methanol (10:1 v:v) and fractions 36–60 (20 mL) afforded 440 mg (23%) of hydrazide **15** on evaporation. Anal. Calcd for $C_{16}H_{23}N_5O_8$: C, 46.48; H, 5.60; N, 16.94. Found: C, 46.90; H, 5.91; N, 16.22. This material was crystallized from ethanolic hydrogen chloride. Anal. Calcd for $C_{16}H_{24}N_5O_8Cl$: C, 42.70; H, 5.37; N, 15.56. Found: C, 42.37; H, 5.77; N, 15.26. $M^{+\cdot}$ 701 (Me_3Si).

Registry No. 1, 11031-38-2; **2a**, 68833-11-4; **2b**, 69279-50-1; **3**, 69282-19-5; **4a**, 71606-18-3; **4b**, 71606-17-2; **4c**, 71606-19-4; **4d**, 71606-16-1; **4f**, 71839-37-7; **4g**, 82597-20-4; **4h**, 79005-87-1; **5**, 68833-57-8; **6**, 68889-77-0; **7a**, 69282-25-3; **7b**, 69282-24-2; **7c**, 69282-18-4; **8a**, 69282-21-9; **8b**, 71502-33-5; **9**, 72670-48-5; **10**, 82537-35-7; **11a**, 69282-23-1; **11b**, 3780-30-1; **11c**, 82537-36-8; **12** (R = CO_2H), 71502-31-3; **13**, 71502-32-4; **14**, 82537-37-9; **15**, 82537-38-0; **16**, 82537-39-1.

Supplementary Material Available: Tables 1–6 listing final atomic coordinates and thermal parameters for nonhydrogen atoms (1), bond lengths (2), bond angles (3), and final atomic coordinates for hydrogen atoms (4) and their respective bond distances (5) and angles (6) for **4c** (6 pages). Ordering information is given on any current masthead page.

Benzidine Rearrangements. 17. The Concerted Nature of the One-Proton *p*-Semidine Rearrangement of 4-Methoxyhydrazobenzene[1,2]

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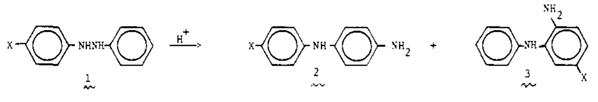
Abstract: The nitrogen kinetic isotope effects (KIE) for the acid-catalyzed rearrangement of 4-methoxyhydrazobenzene (**1b**) into the *p*-semidine (4-methoxy-4′-aminodiphenylamine, **2b**) and *o*-semidine (2-amino-5-methoxydiphenylamine, **3b**) have been measured and are 1.0296 (av) and 1.074 (av), respectively. The carbon KIE for formation of **2b** was found to be 1.039 (av). The results show that *p*-semidine formation is a concerted process. Rearrangements were carried out in 60% aqueous dioxane under conditions of earlier kinetic work. Mixtures of **1b** and [^{15}N,$^{15}N'$]**1b** were used for the nitrogen KIE, measured mass spectrometrically with isolated *N*-benzoyl-**2b**, and mixtures of **1b** and [4′-^{14}C]**1b** for the carbon KIE, measured with scintillation counting on isolated *N*-benzoyl-**2b**. The method of carbon labeling did not allow for a measurement of the KIE for formation of **3b**.

The acid-catalyzed *p*-semidine rearrangement is the rearrangement of a 4-substituted hydrazobenzene (eq 1). The *p*-semidine (**2**) is formed from bonding between the nitrogen attached to one ring and the *p*-carbon atom of the second ring. An *o*-semidine (**3**) is also usually formed.



(1)

For a number of years in the past the *p*-semidine rearrangement was believed not to be a valid member of the class of acid-catalyzed benzidine rearrangements. This belief came about first because it was difficult for early workers to accept that such a remarkable change in geometry could occur intramolecularly and second from a misreading of the early literature by Hammick and Munro.[4] These workers thought that all of the then known cases of *p*-semidine rearrangements had been achieved by the so-called Jacobson method, namely the reaction of an azobenzene with an acid reducing medium, such as aqueous $SnCl_2$–HCl. In this method the azobenzene is reduced to the hydrazobenzene, which next rearranges in the acid solution. Having failed themselves to bring about a purely acid-catalyzed *p*-semidine rearrangement (of 4-ethoxyhydrazobenzene), Hammick and Munro concluded that this type of rearrangement could be successful only by the Jacobson method because the rearrangement required the presence of a heavy-metal ion and was, in fact, an intermolecular one, assisted, in an unspecified Friedel–Crafts way, by the metal ion. Hammick and Munro (and all other later workers) overlooked some very early reports by Jacobson of rearrangements of 4-substituted hydrazobenzenes in acid solution only, for example, of **1a** (X = Cl).[5,6] Consequently, the *p*-semidine rearrangements attracted particular attention, first with attempts to find if they were really members of the family of benzidine rearrangements and next, after this question had been reanswered affirmatively,[6] with attempts to understand how the rearrangements could occur intramolecularly.

It is now known that *p*-semidine rearrangements are not only acid catalyzed but that they have another characteristic of benzidine rearrangements in that some of them are one-proton (e.g., **1b**, X = MeO)[7] and others (e.g., **1a**) two-proton rearrangements.[8,9] Furthermore, Heesing and Schinke have shown with the use of labeled molecules that the rearrangements of **1a**[10] and **1b**[11] are truly intramolecular.

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[1] Part 16: Shine, H. J.; Zmuda, H.; Park, K. H.; Kwart, H.; Horgan, A. G.; Brechbiel, M. *J. Am. Chem. Soc.* **1982**, *104*, 2501.

[2] Supported by the National Science Foundation Grants CHE 78-00813 and 79-11110.

[3] On leave from the Silesian University, Katowice, Poland.

[4] Hammick, D. L.; Munro, D. C. *J. Chem. Soc.* **1950**, 2049.

[5] Jacobson, P. *Liebigs Ann. Chem.* **1909**, *367*, 304.

[6] Shine, H. J. In "Mechanisms of Molecular Migrations"; Thyagarajan, B. S., Ed.; Interscience: New York, 1969; Vol. 2, pp 191–247.

[7] Banthorpe, D. V.; Cooper, A. *J. Chem. Soc., Perkin Trans. 2* **1968**, 605.

[8] Banthorpe, D. V.; Cooper, A. *J. Chem. Soc., Perkin Trans. 2* **1968**, 618.

[9] See Cox and Buncel (Cox, R. A.; Buncel, E. In "The Chemistry of the Hydrazo, Azo and Azoxy Groups"; Patai, S., Ed.; Wiley: New York, 1975; pp 775–859) for the most recent summary of kinetic data.

[10] Heesing, A.; Schinke, U. *Chem. Ber.* **1977**, *110*, 3319.

[11] Heesing, A.; Schinke, U. *Chem. Ber.* **1972**, *105*, 3838.

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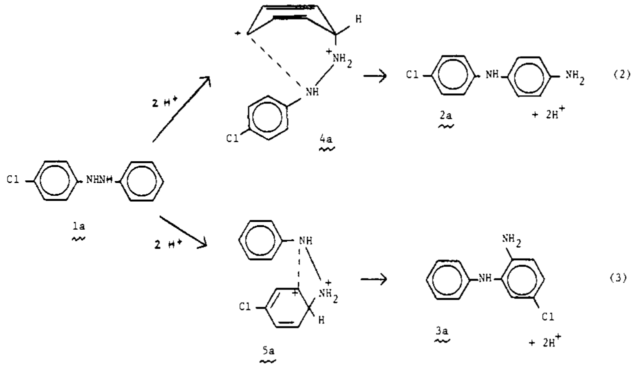
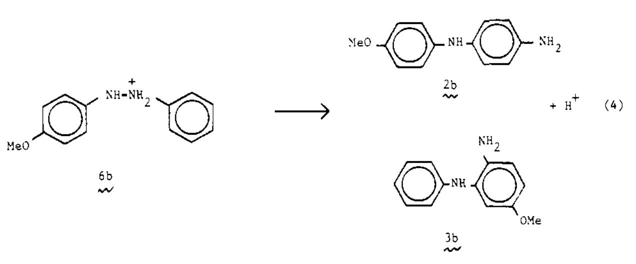
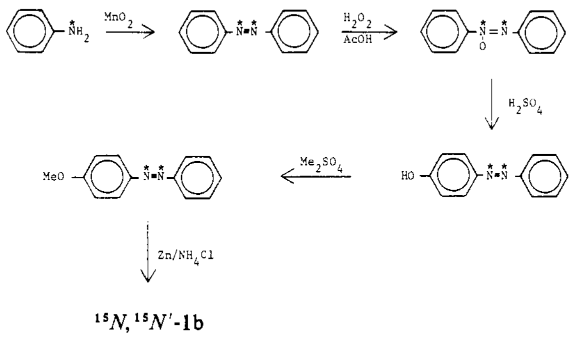
The major question remains therefore: namely, how can *p*-semidine rearrangements occur intramolecularly? Are they concerted processes or do they involve tightly bound fragments formed after breaking of the N–N bond? Difficulties in formulating a satisfactory picture for such a molecular contortion as an intramolecular *p*-semidine rearrangement have made this class of rearrangements a particularly attractive model for the ring-protonation theory. In this theory, as applied to two-proton rearrangements, the second protonation occurs at an ipso position and causes the aryl ring to adopt a bent cyclohexadienyl-like configuration, suited, for example, to the bonding requirements of a *p*-semidine rearrangement.[12,13] This formulation has been adopted for the rearrangement of **1a** by Heesing and Schinke, who represent with **4a** the intermediate that leads to the *p*-semidine (**2a**), eq 2.[10] The rearrangement of **1a** gives not only **2a** but also, in larger yield, an *o*-semidine, **3a**. The pathway to **3a** has been represented also with an ipso-protonated intermediate, but in this case with **5a** (eq 3). Thus, in each case the required bonding positions are viewed as having been brought close together by ring protonation. Whether or not bonding between N and C′ atoms is then concerted with the breaking of the N–N bond has not been investigated, but the implication in the drawings is that it is.



Recently we presented evidence and arguments in the rearrangement of hydrazobenzene itself that the ring-protonation theory, as it applies to that two-proton case, is not valid.[1] We feel that the ring-protonation representation of the rearrangement of **1a** is not likely to be valid either, but arguments on that case must await further study. What about the rearrangement of **1b**, a one-proton case? Here, there is little argument as to where the protonation occurs. Among proponents of the ring-protonation theory, only Lupes[13] applies it to one-proton rearrangements, while others accept, as appears reasonable to us, that the first protonation of a hydrazo aromatic occurs at nitrogen.[1] The question to be answered, therefore, is how does monoprotonated **1b** (**6b**, eq 4) rearrange to **2b**? We have set out to answer that question with measurements of nitrogen and carbon kinetic isotope effects (KIE). We have prepared 4-methoxy[^{15}N,^{15}N′]hydrazobenzene ([^{15}N,^{15}N′]**1b**) and 4-methoxy[4′-^{14}C]hydrazobenzene ([4′-^{14}C]**1b**) and have measured the KIE of their rearrangement. We shall show that the rearrangement to **2b** is a concerted process. We are not able to describe the rearrangement to **3b** completely, since we have not measured its carbon KIE, but from the size of the nitrogen KIE, we feel that it is not a concerted process.



Scheme I



Scheme II

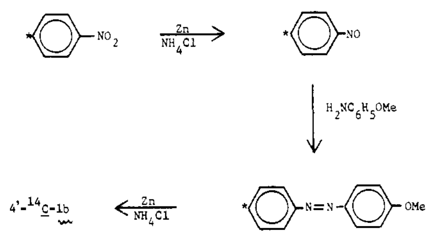


Table I. Kinetic Isotope Effects for the Formation of **2b** and **3b** from **1b** in 60% Aqueous Dioxane at 0 °C

	KIE		
	2b		3b
% conversion	$k(^{12}C)/k(^{14}C)$	$k(^{14}N)/k(^{15}N)$	$k(^{14}N)/k(^{15}N)$
5	1.0368		
10	1.0390	1.0286	1.0671
10	1.0412	1.0305	1.0809

Results and Discussion

[^{15}N,^{15}N′]**1b** was prepared as in Scheme I, beginning with commercially available 99% [^{15}N]aniline. Dilution of the fully doubly labeled product with unlabeled material was carried out at the 4-methoxyazobenzene stage, so that the labeled hydrazo compound used finally for rearrangements contained approximately 5 mol% of [^{15}N,^{15}N′]**1b**.

[4′-^{14}C]**1b** was prepared as in Scheme II beginning with [4-^{14}C]nitrobenzene, which we had prepared earlier and which had an activity of 16 mCi/mol. Again, dilution was carried out at the 4-methoxyazobenzene stage so as to give a final product with an activity of 5 mCi/mol.

Rearrangements were carried out in 60% aqueous dioxane at 0 °C in buffered solutions designed for a pH of 4.43, as described by Banthorpe and Cooper.[7] It was found essential to carry out the rearrangements in an oxygen-free atmosphere, and therefore oxygen-free argon was used.

Rearrangements were stopped after 5% and 10% conversions, the times of conversion being calculated from the published first-order rate constant;[7] 100% conversion was achieved by allowing reaction to go overnight. In previous work with hydrazobenzene the hydrazo compound remaining at low conversions was oxidized to azobenzene with air.[1] This procedure was found to be completely unusable in the present case because both of the semidines were also oxidized very quickly to brown gummy material. Therefore, the products and unrearranged **1b** were benzoylated at the low conversions, while the products were benzoylated at 100% conversion. This is similar to the procedure used in the study of the intramolecularity of the rearrangement by Heesing and Schinke, who acetylated the products at 100% conversion before separating them.[11] We found benzoylation to be more convenient. Our procedure required the separation of mono-*N*-benzoyl derivatives of semidines **2b** and **3b** and mono-*N*-benzoyl derivatives of **1b**. Conditions of separation were worked out with authentic benzoyl derivatives of **1b** and **2b**, prepared

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[12] Allan, Z. J. *Tetrahedron Lett.* **1971**, 4225; *Monatsh. Chem.* **1975**, *106*, 429.

[13] Lupes, M. E. *Rev. Roum. Chim.* **1972**, *17*, 1253.

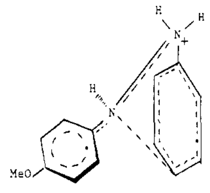
separately. We did not have authentic *N*-benzoyl-**3b**, but this was identifiable in the mixture of the four monobenzoyl derivatives by its difference from the three known ones.

The KIE measured for the formation of **2b** and **3b** are given in Table I. A carbon KIE is not listed for **3b** because our method of labeling **1b** could not have distinguished between the presence and absence of a KIE. Nevertheless, the scintillation counting measurements were made on the isolated samples of *N*-benzoyl[^{14}C]**3b** as a test of the cleanliness of our isolation procedure, and gave as expected $k(^{12}\mathrm{C})/k(^{14}\mathrm{C}) = 1.000$ for each conversion.

The results show that there is a substantial nitrogen and carbon KIE for the formation of **2b**. This means that breaking of the N–N bond and making of the N–4C′ bond are part of the rate-determining transition state, that is, that the formation of **2b** is a concerted process. The sizes of the KIE are similar to those reported for the formation of benzidine from hydrazobenzene, which were 1.022 for the nitrogen and 1.028 for the carbon KIE.[1] These orders in size appear to be diagnostic of the concerted rearrangements. In contrast, the nitrogen KIE for the formation of **3b** is much larger, and also similar to that found for the nonconcerted formation of diphenyline from hydrazobenzene, namely 1.063.[1] Although we have not yet been able to measure a bond-making KIE for the formation of **3b**, because of the difficulty of synthesizing the required labeled precursor, it appears that the size of the nitrogen KIE (av 1.0740) is symptomatic of a dissociative process. The formation of **3b** from **1b** is a [1,3] sigmatropic shift and does not, in fact, conform with a symmetry-allowed concerted suprafacial process.

As for the concerted formation of **2b**, it is now seen, contrary to earlier-held misgivings,[6] that protonated **1b** (i.e., **6b**, eq 4) must be able to adopt the necessary conformation for a [1,5] sigmatropic shift.

It is the practice to represent protonation of **1b** as shown (**6b**) on the less basic nitrogen atom. The reason for this may be that in the heterolytic breaking of the N–N bond according to the polar-transition-state theory the *p*-anisidinyl-like portion of the transition state is better able to support the electron deficiency, which will then develop in its half of the molecule. Heterolysis in this fashion is thought to be more in accord with the formation of the two products (**2b** and **3b**).[9] We have used the customary formulation, but it makes no difference, particularly, in a concerted process which half of the molecule is designated as carrying the positive charge or the pair of electrons. Two representations of the 1,5 shift are shown. In one of them (**7**) the rings are shown as being planar, and in the other (**8**) one of the rings is bent, which may well be the conformation that is adopted in the transition state. The question of ring geometry arises in all of the benzidine rearrangements and has been discussed for the benzidine case itself.[1]



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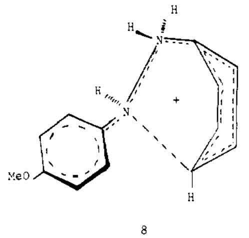

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We have made a calculation of KIE for the transition state (**8**), using the simplified procedures described earlier.[1,14] The procedure used for the breaking of the N–N bond was exactly as described earlier, except of course now for a one-proton process, and gave a calculated nitrogen KIE ($k(^{14}\mathrm{N})/k(^{15}\mathrm{N})$) of 1.0202. In order to calculate the KIE for making the N–4C′ bond, it was necessary to estimate the force constant for the bond in the transition state (**8**) and, therefore, to choose a known vibrational frequency for a C–N bond in a molecule with somewhat similar geometry. We chose the value of 845 cm^{-1} from the spectrum of *N,N*′-tetramethylene-*o*-semidine.[15] The force constant was calculated and half of its value was used for calculating the frequency of the N–4C′ bond in the transition state. The cut-off treatment was used again,[16] and all other assumptions and steps in the calculation were the same as described earlier,[17] giving a calculated value of $k(^{12}\mathrm{C})/k(^{14}\mathrm{C})$ of 1.0367. The calculated value of $k(^{14}\mathrm{N})/k(^{15}\mathrm{N})$ for the dissociative process was 1.0633.

Our conclusion is that in spite of its simplicity and the assumptions involved, the calculation gives results that distinguish between concerted and dissociative processes and that correspond reasonably well with the experimental results. The *p*-semidine rearrangement of **1b**, therefore, is a symmetry-allowed concerted process, while the *o*-semidine rearrangement of **1b** has the earmark of a dissociative process.

Some aspects of the rearrangement of **1b** (and other 4-substituted hydrazobenzenes) remain puzzling. The *o*-semidine (**3b**) is the major product, noted also by Heesing and Schinke.[11] The pathway to **3b** would appear therefore to be the more easily achieved, and perhaps this reflects the difficulty that **6b** has in reaching the geometry of the concerted transition state. Yet, another possible product, allowed by orbital symmetry in a concerted process, the *o*-benzidine, is not formed. It may be that charge or spin densities do not favor 2,2′ bonding,[1] but we do not really know the answer to this part of the benzidine puzzle.

It is interesting to note, finally, that a carbon isotope effect, $k(^{12}\mathrm{C})/k(^{14}\mathrm{C}) = 1.049$, was measured by Volford et al.[18] for the formation of a C–N bond in the thermal cyclization of a picolylaminomethylene malonic ester into a pyrimidinone.

Experimental Section

Materials. Dioxane was distilled over sodium in an argon atmosphere. Pyridine was dried first over potassium hydroxide pellets, and next over barium oxide before distilling. Silica gel (Woelm 04657, 0.063–0.2 mm) was used for column chromatography. Precoated PLC plates, silica gel 60 F 254 (E. Merck, No. 5766), were used for preparative TLC.

[^{15}N,^{15}N′]Azobenzene. A suspension of 10.3 g of active manganese dioxide in a solution of 2 g (21.3 mmol) of [^{15}N]aniline in 150 mL of dry benzene was boiled under reflux for 6 h. The water formed was removed in a Dean–Stark separator. Workup of the benzene solution and column chromatography of the crude product gave 1.86 g (96%) of [^{15}N,^{15}N′]-azobenzene, mp 67 °C.

[^{15}N,^{15}N′]Azoxybenzene was prepared in 75% yield by oxidation of labeled azobenzene in acetic acid with 30% hydrogen peroxide.[19]

4-Hydroxy[^{15}N,^{15}N′]azobenzene. The general procedure for a Wallach rearrangement was followed.[20] A mixture of 1.5 g of doubly labeled and 8.5 g of ordinary azoxybenzene was dissolved in 200 mL of 85% sulfuric acid. After standing for 48 h at room temperature the solution was poured onto 500 g of crushed ice, giving 10.1 g of a dark solid. The solid was extracted with *n*-hexane in a Soxhlet extractor until the extract solution was colorless. Evaporation of the hexane gave a solid residue, which was dissolved in ether. The ether solution was washed first with aqueous sodium bicarbonate to remove sulfonated products, next with water, and last with 10% aqueous sodium hydroxide. Acidification of the sodium hydroxide solution, extraction with ether, and workup of the dried ether solution gave 5.1 g (51%) of 4-hydroxyazobenzene, now containing approximately 15% of the double labeled molecule. This was used without purification to make the *O*-methyl derivative (below). Workup of the bicarbonate extract gave 900 mg of what we think was 4-hydroxyazobenzene-4′-sulfonic acid. Workup of the nonacidic residue in the ether solutions gave 3 g of azobenzene.

4-Methoxy[^{15}N,^{15}N′]azobenzene. To a solution of 3.0 g (15.2 mmol) of the 4-hydroxyazobenzene in 25 mL of 20% aqueous potassium hydroxide at 0 °C was added 2.0 mL of dimethyl sulfate.[21] After the mixture was stirred at room temperature for 18 h the precipitated solid was filtered, washed with water, and dried. Column chromatography

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[14] Shine, H. J.; Zmuda, H.; Park, K. H.; Kwart, H.; Horgan, A. G.; Collins, C.; Maxwell, B. E. *J. Am. Chem. Soc.* **1981**, *103*, 955.

[15] Wittig, G.; Joos, W.; Rathfelder, P. *Liebigs Ann. Chem.* **1957**, *610*, 180.

[16] Stern, M. J.; Wolfsberg, M. *J. Chem. Phys.* **1966**, *45*, 4105.

[17] The term $(m_{\mathrm{H}}^{\ddagger}/m_{\mathrm{L}}^{\ddagger})^{1/2}$, in which $m_{\mathrm{H}}^{\ddagger}$ and $m_{\mathrm{L}}^{\ddagger}$ are the reduced masses in the transition state, thus becomes $[(37 \times 142)/(39 \times 140)]^{1/2}$.[14]

[18] Volford, J.; Meszaros, Z.; Kovacs, G. *J. Labelled Compd.* **1973**, *11*, 231.

[19] Gagnon, P. E.; Newbold, B. T. *Can. J. Chem.* **1959**, *37*, 3661.

[20] Wallach, O.; Belli, L. *Chem. Ber.* **1880**, *13*, 525.

[21] Colombano, A. *Gazz. Chim. Ital.* **1907**, *37*, 471.

with benzene elution gave 2.75 g (12.9 mmol, 85%) of 4-methoxybenzene, mp 56 °C (lit. mp 56 °C).[21] Mass spectrometry showed that this contained approximately 18% of the double labeled molecule.

Crystallization after mixing again with ordinary 4-methoxyazobenzene gave the 5 mol% of doubly labeled starting material.

4-Methoxy[^{15}N,^{15}N′]hydrazobenzene, approximately 5 mol% double labeled, was prepared by reduction of the azo compound in 95% ethanol with zinc dust and saturated aqueous ammonium chloride.[7] The hydrazo compound was precipitated by filtration into degassed aqueous ammonium hydroxide, washed, dried, and used without crystallization, mp 72 °C, 83% yield (lit. mp 72 °C).

Nitroso[4-^{14}C]benzene. Zinc dust (3.8 g) was added in small portions to a stirred suspension of 3.0 g (24.4 mmol) of nitro[4-^{14}C]benzene[1] (approximately 16 mCi/mol) in 50 mL of water containing 1.5 g of ammonium chloride at room temperature. Stirring was continued for 20 min after addition was complete. The suspension was filtered, and the inorganic residue was washed with 60 mL of hot water. To the aqueous solution was added 20 g of crushed ice, and the solution was kept at 0 °C while 7.5 mL of concentrated sulfuric acid and 10 g of crushed ice were added. To the rapidly stirred acid solution was added very rapidly an ice-cold solution of 1.7 g of sodium dichromate dihydrate in 7.5 mL of water. After 3 min the straw-colored precipitate of nitroso[4-^{14}C]benzene was filtered and washed twice with water. Drying in the desicator gave 2.42 g (22.6 mmol, 93%) of nitroso[4-^{14}C]benzene, mp 67 °C.

4-Methoxy[4′-^{14}C]azobenzene.[22] To a solution of 2.5 g (20 mmol) of commercial *p*-anisidine in 20 mL of acetic acid maintained at 40 °C was added 2.4 g (22 mmol) of nitroso[4-^{14}C]benzene. The solution was allowed to stand at room temperature for 2 days and was then poured into 100 mL of water. The product obtained by extracting the aqueous solution with ether was chromatographed (column) with benzene elution, giving 3.4 g (16 mmol, 80%) of 4-methoxy[4′-^{14}C]azobenzene, mp 56 °C.

For KIE measurements this product was diluted with ordinary 4-methoxyazobenzene and crystallized from benzene:hexane (1:1) so as to give a labeled product of ca. 5 mCi/mol activity.

Benzoylation of 4-Methoxyhydrazobenzene (1b). To a solution of 200 mg (0.83 mmol) of **1b** in 2 mL of pyridine was added 0.5 mL of benzoyl chloride. After 4 h the solution was poured into 50 mL of water, and the water solution was extracted with ether. The ether solution was washed with water several times, dried over magnesium sulfate, and evaporated. The residue was separated by preparative TLC into a solid (250 mg, mp 105 °C) and an oily fraction, using a mixture of hexane, ether, and acetone (43:47:10 by volume). The oil was shown by mass spectrometry and repeated TLC to be a mixture of benzanilide and 4-methoxybenzanilide. The low-resolution mass spectrum of the solid had identifiable peaks at m/e 318 (M$^+$, 1.3), 227 (14), 213 (12), 122 (13.3), 105 (C_6H_5CO, 100), and 93 (20.3). This solid is believed to be 1-benzoyl-1-(4-methoxyphenyl)-2-phenylhydrazine.

Anal. Calcd for $C_{20}H_{18}N_2O_2$ (M_r 318); C, 75.5; H, 5.69; N, 8.80. Found: C, 75.7; H, 5.88; N, 8.76.

Benzoylation of 4-Amino-4′-methoxydiphenylamine (2b). Authentic **2b** was obtained as Variamine Blue hydrochloride from Fluka. The free base (**2b**) was liberated with sodium hydroxide, extracted with ether, and benzoylated as above. A solid was precipitated on pouring the pyridine solution into water. This was crystallized from ethanol, giving mp 138 °C. The low-resolution mass spectrum had identifiable peaks at m/e 318 (M$^+$, 11.6), 227 (19.1), 213 (12.5), 122 (1.8), 105 (C_6H_5CO, 100), and 93 (1.9), consistent with the structure of 4-(benzoylamino)-4′-methoxydiphenylamine. This derivative became discolored (violet) on storage.

2-(Benzoylamino)-5-methoxydiphenylamine (*N*-Benzoyl-3b). This was not prepared from authentic **3b** but was isolated from the rearrangement of **1b** and had mp 178 °C (ethanol). The low-resolution mass spectrum had peaks at m/e 318 (M$^+$, 21.2), 301 (20.6), 300 (22.6), 285 (21), 227 (4.3), 213 (39), 212 (37), 198 (4.2), 182 (20.3), 123 (4), 105 (99), 93 (2.4), and 92 (4.3).

Anal. Calcd for $C_{20}H_{18}N_2O_3$ (M_r 318): C, 75.5; H, 5.69; N, 8.80. Found: C, 74.8; H, 5.83; N, 8.51.

The peak at 182 is thought to be from $C_6H_5COC_6H_5$, formed by rearrangement (and fragmentation) of M$^+$.

Rearrangement of Labeled 4-Methoxyhydrazobenzene. Rearrangements were carried out under the conditions of the kinetics reported earlier,[7] and the times of achieving partial conversions were calculated from the reported first-order rate constant.[7] An example is given for isolating products after 10% rearrangement. Rearrangements were carried out under oxygen-free argon because of the high susceptibility of 4-methoxyhydrazobenzene and even higher susceptibility of the semidine rearrangement products to air oxidation, particularly in solution. Also, because the products are so sensitive to air oxidation, it was impossible this time to use the air-oxidation method of handling unrearranged substrate that we adopted with rearrangements of hydrazobenzene.[1] Instead, the products and unrearranged 4-methoxyhydrazobenzene were benzoylated immediately after stopping the rearrangement, and the benzoyl derivatives were separated as described below. The benzoyl derivatives of the *o*- and *p*-semidines were used for KIE measurements. Rearrangements were carried out in solutions buffered for achieving a pH 4.43, the buffer being made by mixing 60 mL of 1.0 N aqueous chloroacetic acid, 18 mL of 1.0 N sodium hydroxide, and 6.5 g of lithium perchlorate hydrate in 22 mL of water.[7]

A solution of 856 mg (4 mmol) of labeled 4-methoxyhydrazobenzene in 300 mL of dioxane and 200 mL of water at 0 °C was mixed quickly with a solution, also at 0 °C, made from 300 mL of dioxane, 100 mL of buffer, and 100 mL of water. The concentration of substrate was thus 4×10^{-3} M. Rearrangement was stopped after 10 min 20 s by adding 30 mL of 40% aqueous sodium hydroxide. The solution was extracted with 450, 150, and 100 mL of ether. The combined ether layer was washed several times with water to remove dioxane, dried over magnesium sulfate, and evaporated. The residue was dissolved in 100 mL of benzene and concentrated to 20 mL by distillation to remove remaining water. Then, 20 mL of pyridine was added, followed by 2 mL of freshly distilled benzoyl chloride. After standing overnight this solution was poured into 100 mL of water and extracted with 2 × 100 mL of benzene. The benzene solution was washed several times with water to remove pyridine, dried, and evaporated. The mixture of benzoylated substrate and products was separated by column (2 × 34 cm) chromatography. Elution with 1 L of hexane gave fraction 1, elution with 600 mL of hexane–ether (1:1) gave fractions 2–5; elution with 1 L of acetone gave fraction 6. The six fractions were monitored with TLC (Eastman's silica gel sheets) and were found to be as follows: fraction 1, mainly 4-methoxyazobenzene; fraction 2, a mixture of 4-methoxyazobenzene and benzoylated 4-methoxyhydrazobenzene; fraction 3, mainly *N*-benzoyl-*o*-semidine and some of the benzoylated hydrazo compound; fraction 4, a mixture of *N*-benzoyl-*o*- and *p*-semidines; fraction 5, a similar mixture, but mainly the *N*-benzoyl-*p*-semidine; fraction 6, the *N*-benzoyl-*p*-semidine and some unknown resinous material. Fractions 3 and 4, and 5 and 6, were combined. Each combination was separated on preparative-scale TLC plates, with hexane–ether–acetone (43:47:10) for development. The appropriate band was removed from the plate material with ether, and the product was crystallized from hexane. In this way the combined fractions 3 and 4 gave 65 mg (51%) of 2-(benzoylamino)-5-methoxydiphenylamine (*o*-semidine), mp 178 °C, while combined fractions 5 and 6 gave 10 mg (7.9%) of 4-(benzoylamino)-4′-methoxydiphenylamine (*p*-semidine), mp 138 °C.

Similar procedures were used for 5% (5 min) and 100% (24 h) rearrangements.

KIE Measurements. For nitrogen KIE's the ratio of light and heavy products obtained at 10% and 100% conversions was measured by whole-molecule mass spectrometry, as described earlier.[1] The ratio $(m/(m+2))$ of masses measured was thus 318/320 for each of the *N*-benzoylated *o*- and *p*-semidine. Because these derivatives had low vapor pressures at ambient temperature, the probe for the mass spectrometer was heated thermostatically during each multiscan run. The number of scans recorded ranged from 15 000 to 30 000. The KIE thus obtained from two separate rearrangements to 10% conversion were, for the *p*-semidine (**2b**), 1.0286 ± 0.0002 and 1.0305 ± 0.0005, and for the *o*-semidine, 1.0671 ± 0.0001 and 1.0801 ± 0.0009.

For carbon KIE the ^{14}C content of a product was measured by scintillation counting,[1] and the KIE was calculated simply by dividing the count at 100% by that at low conversion. Because the concentration and nature of the substrate were the same in each comparison, it was considered not necessary to use an internal standard for absolute count measurements.

Registry No. 1b, 953-12-8; [4′-^{14}C]**1b**, 82582-21-6; [^{15}N,^{15}N′]**1b**, 82582-22-7; **2b**, 101-64-4; **3b**, 82582-23-8; *N*-benzoyl-**3b**, 82582-24-9; 4-(benzoylamino)-4′-methoxydiphenylamine, 55872-66-7; 1-benzoyl-1-(4-methoxyphenyl)-2-phenylhydrazine, 82582-25-0; [^{15}N,^{15}N′]azoxybenzene, 74638-78-1; 4-hydroxy[^{15}N,^{15}N′]azobenzene, 82582-26-1; 4-methyloxy[^{15}N,^{15}N′]azobenzene, 82582-27-2; nitroso[4-^{14}C]benzene, 82582-28-3; nitro[4-^{14}C]benzene, 31141-96-0; 4-methoxy[4′-^{14}C]azobenzene, 82582-29-4; *p*-anisidine, 104-94-9.

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[22] Jacobson, P.; Loeb, A. *Chem. Ber.* **1909**, *42*, 1079.