heated at reflux for 7 hr. The yields were: carbon dioxide, 40%; benzaldehyde, 5.8%; and diphenylmaleic anhydride, 45.7% (vpc).

Attempted Reaction of Pivalic Anhydride and Pivalic Acid with Pyridine N-Oxide. A solution of 0.0613 g (0.645 mmole) of pyridine N-oxide and 0.471 g (2.45 mmoles) of pivalic anhydride[42] in 10 ml of mesitylene was heated at 113° for 4.5 hr under a nitrogen atmosphere. No carbon dioxide and no isobutylene was produced. The reaction mixture was extracted with ether (five 10-ml portions) and the aqueous phase diluted to 100 ml. A portion (2.00 ml) of this solution was diluted to 100 ml and submitted to quantitative ultraviolet analysis using the pyridine N-oxide absorption at 254 mμ. This analysis indicated that 98% of the pyridine N-oxide was recovered.

Carbon dioxide was not produced in a similar reaction for 6 hr in refluxing xylene nor by the use of pivalic acid, acetic anhydride, and pyridine N-oxide in refluxing benzene for 16 hr.

Reaction of 4-Picoline N-Oxide and Pivalic Anhydride in Benzene. A solution of 8.7 g (80 mmoles) of 4-picoline N-oxide, 3.7 g (20 mmoles) of pivalic anhydride,[42] and 180 ml of benzene was heated at reflux for 71 hr. The yield of carbon dioxide was 88.6%.

Reaction of Phenylacetyl Chloride with Pyridine N-Oxide. To a mixture of 38.0 g (0.400 mole) of pyridine N-oxide and 400 ml of chloroform (ethanol-free) was added, dropwise and with stirring, at 30–35°, 15.4 g (0.100 mole) of phenylacetyl chloride. The temperature of the mixture was then raised to the reflux point (65°). The carbon dioxide evolution was, at first, fairly rapid, 1.10 g (25.0% of the theoretical amount) being evolved in the first 1.5 hr. After that, it slowed considerably and, during the final 24 hr of heating, only 0.62 g of additional carbon dioxide was evolved, for a total of 1.72 g (39.1%). The conversion to benzaldehyde was determined by gas chromatographic examination of the reaction mixture (Versamid column at 150°) to be 18.6%.

Reaction of Bicyclo[2.2.1]heptane-2-carboxylic Acid (Mixture of *exo* and *endo*) with Pyridine N-Oxide in Mesitylene. An exploratory run in refluxing benzene indicated that a higher temperature was required for decarboxylation (no carbon dioxide evolution was observed during 24 hr). Accordingly, a solution of 3.5 g (25 mmoles) of norbornane-2-carboxylic acid,[43] 9.80 g (100 mmoles) of pyridine N-oxide, and 7.1 g (70 mmoles) of acetic anhydride in 75 ml of mesitylene was heated at reflux for 45 hr. Carbon dioxide evolution (yield, 30%) appeared to be complete after 35 hr of heating.

Direct vpc analysis on a polyphenyl ether column at 100° showed that norcamphor was not present in the reaction mixture. The possible products norbornane and norbornene could not be determined by vpc since they have the same retention time as mesitylene. No evidence could be found for the presence of an unsaturated acid in the acid fraction of the product.

Reaction of *exo*-Bicyclo[2.2.1]hept-5-ene-2-carboxylic Acid and Pyridine N-Oxide. A solution of 19.3 g (200 mmoles) of pyridine N-oxide, 6.9 g (50 mmoles) of *exo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid,[43] 15.4 g (100 mmoles) of acetic anhydride, and 100 ml of benzene was heated at reflux for 31 hr. The yield of carbon dioxide was 35.4%. The neutral fraction of the product gave negative ketone tests with several reagents and exhibited an infrared spectrum of a mixed anhydride of the starting acid and acetic acid.

Similar runs made in refluxing toluene, xylene, dioxane, and diglyme afforded carbon dioxide and mixed anhydrides, but no condensable material was deposited in ice-cooled traps.

(42) M. F. Ansell, M. A. Davis, J. W. Hancock, W. J. Hickinbottom, P. G. Holton, and A. A. Hyatt, *J. Chem. Soc.*, 2705 (1955).

(43) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett, and R. Armstrong, *J. Am. Chem. Soc.*, 72, 3116 (1950).

The Wallach Rearrangement. II.[1] Kinetics of the Rearrangement of Azoxybenzene and Its Derivatives in Strongly Acidic Solution[2]

Chi Sun Hahn, Kyu Wan Lee, and H. H. Jaffé

Contribution from the Department of Chemistry, Yonsei University, Seoul, Korea, and the Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221. *Received March 7, 1967*

Abstract: A kinetic study of the rearrangement of azoxybenzene and α- and β-4-bromo- and α- and β-4-methylazoxybenzene into the corresponding hydroxyazobenzenes in 20 vol. % ethanol and 80 vol. % aqueous sulfuric acid–water solutions has been undertaken by ultraviolet spectrophotometry. The rate constants obtained show that the rearrangement is an acid-catalyzed pseudo-first-order reaction. The activation parameters of the rearrangement were obtained and several steps in the mechanism of the rearrangement are elucidated.

The investigation of the Wallach rearrangement, the conversion of azoxybenzene and its derivatives into 4-hydroxyazobenzene and the corresponding substituted hydroxyazobenzenes in the presence of strong acid, has recently been approached by two methods. One of these has focused on the position to which the azoxy oxygen atom migrates.[1,3,4] The other method has involved mechanistic studies of the rearrangement using isotopic tracers.[5,6] By the former method, Hahn and Jaffé found that the oxygen atom in the azoxy group of a 4-monosubstituted azoxybenzene migrates to the unsubstituted ring, depending neither on the nature of the substituent already present in the other ring, nor on the relation between the oxygen atom and the available position. It was found,

(1) Part I in the series: C. S. Hahn and H. H. Jaffé, *J. Am. Chem. Soc.*, 84, 946 (1962).

(2) (a) This investigation was financially supported by the United Board for Christian Higher Education in Asia and the Graduate School of Yonsei University. (b) This paper comprises a portion of the dissertation submitted by K. W. Lee in partial fulfillment of the requirements for the M.S. degree in the Graduate School of Yonsei University, Seoul, Sept 1966. (c) Presented at the 16th and 17th Annual Meeting of the Korean Chemical Society, 1965 and 1966.

(3) L. C. Behr, E. G. Alley, and O. Levand, *J. Org. Chem.*, 27, 65 (1962).

(4) J. Singh, P. Singh, J. L. Boivin, and P. E. Gagnon, *Can. J. Chem.* 41, 499 (1963).

(5) M. M. Shemyakin, V. I. Maimind, and B. V. Vaichunaite, *Chem. Ind.* (London), 755 (1958); *Zh. Obshch. Khim.*, 28, 1708 (1958).

(6) M. M. Shemyakin, Ts. E. Agadzhanyan, V. I. Maimind, and R. V. Kudryavtsev, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1339 (1963).

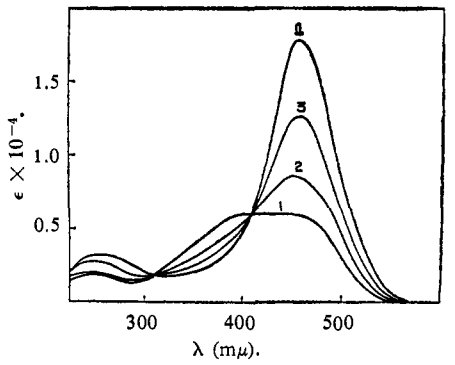


Figure 1. Absorption spectra of azoxybenzene (5.0×10^{-5} *M*) in: 1, 20 vol. % EtOH–90% H_2SO_4 (immediately); 2, 20 vol. % EtOH–100% H_2SO_4 (immediately); 3, 20 vol. % EtOH–90% H_2SO_4 (after 12 hr); 4, 20 vol. % EtOH–100% H_2SO_4 (after 12 hr).

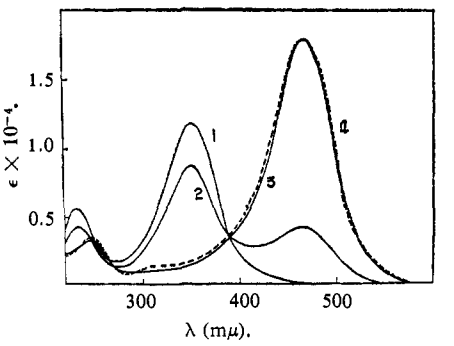
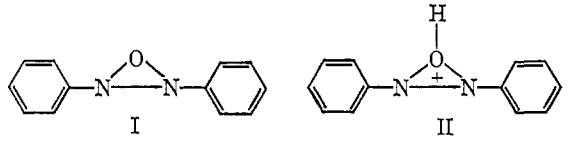


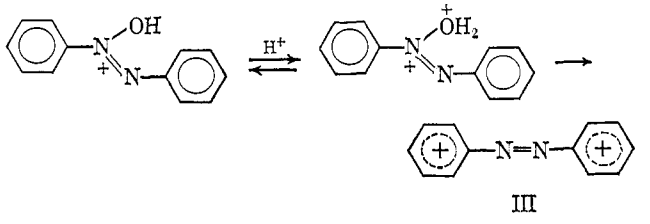
Figure 2. Absorption spectra of 4-hydroxyazobenzene (5×10^{-5} *M*) in: 1, EtOH; 2, 20 vol. % EtOH–10% H_2SO_4; 3, 20 vol. % EtOH–90% H_2SO_4; 4, 20 vol. % EtOH–100% H_2SO_4.

however, that the position in the open ring, *ortho* or *para*, to which the oxygen atom migrates depends on the nature of the substituent already present in the other ring. These findings, however, remain unexplained, and the method above does not permit elucidation of the mechanism. Using the isotopic labeling method, Shemyakin and co-workers,[5,6] and Oae, *et al.*,[7] have proposed mechanisms for the rearrangement of azoxybenzene. Both mechanisms involve a mechanistic intermediate: a three-membered ring N,N,-oxide I and its protonated N,N-hydroxide II.



I II

In contrast with these intermediates, Gore, *et al.*,[8] postulated a dicationic species III as a possible intermediate. However, none of the proposals have been based upon kinetic data except the recent work of Buncel and Lawton,[9] in which they have dealt only with unsubstituted azoxybenzene, and who proposed the following mechanism.



III

Following up one of the authors' previous work on azoxybenzene and its monosubstituted derivatives,[1] we have studied the kinetics of the Wallach rearrangement in order to obtain information bearing on the mechanism of the reaction.

Results and Discussion

Spectroscopic Observations. Gore and Hughes[10] have found that azobenzene, azosulfonic acid, aniline, and a polymer are produced as by-products in the rearrangement of azoxybenzene. However, our previous study[1] and Buncel's work[9] have shown that none of these side products were obtained under the conditions used. The present work again confirmed that the rearrangement is quantitative under kinetic conditions in all compounds investigated here, and in the concentrations used.

The spectra in Figure 1 show the extent of completion of the rearrangement of azoxybenzene (5×10^{-5} *M*) in 20 vol. % ethanol–80 vol. % 90% aqueous sulfuric acid and 20 vol. % ethanol–80 vol. % 100% sulfuric acid, respectively (since all solvent in the present work consists of ethanol and aqueous sulfuric acid in the ratio 1:4, only the concentration of sulfuric acid in the aqueous fraction will be indicated hereafter). Spectrum 1 in Figure 1 (1-1) is taken immediately after the solution was prepared and shows broad absorption in the range between 395 and 460 mμ. It seems likely that this is a superposition of the $\pi \rightarrow \pi^*$ transitions of the conjugate acids of azoxybenzene and 4-hydroxyazobenzene.[11]

The spectrum 1-2 was also taken immediately in "100% sulfuric acid." It can be seen that the intensity of the absorption peak at 395 mμ is decreased. On the other hand, the absorption peak at 460 mμ, which is undoubtedly due to the conjugate acid of 4-hydroxyazobenzene, is increased. This trend is continued in the spectra 1-3 and 1-4, which were taken after the solutions had been allowed to stand for 12 hr at room temperature.

The fact that the 460-mμ bands in the spectra 1-2, 1-3, and 1-4 are not attributable to the conjugate acid of azoxybenzene but to the conjugate acid of 4-hydroxyazobenzene is confirmed by an examination of the spectra in Figure 2, in which the spectra of the free base and the conjugate acid of authentic 4-hydroxyazobenzene are shown. The main band of the free base of 4-hydroxyazobenzene, which appeared at λ_{max} 350–351 mμ, is shifted markedly to longer wavelength, λ_{max} 460 mμ, in "90%" and "100% sulfuric acid" solutions. This wavelength coincides precisely with the absorption maxima of the spectra 1-2, 1-3, and 1-4. These facts confirm unequivocally that azoxybenzene in strongly acidic solution rearranges into 4-hydroxyazobenzene, the faster the more concentrated the acid.

(7) S. Oae, T. Fukumoto, and M. Yamagami, *Bull. Chem. Soc. Japan*, 36, 601 (1963).
(8) P. H. Gore, *Chem. Ind.* (London), 191 (1959).
(9) (a) E. Buncel and B. T. Lawton, *ibid.*, 1835 (1963); (b) E. Buncel and B. T. Lawton, *Can. J. Chem.*, 43, 863 (1967).
(10) P. H. Gore and G. K. Hughes, *Australian J. Sci. Res. Ser. A*, 3, 136 (1950).
(11) (a) H. H. Jaffé, S. J. Yeh, and R. W. Gardner, *J. Mol. Spectry.*, 2, 120 (1958); (b) C. S. Hahn, *J. Korean Chem. Soc.*, 6, 170 (1962).

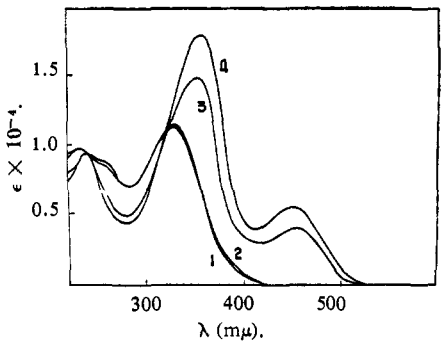


Figure 3. Absorption spectra of azoxybenzene (1.0×10^{-5} *M*) in: 1, original 9% H_2SO_4–20 vol. % EtOH; 2, original 10% H_2SO_4–20 vol. % EtOH; 3, diluted 9% H_2SO_4–20 vol. % EtOH from 90% H_2SO_4 (after 12 hr); 4, diluted 10% H_2SO_4–20 vol. % EtOH from 100% H_2SO_4 (after 12 hr).

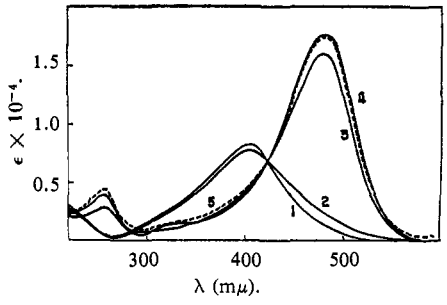


Figure 4. Ultraviolet spectra of α-4-bromoazoxybenzene by elapsing time at room temperature in: 1, 20 vol. % EtOH–90% H_2SO_4 (immediately); 2, 20 vol. % EtOH–100% H_2SO_4 (immediately); 3, 20 vol. % EtOH–90% H_2SO_4 (2 days after); 4, 20 vol. % EtOH–100% H_2SO_4 (2 days after); 5, ultraviolet spectrum of 4-bromo-4′-hydroxyazobenzene in 20 vol. % EtOH–100% H_2SO_4.

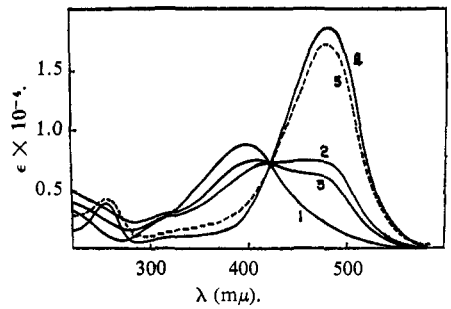


Figure 5. Ultraviolet spectra of β-4-bromoazoxybenzene by elapsing time at room temperature in: 1, 20 vol. % EtOH–90% H_2SO_4 (6 hr after); 2, 20 vol. % EtOH–100% H_2SO_4 (6 hr after); 3, 20 vol. % EtOH–90% H_2SO_4 (3 days after); 4, 20 vol. % EtOH–100% H_2SO_4 (3 days after); 5, ultraviolet spectrum of 4-bromo-4′-hydroxyazobenzene in 20 vol. % EtOH–100% H_2SO_4.

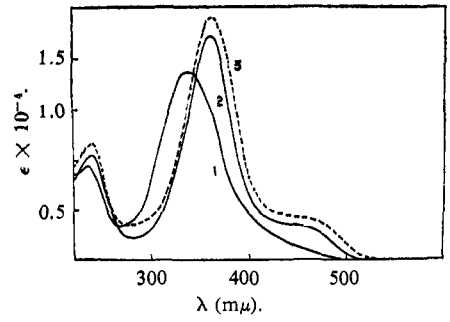


Figure 6. Ultraviolet spectra of β-4-bromoazoxybenzene (1.0×10^{-5} mole) in: 1, 20 vol. % EtOH–10% H_2SO_4 diluted from 20 vol. % EtOH–100% H_2SO_4 (immediately); 2, same solution (3 days after); 3, ultraviolet spectrum of 4-bromo-4′-hydroxyazobenzene in 20 vol. % EtOH–10% H_2SO_4.

This conclusion is further confirmed by an examination of the spectra in Figure 3. There is no appreciable difference between spectra of azoxybenzene prepared in originally 9 and 10% sulfuric acid (3-1 and 3-2). The spectra of azoxybenzene dissolved in 90 and 100% sulfuric acid and subsequently diluted tenfold with 20% ethanol (3-3 and 3-4), show no resemblance to 3-1 and 3-2, but are identical with the spectrum of 4-hydroxyazobenzene (2-2). The spectra in Figures 4, 5, and 6 show exactly the same trend for α- and β-4-bromoazoxybenzene.

By analogous experiments it is shown that, in α- and β-4-methylazoxybenzene, the azoxy oxygen atom migrates to the 2′ position (rather than to the 4-position, as in the other compounds), yielding 4-methyl-2′-hydroxyazobenzene, in confirmation of our previous observation.[1]

Kinetics. The above data show that we are dealing with two reactions: a very rapid acid-base equilibrium[12] and a much slower rearrangement.

These facts strongly support the feasibility of a kinetic study of the rearrangement, and since the optical density of the conjugate acid of the rearranged product of azoxybenzene at 460 mμ increases as the rearrangement proceeds, the rate of the rearrangement was measured at this wavelength. In the cases of α- and β-4-bromoazoxybenzene and α- and β-4-methylazoxybenzene, the rates were measured at 476 and 450 mμ, respectively. Preliminary tests showed that the rate in "100% sulfuric acid" solution was too rapid and impractical to follow, so the kinetic runs were carried out with below "90% sulfuric acid" solutions at various temperatures. The result of one of these runs, using "80% sulfuric acid" at 50°, is tabulated in Table I.

Table I. Pseudo-First-Order Rate Constants of the Rearrangement of Azoxybenzene (5×10^{-5} *M*) in a Mixture of 20 vol. % EtOH–80 vol. % 80% H_2SO_4–H_2O at 50° in Sealed Ampoules

Time, hr	OD at 460 mμ	$\log \frac{D_\infty - D_0}{D_\infty - D_t}$	$k \times 10^5$ sec^{-1}
0	0.138		
1	0.214	0.0187	1.20
2	0.304	0.0418	1.33
3	0.370	0.0595	1.26
4	0.438	0.0786	1.25
5	0.506	0.0986	1.22
6	0.540	0.1090	1.27
7	0.616	0.1330	1.21
8	0.659	0.1473	1.18
9	0.715	0.1664	1.18
10	0.776	0.1885	1.21
T_∞	1.950		
		Av = 1.22 ± 0.04(s)	

The pseudo-first-order rate constants for the rearrangement in a series of sulfuric acid solutions at various temperatures measured by the same method are summarized in Table II, and a pseudo-first-order plot for the rearrangement of α- and β-4-bromoazoxybenzene is displayed in Figure 7, as an example.

(12) C. S. Hahn and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 949 (1962).

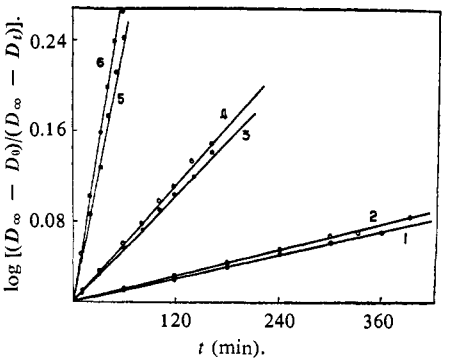


Figure 7. Pseudo-first-order plot of the Wallach rearrangement of α- and β-bromoazoxybenzene (5.0×10^{-5} M) at 50°. Measured at 476 mμ; ● for α, ○ for β; 1, 2 for 80%; 3, 4 for 85%; 5, 6 for 90% H_2SO_4.

It should be noted that the differences between the rates of the two isomer pairs at each temperature are extremely small, although they quite apparently exceed the experimental error. It is further interesting to note that the ratios of the rates of α to β compounds are fairly constant; the average is 0.93 for the bromo, 1.68 for the methyl compounds. These ratios correspond, oddly enough, closely to the ratios of the corresponding basicity constants (*i.e.*, the reciprocal of the K_a's) of the azoxy compounds, 0.95 and 1.3, respectively.

Table II. Pseudo-First-Order Rate Constants for the Rearrangement[a]

Vol. % H_2SO_4	At 50° k	At 75° k
Azoxybenzene,[b] $pK_a = -6.45$		
75	0.134	3.30
80	0.479	10.1
83	2.18	36.5
85	2.53	43.2
88	4.55	74.0

	At 50°		At 65°	
	k_α[d]	k_β[e]	k_α[d]	k_β[e]
α- and β-4-Bromoazoxybenzene,[c] $pK_a = -7.01$ and -6.94, respectively				
80	0.86	0.92	5.75	5.95
85	3.32	3.70	21.5	22.5
90	14.8	16.8	89.4	92.1
α- and β-4-Methylazoxybenzene,[f] $pK_a = -6.04$ and -6.16, respectively				
75	1.77	1.18	8.90	6.38
78	4.65	2.05	20.9	10.2
80	5.62	3.37	25.0	15.3
85	26.0	14.0	105.0	61.5
90	45.6	32.7	171.0	128.0

[a] All rate constants are given as $k \times 10^5$ sec^{-1}. [b] Measured at 460 mμ. [c] Measured at 476 mμ. [d] For α isomer. [e] For β isomer. [f] Measured at 450 mμ.

Measurement of the rates at several temperatures has permitted the estimation of enthalpies and entropies of activation; the values obtained are presented in Table III. It should be noted that the values for each isomer pair are extremely similar, while there is a rather large difference between the values for the methyl-substituted compounds and the others. This difference will be further discussed below.

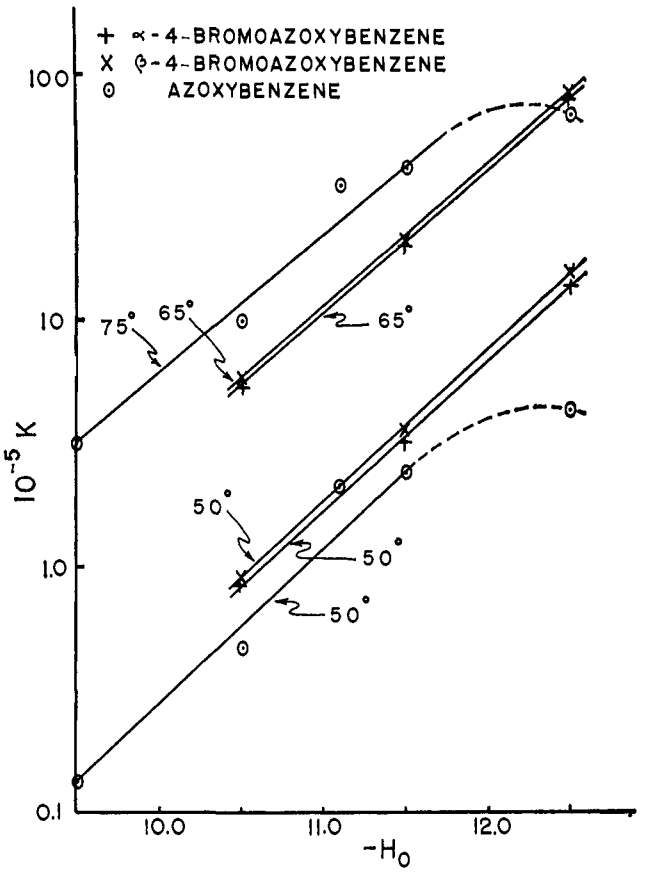


Figure 8. Plot of the logarithm of the rate constants for the Wallach rearrangement of azoxybenzene and its α- and β-4-bromo derivatives *vs.* H_0.

Next, it is interesting to examine the dependence of the rates on acidity. Figures 8 and 9 show that the logarithms of all the rates are roughly linear with H_0, at least up to "85 vol. %" sulfuric acid, and all have virtually the same slope, −0.55.

Table III. Activation Parameters of the Rearrangement of Azoxybenzene and Its Bromo and Methyl Derivatives

Vol. % H_2SO_4	E_a, K cal/mole	$\Delta S^\ddagger$, eu
Azoxybenzene		
75	28.6	1.5
80	27.7	1.1
83	25.7	−2.5
85	25.3	−3.8
88	24.9	−4.0

	E_a, K cal/mole		$\Delta S^\ddagger$, eu	
	α	β	α	β
α- and β-4-Bromoazoxybenzene				
80	27.5	27.0	0.8	−0.2
85	27.0	25.8	2.4	−0.5
90	26.0	24.6	2.2	−2.5
α- and β-4-Methylaxoybenzene				
75	22.0	24.4	−11.0	−7.8
78	21.7	23.2	−13.3	−10.3
80	21.6	21.9	−13.4	−13.8
85	20.2	21.4	−14.6	−16.8
90	19.1	19.7	−16.9	−17.9

The pK_a's of azoxybenzene and its derivatives in the solvent system used in the present investigation have

been determined by one of the authors,[12] using the H_0 function in the solvent system used here,[13] and the pK_a of azoxybenzene was found to be −6.45. Recently, Buncel and Lawton[9b] have determined the pK_a in an aqueous medium using the normal H_0 function[14] and found it to be −5.15. The difference of the pK_a values between the two investigations seems largely due to the difference between the two solvent systems.[5] The pK_a values of the other compounds used here have also been reported previously[12] and are included in Table II.

Mechanism. It remains to examine the implications of these findings on the mechanism of the reaction and to compare these findings with previous experience. It is quite apparent from the strong acid catalysis and the linear log k *vs.* H_0 plots that a protonation step must precede the rate-determining step of the reaction. This is obviously *not* the conversion of azoxybenzene to its first conjugate acid, since, under our experimental conditions, much less than 1% of the substrate exists as free base. Thus one is forced to the conclusion that a diprotonated species (second conjugate acid) must be an intermediate. This conclusion is in agreement with Buncel's results.[9]

Next, one is struck by the extreme similarity of the rates of isomeric α and β pairs of compounds. If one assumes further that the second basicities of the isomer pairs have the same ratio as the first basicities, the remaining difference between the pairs virtually disappears, and the rates for isomer pairs become indistinguishable. This implies that a symmetric intermediate must be involved, in agreement with the conclusions by Shemyakin, *et al.*,[6] and by Gore,[8] that a symmetric stage must be involved somewhere in the reaction, but indicates further that this stage occurs *prior* to the rate-determining step. Whether this symmetrical intermediate occurs before or after the second protonation is difficult to decide at this point. However, the slight but significant rate differences between isomer pairs, which disappear on correction for an assumption of different pK's for the members of the pair, strongly suggests that the second conjugate acids are still distinct, and leads us to postulate the following steps.

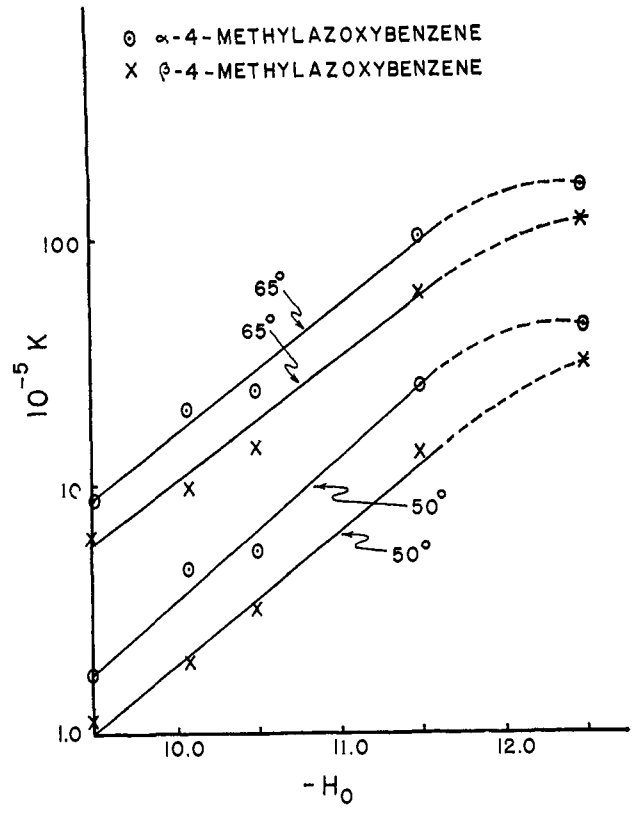
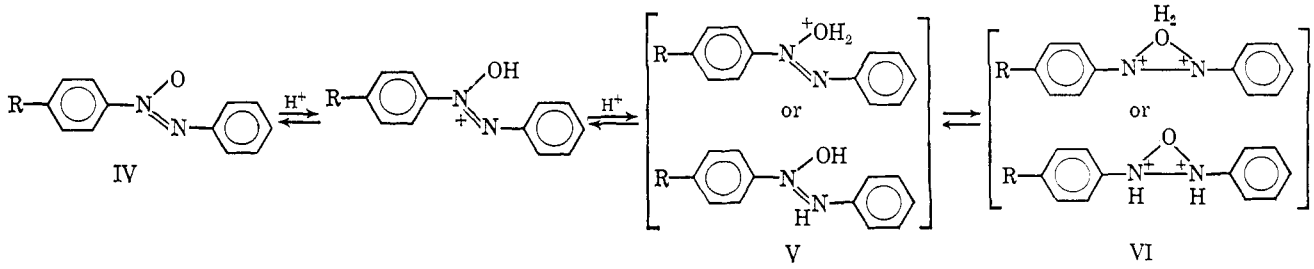


Figure 9. Plot of the logarithm of the rate constants for the Wallach rearrangement of α- and β-4-methylazoxybenzene *vs.* H_0.

pounds up to "90%." Unfortunately no direct evidence for the second protonation equilibria exists, so that no estimate of the pK's are available. It is suggested that the first compounds are protonated to such an extent in "90%" sulfuric acid that the simple preequilibrium formulation no longer holds. The bromo compound, which should be the weakest base, then does not seem to become sufficiently protonated for this simple formalism to fail until a slightly higher acidity is reached.

The postulation of a triangular symmetric intermediate prior to the rate-determining step suggests that un-



The experimental data give no information concerning the structure of the second conjugate acid V or the symmetric triangular intermediate VI, for both of which two conceivable structures have been written.

The plots of log k *vs.* H_0 are linear for the azoxybenzene and its methyl derivative only up to "85%" sulfuric acid, while they are linear for the bromo compound. symmetrically substituted azoxy compounds should rearrange from α to β forms and *vice versa* by treatment with strong acid. Some evidence that such rearrangements occur is available,[15] since it has been observed that the isomeric purity of these compounds decreases with time; also, it has been reported that β-*p*-nitroazoxybenzene rearranges to the α isomer in acid solution.[5,6,8] No other study of recovery of starting material in partially reacted Wallach reaction mixtures

(13) (a) H. H. Jaffé and R. W. Gardner, *J. Am. Chem. Soc.*, **80**, 319 (1958); (b) S. J. Yeh and H. H. Jaffé, *ibid.*, **81**, 3274 (1959); (c) M. Isaks and H. H. Jaffé, *ibid.*, **86**, 2209 (1964).

(14) M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 935 (1957).

(15) Unpublished results.

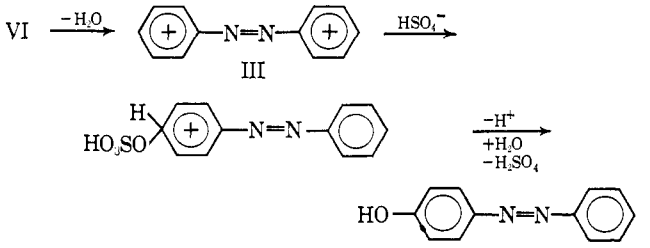
seems to have been undertaken. Such a study might shed further light on the order of the steps of conversion of IV to V to VI and the possibility of a prior triangular intermediate II which has also been postulated. However, the extreme similarity of the α and β isomers makes such a study extremely difficult.

Finally, it remains to speculate about the rate-determining step in the Wallach rearrangement. The fact that the products from the methyl compound differ from the products of the other three compounds suggests that either a different transition state may be involved, or that a similar transition state may decompose in a different manner, or again that the rate-determining step leads to a further intermediate which then reacts in different ways. A strong implication that the first of these alternatives applies, *i.e.*, that the transition state for the methyl compounds is different from the others, is contained in the activation parameters of Table III. There it is seen that activation energy and entropy for the methyl compounds differ strikingly from values for the unsubstituted and bromo compounds.

This conclusion is confirmed by an examination of substituent effects. Table II shows that, for any set of comparable conditions, both the methyl and bromo derivatives react substantially faster than the unsubstituted compound. This is an unusual situation, since the methyl group is generally electron donating, the bromo substituent net electron withdrawing. Since the rate-determining step is preceded by a protonation equilibrium, it is well to correct the rates for an estimate of the difference of the equilibrium constants. Assuming, as above, that the basicity ratios are the same for first and second basicity, we must decrease the apparent rates of the methyl compounds by a factor slightly less than 3, increase those of the bromo compounds by a factor slightly larger than 3, relative to the unsubstituted compound. This gives us relative rates of about 4:1:5 for the intrinsic rates of the methyl, unsubstituted, and bromo compounds, respectively.

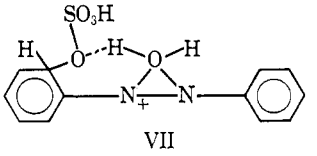
The demonstration of a dual mechanism and the substituent effects focuses again on the apparent paradox, observed earlier,[12] that the strongly electron-donating methoxy group directed the reaction into the path of electron-withdrawing substituents. The problem is probably solved by the recognition that the reaction requires formation of the second conjugate acid. The methoxy group itself can act as a basic center; the pK of anisole has been reported as -6.54 in aqueous sulfuric acid.[16] Accordingly it appears highly reasonable that the methoxy group is protonated before the protonation of the azoxy group, and that consequently the effective substituent is the strongly electron-withdrawing methyloxonio group ($MeHO^+$); thus the direction of the rearrangement of the methoxy compounds also finds a reasonable explanation. Another strongly electron-withdrawing group, *m*-nitro, also directs the rearrangement into the 4′ position.[3]

It now remains to propose plausible mechanisms for the two reaction paths, such that one should be favored by electron-withdrawing, the other by electron-releasing substituents. Although we are unable to provide much evidence for the details, we propose that electron withdrawal favors loss of water from VI to give the dication III, which then undergoes nucleophilic attack. While the attacking reagent is unknown, sulfate or bisulfate ion appears as a logical choice. Hence the mechanism might be as follows.



This mechanism is consistent with Shemyakin's findings[6] by isotope experiments that the mechanism leading to 4′-hydroxy substitution is intermolecular.

In the case of electron-repelling substituents, the situation is considerably more complicated. The more negative activation entropy suggests that the transition state must be considerably more complex and structured. For some cases of 2′-substitution, isotope experiments have shown that the hydroxy oxygen atom is largely or completely the azoxy oxygen atom, although, in the case of 4,4′-dimethylazoxybenzene, Shemyakin found only 30% intramolecular rearrangement.[6] Anyway, such an intramolecular mechanism, involving a tight cyclic transition state in which the oxygen is bound by the azo group and the ring, may well be expected to have a large negative entropy. Alternately a transition state in which a solvent molecule (possibly again SO_4H^- or SO_4^{2-}) is hydrogen bonded to the diprotonated azoxy group and attacking the adjacent ring, such as VII, is conceivable.



VII

Experimental Section

Materials. All chemicals used were Wako (Japanese) special grade, except absolute alcohol and sulfuric acid (Merck special grade), and were used without further purification.

Compounds. The preparation of all the azoxybenzene derivatives under investigation are described in previous papers.[1,12]

Preparation of Solution. Preliminary tests showed that 5×10^{-5} M solutions are best suited for kinetic measurements. Stock solution (5 ml) of azoxybenzene (1.0×10^{-3} M in ethanol) was pipetted into a series of 50-ml volumetric flasks into which were added 5 ml of ethanol and aqueous sulfuric acid solutions of appropriate concentration to make 1×10^{-4} M solution (stock solution no. 2); during this step the solutions were cooled so that the rearrangement would not commence before the kinetic run was started. Stock solutions (no. 2) were then further diluted to five times their volume with 20% ethanol; the final solvent consisted of 20 vol. % of ethanol and 80 vol. % of the appropriate aqueous sulfuric acid. Solutions of 4-hydroxyazobenzene were also prepared in the same manner.

Kinetic Measurements. A Shimadzu Model 1 QR-50 spectrophotometer with glass-stoppered 1-cm silica cells was used for the kinetic runs. Aliquots were pipetted from the final solution (5×10^{-5} M) at room temperature into a series of ampoules. The sealed ampoules were placed in a constant-temperature bath at

(16) E. M. Arnett and C. Y. Wu, *J. Am. Chem. Soc.*, **82**, 5660 (1960); **84**, 1680 (1962).

once and individual ampoules were removed at recorded times and plunged into ice-cold water. The thermostat used regulated the temperature within 0.05°. The rate of the rearrangement was determined by measuring the change in absorbance at 460, 476, and 450 mμ, respectively, for the different compounds.

Acknowledgment. The financial support from the United Board for Christian Higher Eduction in Asia and the Graduate School of Yonsei University is gratefully acknowledged.

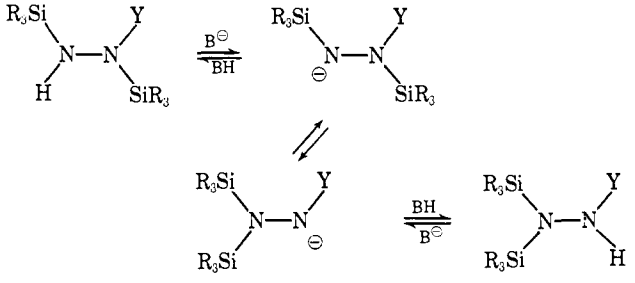
New Anionic Rearrangements. V. Anionic Rearrangement of *t*-Butyldimethylsilylhydrazines[1,2]

Robert West and Mitsuo Ishikawa

Contribution from the Department of Chemistry, The University of Wisconsin, Madison, Wisconsin 53706. *Received May 5, 1967*

Abstract: The synthesis and properties of a series of *t*-butyldimethylsilylhydrazines are described. These compounds undergo catalyzed anionic rearrangement with migration of silicon as do other silylhydrazines, but the bulky *t*-butyldimethylsilyl group both retards the rate of rearrangement and alters the equilibrium isomer ratio. Nmr studies of competitive and sequential migration of trimethylsilyl and *t*-butyldimethylsilyl groups in hydrazines containing both substituents support the mechanism proposed for the rearrangement, in which protonation and deprotonation are the rate-determining steps.

Earlier papers in this series have shown that organosilylhydrazines undergo rapid equilibration in the presence of strong bases.[2-4] As explained previously, the silyl groups are believed to migrate from one nitrogen to the other in the hydrazide anion.

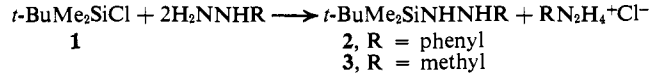


Y = H, CH_3, or C_6H_5

In the above reaction where Y = H or CH_3 and R_3Si = trimethylsilyl or ethyldimethylsilyl, the amounts of 1,1- and 1,2-bis(silyl) isomers present in the equilibrium mixture are nearly equal.[5] Thus the steric preference for one isomeric form over the other appears to be negligible in these cases.

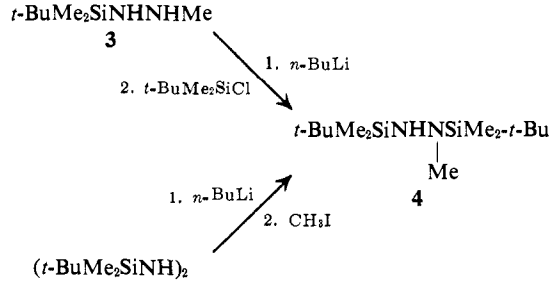
To investigate steric hindrance in the silylhydrazine rearrangement, we decided to employ a much bulkier migrating substituent, the *t*-butyldimethylsilyl group. This paper reports the synthesis and characterization of a number of *t*-butyldimethylsilylhydrazines, all of which are new compounds, and a study of their behavior in the anionic rearrangement reaction.

Synthesis. Most syntheses followed methods developed earlier, based originally on those of Wannagat and his co-workers.[6] In an earlier paper we showed that phenylhydrazine reacts with trimethylchlorosilane or ethyldimethylchlorosilane to form the 1,2-disubstituted product exclusively.[5] Similarly, phenylhydrazine reacts with *t*-butyldimethylchlorosilane (**1**) to give only 1-*t*-butyldimethylsilyl-2-phenylhydrazine (**2**).



However, the bulky *t*-$BuMe_2Si$ group stabilizes certain hydrazines which cannot be prepared with nonhindering Si substituents. When methylhydrazine (R = CH_3) was used in the above reaction in place of phenylhydrazine, 1-*t*-butyldimethylsilyl-2-methylhydrazine (**3**) was produced. The analogous trimethylsilyl- and ethydimethylsilylmethylhydrazines are unstable toward further condensation, and we were unable to isolate them.[5] Both of the *t*-$BuMe_2Si$ compounds were shown to have the 1,2 structure from their proton nmr spectra, which contained two peaks in the N–H region (Table I).

When **3** is treated with 1 equiv of *n*-butyllithium followed by 1 equiv of **1**, the product is 1,2-bis(*t*-butyldimethylsilyl)-1-methylhydrazine (**4**) formed in 99% isomeric purity. The structure follows unambiguously from the nmr spectrum, which shows two peaks for Me_2Si protons and two for *t*-BuSi protons (Table I). The same compound was obtained by metalation and



(1) Research sponsored by Air Force Office of Scientific Research (SRC)-O.A.R., USAF, Grant No. AF-AFOSR 1061-66.

(2) Previous paper in this series: R. West, M. Ishikawa, and R. E. Bailey, *J. Am. Chem. Soc.*, **89**, 4072 (1967).

(3) R. E. Bailey and R. West, *ibid.*, **86**, 5369 (1964).

(4) R. West, M. Ishikawa, and R. E. Bailey, *ibid.*, **88**, 4648 (1966).

(5) R. West, M. Ishikawa, and R. E. Bailey, *ibid.*, **89**, 4068 (1967).

(6) U. Wannagat and W. Liehr, *Z. Anorg. Allgem. Chem.*, 274, 129, 133 (1958); **299**, 341 (1959); U. Wannagat, C. Krüger, and H. Niederprum, *ibid.*, **321**, 198 (1963); U. Wannagat, *Advan. Inorg. Chem. Radiochem.*, **6**, 225 (1964).