Mechanism of Benzidine and Semidine Rearrangements. Part XXVII.[1] Kinetics, Products, and Solvent Isotope Effects for Acid-catalysed Rearrangements of Some *N*-Substituted Hydrazoarenes

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The acid-catalysed rearrangements and accompanying reactions of *NN'*-dimethylhydrazobenzene at acidities convenient for kinetic measurements were first order in acid and had a solvent isotope effect (k_{D_2O}/k_{H_2O}) of 2·3. A large proportion of products (*ca.* 38%) comprised compounds, *e.g. o*-benzidine, semidines, fission amine, and tar, that are not typically found in acid-catalysed reactions of hydrazoarenes but the reaction was intramolecular and addition of scavengers provided no evidence for radical intermediates. Acid treatment of *NN*-dimethyl-1,1'-hydrazonaphthalene, *N*-methylhydrazobenzene, and *N*-acetylhydrazobenzene promoted reactions first, second, and second order respectively in acid with solvent isotope effects of 2·3, 4·0, and 3·1. No unusual products were now formed. The kinetic form, products, and isotope effects of these reactions are discussed on the basis of the previously suggested polar transition state mechanism.

THERE is considerable evidence that with one exception the acid-catalysed rearrangements of hydrazoarenes that have been investigated are intramolecular and radical intermediates are not involved.[2,3] The exception is tetraphenylhydrazine, for which there is chemical and physical evidence that suggests an intermolecular radical mechanism.[4-6] The latter reaction also differs from the rest of the class in that considerable amounts of fission amine (diphenylamine) and semidines were formed, whereas fission amines are never formed on acid treatment of hydrazoarenes except when a disproportionation process occurs which yields equivalent amounts of azo-compounds[3] (a reaction not possible for tetraphenylhydrazine). Semidines are rarely found as main products and only then if substituents block the 4-positions of the aromatic rings.

Brief reports that acid treatment of *NN*-dimethylhydrazobenzene gave considerable amounts of semidines

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[1] Part XXVI, D. V. Banthorpe and J. G. Winter, *J.C.S. Perkin II*, 1972, 874.

[2] D. V. Banthorpe, *Topics Carbocyclic Chem.*, 1969, **1**, 1.

[3] D. V. Banthorpe and J. G. Winter, *J.C.S. Perkin II*, 1972, 868.

[4] G. S. Hammond, B. Seidel, and R. E. Pincock, *J. Org. Chem.*, 1963, **28**, 3275.

[5] P. Welzel, *Chem. Ber.*, 1970, **103**, 1318.

[6] F. A. Neugebauer and S. Bamberger, *Chem. Ber.*, 1972, **105**, 2058.

and fission amines[7] and that photolysis of the same compound gave the same products in reactions that probably involved radicals,[8] led us to examine this substrate and certain other *N*-substituted hydrazoarenes for the occurrence of acid-catalysed radical mechanisms of intermolecular rearrangement.

The only previous studies on rearrangements of *N*-substituted hydrazoarenes in addition to those mentioned above are semi-quantitative product analyses from reactions of *NN'*-dimethylhydrazobenzene,[9] *N*-methylhydrazobenzene,[10] and *N*-acetylhydrazobenzene[11,12] and a very brief kinetic investigation on *N*-methylhydrazobenzene.[13]

RESULTS

(a) *Kinetics.*—All kinetic runs were carried out using 60% (v/v) dioxan–water as solvent and with the initial concentration of the substrate *ca.* 10^{-3}M. Pseudo first-order rate constants (s^{-1}) are recorded for the disappearance of *NN'*-dimethylhydrazobenzene (I), *N*-methylhydrazobenzene (II), *N*-acetylhydrazobenzene (III), and *NN'*-dimethyl-1,1'-hydrazonaphthalene (IV) in Table 1. All runs were carried out at an ionic strength (μ) buffered by the addition of lithium perchlorate except for those involving (III); for these the acidities were above those at which a formal μ can be taken to control the properties of solutions independent of the nature of the ionic composition and so μ was not here kept constant in the different runs.

TABLE 1

Kinetics of reaction of *N*-substituted hydrazoarenes in 60% (v/v) dioxan–water

Substrate (I)	Rates at 0°; catalyst perchloric acid; μ 0·100					
$10^3[\overset{+}{H}]$/M	9·5	30·5	49·8	69·7	100	Order [a]
$10^5\ k_4/s^{-1}$	11·0	37·2	61·2	83·2	113	1·03 ± 0·10
Substrate (II)	**Rates at 0°; catalyst perchloric acid; μ 0·32**					
$10^2[\overset{+}{H}]$/M	5·11	8·00	15·1	23·0	32·2	Order [a]
$10^5\ k_4/s^{-1}$	4·37	10·6	39·9	103	175	2·00 ± 0·08
Substrate (III)	**Rates at 25°; catalyst sulphuric acid; μ variable**					
$[\overset{+}{H}]$/M	3·00	3·11	3·36	3·60		Order [a] 2·21 ± 0·09
H_0 (rel) [b]	0·73	0·49	0·25	0·00		
$10^5\ k_4/s^{-1}$	5·62	17·8	70·9	225		
Substrate (IV)	**Rates at 0° in phthalate buffer; μ 0·025**					
pH (corrected) [c]	4·12	3·21	3·10	2·75	2·36	Order [a]
$10^5\ k_4/s^{-1}$	2·60	19·8	25·1	56·3	152	1·02 ± 0·03

[a] See text. [b] Relative H_0 values (see Experimental section). [c] Corrected pH values (see Experimental section).

In addition to measuring the rate of disappearance of (I), measurements at 0·0498- and 0·100M-$\overset{+}{H}$ were made for the rate of formation of 4,4'bismethylaminobiphenyl. Values of $10^5 k_1$ of 24·1 and 46·1 respectively were obtained.

In all cases plots of log k_1 *versus* log $[\overset{+}{H}]$, -H_0, or -pH, as appropriate, were linear and the slopes are in Table 1 under ' order '.

(b) *Products.*—Treatment of compound (I) with 0·100M-$\overset{+}{H}$ under the conditions in Table 1 gave (yields based on substrate consumed): 4,4'-bismethylaminobiphenyl (40%; 4,4'-linkage of substrate); 2,4'-bismethylaminobiphenyl (19%; 2,4'-linkage); 2,2'-bismethylaminobiphenyl (1%); 2,2'-linkage); *N*-methyl-(2-methylaminophenyl)phenylamine (23%; *o*-semidine linkage); *N*-methyl-(4-methylaminophenyl)phenylamine (3%; *p*-semidine linkage); *N*-methylaniline (6%; fission amine); and tar (5%).

Products from treatment of (II) with 0·32M-$\overset{+}{H}$ were: 4-amino-4'-methylaminobiphenyl (76%; 4,4'-linkage) and 2-(or 4-)amino-4'-(or 2'-)methylaminobiphenyl (23%; position of methylation undetermined).

Products from treatment of (III) with 3·00M-$\overset{+}{H}$ were: 4-acetylamino-4'-aminobiphenyl (96%; 4,4'-linkage); 2(or 4)-acetylamino-4'-(or 2'-)aminobiphenyl (2%; position of acetylation undetermined); and 4,4'-diaminobiphenyl (2%; 4,4'-linkage: deacetylated product).

Products from treatment of (IV) at pH 2·36 were: 2,2'-bismethylaminobinaphthyl (52%; 2,2'-linkage); 4,4'-bismethylaminobinaphthyl (35%; 4,4'-linkage); *N*-methyldibenzo[*a*,*i*]carbazole (10%; 2,2'-linkage).

(c) *Solvent Isotope Effects.*—Rate constants of reactions in solvents containing 60% dioxan and the remainder either water or deuterium oxide (v/v) but otherwise in identical conditions are in Table 2. All rate constants are the mean of three determinations.

TABLE 2

Solvent isotope effects for reactions in dioxan–water and dioxan–deuterium oxide [a]

Substrate	[Acid] (H^+ or D^+)/M	T/°C	k_{D_2O} [b]	k_{H_2O} [b]	k_{D_2O}/k_{H_2O}
(I)	$4·98 \times 10^{-2}$	0	14·1	6·12	2·3
(II)	$2·31 \times 10^{-1}$	0	41·3	10·3	4·0
(III)	3·36	25	21·9	7·09	3·1
(IV)	$1·78 \times 10^{-3}$	0	12·9	5·63	2·3

[a] Solvent, acid, temperature *etc.* as in the corresponding entry in Table 1. [b] Rate constant: $10^4\ k/s^{-1}$.

(d) *Intramolecularity.*— *NN'*-Dimethylhydrazobenzene was added to an equimolar quantity of its 2,2',4,4',6,6'-hexadeuteriated homologue and 4,4'-bismethylaminobiphenyl was isolated after treatment of the mixture with 0·100M-$\overset{+}{H}$ under the conditions specified in Table 1. The mass spectrum of this product determined at low (*ca.* 20 eV) ionising potential revealed parent peaks at *m/e* 212 and 218. When allowance was made for peaks at intermediate masses corresponding to the small percentage of incompletely deuteriated substrate and for fragmentation of the parent ion of higher mass number, it was found that there was no detectable peak at *m/e* 215 that would have resulted from cross-over products. Occurrence of a species at this mass corresponding to 2% of the total reaction would have been detected.

In another experiment, 2,4,6-trideuterio-*NN'*-dimethylhydrazobenzene was similarly rearranged and the 4,4'; 2,*N'*; and 4,*N'*-linked products were found to give parent peaks at *m/e* 215 under electron impact unaccompanied by any detectable peaks at *m/e* 218 or 212 due to hexadeuteriated

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[7] W. N. White and E. E. Moore, *J. Amer. Chem. Soc.*, 1968, **90**, 526.

[8] J. F. Sullivan, K. Hailey, and H. J. Shine, *Tetrahedron Letters*, 1970, 2007.

[9] G. Wittig, W. Joos, and P. Rathfelder, *Annalen*, 1957, **610**, 180.

[10] B. Rassow and K. Berger, *J. prakt. Chem.*, 1911 (ii), **84**, 260.

[11] A. Pongratz and K. Scholtis, *Ber.*, 1942, **75**, 138.

[12] D. W. Davies and D. Ll. Hammick, *J. Chem. Soc.*, 1954, 475.

[13] W. N. White and R. Preisman, *Chem. and Ind.*, 1961, 1752.

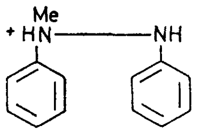
or isotopically normal products respectively. Again, peaks at these mass numbers corresponding to *ca.* 2% of the total reaction would have been detected.

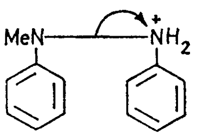
(e) *Experiments using Radical Scavengers.*—The reaction of *NN'*-dimethylhydrazobenzene with 0·100M-$\overset{+}{\mathrm{H}}$ under the conditions previously specified was carried out in the presence of three-fold molar excesses of (a) galvinoxyl and (b) 9,10-dihydroanthracene. The product proportions were unchanged (within ±1% actual value) in each case from those recorded in Table 1.

Rearrangements of the substrate in both 60% (v/v) dioxan–water and 100% dioxan with 0·100M-$\overset{+}{\mathrm{H}}$ as catalyst were also carried out between the pole pieces of an e.s.r. spectrometer, but no signals attributable to radical species could be detected.

DISCUSSION

Kinetics.—The reaction of *N*-methylhydrazobenzene was second order in acid in the solvent (60% dioxan–water) that we have routinely used in these studies. Hydrazobenzene showed the same kinetic form in the same solvent at acidities convenient for kinetic measurements.[14] In contrast, the former compound was reported to react in more aqueous media with orders between one and two in acid, depending on the actual acidity used.[13] An *N*-methyl group slightly increases the basicity of aniline (aniline pK_a 4·58; *N*-methylaniline 4·86: all pK_a values are from ref. 15) and presumably similarly effects hydrazobenzene. Consequently, monoprotonation probably predominantly gives (I) wherein electron release from the methyl group to aid N–N fission cannot occur as in the less favoured species (II): in order to achieve N–N fission and subsequent reaction by the processes that have been previously described in detail[16] a dication must be formed under our conditions, as for hydrazobenzene, by uptake of a second proton.


(I)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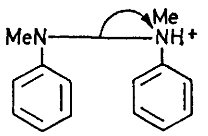
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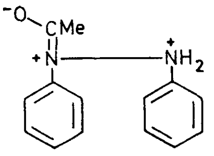
(IV)

On the other hand, uptake of one proton by *NN'*-dimethylhydrazobenzene gives an intermediate in which one *N*-methyl group can aid N–N fission [*cf.* (III)] and so a rearrangement that is first order in acid resulted. The approximate relative rates (at $\mu = 0\cdot100$; $[\overset{+}{\mathrm{H}}]$ 0·100M) 1 : 2·5 : 14 for hydrazobenzene and its *N*-methyl and *NN'*-dimethyl homologues reflect these polar effects on rate.

At two acidities the component of the rate of disappearance of *NN'*-dimethylhydrazobenzene to give 4,4'-linked product (numbering as in the substrate) was shown to be equal (±1%) to the rate of formation of the product and so no build up of intermediate could be inferred.

1,1'-Hydrazonaphthalene has been found to give a first-order reaction in acid in 60% dioxan–water.[17] The *NN'*-dimethyl compound has a similar kinetic form and reacted faster (at $\mu = 0\cdot025$; pH 2·36) by 1·5-fold, which makes it the most reactive hydrazoarene to undergo a one-proton mechanism. The latter compound is probably a slightly weaker base than 1,1'-hydrazonaphthalene (1-naphthylamine pK_a 3·96; *N*-methyl-1-naphthylamine 3·67) but electron release from the methyl group situated on the unprotonated nitrogen may facilitate N–N fission and over-ride the basicity effect.

N-Acetylhydrazobenzene underwent rearrangement that was second order in acid and reacted some 10-fold slower than the (also second order) rearrangement of 4-nitrohydrazobenzene[18] under comparable conditions ($[\overset{+}{\mathrm{H}}]$ 3·00M). It is thus the most unreactive hydrazoarene that has been studied to date and this is presumably a consequence of its low basicity (acetanilide pK_a 0·5; 4-nitroaniline 1·0). The need for uptake of the second proton indicates that possible formation of a ' dication ' structure such as (IV) from the monoprotonated substrate is insufficient to promote rearrangement.

Thus the kinetic forms for the four hydrazo-compounds fell in a readily rationalised pattern.

Solvent Isotope Effects.—The values of the solvent isotope effects for *NN'*-dimethylhydrazobenzene,

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[14] D. V. Banthorpe, E. D. Hughes, C. K. Ingold, and J. Roy, *J. Chem. Soc.*, 1962, 3294.

[15] D. D. Perrin, ' Dissociation Constants of Organic Bases in Aqueous Solution,' Butterworths, London, 1965.

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

[17] D. V. Banthorpe, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 1962, 2386.

[18] D. V. Banthorpe, A. Cooper, and M. O'Sullivan, *J. Chem. Soc. (B)*, 1971, 2054.

N-methylhydrazobenzene, and *NN*′-dimethyl-1,1′-hydrazonaphthalene (Table 2) indicate a factor of acceleration for transfer of each proton of 2·0—2·3 when water in the solvent was replaced by deuterium oxide; this is as expected if the one or two protons (in the reactions which are first and second order in acid) are transferred in pre-equilibria.[2] The solvent isotope effect for the two-proton reaction of *N*-acetylhydrazobenzene was however low for a reaction with two pre-equilibria, but falls in line with recent observations of similarly low effects for two-proton rearrangements of feebly basic hydrazoarenes. This reinforces the previous suggestion [1] that the second protonation could become rate limiting for such substrates.

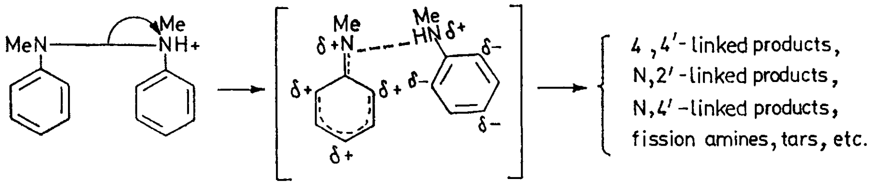
It has been suggested [19] that the large solvent isotope effect (k_{D_2O}/k_{H_2O} 4·8) for the two-proton reaction of hydrazobenzene need not indicate the occurrence of two pre-equilibria but rather reflects a change of basicity of the substrate on moving from protium to deuterium-containing solvents where an imino hydrogen atom could exchange for deuterium. This suggestion seems unlikely, as secondary isotope effects could hardly account for the observed large changes of rate, and the suggestion is excluded by our observation of entirely normal values for the reactions of the *NN*′-dimethylated substrate where no imino hydrogen atom is available for exchange.

Products.—Most of the products from these rearrangements are either new compounds or are reported compounds which have uncertain structure. Structures were assigned by exhaustive methylation of the products to give ′onium compounds and demethylation of the latter to give tertiary arylamines. Both these derivatives were compared chromatographically with corresponding ′onium compounds and amines prepared from rearrangement products from hydrazobenzene and 1,1′-hydrazonaphthalene. This method usually allowed unambiguous assignment of the products from *N*-substituted substrates, but in some cases the position of *N*-substitution remained unknown. Thus, a product from rearrangement of *N*-methylhydrazobenzene could be shown to have 2,4-linking of the aryl residues by the identity of its derivatives with those from 2,4′-diaminobiphenyl (a known rearrangement product of hydrazobenzene) but the location of the *N*-methyl group could not be determined.

Our results showed that 4,4′-linking of the aromatic rings predominated for *N*-acetylhydrazobenzene and *N*-methylhydrazobenzene with lesser extents of 2,4′-products. In addition, some deacetylated products occurred for the former substrate. *NN*′-Dimethyl-1,1′-hydrazonaphthalene gave predominantly the 2,2′-linked product and lesser amounts of the 4,4′-linked product; the carbazole was a direct product as control experiments showed that the 2,2′-bismethylaminonaphthyl was not converted into it under the conditions of rearrangement.

These products parallel in structure and proportions those from hydrazobenzene and 1,1′-hydrazonaphthalene.[14,17] However, rearrangement of *NN*′-dimethylhydrazobenzene gave a different pattern. A considerable (*ca.* 38%) proportion of products consisted of 2,2′-linked (*o*-benzidine), 2,N′-linked (*o*-semidine), and 4,N′-linked (*p*-semidine) products, together with fission amine and tar. Such compounds are rarely found in products of rearrangement of hydrazoarenes (see introductory paragraphs) but our results are similar to those obtained under quite different conditions.[7]

If *NN*′-dimethylhydrazobenzene is presumed (see next section) to rearrange intramolecularly *via* the polar transition state mechanism, an explanation for the formation of these ′ unexpected ′ products is as follows: as the transition state is attained, interactions between the methyl groups cause a relative displacement and rotation of the aryl residues [*cf.* (V)] that is absent in hydrazobenzene and which leads to enhancement of 2,N′- and 4,N′-linked products amongst the initially-formed quinonoid intermediates. If a proportion of molecules undergoing reaction suffers sufficient relative displacement of the rings, kinetically-free fission amine and an imino-cation could be formed. The latter would react with water to give *N*-methylphenylhydroxylamine which is known readily to form tars in the presence of acid.



(V)

′ Unexpected ′ products are not formed on rearrangement of *NN*′-dimethyl-1,1′-hydrazonaphthalene. Here relative displacement of the aryl groups might be prevented by the increased electrokinetic interactions between the naphthyl rings as the molecule folds into the transition state.

Intramolecularity.—Previous methods of demonstrating the intramolecularity of the benzidine rearrangement have sought to prove the absence of cross-over products AB from the concurrent rearrangements of AA and BB.[20] A condition of this method is that the rates of rearrangement of the two compounds must be similar. The absence of products AA and BB from an unsym-

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[19] M. J. S. Dewar in ′ Molecular Rearrangements,′ ed. P. de Mayo, Interscience, New York, 1963, vol. p. 323.

[20] D. V. Banthorpe, *J. Chem. Soc.*, 1962, 2413.

metrically-substituted substrate AB is no proof of intramolecularity as heterolytic cleavage could occur essentially only in one direction resulting in only one mode of recombination of the charged fission fragments and lack of cross-over products even in an intermolecular process.

Our present method of rearranging either (AA + A′A′) or AA′ where the group A′ differs from A in being deuteriated, and assaying the products (*via* mass spectrometry) for AA′ and A′A′ respectively replaces the use of concurrent rearrangement of different hydrazo-compounds and also eliminates differences in selectivities of coupling that could occur between different possible fission fragments.

Our results show that $<2\%$, if any, of *NN*′-dimethylhydrazobenzene could have undergone intermolecular rearrangement. In addition, the observation of an identical (within experimental error) pattern of products when rearrangement was effected in the presence or absence of radical scavengers rules out intermolecular radical mechanisms and makes unlikely intramolecular routes progressing through hypothetical radicals such as PhNMe$\overset{+}{\mathrm{N}}\overset{\bullet}{\mathrm{M}}$ePh, analogous to those recently suggested for the rearrangement of tetraphenylhydrazine.[21]

Mechanisms.—The above results exclude radical processes for the rearrangement of *NN*′-dimethylhydrazobenzene such as are believed to occur for tetraphenylhydrazine. Despite the unusual products obtained from the former substrate, it is likely that this and the other *N*-substituted compounds that were investigated rearrange *via* the polar transition mechanism which satisfactorily accounts [2] for kinetic and product data for all other hydrazoarenes (except tetraphenylhydrazine) that have been examined to date.

EXPERIMENTAL

(i) *Preparations*.—All m.p.s are uncorrected and agreed to ±1 °C with literature values unless otherwise specified.

N*N*′-*Dimethylhydrazobenzene*. This was prepared either by methylation of the dilithium salt of hydrazobenzene (formed from reaction of the hydrazo-compound with methyl lithium) [22] with dimethyl sulphate in ether [9] or by reaction of the disodium–azobenzene adduct with dimethyl sulphate in dioxan.[23] The product was purified by repeated precipitation from benzene with light petroleum (b.p. 40—60°) (yield 60 or 95% respectively), m.p. 34° (from benzene) (Found: C, 79·0; H, 7·6; N, 13·2. Calc. for $C_{14}H_{16}N_2$: C, 79·3; H, 7·5; N, 13·2%).

N-*Methylhydrazobenzene*. This was prepared by a modification in the second method for the previous compound [23] that gave *NN*′-dimethylhydrazobenzene (50%) and *N*-methylhydrazobenzene (25%). The product was purified as for its *NN*′-dimethyl homologue, m.p. 75° (from benzene) (Found: C, 78·6; H, 7·0; N, 14·0. Calc. for $C_{13}H_{14}N_2$: C, 78·6; H, 7·1; N, 14·3%).

N-*Acetylhydrazobenzene*. This was prepared by the action of acetic anhydride in 3-fold excess on hydrazobenzene [24] (yield 23%), m.p. 159° (from ethanol) (Found: C, 74·0; H, 6·2; N, 12·5. Calc. for $C_{14}H_{14}N_2O$: C, 74·3; H, 6·2; N, 12·4%).

NN′-*Dimethyl*-1,1′-*hydrazonaphthalene*. This was prepared by oxidation of methyl-(1-naphthyl)amine with potassium permanganate in acetone [25] (yield 12%), m.p. 190° (from benzene) (lit.,[25] 187—190°) (Found: C, 84·2; H, 6·3; N, 8·9. Calc. for $C_{22}H_{20}N_2$: C, 84·6; H, 6·4; N, 9·0%).

(ii) *Kinetic Methods*.—Aliquot portions (5 ml) of the reaction mixture were removed and were basified with aqueous sodium hydroxide and the products and unchanged substrate were extracted with benzene (1 ml). After most of the solvent had been removed, the mixture was separated by chromatography on Whatman No. 4 paper that had been impregnated with 10% formamide in ethanol using cyclohexane as eluant,[26] and the uncharged substrate, or in two runs (see Results section) a product, was eluted. R_F Values were irreproducible from paper to paper, as has been our previous experience with these systems,[17] and for each separation the desired compound was located by running standards on each side of the mixture spot, cutting the paper into strips after development of the chromatogram, and determining the R_F value by exposing the standards to nitrous fumes when the components were revealed as yellow spots. Once located the unchanged substrate (or product) was eluted with methanol (10 ml) and the optical density of the solution was measured at 262, 265, 273, 285, and 295 nm for *NN*′-dimethylhydrazobenzene, *N*-methylhydrazobenzene, *N*-acetylhydrazobenzene, *NN*′-dimethyl-1,1′-hydrazonaphthalene, and 4,4′-bismethylaminobiphenyl respectively.

Rate constants, reproducible in duplicate runs to ±3%, were calculated from these extinction measurements using Guggenheim's method [27] for the pseudo-first-order reactions.

Comparison of the u.v. absorption curves and of chromatographic properties on a variety of thin layer and paper systems of these separated components with those of the rigorously purified starting materials showed that the separation method described gave pure materials.

H_0 Values relative to that of the most concentrated acid solution used (for reactions of *N*-acetylhydrazobenzene) were measured by indicator studies using 2-nitroaniline. ' Corrected ' pH values for the phthalate buffers in 60% dioxan–water were obtained as previously described [17] from pH-meter readings carried out at 20°.

(iii) *Products*.—The hydrazo-compound (2 g) was rearranged and tar (if present) was removed by passage of a benzene solution of the basified products through an alumina column (Brockman grade III; 10 cm × 1 cm o.d.). Rearrangement products were separated using preparative t.l.c. on Merck Silica Gel H or alumina with benzene–ether [9 : 1 (v/v)] or benzene–ethyl acetate mixtures [9 : 1 to 5 : 1 (v/v), variously] as eluants. After each product had been recovered from the chromatogram it was extensively pumped down to remove volatile impurities and the residue was weighed using a Cahn microbalance. In

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[21] U. Svanholm, K. Prechgaard, O. Hammerich, and V. N. Parker, *Tetrahedron Letters*, 1972, 3675.

[22] G. Wittig and J. E. Grolig, *Chem. Ber.*, 1961, **94**, 2148.

[23] J. W. B. Reesor and G. F. Wright, *J. Org. Chem.*, 1957, **22**, 375.

[24] S. Goldschmidt and K. Euler, *Ber.*, 1922, **55**, 616.

[25] E. Lieber and S. Somasekhara, *J. Org. Chem.*, 1959, **24**, 1775.

[26] M. Vecera, J. Petranek, and J. Gasparic, *Coll. Czech. Chem. Comm.*, 1957, **22**, 1603.

[27] E. A. Guggenheim, *Phil. Mag.*, 1926, **2**, 538.

order to obtain the values recorded in the Results section controls were carried out to determine the percentage recovery from the chromatographic systems: these were generally >90% and the total corrected product balance accounted for 95—99% of the reaction.

As explained in the Discussion section, the structures of isomeric rearrangement products not previously investigated were assigned by chromatographic comparison with compounds prepared from (available) known rearrangement products of the non-methylated homologues of the substrates. Each unknown compound (20 mg) was exhaustively methylated by heating (80°) with portions of methyl iodide in nitromethane, each treatment being followed by addition of sodium hydrogen carbonate solution to neutralise the acid generated in the methylation process. The resulting 'onium iodides were compared with standards (which had been treated similarly) by chromatography using Whatman No. 1 paper and the following two solvents: (a) butan-1-ol : acetic acid : water [5 : 1 : 4 (v/v)] and (b) propan-1-ol : ammonia : water [6 : 3 : 11 (v/v)], with a spray of aqueous potassium chloroplatinate [5% (v/v)] as detecting agent. The 'onium compounds were then demethylated by treatment with sodium thiophenoxide in butan-2-one at reflux under nitrogen for 30 h.[28] to give tertiary amines in *ca.* 90% yield. These were not purified but were compared with standards prepared in the same way, using t.l.c. on silica gel H with ether–benzene [3 : 7, 1 : 1, 7 : 3 (v/v)] and chloroform as eluants. A check was made that the i.r. and u.v. spectra of the respective pairs (experimental and controls) of compounds were identical.

In addition, 2,2'-linked products were further characterised by their conversion into the corresponding carbazole which slowly precipitated on refluxing an acid solution of the appropriate compound.

In this manner, products (all recrystallised from methanol or benzene) from *NN'*-dimethylhydrazobenzene were shown to be 2,2'-bismethylaminobiphenyl, m.p. 103°, 2,4'-bismethylaminobiphenyl, m.p. 108°, 4,4'-bismethylaminobiphenyl, m.p. 90° (lit., 76°,[9] 92° [29]), *N*-methyl-(2-methylaminophenyl)phenylamine, m.p. 83°, *N*-methyl-(4-methylaminodiphenyl)phenylamine, m.p. 137°, and *N*-methylaniline.

Products from *N*-methylhydrazobenzobenzene were: 4-amino-4'-methylaminobiphenyl, m.p. 85° (lit.,[10] 83°), 2-(or 4-)amino-4'-(or 2'-)methylaminobiphenyl, m.p. 123° (lit.,[10] 124°), and benzidine, m.p. 127°.

Products from rearrangement of *N*-acetylhydrazobenzene were characterised by comparison using the chromatographic systems described above with the products of reaction of acetic anhydride on benzidine and 2,4-diaminobiphenyl.[30] They were 4-acetylamino-4'-aminobiphenyl, m.p. 132° and 2-(or 4-)acetylamino-4'-(or 2'-)aminobiphenyl, m.p. 143° (lit.,[30] 139°).

Products from rearrangement of *NN'*-dimethyl-1,1'-hydrazonaphthalene were 2,2'-bismethylaminobinaphthyl, m.p. 163°, 4,4'-bismethylaminobinaphthyl, m.p. 170°, and *N*-methyldibenzo[*a,i*]carbazole, m.p. 123°.

(iv) *Intramolecularity of Rearrangement.*—2,4,6-Trideuterioaniline (99 ± 2% deuterium in these positions, by n.m.r. analysis) was prepared [31] and was converted into hydrazobenzene by a method known to retain the deuterium.[32] This product was in turn converted into *NN'*-dimethylhydrazobenzene as described in part (i) of this section, and the product was shown by n.m.r. and mass spectroscopy to contain 98 ± 2% deuterium at the 2,2',4,4',6,6'-positions.

2,4,6-Trideuterioaniline was coupled with nitrosobenzene [33] to give 2,4,6-trideuterioazobenzene which also converted into 2,4,6-trideuterio-*NN'*-dimethylhydrazobenzene. This product contained 98 ± 2% label at the specified positions.

After the rearrangement using these labelled species had been carried out the products were separated and analysed using a Metro-Vick MS9 mass spectrometer with an ionising potential of 20 eV.

(v) *Miscellaneous.*—Experiments with scavengers were carried out in three-necked flasks, the compartments of which contained the substrate, the catalysing acid, and the trapping agent respectively. The last was used in 3-fold molar excess over the substrate. The three solutions were then simultaneously mixed and the reaction was carried to completion.

In the e.s.r. studies, cooled deoxygenated solutions of the catalysing acid and the hydrazo-compound were mixed in the probe of the spectrometer and were scanned at 5 min intervals during 30—60 min. A modified Varian 4500 spectrometer was used with a 100 kHz modulation unit. Radical concentrations down to 10^{-9}M were detectable in controls.

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