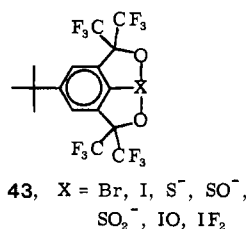


adjacent to the sulfonyl sulfur, consistent with a cycle 10-S-5 transition state.

The effectiveness of the tridentate ligand of 43 is dramatized



by characterizing the tridentate ligand as a host and the nonmetal X as a guest, using the nomenclature of Cram.³⁷ The host is

geometrically constrained to have almost the same geometry as it does in the host-guest complex, thus minimizing disadvantageous entropic factors in the formation of the complex while all the enthalpic advantages of the bonds around the central atom add to its stability. The host exerts a viselike grip on his guest.

The existence of 10-S-3 sulfuranides, 10-S-4 sulfuranide oxides, and 10-S-5 sulfuranide dioxides as single energy minimum ground-state structures indicates that other 10-S-3, 10-S-4, and 10-S-5 species may be energetically stable enough to exist as intermediates. It does not, however, prove the existence of an intermediate in any particular associative nucleophilic reaction at sulfur, except the ones forming 1-3.

Acknowledgment. This research was supported by a grant from the National Science Foundation (CHE 79-07-7905692). The NMR spectra were provided by the University of Illinois NSF Regional Instrumentation Facility (Grant CHE 79-16100) and mass spectra by facilities supported by grants from the National Institutes of Health (Grants CA 11388 and GM 16864). The assistance of A. J. Arduengo in obtaining the KANVAS drawings of 1, 2, and 3 is gratefully acknowledged.

Registry No. 1, 84649-56-9; 2, 96129-80-5; 3, 96129-82-7; 11, 84649-61-6; 12, 84649-62-7; 13, 84649-63-8; 14, 84649-59-2; 15, 84649-60-5; 16, 96129-83-8; 17, 96129-84-9; HFA, 684-16-2; sulfur, 7704-34-9.

Supplementary Material Available: A listing of positional parameters for 1, 2, and 3 (Tables I-III) and thermal parameters for 1 (Table V), 2 (Table VI), and 3 (Table VII), complete bond lengths and angles for 1 (Table VIII), 2 (Table IX), and 3 (Table X), observed and calculated structure factors for 1 (Table XI), 2 (Table XII), and 3 (Table XIII), and calculated H positions for 1 (Table XIV), 2 (Table XV), and 3 (Table XVI) (56 pages). Ordering information is given on any current masthead page.

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Heavy-Atom Kinetic Isotope Effects in the Acid-Catalyzed and Thermal Rearrangements of 2,2'-Hydrazonaphthalene. Transition-State Differences in Their Concerted Rearrangements¹

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Abstract: Acid-catalyzed (70% aqueous dioxane at 0 °C) and thermal rearrangement (95% ethanol at 80 °C) of 2,2'-hydrazonaphthalene (1) into 2,2'-diamino-1,1'-binaphthyl (2) have been shown to be concerted, [3,3]-sigmatropic shifts. This was accomplished by measuring the nitrogen and carbon kinetic isotope effects (KIE), for which purpose mixtures of 1 with [¹⁵N,¹⁵N']1 and [1,1'-¹³C₂]1 were used. KIE were calculated from whole-molecule mass ratios, measured by multiscan mass spectrometry, in the bis(trifluoroacetyl) derivative of product 2, isolated after low and high conversions. The results (averaged) were, for two isotopic atoms, $k(^{14}\text{N})/k(^{15}\text{N}) = 1.0904$, $k(^{12}\text{C})/k(^{13}\text{C}) = 1.0086$ in the one-proton, acid-catalyzed rearrangement and 1.0611 and 1.0182, respectively, in the neutral, thermal rearrangement. These results indicate that although the rearrangements are concerted processes, the breaking of the N-N bond and the forming of the C-C bond proceed to different extents in the transition states. Furthermore, the difference in the timing of these events is greater in the acid-catalyzed than in the thermal rearrangement, a difference which may be attributable to earlier C-C bonding in the polar transition state of the former.

Among benzidine rearrangements⁵⁻¹⁵ those of hydrazoarenes which contain the 2-naphthyl group constitute a unique class. First, in acid-catalyzed rearrangements in the usual solvents

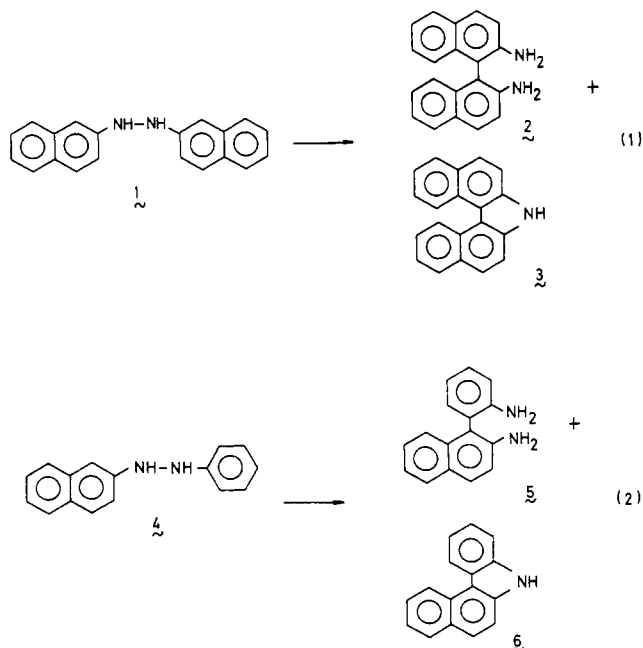
(aqueous ethanol or aqueous dioxane), they undergo almost complete *o,o'*-bonding with little or no concomitant dispro-

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(1) Previous paper: Shine, H. J.; Park, K. H.; Brownawell, M.; San Filippo, J., Jr. *J. Am. Chem. Soc.* 1984, 106, 7077.

portionation. Second, they undergo equally clean thermal rearrangements with formation of the same products. Particularly striking among these rearrangements are those of 2,2'-hydrazonaphthalene (**1**) and *N*-2-naphthyl-*N'*-phenylhydrazine (**4**). Each rearranges in acid solution at 0 °C to give the *o,o'*-biaryl-linked diamine and smaller amounts of the corresponding carbazole (eq 1 and 2). Each rearranges when heated in ethanol to the same



products as in acid catalysis, although the amounts of carbazole are somewhat greater. These similarities have been discussed by Shine and co-workers in work with **1**^{16,17} and in more detail, in their classic paper, by Banthorpe, Hughes, and Ingold.¹⁰ Shine held the view that in neutral alcohols thermal rearrangement of **1** was initiated by hydrogen bonding with the hydroxylic hydrogen atom and thus proceeded much in the way of acid catalysis. A broader view was taken by the English school, not only of the rearrangements of **1** and **4** but also of other hydrazoarenes. This view was that all benzidine rearrangements are essentially heterolytic, the meaning of this view being that both thermal and the better-known acid-catalyzed rearrangements could be described by the polar-transition-state theory.¹⁸ An essential feature of the polar-transition-state theory is that it regarded all benzidine rearrangements as being concerted processes. This view, though,

(2) Supported by the National Science Foundation, Grants CHE-8026576 and CHE-8314947.

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(4) Supported by the National Science Foundation, Grant CHE 8312730.

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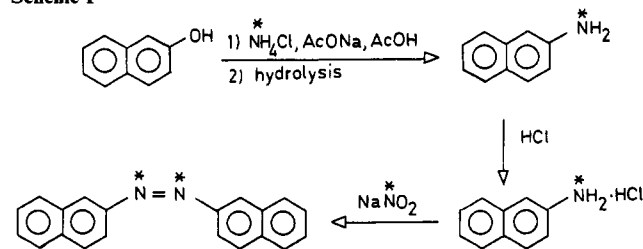
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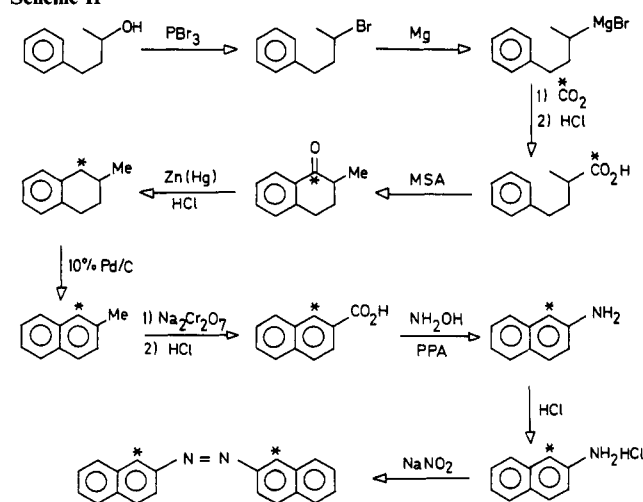
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(18) The possibility that hydrazonaphthalenes might rearrange in hydrocarbon solvents by a homolytic mechanism was noted, however.¹⁹

Scheme I



Scheme II



is being questioned in present times and was recently found to be invalid for the acid-catalyzed rearrangement of hydrazobenzene into diphenylene.¹⁹ The pattern of acid-catalyzed benzidine rearrangements that is emerging^{1,19,20} is that they are truly sigmatropic rearrangements, controlled by requirements of orbital symmetry. The rearrangements of 2-naphthylhydrazoarenes invite investigation, therefore, since in this pattern they should be allowed [3,3]-sigmatropic shifts. Furthermore, the cleanliness of both the acid-catalyzed and thermal rearrangements allows for probing the concertedness of each and for asking if differences in the transition states of acid-catalyzed and thermal rearrangements can be found. We set out to answer the questions of concertedness and transition-state differences by measuring nitrogen and carbon kinetic isotope effects (KIE) in the rearrangements of **1**. We have been able to show that the rearrangements are, indeed, concerted and that there is a difference in transition states.

The kinetics and products of the acid-catalyzed rearrangement of **1** in 60% and 70% aqueous dioxane were reported by Banthorpe.²¹ At low acidities, in the range 10⁻²-10⁻¹ M perchloric acid, the rearrangement is first order in acid. At low acidities in 60% aqueous dioxane, the diamine (**2**) and the carbazole (**3**) were the major products in yields averaging approximately 94% and 5.5%, respectively. A third, unidentified product was also obtained but in very small amounts. The kinetics and products of the thermal rearrangement of **1** have been reported by Shine and Trisler^{16,17} and by Banthorpe.²² Little substantive difference is to be found in the results of the two investigations. The thermal rearrangement was first order in **1** and at 80 °C in ethanol gave only **2** and **3** in yields, respectively, of approximately 86% and 13%¹⁷ and 81% and 18%.²²

The background for our measurements of heavy-atom KIE was thus clearly established. The approach taken was to synthesize [¹⁵N,¹⁵N']**1** and [1,1'-¹³C₂]**1** beginning with precursors containing

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(22) Banthorpe, D. V. *J. Chem. Soc.* **1964**, 2854.

99% isotopic enrichment. Thereafter it was possible to carry out rearrangements of mixtures of **1** and labeled **1**, containing approximately 5 mol % of the doubly labeled isomer, under established kinetic conditions,^{17,21} and to calculate KIE from the relative abundances of **2** and doubly labeled **2** which were formed after selected conversions.

Results

Syntheses of Labeled 1. The primary objective in the labeling work was to prepare the appropriately labeled 2,2'-azonaphthalenes, since these could be reduced easily as needed to labeled **1**. The only convenient method of preparing 2,2'-azonaphthalene is by the diazotized coupling of 2-naphthylamine.²³ Consequently, the labeling syntheses were directed toward [¹⁵N]- and [1-¹³C]-2-naphthylamine. These were synthesized as shown in Schemes I and II. Details of the successful syntheses are given elsewhere.²⁴ The synthesis of [¹⁵N]-2-naphthylamine via a Bücherer reaction gave no trouble. In the synthesis of [1-¹³C]-2-naphthylamine, we planned at first to make 2-methyl-4-phenyl-[1-¹³C]butyric acid from the corresponding 2-methyl-4-phenylbutyronitrile. Untch had shown that alicyclic nitriles could be obtained readily from alcohols by in situ formation and reaction of their trimethylsilyl ethers with cyanide ion.²⁵ This reaction was tried, therefore, with commercially available 2-methyl-4-phenylbutanol but without satisfying results after several attempts. Complete conversion of the alcohol was not achieved, even after lengthy reaction times. Furthermore, a product was obtained which, when separated from unreacted alcohol by column chromatography and hydrolyzed by heating with 2 N sulfuric acid, gave (presumed) 2-methyl-4-phenylbutyric acid which resisted clean cyclization to 2-methyltetralone. This route to 2-methyltetralone was abandoned, therefore, in favor of the one shown in Scheme II. In that route, it was necessary to carry out carbonation on a large excess of the Grignard agent. This was wasteful in Grignard agent but productive (87% yield) in terms of ¹³CO₂.

Scheme II shows the conversion of 2-naphthoic acid into 2-naphthylamine by heating with hydroxylamine (used as the hydrochloride) in polyphosphoric acid (PPA). This was achieved in 82% yield by Snyder,²⁶ a result that we found possible to duplicate only if freshly opened bottles of PPA were used. Attempts to make 2-naphthylamine by Hofmann rearrangement (sodium hypobromite) of 2-naphthoic acid amide were unsuccessful. Reaction of 2-naphthoic acid with nitromethane (as a source of hydroxylamine) in PPA²⁷ gave only a 31% yield of 2-naphthylamine and was not pursued.

The diazotized coupling of 2-naphthylamine as the route to [¹⁵N,¹⁵N']**1** required the use of Na¹⁵NO₂ and was thus wasteful in ¹⁵N. Nevertheless, this was necessary to obtain mainly (98%) doubly labeled **1** and thus avoid complications later in mass spectrometric measurements.

Rearrangements. Thermal rearrangement was carried out at 80 °C in 95% ethanol under oxygen-free argon, with initial concentration of 0.01 M **1**. The rate constant¹⁷ for rearrangement under these conditions is given as $9.76 \times 10^{-3} \text{ min}^{-1}$, and this was used for calculating the times for quenching rearrangement by cooling the solution in the water. For example, the times for 10% and 100% conversion were calculated as 10.75 min and approximately 8 h, respectively. However, calculated times, particularly for low conversions, were used only as guides, and the real extent of a rearrangement was calculated from the sum of the yields of isolated **2** and **3**, as well as from unused **1**, recovered as azonaphthalene.

After quenching the rearrangement by cooling, the solution was made alkaline and unrearranged **1** was oxidized by air to azonaphthalene. Separation of **2**, **3**, and azonaphthalene was ac-

Table I. Yields of Products and Conversions in the Thermal^a and Acid-Catalyzed^b Rearrangements of 2,2'-Hydrazonaphthalene (**1**)

run	type, isotope	tot recovery, % ^c	distribution, %			ratio (%) 2/(2+3)	conv, % ^d
			2	3	azo		
1	Δ, ¹⁵ N	97.2	5.2	1.2	93.6	81.2	6.4
		96.1	82.4	15.4	2.2	84.3	98
2	Δ, ¹⁵ N	98.9	7.4	1.7	90.9	81.3	9.1
		96.5	80.1	15.5	4.4	83.8	96
3	Δ, ¹³ C	99.1	8.3	1.9	89.8	81.4	10
		96.5	81.2	15.1	3.7	84.3	96
4	Δ, ¹³ C	98.4	11.9	2.1	86.0	85.0	14
		96.5	81.2	15.1	3.7	84.3	96
5	H ⁺ , ¹⁵ N	99.3	11.5	1.5	87.0	88.5	13
		98.8	79.8	11.0	9.2	87.9	91
6	H ⁺ , ¹⁵ N	99.3	20.8	3.0	76.2	87.4	24
		97.5	83.4	11.8	4.8	87.6	95
7	H ⁺ , ¹³ C	98.7	12.0	1.6	86.4	88.2	14
		91.2	84.6	9.5	5.9	89.9	94
8	H ⁺ , ¹³ C	97.9	9.3	1.2	89.5	88.1	10
		97.2	82.8	10.9	6.3	88.4	94

^aAt 80 °C in 95% ethanol. ^bAt 0 °C in 70% aqueous dioxane. ^cSum of **2**, **3**, and 2,2'-azonaphthalene isolated. ^dBased on distribution of isolated products.

complished quantitatively in standard ways. The crude **2**, mp 190–191 °C, was converted quantitatively into its bis(trifluoroacetyl) derivative which was purified for mass spectrometry.

The data in Table I report the yields of products isolated. Runs which were carried to 100% conversion were found to have given 2–4% of azonaphthalene after workup. We are uncertain as to whether this represents unrearranged **1** which was oxidized to azonaphthalene after rearrangement was quenched or whether the azonaphthalene was formed by adventitious oxidation during rearrangement. Thus, our 100% conversions may have been 96–98% conversions in reality. This possibility affects the size of the calculated KIE and is discussed below.

The rate of rearrangement of **1** in acid solution is quite fast. In order to have reasonable times for low conversions, therefore, it was necessary to use low acid concentrations. At the same time, reasonably high concentrations of **1** were needed in order to give enough product at low conversions for isolation and purification for mass spectrometry. The concentration of **1** which was chosen was $4 \times 10^{-3} \text{ M}$ in 70% aqueous dioxane, as described by Banthorpe.²¹ In the region of 10^{-2} M perchloric acid concentrations, the order in acid was reported by Banthorpe to be 1.16. We selected an acid concentration of 10^{-3} M to obtain a slower rate of reaction and calculated this, from Banthorpe's data, to be $1.2 \times 10^{-3} \text{ s}^{-1}$. Times of low conversion were then calculated with this rate constant, e.g., 7 and 15 min for 5% and 10% conversions, but the conversions which were obtained were calculated finally from the amounts of products isolated. These are given in Table I. The low acid concentration, smaller in fact than the initial concentration of **1**, must have resulted in a falloff in rate beyond the early conversions because the product **2** is a diamine and also because ammonia is liberated in the formation of **3**. In order to achieve 100% conversion, therefore, solutions were kept at 0 °C for 24 h. This approach appears to have been faulty, however, because air oxidation of a 100% rearrangement solution after basification always gave some azonaphthalene (5–9%). It is probable that this arose from unrearranged **1**, and in that case the projected 100% conversions were, in fact, in the range of 91–95%. The conversions are given in Table I and have been taken into account in calculating KIE.

The data in Table I show that the ratio of yields of **2** and **3**, namely approximately 83:17 for the thermal and 88:12 for the acid-catalyzed rearrangement, are analogous to those reported earlier.^{16,17,21,22} The ratio in the acid-catalyzed rearrangements is not affected by the extent of rearrangement. This confirms earlier findings that **3** is not formed from **2** under the conditions of rearrangement but that, as suggested earlier, arises from a bifurcation in pathway after C–C bonding has occurred.¹⁰ The proportion of **2** formed at low conversions in the thermal rearrangements was a little lower on the average than at high con-

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(26) Snyder, H. R.; Fishel, D. L.; Schechter, H. *J. Org. Chem.* **1965**, *30*, 1453.

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Table II. KIE^a for the Thermal^b and Acid-Catalyzed^c Rearrangements of 2,2'-Hydrazonaphthalene (1)

run	type	isotope	conv, % ^d	KIE _{app} ^e	KIE ^f	10 ⁴ σ ^g
1	Δ	¹⁵ N	6.4/98	1.0554	1.0610	3.9
2	Δ	¹⁵ N	9.1/96	1.0518	1.0612	5.2
3	Δ	¹³ C	10/96	1.0157	1.0183	12
4	Δ	¹³ C	14/96	1.0154	1.0181	11
5	H ⁺	¹⁵ N	13/91	1.0676	1.0942	6.7
6	H ⁺	¹⁵ N	24/95	1.0691	1.0866	6.8
7	H ⁺	¹³ C	14/94	1.0072	1.0089	6.7
8	H ⁺	¹³ C	10/94	1.0067	1.0082	7.3

^a k_1/k_2 for two isotopic atoms in [¹⁵N,¹⁵N']1 and [1,1'-¹³C₂]1. ^b At 80 °C in 95% ethanol. ^c At 0 °C in 70% aqueous dioxane. ^d Low and high conversions based on isolated yields of products and 2,2'-azobenzene. ^e Calculated with eq 3 and assuming high conversion was 100%. ^f Calculated with eq 4 by using conversions as shown in the table. ^g Standard deviation in KIE calculated from standard deviations of the mean in mass ratio measurements; see Experimental Section.

versions, suggesting that, in addition to the dual pathways, some thermal conversion (1–2%) of 2 into 3 may have occurred.

KIE Measurements and Calculations. The ratio of masses ($M + 2$)/ M in the product was measured by high-precision, multiscan, whole-molecule mass spectrometry. Initially, these measurements were carried out on 2 itself. Nitrogen KIE of the order 1.07 were obtained, but the precision and reproducibility in measuring the relative abundances of the ions 286 and 284 were not satisfactory. These problems were attributed to errors in measuring the abundance of the ($M - 1$) ion and their effect on calculating the relative abundances of the ($M + 2$) and M ions. Consequently, after separation and isolation, 2 was converted into its bis(trifluoroacetyl) derivative in whose mass spectrum the ($M - 1$) peak is negligibly small. Thereafter, measurements of the abundances of the ions 478 and 476 were reproducible and could be carried out with highly satisfactory precision. The enrichment of the mass 478 in the bis(trifluoroacetyl) derivative was then obtained by normalizing for the natural abundances, giving us eventually ($M + 2$)/ M ratios arising from heavy-atom substitution, from which KIE could be calculated. Calculations have been made in two ways. Equations for calculating KIE are well-known and depend, as they relate to product, upon one's knowing isotopic enrichments in the product at low and 100% conversions. We have assumed, then, that our 100% conversions were indeed 100% and have calculated KIE from eq 3.²⁸ In this equation R_p and R_0 are the

$$R_p/R_0 = [1 - (1 - F)^{k_2/k_1}] / F \quad (3)$$

normalized abundances ($M + 2$)/ M in the product at molar conversions F and 1.0. In our case, we have assumed, first, that the conversion of 1.0 was reached and the results, expressed as KIE_{app}, are given in Table II.

If, as seems probable, our projected complete conversions did not reach 100% (a molar conversion of 1.0), it becomes necessary to be able to calculate KIE from mass ratio data of low and high conversions. To our knowledge, no treatment of data in this way has been reported hitherto, but one has been devised by Prof. W. H. Saunders, Jr., and is used here.²⁹ In this treatment, R'_p/R_0 is expressed in a second equation (3a, not shown) for a new, incomplete conversion F' . By dividing eq 3 by eq 3a, we arrive at eq 4 in which R_p and R'_p are the measured, normalized mass ratios ($M + 2$)/ M at conversions F and F' , respectively, and k_2/k_1 is the KIE (k_H/k_L) for the reaction. An explicit solution to eq

$$\text{ROBS} = R_p/R'_p = \frac{F'[1 - (1 - F)^{k_2/k_1}]}{F[1 - (1 - F')^{k_2/k_1}]} \quad (4)$$

4 cannot be found, but the value of k_2/k_1 fitting ROBS can be obtained by computer iteration between reasonable limits in the value of k_2/k_1 . Reasonable limits were obtained in our case from

(28) Melander, L.; Saunders, W. H., Jr. "Reaction Rates of Isotopic Molecules"; Wiley: New York, 1980; p 100.

(29) We are indebted to Prof. Saunders for proposing this solution and for supplying an Apple-II program for carrying out the necessary iterations.

the value of KIE_{app} obtained as described above. Further details are given in the Experimental Section. In this way KIE were obtained which are based on yield-derived conversions (Table I) and are given in Table II (but as k_1/k_2). It can be seen that these KIE are larger, as would be expected, than the values of KIE_{app}. We regard them as the real KIE for the rearrangements. Regardless of the absolute values of the KIE, the surprising revelation of the results is in the relative sizes of the KIE for breaking the N–N bond and making the C–C bond. In the thermal rearrangement, the isotope effect averages 6.11% for nitrogen and 1.83% for carbon, while in the acid-catalyzed rearrangement the averages are 9.04% and 0.85%. The results show that both classes of rearrangement are concerted but that, in each case, there is a difference in the timing of breaking the N–N bond and forming the C–C bond and that this difference is greater in the acid-catalyzed than in the thermal rearrangement.

Discussion

o-Benzidine rearrangements are not often encountered in the rearrangement of hydrazoarenes in aqueous or alcoholic acid solutions. No case of *o,o'*-bonding is to be found, for example, for rearrangements of hydrazobenzenes in Jacobson's 1922 classic collection of recorded rearrangements.³⁰ Since that time examples of *o*-benzidine rearrangement have been reported, particularly in the 3,3',5,5'-tetramethyl- and tetrahalogenohydrazobenzenes, which when heated in strong aqueous sulfuric acid gave yields of *o,o'*-bonded product of 2–16%.³¹ *o*-Benzidine rearrangements among monosubstituted hydrazobenzenes are much less common when rearrangements are carried out in acidic aqueous alcoholic solutions. Večeřa and co-workers have reported that traces of *o*-benzidines were obtained from rearrangements of 2- and 4-methyl-, 3,3'-dichloro-, and 2,2'- and 4,4'-dimethylhydrazobenzene.^{32,33} The largest reported yield of *o,o'*-bonding in a hydrazobenzene rearrangement is of 40% from 3,3'-diaminohydrazobenzene.^{34,35} Rearrangement of hydrazobenzene itself in aqueous alcoholic solutions is often described as giving only benzidine and diphenylene as products,¹¹ but traces of *o*-benzidine have, in fact, been found.³² This rarity of *o,o'*-bonding in rearrangements of simple hydrazobenzenes³⁷ is surprising in view of the fact that such bonding would result from an allowed [3,3]-sigmatropic shift. In the case of hydrazobenzene one of us has speculated earlier that the virtual absence of *o,o'*-bonding arises from the large distance which separates *o,o'*-positions in the bent, cyclohexadienyl-like rings of a diprotonated transition state.¹⁹

The rearrangements of hydrazonaphthalenes are striking, therefore, in their contrast, since in these cases *o,o'*-bonding occurs almost entirely.⁴⁰ Cox and Buncl¹⁵ have suggested that the reason

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(31) Carlin, R. B.; Forshey, W. O., Jr. *J. Am. Chem. Soc.* **1950**, 72, 793. Carlin, R. B.; Heinger, S. A. *J. Am. Chem. Soc.* **1955**, 77, 2272. Carlin, R. B.; Foltz, G. E. *J. Am. Chem. Soc.* **1956**, 78, 1992.

(32) Večeřa, M.; Petraňek, J.; Gasparič, J. *Collect. Czech. Chem. Commun.* **1957**, 22, 1603.

(33) Večeřa, M.; Petraňek, J. *Collect. Czech. Chem. Commun.* **1960**, 25, 1992.

(34) Clovis, J. S.; Hammond, G. S. *J. Org. Chem.* **1963**, 28, 3290.

(35) The report of 100% yield by Shine and Chamness³⁶ for the rearrangement of 4,4'-divinylhydrazobenzene should be regarded as speculative since it was based only on the similarities in the infrared spectra of the polymeric product and poly(vinylaniline).

(36) Shine, H. J.; Chamness, J. T. *J. Org. Chem.* **1963**, 28, 1232.

(37) It is surprising, though, that treatment of simple hydrazobenzenes with acid in uncommon ways does give *o*-benzidines. Thus, reaction of solid hydrazobenzene (in dry sand) with dry hydrogen chloride gave a large proportion of *o*-benzidine as well as substantial proportions of all other possible rearrangement products.^{32,38} Also, reactions of hydrazobenzene and *m*-hydrazotoluene³⁹ with hydrogen halides in benzene, toluene, and ether at low temperatures gave *o*-benzidines. These findings would appear to support belief that [3,3]-sigmatropic rearrangements should occur, but nothing at all is known about the mechanism of rearrangement in these circumstances.

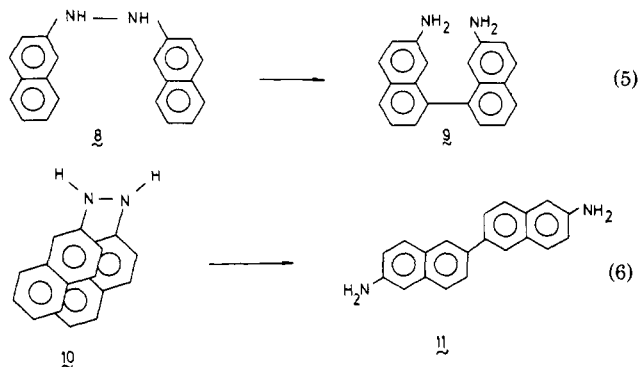
(38) Večeřa, M.; Gasparič, J.; Petraňek, J. *Collect. Czech. Chem. Commun.* **1958**, 23, 249. *Chem. and Ind.* **1957**, 299.

(39) Lukashovich, V. O. *Tetrahedron*, **1967**, 23, 1317; *Russ. Chem. Rev. (Engl. Transl.)* **1967**, 36, 895.

(40) Traces of products other than from *o,o'*-bonding were found in the present and earlier²¹ work but have never been characterized.

for this is that in the hydrazonaphthalenes, "folding over" of the rings is less pronounced for steric reasons, leading to more *o*,-*o'*-bonding because these positions are simply closer together.

In attempting to visualize the structure of a transition state which is consistent with preferred *o*,-*o'*-bonding, we need also to rationalize the large differences in the sizes of the nitrogen and carbon KIE. These differences indicate, as pointed out earlier, that N-N bond breaking and C-C bond formation do not occur to comparable extents in the transition states. The relatively large nitrogen but small carbon KIE may be understood in either of two ways. They are that, in comparison with the breaking of the N-N bond, the C-C bond may be only little formed or may be well formed in a transition state. Ways of representing these transition states are shown in skeletal form in **7a** and **7b**, in each of which the member atoms of the [3,3]-sigmatropic shift have been positioned in a distorted chair conformation. In model **7b**, in which the C-C bond is only little formed, the planes of the naphthyl rings have been oriented at an angle so as to emphasize the difference in extents of N-N and C-C bonding. One can use this model to understand why "allowed" modes of C-C bonding, other than at the 1,1'-carbon atoms, do not occur to a significant extent. Alternative modes of C-C bonding which are allowed by the principles of orbital symmetry are at the 8,8'- and 6,6'-carbon atoms. These would result from [5,5]- and [7,7]-sigmatropic shifts, respectively, and lead to 7,7'-diamino-1,1'- (**9** eq 5) and 6,6'-diamino-2,2'-binaphthyl (**11**, eq 6). It can be seen in model **7b**



that the distances separating the 8,8'- and 6,6'-carbon atoms are greater than that which separates the 1,1'-carbon atoms. We can rationalize, therefore, that **2** (1,1'-carbon bonding) is the major product of rearrangement of **1** and that **9** and **11** have never been identified as products and, if formed, must be in trace amounts only.

Model **7a** represents C-C bonding which is already much advanced when N-N bond breaking makes its large contribution to the transition state. Although not so evident from the projection, the distances separating the 8,8'- and 5,5'-carbon atoms are again the larger, and we can once more rationalize the preferred formation of product **2** over **9** and **11**.

Last in the models is **7c** which represents the opposite extreme of folding over of the naphthyl rings, that in which maximum overlap of the π systems may occur. In this case the member atoms of the [3,3]-sigmatropic shift adopt a boatlike conformation. It may be, as Cox and Buncel have suggested, that this folding over is inhibited for steric reasons.¹⁵ But, in any case, one may rationalize here, too, that the rings are so oriented as to place the bonding carbon atoms for [5,5]- and [7,7]-sigmatropic shifts too far away from each other to compete with the [3,3]-sigmatropic one.

Lacking better vision of the transition states, we have represented the naphthyl rings in them as being planar rather than nonplanar networks of conjugated atoms, which may, in fact, exist in the transition states.

The difference in the size of the nitrogen and carbon KIE is greater in the acid-catalyzed than in the thermal rearrangement. Does this mean that the C-C bond is more, or less, formed in the transition state of the acid-catalyzed than in the thermal rearrangement? In fact, can the KIE data show how the transition

states of the two rearrangements differ? The acid-catalyzed is a one-proton rearrangement, so that one-half of the heterolyzing molecule is positively charged and the other half is like 2-naphthylamine. That is, the transition state has the polar character attributed in earlier years to all rearrangements by Banthorpe, Hughes, and Ingold.¹⁰ One would think, therefore, that the two halves of the transition state would be more closely linked by attraction than the two halves of the transition state in the thermal rearrangement. Furthermore, the transition state may be better represented by model **7a**, in which C-C bonding is well advanced, than by model **7b**.⁴¹

In summary, some understanding of the cleanliness and stereoselectivity of these uncommon rearrangements is now at hand. Bond breaking and making are concerted but do not occur to equal extents in the transition states. In this, concertedness constraints are placed on the geometry of the transition states, leading to *o*,-*o'* rather than other "allowable" concerted approaches to bonding. It will be interesting to find out whether or not similar transition-state characteristics exist in analogous [3,3]-sigmatropic rearrangements, particularly whether the extents of bond breaking and making also differ in the transition states of the well-known Claisen rearrangements.

Experimental Section

Dioxane was distilled from lithium aluminum hydride just before use. Silica gel for column chromatography was from Woelml (No. 402809). Eastman "Chromagram" silica gel sheets were used for TLC monitoring. Precoated plates of silica gel (Merck PLC 60F 254) were used for preparative TLC. Flash chromatography was carried out with J. T. Baker Co. apparatus and silica gel (25–40 μ m).

[¹⁵N,¹⁵N]- and [1,1'-¹³C₂]-2,2'-Azonaphthalene were prepared as shown in Schemes I and II.²⁴ Mass spectrometric analyses showed the former to be 99.4% ¹⁵N₂ and 0.80% ¹⁵N₁. Analysis of the latter showed it to be 95.2% ¹³C₂ and 4.3% ¹³C₁.⁴² Mixtures of enriched and nonenriched azonaphthalene were made and crystallized so as to give homogeneous mixtures containing approximately 5 mol % of the enriched molecule. The mixtures were used for preparing enriched 2,2'-hydrazonaphthalene (**1**) by reduction with zinc dust and ammonium chloride as described earlier.¹⁷ The slightly yellow product, mp 136–138 °C, 97% yield, was used without further purification.

Acid-Catalyzed Rearrangement of 1. A solution of 1.136 g (0.004 mol) of enriched 2,2'-hydrazonaphthalene in 500 mL of 70% aqueous dioxane was cooled to 0 °C. A solution of 21.2 g (0.199 mol) of lithium perchlorate and 0.142 g (0.001 mol) of 71% perchloric acid in 500 mL of 70% aqueous dioxane was similarly cooled. The two solutions were then mixed quickly in a flask equipped with stirrer and standing in an ice bath. The solution was stirred under oxygen-free nitrogen at 0 °C. After a few minutes, 200 mL of solution was pumped out for 100% conversion. This solution was kept under oxygen-free nitrogen at 0 °C for 24 h. The solution remaining in the reaction flask was quenched after adequate time for low conversion by addition of 40% aqueous sodium hydroxide to alkaline pH. The unrearranged 2,2'-hydrazonaphthalene in an alkaline, quenched aliquot was next oxidized to 2,2'-azonaphthalene by bubbling oxygen for 4 to 5 h. Conversions were calculated from the yields of isolated products.

The mixture of products was separated as follows. The oxidation solution was evaporated to dryness at room temperature in a rotary evaporator, and the residue was extracted with benzene. The diamine (**2**) in the benzene solution was extracted with 10% hydrochloric acid. The acid solution was neutralized with ammonium hydroxide, and the precipitated diamine was collected, washed, and dried. The crude 2,2'-diamino-1,1'-binaphthyl had mp 190–191 °C. The remaining benzene solution was evaporated to dryness at room temperature, and the residue was taken up in the minimum amount of hot 95% ethanol. 2,2'-Azonaphthalene crystallized out and was collected. The residual ethanol solution was evaporated to dryness, giving a dark brown solid. This solid was dissolved in ether, a small amount of insoluble material was filtered

(41) A referee has commented that "a high nitrogen and low carbon KIE would seem to be highly consistent with a loose transition state having much N-N bond breaking and little C-C bond formation. A loose transition state seems consistent with the postulated steric repulsions, and it seems likely that the transition state would be looser in the case of acid catalysis, since the electron withdrawal by the H⁺ would leave lessened electron density for bonding".

(42) We thank Dr. Frank W. Crow, Midwest Center for Mass Spectrometry, and NSF Regional facility, Department of Chemistry, University of Nebraska, Lincoln, NE, for these analyses.

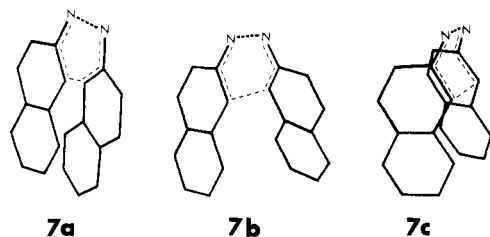


Figure 1. Representations, in skeletal form, of possible transition states in the [3,3]-sigmatropic rearrangement of 2,2'-hydrazonaphthalene. **7a** represents a distorted chair conformation in which C-C bonding is advanced before N-N bond breaking has its effect on the transition state, with little overlap of the naphthyl rings. **7b** represents a distorted chair conformation in which little C-C bonding has occurred during N-N bond breaking, also concomitant with little overlap of the naphthyl rings. **7c** represents a boat conformation leading to maximized overlap of the naphthyl rings.

off, and the ethereal filtrate was evaporated to dryness. The residue, a mixture of the dibenzocarbazole and azonaphthalene, was separated by column chromatography (silica gel, cyclohexane/ether 1:1). The separated 3,4:5,6-dibenzocarbazole had mp 153–155 °C. In most cases, the sum of all products isolated accounted for 97–99% of the 2,2'-hydrazonaphthalene which was used.

The diamine (**2**) was converted quantitatively into its bis(trifluoroacetyl) derivative by heating with trifluoroacetic anhydride in benzene. The derivative crystallized on cooling the solution and was recrystallized from benzene, mp 194–195 °C.

Thermal Rearrangement of 1. Rearrangement was carried out in boiling 95% ethanol under argon. The rate constant for this rearrangement at 80 °C has been given as $9.7 \times 10^{-3} \text{ min}^{-1}$,¹⁷ and this was used for calculating the times for our low and 100% conversions. Again, however, the actual extents of conversion were calculated from the sum of the products obtained. For complete conversion, the solution was heated for 9 h. Product workup at this conversion gave 3–4% azonaphthalene. Initially, we attempted to carry out rearrangements in sealed vessels and also in an autoclave. However, the time lag in bringing the solution to 80 °C in sealed vessels was too large for obtaining predictable conversions. Therefore, introduction of solid **1** into preheated solvent was used. A typical experiment is described.

A flask containing 200 mL of 95% ethanol and fitted with reflux condenser and argon inlet was placed in an oil bath kept at 80 °C. A slow stream of oxygen-free argon was passed through boiling ethanol and into the flask. Solid **1**, 568 mg (2 mmol), was added in one batch to the heated, stirred ethanol. After an appropriate time, the solution was cooled quickly in an ice bath, poured into 40 mL of distilled water, and

made alkaline with a few milliliters of sodium hydroxide solution. Unconverted **1** was then oxidized by bubbling air through the solution for 5 h. For 100% conversion, the same procedure was used but with 284 mg of **1** and 100 mL of ethanol.

After air oxidation, the solution was evaporated to dryness on a rotary evaporator. The residue was dissolved in benzene, and the benzene solution was extracted with 10% hydrochloric acid. Further separations were carried out as described above.

KIE Measurements. Mass ratios were determined with a Hewlett-Packard Model 5985B mass spectrometer. All samples were introduced into the mass spectrometer via the solid-sample inlet. Samples were heated as required to maintain a constant source pressure of 8×10^{-7} torr. Data collection was achieved by monitoring the absolute abundances of appropriate ions at 70 eV. A total of 19 950 repetitive scans per sample was obtained with an average dwell time of 50 ms/ion. The resulting data were analyzed in blocks of 750 scans, the absolute abundances being added and then averaged for each block to yield the mean and its standard deviation, from which the ratio of masses was calculated by routine statistical methods. KIE were then calculated from these ratios as described in the results section. For solving eq 4 by iteration, the limits of k_2/k_1 were initially chosen as 0.90 and 1.0. Iterations were then carried out by increasing k_2/k_1 in increments of 0.0005. Having thus obtained a value of k_2/k_1 satisfying eq 4, new but narrower limits were chosen which embraced the value of k_2/k_1 , and iterations were repeated in increments of 0.00001. This procedure was adopted because of limitations in computer capacity and time. The value of k_2/k_1 so obtained was inverted (k_1/k_2) and is expressed as KIE in Table II. Standard deviations in KIE arising from errors in mass measurements and given in Table II were calculated from the standard deviation of the mean in the mass spectrometric data. We have made these calculations as they pertain to the value of ROBS used in eq 4. That is $\text{ROBS} = R_p/R'_p$, in which R_p is the normalized ratio $(M+2)/M$ at conversion F and R'_p is the ratio at conversion F' . The normalized ratio $(M+2)/M$ is $[(M+2)_{\text{exp}} - (M+2)_{\text{std}}] / [(M+2)_{\text{exp}} - (M+2)_{\text{std}}]_F$. Each $(M+2)$ term in this expression has its own standard deviation of the mean. Therefore, the standard deviation in ROBS was calculated by routine statistical methods for the mean and variance in the difference and quotient of two random variables.⁴³

Registry No. 1, 613-64-9; **2**, 4488-22-6; **2** *N,N'*-bis(trifluoroacetyl) derivative, 62542-24-9; **3**, 194-59-2; ¹⁵N, 14390-96-6; ¹³C, 14762-74-4; 2,2'-azonaphthalene, 582-08-1.

(43) Mood, A. M.; Graybill, F. A.; Boes, D. C. "Introduction to the Theory of Statistics", 3rd ed.; McGraw-Hill: New York, 1974; pp 178–181.