does not belong to the subject of this Section, because the preparative methods did not involve the reductive coupling of diazonium ions, we may mention that we have similarly checked by infrared analysis the products of rearrangement of the deuterated hydrazobenzenes described in Part X,[1] showing, for instance, that the 4,4′-dideuterohydrazobenzene gave a benzidine containing undetectably little deuterium. These experiments are not described, as their effect was only further to confirm already certain conclusions.

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