1318. *The Rearrangement of Aromatic* N-*Nitroamines. Part V.*[1] *The Acid-catalysed Rearrangements of* N-*Nitro-*1-*naphthylamine and its* N-*Methyl Homologue*

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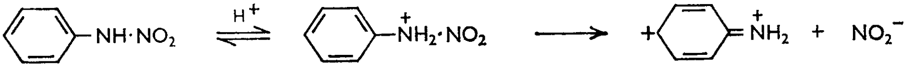
The kinetics and products of the rearrangements of the title compounds and of 2,4-dideutero-*N*-nitro-1-naphthylamine have been studied at various acidities. These reactions closely resemble those of *N*-nitroaniline and probably proceed by a similar mechanism with *C*-nitrites as intermediates. The existence of *N*-nitrites as precursors of the *C*-nitrites seems unlikely and a direct *N*-nitro to *C*-nitrite shift is suggested. There is much evidence against a π-complex mechanism, and a radical-cage mechanism cannot accommodate all the observations.

It has been suggested that the acid-catalysed intramolecular rearrangement of *N*-nitroaniline involves *C*-nitrites and perhaps an *N*-nitrite as intermediates on the path to *C*-nitroamines.[2] Accompanying reactions were considered to derive from disproportionation (reaction 1) to an aromatic dication for which there is independent evidence.[3–5] We have also shown that the rearrangements of *N*-nitro-1-naphthylamine (I) and *N*-methyl-*N*-nitro-1-naphthylamine (II) are intramolecular at widely different acidities.[1] As the extension of studies on the benzene series to the naphthalene series has been very fruitful in the elucidation of the mechanism of the related benzidine rearrangement,[3] we have carried out a kinetic and product study of these two naphthyl compounds. Previous workers had reported that only the 2-nitro-isomers were formed on treatment of (I) and (II) with concentrated acids.[6]



(I)

Results

Kinetics of Rearrangement.—These were studied over as wide a range of concentrations of perchloric acid as possible in 60% dioxan (v/v) at 0°. Good first-order plots and a Hammett dependence of rate on acidity were obtained for (II), but at a particular acidity the rate constant was a function of the initial substrate concentration; *e.g.*, k_1 was approximately doubled by a 5-fold increase in substrate concentration; and the Guggenheim method of calculation had to be used as the " infinity values " drifted with time. Products of a reaction similar to (1) were suspected to be interfering with the method of analysis, and the rearrangements were studied in the presence of an excess of sodium azide. This would destroy any nitrous acid* and would probably couple with the dication to form an aromatic azide; it but does not attack the substrate, its conjugate acid, or the rearrangement products. At a particular acidity, the addition of a 3- to 10-fold excess of azide ion caused k_1 to decrease by about 10%, but the reaction became strictly first-order in substrate and showed the same Hammett-dependence as in the absence of scavenger. Also, the usual graphical method of calculation could now be used as the " infinity " values were constant. Similar phenomena occurred with (I). Results are given in Table 1.

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* Reference to nitrous acid includes any species derivable from this in acidic media.

[1] Part IV, D. V. Banthorpe, J. A. Thomas and D. L. H. Williams, *J.*, 1965, 6135.

[2] D. V. Banthorpe, E. D. Hughes, and D. L. H. Williams, *J.*, 1964, 5349, and references therein.

[3] D. V. Banthorpe, E. D. Hughes, and C. K. Ingold, *J.*, 1964, 2864.

[4] R. Adams *et al.*, *J. Amer. Chem. Soc.*, 1962, **84**, 2058, 2061, 2065.

[5] R. R. Rafos, *Diss. Abs.*, 1964, **22**, 4189.

[6] E. Bamberger *et al.*, *Ber.*, 1894, **27**, 697; 1920, **53**, 2321; 1922, **55**, 3383.

The Hammett slopes for (*a*), (*b*), and (*c*) are 1·31, 1·30, and 1·37 (all ±0·10), respectively. The solvent isotope-effects $(k_{D_2O}/k)_{H_2O}$ were 2·30 for (I), and 1·70 for (II), when measured in 1·75 and 3·25M perchloric acid in 60% dioxan–water at 0° at molar fractions of D_2O of 0·77 and 0·69, respectively. These correspond to effects of about 3·1 and 2·5 for a completely deuterated aqueous fraction of the solvent.[7]

Compound (I) rearranges more readily than (II) despite its considerable acidity, and these results are very similar to those for *N*-nitroaniline [2] and its *N*-methyl homologue,[8] and indicate a similar *A*1-like decomposition of a protonated intermediate formed in pre-equilibrium.*

TABLE 1

Kinetics of rearrangement of the *N*-nitroamines in 60% dioxan–water at 0°

(*a*) [*N*-Methyl-*N*-nitro-1-naphthylamine]$_0$ = 1·0 × 10^{-3}M; [NaN_3]$_0$ = 0

[$HClO_4$] (M)	1·26	1·48	1·75	2·01	2·27	2·49	2·76	2·98	3·24
10^3k_1 (sec.$^{-1}$)	0·032	0·050	0·106	0·215	0·422	0·848	1·73	3·45	5·07

(*b*) [*N*-Methyl-*N*-nitro-1-naphthylamine]$_0$ = 1·0 × 10^{-3}M; [NaN_3]$_0$ = 3·0 × 10^{-3}M

[$HClO_4$] (M)	1·85	2·38	3·25
10^3k_1 (sec.$^{-1}$)	0·098	0·48	4·00

(*c*) [*N*-Nitro-1-naphthylamine]$_0$ = 0·57 × 10^{-3}M; [NaN_3]$_0$ = 2·3 × 10^{-3}M

[$HClO_4$] (M)	0·995	1·25	1·49	1·75	1·99	2·25
10^3k_1 (sec.$^{-1}$)	0·036	0·079	0·197	0·437	0·762	1·77

Products of Rearrangement.—Side-reactions, including tar formation, accompany the rearrangements of both (I) and (II), but are less important in more concentrated acids. Such disproportionation is more extensive for (I) and in the absence of azide ion much tar and 8 yellow bands of comparable intensity can be resolved from the reaction mixtures by chromatography on alumina. However, our tracer work has shown that even under such conditions the 2- and 4-nitro-substituted rearrangement products are not formed intermolecularly.[1] In the presence of azide or of urea, only these two products, together with less than 1% of an unidentified nitro-isomer and a trace of tar are formed, and the recovery of rearrangement products is increased. Some results are given in Table 2 for compound (II). Compound (I) shows similar trends.

TABLE 2

Products of rearrangement of compound (II)

[Acid] (M)	1·50 *	1·85 *	2·38 *	3·00 *	16·1 †
Recovery (%), no NaN_3	69	60	80	91	86
Recovery (%), NaN_3 added	78	80	90	91	92

[(II)]$_0$ = 1 × 10^{-3}M; [NaN_3]$_0$ = 5 × 10^{-3}M.

* $HClO_4$ in 60% dioxan–water at 0°. † H_2SO_4 in water at 0°.

Below about 2·5M-acid, any nitrous acid generated by disproportionation destroys an equimolar quantity of rearrangement products and the dication presumably forms hydroxyarylamines which decompose to tar. At 3·0M-acid such destruction of products [from both (I) and (II)] was inappreciable during the rearrangement conditions, and a similar situation would be expected at higher acidities.[10, 11] Nevertheless, the addition of azide ion significantly altered

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* Orton reported general acid catalysis for the rearrangement of certain halogenated *N*-nitroamines,[9] but by this he meant that the reaction was catalysed by any acid as compared to the " specific " catalysis by hydrochloric acid of the rearrangement of *N*-chloroacetanilides. This statement has often been confused with the later Brönsted definitions of these terms. A second-order dependence of rate on acid concentration at low concentrations of mineral acid in acetic acid–water mixtures was also claimed. It is possible, though rather unlikely, that cross-nitration between substrate molecules occurs under these conditions.

[7] K. Wiberg, *Chem. Rev.*, 1955, **55**, 713.
[8] W. N. White *et al.*, *J. Amer. Chem. Soc.*, 1961, **83**, 2024; 1964, **86**, 1517.
[9] K. J. P. Orton, *Chem. News*, 1912, **106**, 236; *Report. Brit. Assoc.*, 1912, 117.
[10] B. C. Challis, Ph.D. Thesis, London, 1960.
[11] E. Kalatzsis, Ph.D. Thesis, London, 1963.

the product yields over ranges extending to quite high acidity. The total recovery of rearrangement products was determined in only a few instances, but the ratio of 2- to 4-nitro-isomers (for the determination of which a particularly convenient analytical method was available) was measured over a wide range, and the results are summarised in Table **3**. Several measurements were made in each of the ranges of acidity shown.

As a specific example, in 12·5M-sulphuric acid at least 18% of the reaction of (II) leading to the 4-isomer was diverted in the absence of azide ion, although we know [11] that *N*-nitrosation is negligible under these conditions. These results illustrate that the true rearrangement can only be isolated in the presence of scavengers, and we have shown that azide ion reacts with neither the substrate nor the rearrangement products at the acidities used.

The mode of destruction of rearrangement products is obscure. Presumably nitrous acid is not implicated, and the only culprit seems to be the aromatic dication, which we believe also to be scavenged by azide ion. Certainly no nitrous acid, which is probably formed in the fraction of reaction not leading to rearrangement, can be detected over wide acidity ranges (see next section). As this nitrous acid does not attack the substrate (as shown by experiments detailed in the Experimental section, and by the absence of nitrate ion which would be generated, as the naphthyldiazonium nitrate, by this reaction [12]) and as it does not react with the aromatic dication to form *C*-nitroso- or *C*-nitro-arylamines,[1] this species must react with products of reaction of the dication in some undetermined fashion, perhaps to add to the complexity of the tars.

TABLE 3

Products of rearrangement

			2-Isomer (%) *	
Compound	Acid range	Conditions	Without azide	With azide †
(II)	0·5—10·3M-H_2SO_4	A, B	73—85	—
,,	7·6—17·7M-H_2SO_4	C	91—99	77 (at 12M)
,,	1·9—9·7M-H_2SO_4	A, D	69—77	64—72
,,	2·4—11·9M-HCl	D	73—77	69—73
,,	Glacial AcOH	E	35	—
(I)	3·2M-$HClO_4$	F	79	76
,,	2·5—15M-H_2SO_4	C	85—82	78—71
,,	16M-H_2SO_4	G	84	84
,,	18·2M-H_2SO_4 ‡	C	—	98

A = 5 ml. EtOH added to 25 ml. acid to ensure solubility at 0°. B = 20 ml. EtOH added to 25 ml. acid to ensure solubility at 0°. C = No EtOH added, at 0°. D = 10 ml. EtOH added to 25 ml. acid to ensure solubility at 0°. E = No EtOH added, at 20°. F = 60% dioxan–water at 0°. G = No EtOH added, at −20°.

* The percentage of the 2-isomer in the rearrangement products: the balance is the 4-isomer. † 2—5M Excess of azide over substrate. ‡ In 98% H_2SO_4 (18·2M), no reaction occurred with (II) in the absence of azide, but a few percent of the 2-isomer was formed on addition of scavenger. Compound (I) gave a small yield of almost entirely the 2-isomer in the presence of additive.

Investigation of the Side Reactions and Possible Intermediates.—The nature of the side reactions was studied and attempts were made to detect certain likely intermediates. Such investigations provide information concerning possible mechanisms (see Discussion and ref. 2).

(*a*) *Disproportionation products.* Less than 1%, if any, of reaction leading to the amine formed from the denitration of (I) and (II), or to benzidine-like products (such as would result from the dimerisation of anilino-radicals generated as intermediates in the rearrangement) could be detected in the range 1—18M-acid with various acids (HCl, $HClO_4$, H_2SO_4) in the presence or absence of sodium azide. Either no nitrate ion or only traces, corresponding to less than 0·1% decomposition of the substrate, could be detected over similar ranges for (I) and (II). In the absence of azide ion, less than 1% disproportionation to nitrous acid was detected in the range 1—18M-acid for (I); and 1—10M-acid for (II); but for the latter compound considerably more occurred at greater acidities, *e.g.*, 10—15% at 12·5M- and 68—75% at 18·2M-sulphuric acid. Disproportionation under the latter conditions could generate a dication which deprotonates to form *N*-methylene-1-naphthylamine on dilution, and subsequently yields tars and polymers in the presence of nitrous acid. However, blank experiments with the

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[12] A. H. Lamberton, *Quart. Rev.*, 1951, **5**, 75.

authentic azomethine and concentrated sulphuric acid containing sodium nitrite did not give these characteristic products.

(*b*) Attempts to detect radicals. Deep maroon colours, not attributable to rearrangement products, developed during and after rearrangement of (I) and (II). These were discharged by addition of hydroquinone, ascorbic acid, *p*-cymene, and azide ion, and partly so by benzoin and cyclohexene, to give the yellow colour characteristic of *C*-nitro-arylamines. Similar colours during other rearrangements have been attributed to side reactions, probably oxidation.[2] They are not necessarily evidence for radical or mesomeric intermediates.

The addition of radical scavengers such as cyclohexene had no effect on the rate of rearrangement or on the percentage recovery or composition of the rearrangement products. But additives that could destroy nitrous acid, *e.g.*, hydroquinone or ascorbic acid, reduced the rate of rearrangement by 10—20%; *i.e.*, they had the same effect as sodium azide.

Acrylonitrile and methyl methacrylate were not polymerised when added to rearranging mixtures, and no electron spin resonance signals attributable to likely radicals could be detected from rearrangements in 1M-, 2M-, or 18M-sulphuric acid. In the last experiments, a signal due to carbon, formed by charring, was recorded. Electrolysis of the hydrochloride of (II) in a silica cell with platinum electrodes, carried out between the pole-pieces of the magnet, did not generate signals of the type characteristic of intermediates of the radical-cage mechanism: [13] a broad signal with no fine structure was detected.

(*c*) Attempted preparation of *N*- and *C*-nitrites. *N*-Nitrites have been previously proposed as intermediates.[2] Such compounds have never been isolated, and *N*-nitroamines cannot significantly occur in this isomeric form, for they are quite stable to base: but there is some spectroscopic evidence [14] for such species in oxides of nitrogen and some indirect evidence [15] for their occurrence as transient intermediates in the formation of *N*-nitro-derivatives by the nitrosation of certain oximes.* Attempts were made to synthesise these compounds or the products of their ready rearrangement. Treatment of *N*-phenylhydroxylamine or *N*-ethylphenylhydroxylamine with nitrosyl chloride in pyridine under various conditions gave only intractable red tars and products isomeric with the starting materials: no *N*-nitrite or product of its decomposition could be isolated. However, dimethylaniline oxide or its hydrochloride reacted under the above conditions or with concentrated sulphuric acid containing sodium nitrite to give about 80% of *p*-nitrodimethylanilide and traces of the *o*-isomer. These must have arisen *via* transient formation of the *N*-nitrite (followed by disproportionation and intermolecular nitration?) but the low yield of *o*-isomer suggests that such an *N*-nitrite is probably unimportant in the intramolecular rearrangement process, although the influence of the two *N*-methyl groups in directing disproportionation rather than intramolecular rearrangement cannot be convincingly assessed,† and steric influences could lead to the preferential conversion of a 2-nitrite into a 4-nitrite rather than into a 2-nitro-compound.

Model systems for the *C*-nitrites (containing a cyclohexadienyl system) which are believed to exist as rearrangement intermediates, are not easy to devise; but reaction of nitrosyl chloride and phenols was reported to give benzo- and chloro-quinones very similar to the side-products obtained from certain *N*-nitroamine rearrangements.[17] Accordingly, attempts were made to synthesise aromatic *C*-nitrites to see if they rearrange to nitro-derivatives or disproportionate to phenols: such compounds are not recorded in the literature, as far as we are aware. Phenols of widely differing acidity, 1-naphthol, *p*-nitrophenol, *p*-methoxyphenol, and *s*-tribromophenol were treated with nitrosyl chloride in pyridine, under various sets of conditions, but only red tars or ill-defined red compounds, probably substituted phenols contaminated with nitrosopyridines, were isolated.

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* Cautious acidification of the sodium salt of a 2,4,6-trisubstituted *N*-nitro-amine (which could not readily rearrange) gave a colourless form of *N*-nitroamine which changed to a yellow form on standing.[16] The yellow material was formed on rapid acidification. This could be an example of the less stable nitrito-isomer being formed preferentially in a kinetically-controlled process, but ultimately reverting to the more stable nitro-form.

† The introduction of an *N*-methyl group into *N*-nitroaniline greatly increases the amount of disproportionation.[2,8]

[13] D. H. Geske and A. H. Maki, *J. Amer. Chem. Soc.*, 1960, **82**, 2671.
[14] W. G. Fateley, H. A. Bent, and B. Crawford, *J. Chem. Phys.*, 1959, **31**, 204.
[15] J. W. Suggett, C. S. Meyers, and G. F. Wright, *J. Org. Chem.*, 1947, **12**, 373.
[16] K. J. P. Orton, *J.*, 1902, **81**, 490, 806, 965.
[17] W. A. Tilden, *J.*, 1874, **27**, 851.

Reactions of 2,4-*Dideutero*-N-*nitronaphthylamine*.—We have recently shown [2] that product isotope-effects of different values occur for *o*- or *p*-deuteration of *N*-nitroaniline, and that the existence of such effects is incompatible with mechanisms incorporating π-complexes or caged radicals.

N-Nitronaphthylamines deuterated solely in the 2- or 4-position were unavailable, but any differential isotope-effect between these two positions should be measurable in 2,4-dideutero-compounds. Results for the 2,4-dideutero-derivatives of (I) are given in Table 4. The difference of rate-constant between the two isotopic forms is within the experimental error, but the effect on the proportions of rearrangement products is probably significant and there is a large effect on the total proportion of reaction leading to rearrangement. If no isotope effect on the side reactions is assumed, product isotope-effects (k_H/k_D) of 4·3 and 8·3 on the total fraction of reaction leading to rearrangement can be calculated at the two acidities.

TABLE 4

Kinetics and products * of normal and di-deuterated *N*-nitro-1-naphthylamine

	Normal compound	Dideutero-compound
(*a*) k_1 (sec.$^{-1}$) in 60% dioxan at 0°		
[H^+] = 1·97M; [N_3^-] = 2·3 × 10^{-3}M	8·0 × 10^{-4}	7·7 × 10^{-4}
(*b*) In 3·0M-$HClO_4$; 60% dioxan at 0°		
Rearrangement (%)	91	69
2-Isomer (%)	75	77
(*c*) In 15·6M-H_2SO_4; at 0°		
Rearrangement (%)	93	61
2-Isomer (%)	84	87

* The percentage of 2-isomer in the rearrangement fraction is recorded. The balance is the 4-isomer.

DISCUSSION

Various *N*-nitroamines have been shown [1,2] to rearrange intramolecularly over a wide acidity range and these compounds clearly possess some property denied to other *N*-substituted arylamines (*e.g.*, *N*-chloro-, nitroso-, and hydroxy-compounds) which react intermolecularly.[18] Three routes have been suggested; a " cartwheel," [2,19] a radical-cage,[8] and a π-complex mechanism,[20] but only the first accounts for the unique behaviour of *N*-nitroamines. On this scheme the intramolecularity can be attributed to rearrangement through the intermediacy of *o*- or *p*-*C*-nitrites formed by means of strainless, cyclic transition states, and there is no reason to believe that the mechanism changes in different ranges of acidity.

Detailed results for *N*-nitroaniline could only be accommodated on the " cartwheel " mechanism,[2] and the close similarity of the rearrangements of (I) and (II) to this previously studied example, strongly suggest a similar route. The kinetic form, trends and type of rearrangement products, intramolecularity, lack of detectable radical intermediates, nature of side-products and occurrence and size of isotope effects are all very similar for the three substrates. A full interpretation of the previously obtained results in terms of the " cartwheel " mechanism has been given,[2] and the routes of formation of the various side-products—diazonium salts, iminoquinones with rearranged substituents, imines, etc.—that have been reported for other *N*-nitroamine rearrangements have been outlined.[21] The occurrence of such products is consistent with the cartwheel or radical-cage mechanisms, but not with the π-complex theory.

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[18] C. K. Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1953, ch. 11.

[19] E. D. Hughes and C. K. Ingold, *Quart. Rev.*, 1952, **6**, 34.

[20] For the most recent summary see M. J. S. Dewar in de Mayo's " Molecular Rearrangements," Academic Press, New York, 1963, vol. 1, p. 295.

[21] J. A. Thomas, Ph.D. Thesis, London, 1964, p. 44.

The large deuterium-isotope effect on the competition between rearrangement and the side reactions shows that the latter must largely arise from steps other than an initial disproportionation as in reaction (1). Presumably an intermediate on the rearrangement pathway is partitioned between the two processes and no isotope effect occurs in the branch leading to side products. The aromatic dication and nitrous acid thus probably arise from disproportionation of a *C*-nitrite rather than an *N*-nitrite. The experiments with amine oxides (see section on side reactions) also make the existence of *N*-nitrites as rearrangement intermediates seem unlikely; as previously suggested,[2] a direct *N*-nitro to *C*-nitrite shift is probable, and this is quite feasible stereochemically.

The isotope effect caused by 4-deuteration is greater than that caused by 2-deuteration, as for *N*-nitroaniline. But unlike the latter example, an effect was detected in concentrated acid. As previously pointed out,[2] the radical and π-complex mechanisms cannot accommodate an isotope effect on products. The effects are, however, qualitatively what would be expected on the cartwheel theory,[2] although exact calculation of the effects for individual 2- and 4-deuteration cannot be made from our experimental results.

The main evidence on which the caged-radical theory is based is the trapping of the 10—15% of the radicals that had supposedly escaped from the solvent cage, either by added scavengers or by reduction (to nitrous acid and the amine from the denitration of the substrate).[8] These observations are, however, also consistent with the trapping of the fragments of the disproportionation reaction (1): no reduction of the dication to amine takes place under our conditions (0°) but it might well occur at the higher temperature (40°) of the former experiments.

Any anilino and nitrogen dioxide radicals formed within a solvent cage which react after repeated collisions[8] would be expected to produce a statistical distribution of 2- and 4-isomers for benzene derivatives, *i.e.*, 67 and 33%, and the product ratios should be almost independent (when allowance is made for available positions) of the structure of the substrate: this is close to the observed values (61%, 39%) for *N*-methyl-*N*-nitroaniline, but appreciably different for the values recorded for *N*-nitroaniline.[2] For the naphthalene derivatives an isomer ratio of 50% : 50% would be predicted by the radical theory, quite different from that observed.* The dependence of isomer ratio on solvent is also difficult to accommodate on this theory, and isomers formed by migration of the nitro-group to the 5- or 7-position should be found. In practice only the 2- and 4-nitro-isomers and a trace of a third, probably the 5-isomer, are present: the latter probably arises from three " cartwheels " *via* the 2- and 4-*C*-nitrites. If *N*-nitroamines reacted through caged-radical mechanisms, there seems no reason why *N*-chloro- and especially *N*-nitroso-amines should not follow suit and so rearrange intramolecularly, rather than intermolecularly.

The lack of appreciable migration to the 5-, 6-, 7-, or 8-positions of the naphthalene nucleus is also inconsistent with the π-complex mechanism; *e.g.*, rearrangement of (I) in strong acids by this scheme would be expected to form similar products, mainly the 5- and 8-nitro-isomers, as obtained by nitration of 1-naphthylamine under similar conditions,[22] especially as this nitration, in common with other electrophilic substitutions (and indeed with almost all organic reactions) are considered by the originator of this theory to proceed *via* a π-complex. The π-complex mechanism also cannot explain the strict intramolecularity of the *N*-nitroamine rearrangements as compared with the exclusive intermolecular nature of those of other *N*-substituted amines, particularly *N*-phenylhydroxylamines and *N*-nitrosoamines.

Most of the available evidence summarised here and elsewhere[2] is completely inconsistent with the π-complex theory, and whereas a considerable body of data can be accommodated by a radical-cage mechanism, there is much that is incompatible with it. The

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* The protagonists of the radical theory have suggested multiple collisions before reaction in the solvent cage. Alternatively, one could argue that radical pairing would occur at the encounter rate: now, an overwhelming preponderance of 2-isomer would be expected at all acidities.

[22] H. H. Hodgson and W. Davey, *J.*, 1939, 348.

cartwheel theory does, however, account for all the data. We hope to test this conclusion by the study of 9-amino-*N*-nitroanthracene. If the cartwheel mechanism applies, this should not rearrange, but should either remain unchanged or disproportionate on treatment with acid. In the event of π-complex or radical routes, normal rearrangement should occur.

EXPERIMENTAL

(a) *Preparations.*—Compounds (I) and (II) were prepared as previously described.[1]

2,4-*Dideutero*-1-*naphthylamine.* 1-Naphthylamine hydrochloride (7 g.) was heated with deuterium oxide (50 ml.; 99·8% w/w) in a sealed tube at 106° for 7 hr. and the extracted deuterated amine converted into the sodium salt of the *N*-nitroamine. Mass-spectrometry of the *N*-nitro-compound and *C*-nitro-isomers formed on rearrangement showed that the sodium salt consisted of 92% 2,4-dideutero-, 2% 2-deutero-, 2% 4-deutero-, 1% monodeutero-, and 3% monodeutero-isomers with the tracer at other ring positions. These analyses prove also the absence of deuterium loss by exchange for protium during the conversion into the sodium salt or in the acidic conditions of the rearrangement. Elemental analysis showed the compound to be *ca.* 95% pure, but it was not recrystallised as this led to slight decomposition. The m. p. was 120°.

Three attempts were made to prepare naphthylamine labelled uniquely in one position.* (*a*) The sodium salt of 1-naphthylamine-2-sulphonic acid was distilled with deuterated calcium hydroxide;[23] and (*b*) 1-naphthylamine-4-sulphonic acid was reduced with sodium amalgam in alkaline deuterium oxide in an atmosphere of carbon dioxide;[24] or (*c*) in the lead anode-chamber of a cell containing sodium carbonate in deuterium oxide, with a current density of 0·04 amp./cm.^{2} for 1½ hr.[25] All methods gave 20—55% yields of 1-naphthylamine, but (*a*) and (*b*) gave unspecific labelling, and (*c*) gave a product with only about 0·33 g.-atom of deuterium per mole in the aromatic ring. Presumably radical processes had led to these results. Deuterium was estimated in these products by combustion in a Pregl-type cracking-line and infrared examination of the resulting water. The height of the peak at 3·95 μ was measured on a Grubb–Parsons S2 spectrometer, using 0·1 mm. sapphire cells, and the percentage of deuterium oxide present was estimated from a calibration graph. Solutions were diluted to contain 0·1 to 0·8% (w/w) deuterium oxide in which range the calibration graph was linear.

N-*Methyl*-4-*nitro*-N-*nitroso*-1-*naphthylamine.* This *amine* was formed on dilution of the product of reaction of equimolar parts of sodium nitrite and the 4-nitroamine in 2·27M-perchloric acid in 60% aqueous dioxan at 0°; yield 100%, m. p. (from ethanol) 65—66° (Found: C, 57·2; H, 3·9; N, 17·5. $C_{11}H_9N_3O_3$ requires: C, 57·1; H, 3·9; N, 18·2%).

N-*Methylene*-1-*naphthylamine.*[26] 1-Naphthylamine (4·7 g.) in acetic acid (70 ml.) reacted with 40% aqueous formaldehyde (2·4 g.) at 20°. A white precipitate was immediately formed which polymerised on attempted determination of melting point. Attempts at recrystallisation also led to polymerisation and decomposition (Found: C, 85·3; H, 5·7; N, 9·3. Calc. for $C_{11}H_9N$: C, 85·1; H, 5·8; N, 9·0%).

Attempted Preparation of N- *and* C-*Nitrites.*—The chosen phenol (0·5 g.) was dissolved in sodium-dried ether (50 ml.) containing a molar proportion of pyridine, and nitrosyl chloride was passed until no more was absorbed. The solution was filtered, diluted with water, and the ether extract examined. Experiments were performed at 20° and −20° and also in the presence of a four-molar excess of pyridine. 1-Naphthol and *p*-methoxyphenol gave red tars, soluble in dilute alkali, that could have contained *C*-nitrites or nitro-phenols, but no compound could be characterised. *S*-Tribromophenol gave a red solid, apparently an ill-defined polymer, and *p*-nitrophenol did not react.

Nitrosyl chloride was similarly passed through solutions containing *N*-phenylhydroxylamine[27] (1 g.) or its *N*-ethyl homologue[28] and pyridine (2 ml.) in ether (50 ml.). The former

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* This could be achieved by reductive deamination of suitable nitronaphthyldiazonium ions with deuterated hypophosphorous acid and reduction of the nitro-group, but the method is expensive and very time-consuming.[3]

[23] Elseviers' Encyclopaedia of Organic Chemistry, Amsterdam, 1955; vol. 12B, p. 5029.
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[27] G. H. Coleman, C. M. McCloskey, and F. A. Stuart, *Org. Synth.*, 1945, **25**, 80.
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compound yielded an intractable brown tar, but the latter gave a red oil which, after purification on alumina, was characterised as an isomer of the starting material (Found: C, 70·8; H, 6·8; N, 10·0. Calc. for $C_8H_{11}NO$: C, 70·0; H, 8·0; N, 10·2%).

Nitrosyl chloride with dimethylaniline oxide or its hydrochloride[29] formed *NN*-dimethyl-*p*-nitroaniline in 80% yield under the same conditions (Found: C, 57·4; H, 5·9; N, 16·7. Calc. for $C_8H_{11}N_2O_2$: C, 57·5; H, 6·6; N, 16·8%). This was characterised by comparison of its infrared spectrum with an authentic specimen. Small amounts of the *o*-isomer were detected by chromatography on alumina. An 80% yield of the *p*-isomer also resulted from the treatment of the amine oxide (1 g.) with 98% sulphuric acid (10 ml.) containing sodium nitrite (2 g.) at 0°.

Products of Rearrangement.—The products were extracted from the reaction mixture and the ratio of the 2- and 4-nitro-isomers, which in total accounted for over 99% the rearrangement fraction, was determined by a paper-chromatographic technique.[1] For compound (II) the extract (*ca.* 0·3 ml.) was spotted along the base-line and an elution method was applied as previously described.[1] Good separation (*e.g.*, R_F values for the denitrated substrate, 2-isomer, and 4-isomer of 1·00, 0·97, and 0·11, respectively) was achieved, the papers were dried, the bands cut out and eluted with 95% ethanol–water, and the optical densities measured on a Unicam S.P. 500 spectrophotometer. Spectroscopic data are given in Table 5. Control experiments indicated that the method was reliable to ±1% actual values. Analysis of the products of rearrangement of (I) was similar but the moving phase was a mixture of ether 35%, and light petroleum (b. p. 40—60°) 65%.

The percentage of the reaction leading to rearrangement was determined by (*a*) product-isolation from column chromatography, (*b*) quantitative paper-chromatographic analysis, or (*c*) comparison of the optical density of " infinity " tubes at the isosbestic point of rearrangement products (as calculated from the intercept of a Guggenheim plot), with that calculated on the assumption of 100% rearrangement.

TABLE 5

Spectrophotometric results for 2- and 4-nitro-isomers

Compound	Solvent	$\lambda_{max.}$	$\lambda_{isosbestic}$ *	$10^{-4}\varepsilon_{440}$	$10^{-4}\varepsilon_{462}$	$10^{-4}\varepsilon_{475}$
2-Nitro-isomer from (II)	60% Dioxan	462	475	0·63	0·72	0·69
4-Nitro-isomer from (II)	,,	440		2·10	1·50	0·69
				$10^{-4}\varepsilon_{452}$	$10^{-4}\varepsilon_{432}$	
2-Nitro-isomer from (II)	95% EtOH	452	—	10·72	—	—
4-Nitro-isomer from (II)	,,	432		—	2·03	—
				$10^{-4}\varepsilon_{434}$	$10^{-4}\varepsilon_{433}$	
2-Nitro-isomer from (I)	,,	434	—	0·93	—	—
4-Nitro-isomer from (I)	,,	433	—	—	1·83	—

* All wavelengths in mμ.

Side Reactions.—Denitrated substrate and benzidine-like products were sought by paper chromatography.[2] Nitrate ion was detected by the colorimetric test with diphenylamine after nitrite had been removed with sulphanilic acid. At low acidities, tar prevented the satisfactory determination of nitrous acid by diazo-coupling, but nitrogen oxides could be aspirated in a stream of nitrogen, collected in alkali, and spot tests with sulphanilic acid and 1-naphthylamine then applied.

Nitrite and nitrate were also determined polarographically. In concentrated acids NO^+ and NO_2^+ give a common wave at the beginning of the polarogram, and for a given capillary, head of mercury, solvent, potential difference, and temperature, the diffusion current is proportional to the sum of the concentrations of these species. NO^+ is polarographically active down to 1M-acid (nitrite ion is in equilibrium with traces of NO^+ which is reduced at the falling-drop electrode) but NO_2^+ is only active above 15M.[30] Thus nitrite could be estimated (in tarry solutions, if necessary) in the range 1—18M-acid; and nitrate could be estimated above 15M-acid by measuring the diffusion current in the highly acid solution, and then diluting accurately to about 12M-acid and repeating the measurement. Any difference in the diffusion

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current in the two measurements, when allowance was made for the dilution factor, was due to NO_2^+. A Cambridge recording polarograph was used, and all polarographic waves were referred to a standard mercurous sulphate electrode made up in sulphuric acid of the same concentration as was present in the solution to be tested. All solutions were made oxygen-free in the usual manner. The mean diffusion current at $-0{\cdot}1$V was determined at the various acidities and the concentrations were read from a calibration graph, which was linear in the range 10^{-4}—10^{-5}M-nitrate or -nitrite. As expected, the addition of azide ion immediately destroyed the polarographic wave.

Tests for radicals were made by conducting reactions between the pole-pieces of a Varian E.S.R. spectrometer, and all solutions were degassed and made up at 0°. Polymerisation tests were made with a 40-molar excess of the monomer present. Experiments were restricted to acidities such that acid-catalysed polymerisation did not occur, and the reaction solutions were filtered through black filter-paper to enable any polymer formed to be more readily detected. Much disproportionation of (II) occurred on solution in 18·2M-sulphuric acid and, on dilution at 0°, an orange solid which decomposed to tar was thrown down. When the reaction was carried out in a Thunberg tube and the dilution was conducted in the absence of oxygen, a dark brown polymer was isolated which possessed no simple molecular formula and was too involatile for mass-spectrometric examination. When *N*-methylene-1-naphthylamine was added to concentrated acid containing sodium nitrite, a quite different green tarry material resulted.

A series of experiments to give information about attack of nitrous acid on the substrate was carried out. Over a range of acidities the profiles of the ultraviolet spectra in the range 250—600 mμ of solutions of (I) and (II) with an excess of sodium nitrite added were nearly identical with those of a superimposition of the spectra of the 2- and 4-nitro-isomers, in proportions corresponding to the rearrangement products and also treated with sodium nitrite at the same acidity. This suggests that (I) and (II) rearrange before they are attacked by nitrous acid. Additions of large excesses of sodium nitrite could not divert the decomposition of (I) and (II) from rearrangement products, which were then promptly nitrosated.

Kinetics.—These were studied in 60% dioxan–water mixtures, the solvents being purified, degassed, and stored under nitrogen. Aliquot portions were taken using a jacketed pipette, quenched in alkali, and the optical density was measured at 440 mμ for reactions of (II). First-order rate constants were calculated by the Guggenheim method, because side reactions affected the " infinitely " values for the slower runs. Good linear plots were obtained and k_1 agreed to ±2% within duplicate runs and when calculated (if possible) by both the Guggenheim and the normal graphical methods at 440 mμ or at the isosbestic point. For the rearrangement of (I), optical density was measured at 437 or 470 mμ; first-order rate constants calculated at both wavelengths were identical for a particular acidity.

We thank Sir Christopher Ingold for helpful discussions; Dr. J. Pannell of Imperial Chemical Industries Limited (Plastics Division) for the e.s.r. measurements; Dr. J. Masek of the Polarographic Institute, Prague, for advice concerning polarography; and the D.S.I.R. for a research studentship (to J. A. T.).

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[*Received, June* 23*rd*, 1965.]