constants determined at high imidazole concentration are not very accurate because the rate of reaction is too fast at this high concentration and difficult to measure with our experimental technique; thus we regard the value of k_1 as only approximate and so of course the other parameters which are calculated from it.

Experimental Section

Materials. Benzene (Erba) was shaken repeatedly with sulfuric acid to remove thiophene[13] and distilled before use from Na wire. Chloroform (Erba) was obtained free of ethanol by washing it several times with water; it was dried with $CaCl_2$ and stored in the refrigerator under N_2 in the dark. We noted that when this care was not taken the solutions of 1-chloro-2,4-dinitrobenzene or imidazole in this solvent turned yellow. The purified chloroform was used at most over 10 days. 1-Fluoro-2,4-dinitrobenzene (Merck) was distilled under vacuum. 1-Chloro-2,4-dinitrobenzene (Merck) was twice recrystallized from absolute ethanol. Dabco was sublimed at 40 °C (10 Torr). Pyridine was left over potassium hydroxide for 2 days and distilled under N_2 from KOH before use. Imidazole was recrystallized several times from benzene and then sublimed under vacuum. *N*-2,4-Dinitrophenylimidazole was prepared from 5 mmol (340 mg) of imidazole dissolved in 2 ml of dry benzene and 1-chloro-2,4-dinitrobenzene (2.5 mmol). The solution was boiled for 30 min and the benzene was evaporated. This yellow residue was recrystallized several times from methanol, yield 60%, mp 141–142.5 °C (lit.[14] 146–148 °C). During the synthesis and workup, the product was protected from light.

Kinetics. The product *N*-2,4-dinitrophenylimidazole has no absorption maximum in the spectral region available for examination in benzene or chloroform. Moreover, at the wavelength useful for examination (where the difference in the extinction coefficient of starting material and product is higher) the extinction coefficient of the *N*-2,4-dinitrophenylimidazole is quite low (ca. 2500 M^{-1} cm^{-1}); thus the total change in optical density over the reaction is also low. Thus we decided to monitor the concentration of 1-chloro-2,4-dinitrobenzene making use of its fast reaction with piperidine. In all the reactions in benzene or chloroform with imidazole with or without other bases added, the sealed ampule technique was utilized. The reactions at low base concentration were followed over ca. 10% conversion; after the desired time the ampule was cooled to room temperature and 1.0 ml of its contents was added to about 8 ml of benzene or chloroform contained in a 10-ml volumetric flask. Then 0.2 ml of piperidine was added and the flask diluted to the mark. After about 10 min all the 1-chloro-2,4-dinitrobenzene has reacted and the optical density of the product, *N*-2,4-dinitrophenylpiperidine, formed was measured at its maximum (380 nm). *N*-2,4-Dinitrophenylimidazole does not react with piperidine under these conditions during about 1 h. The rate constant was reckoned as 2.3 times the slope of the plot of log *A* vs. time. All the reactions were carried out under pseudo-first-order conditions. The reactions of 1-fluoro-2,4-dinitrobenzene with imidazole were carried out in the thermostated cell of the spectrophotometer.[15]

Acknowledgment. We thank Professor Claude F. Bernasconi for criticism of the manuscript.

Registry No.—Imidazole, 288-32-4; 1-chloro-2,4-dinitrobenzene, 97-00-7; 1-fluoro-2,4-dinitrobenzene, 70-34-8.

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The Acid-Catalyzed Nitramine Rearrangement. 8. Solvent Viscosity Effects[1,2]

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The rearrangement of *N*-nitro-*N*-methylaniline in methanol–glycerol mixtures of various compositions and viscosities was studied. In the presence of hydroquinone (which eliminates the intermolecular portion of the rearrangement), the yields of nitroanilines and the ortho to para isomer ratio increased with viscosity. The enhanced yield is explained by the lessened tendency of the intermediate solvent caged particles to dissociate in the higher viscosity solvents. The greater ortho to para isomer ratio must be caused by solvent interference to the migration of the nitro group within the solvent cage to the more distant para position. This hindrance increases with solvent viscosity. Rearrangement in the absence of hydroquinone scavenger yields similar results although more nitrated product is formed. The data can be quantitatively accounted for in terms of the mechanism shown in Chart II. This mechanism postulates a solvent viscosity effect within the solvent cage.

The outcome of the nitramine rearrangement frequently appears to be affected by the nature of the solvent. For example, the isomerization of *N*,2,4-trinitro-*N*-methylaniline proceeded normally in 80 or 96% sulfuric acid to yield 2,4,6-trinitro-*N*-methylaniline.[3] However, only the denitrated product, 2,4-dinitro-*N*-methylaniline, was formed from the same nitramine in 1:1 sulfuric acid–acetic acid mixture or in hot dilute hydrochloric acid. Rearrangement of 2,4,6-tribromo-*N*-nitroaniline in aqueous acids produced the expected mixture of isomeric nitrodibromoanilines.[4] Different products, 2,4,6-tribromobenzenediazonium ion and a quinoneanil, were formed when the medium was changed to acetic acid–sulfuric acid. Rearrangement of *N*-nitroaniline is also affected by the solvent.[5] Decreasing the molarity of the acid catalyst lowered the yield of nitrated products from 95% to 60% and changed the ortho–para ratio from 19.0 to 3.5. Similar behavior was noted in the rearrangements of *N*-nitro-1-naphthylamine and *N*-nitro-*N*-methyl-1-naphthylamine.[6]

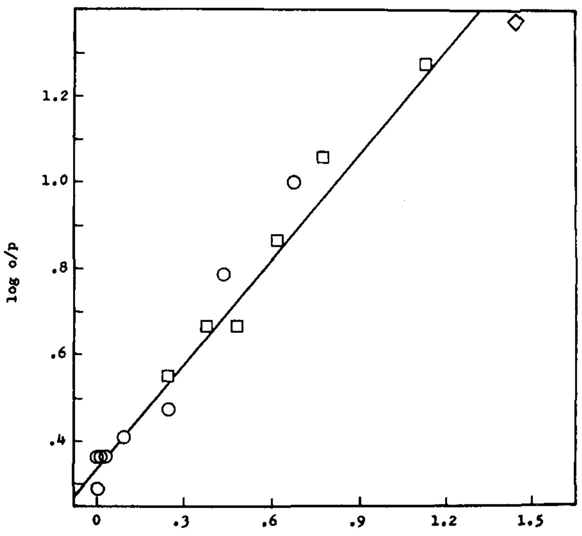


Figure 1. Ratio of percent *o*-nitroaniline to percent *p*-nitroaniline (*o*-/*p*-) from rearrangement of *N*-nitroaniline in acid media of different viscosities. □, H_2SO_4; ○, $HClO_4$; and ◇, H_3PO_4. Equation of the curve: $o\text{-}/p\text{-} = (\eta + 0.4)/(0.008\eta + 0.6)$.

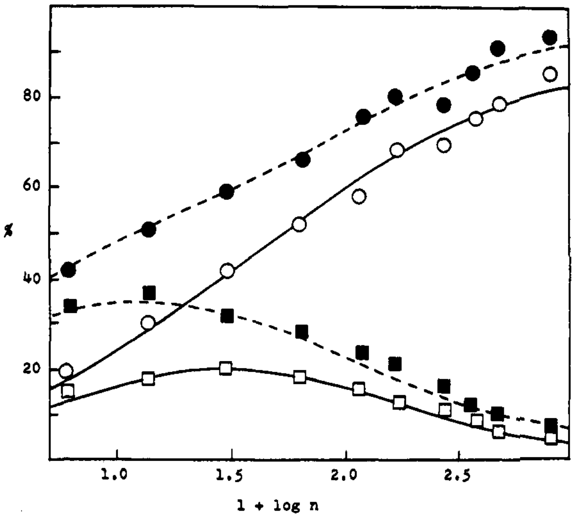


Figure 2. Yields of *o*- and *p*-nitro-*N*-methylanilines in methanol-glycerol solutions of various viscosities: ● and ■, ortho and para isomer, respectively, in the absence of hydroquinone scavenger; ○ and □, ortho and para isomer, respectively, in the presence of hydroquinone scavenger. Curves were calculated from the kinetics of the mechanism of Chart II using the relative rate constants in Table I.

Results and Discussion

The influence of acid concentration on the isomer ratio obtained from *N*-nitroaniline has been attributed to the effect of the acid medium's base strength on proton loss from the ortho and para σ-bonded intermediates.[5] Analysis of the results shows that the change in the ortho–para ratio cannot be interpreted in terms of the base strength of the solvent. The suggested proton abstraction[5] would be similar to that in an A-2 type mechanism.[7] Both the Zucker–Hammett hypothesis[7] and the Bunnett equation[8] require that the logarithm of the ortho–para ratio for such a process have a linear relationship to the logarithm of water activity in the various media. However, a plot of these two quantities shows a great deal of scatter (correlation coefficient $r = 0.75$). A graph of the logarithm of the isomer ratio vs. H_0 is of similar quality ($r = 0.73$).

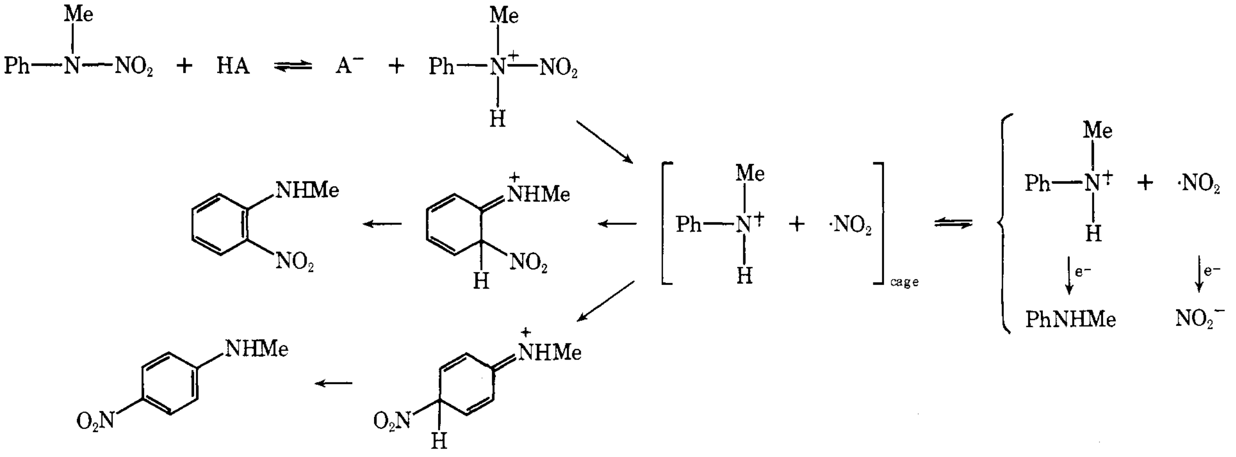
Previous studies[2a–g] of the aromatic nitramine rearrangement have shown that it involves the decomposition of the protonated nitramine to form a pair of caged radicals which may either dissociate to free radicals or recombine to yield nitrated products (Chart I). It would be expected that the competition between these latter processes would be affected by the solvent property known as viscosity. Viscosity increases should strengthen the solvent cage, hinder dissociation, and thus favor recombination. High-viscosity solvents should improve the yields of nitrated products. In fact, the yield of *o*- and *p*-nitroaniline from *N*-nitroaniline did increase from 60 to 95% as the concentration, and the viscosity, of the catalyzing acid was increased.[5]

Interestingly, although the observed ratios of products from *N*-nitroaniline cannot be correlated with the acidities or basicities of the acid media, a plot of these isomer ratios vs. the viscosities of the acid solutions provides a smooth curve even though three different acids were involved (Figure 1, correlation coefficient $r = 0.98$).[9]

These limited correlations suggested a more thorough investigation in which solvent viscosity was changed while other properties of the medium were kept almost constant. For this purpose, the rearrangement of *N*-nitro-*N*-methylaniline in a series of methanol–glycerol solutions of varying composition was chosen for study. Methanol and glycerol have very similar polarities as indicated by their *Z* values (83.6 and 85.3 kcal/mol, respectively), but very different viscosities (0.55 and 954 cP, respectively). Rearrangements were carried out both with and without the addition of hydroquinone as a scavenger. The results are shown graphically in Figure 2.

The data obtained in presence of hydroquinone are the most revealing and the least ambiguous. Hydroquinone eliminates the intermolecular portion of the rearrangement so that the

Chart I



yield of nitrated material is a measure of the extent of the intramolecular (cage) process. Figure 2 shows that the total yield of nitroanilines increases as the medium viscosity becomes greater. A higher viscosity does not change the rate of geminate recombination of the anilinium radicals and nitrogen dioxide within the solvent cage to form nitrated anilines, but does decrease the rate of escape of these species from the cage. The liberated free radicals react with hydroquinone, are reduced, and do not recombine. Therefore, they do not contribute to the yield of nitroaniline. Since this latter unproductive side reaction (diffusion from the cage and reduction) is disfavored in higher viscosity solvents, the yields of nitroaniline rise with increasing viscosity.

There is a marked change in the ortho to para isomer ratio as the viscosity is changed. An increase in viscosity of 135-fold causes a 14-fold enhancement of the ortho to para ratio—the increment being the greatest in the high viscosity range. It appears that high viscosity not only interferes with the diffusion of particles out of the solvent cage, but also hinders the movement of those particles with respect to each other in the cage. In very low viscosity solvents, the ortho to para ratio will be dictated mainly by electronic, steric, and statistical factors. However, as the viscosity increases, the movement of the caged particles will become more restricted. Since the ortho position is closer to the origin of the nitro group than is the para position, the opportunity for the nitrogen dioxide radical to approach the para position before reaction occurs at the nearer ortho position of the anilinium radical is decreased. As a result the relative amount of ortho isomer increases with the viscosity.[10]

The rearrangement of *N*-nitro-*N*-methylaniline in methanol–glycerol mixtures in the *absence* of hydroquinone yielded similar results (Figure 2). In these experiments, there was a smaller decrease in the yields of nitroanilines as the viscosity was reduced because the intermolecular portion of the rearrangement is not eliminated. The behavior of the ortho to para isomer ratio was much the same as that observed in the presence of hydroquinone, but less dramatic (a change of 11-fold over a viscosity range of 0.61–80.5 cP). This latter result is in agreement with the suggested course of the reaction since recombination of the dissociated free radicals which occurs in the absence of hydroquinone would not be expected to discriminate between the ortho and para positions as severely as intracage recombination.[1g]

Table I. Relative Rate Constants [a] for the Mechanism of Chart II

MeOH–glycerol	H_2O–glycerol
$k_3 = 7.1k_7$	$k_3 = 7.7k_7$
$k_4 = 16k_{15} - 8.1k_9$	$k_4 = 5.4k_{15} - 8.7k_9$
$k_5 = 4.0k_{15}$	$k_5 = 3.0k_{15}$
$k_6 = 5.1k_{16}$	$k_6 = 5.6k_{16}$
$k_8 < 0.3\sqrt{k_{13}k_{14}}^b$	$k_8 < 0.1\sqrt{k_{13}k_{14}}^b$
$k_{10} = 7.5\sqrt{k_{13}k_{14}}^b$	$k_{10} = 3.1\sqrt{k_{13}k_{14}}^b$
$k_{11} < 0.2k_{16}$	$k_{11} < 0.3k_{16}$
$k_{12} = 2.5\sqrt{k_{13}k_{14}}^b$	$k_{12} = 1.9\sqrt{k_{13}k_{14}}^b$

[a] The rate constants of steps 3–14 are for unit viscosity (1 cP). Rate constants at other viscosities (k_i') are obtained by dividing the listed rate constants by viscosity (k_i/η). [b] In the presence of hydroquinone scavenger, k_{13} and k_{14} will both be very much larger than k_8, k_{10}, and k_{12}.

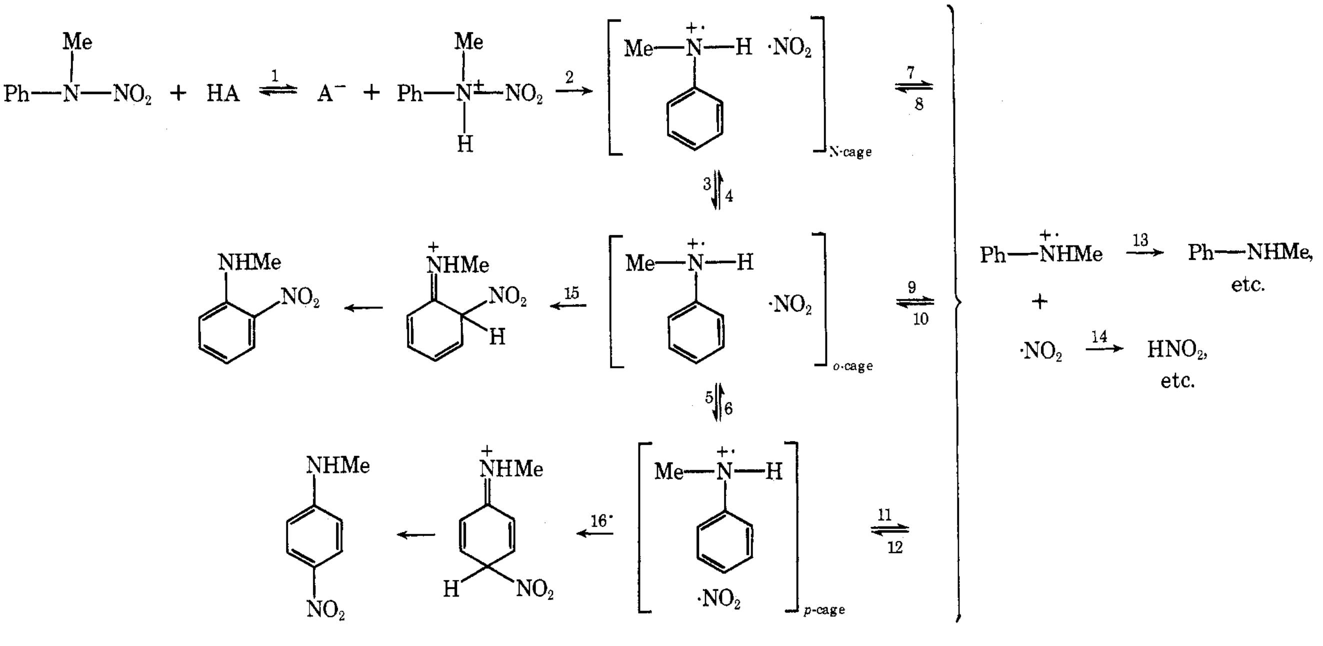
These conclusions were put on a more quantitative basis by use of the mechanism shown in Chart II. The mechanism supposes three more or less distinct cage species—one formed directly from the protonated nitramine with the NO_2 radical close to the amino nitrogen (N-cage), one that collapses to the ortho isomer with nitrogen dioxide in the region of the ortho positions (*o*-cage), and one that yields the para compound with the free nitro group in proximity to the para position. Application of steady-state kinetic methods to this scheme permitted the derivation of expressions for the percentage of each product in terms of the rate constants for each step and power terms involving the viscosity of the medium. The rate constants for steps 3–14 were assumed to have the following dependence on viscosity:

$$k_i' = k_i/\eta = \text{rate constant of step } i$$

Substitution of the experimental isomer yields in these equations allowed the evaluation of the relative rate constants (Table I). The theoretical curves defined by these rates parameters are those drawn in Figure 2.

Some interpretation of the relative values of the rate constants in Table I is possible. The smallness of k_8 is probably due to the fact that the positive nitrogen atom in the *N*-methylanilinium radical binds solvent so strongly that the NO_2 radical cannot easily diffuse back to reform the N-cage species. If this is so, it seems likely that k_4, which involves a

Chart II



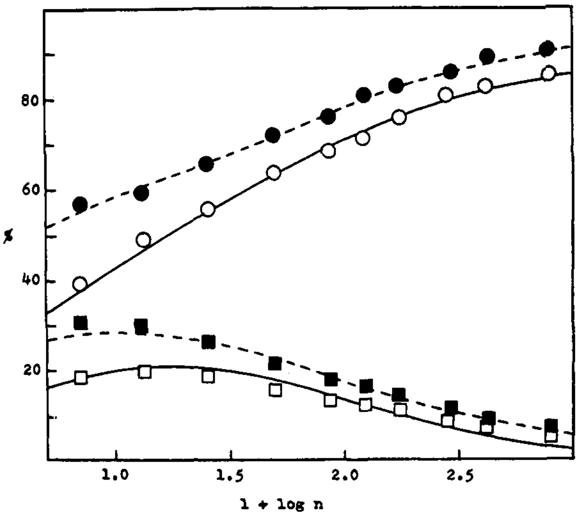


Figure 3. Yields of *o*- and *p*-nitro-*N*-methylanilines in water–glycerol solutions of various viscosities: ● and ■, ortho and para isomer, respectively, in the absence of hydroquinone scavenger; ○ and □, ortho and para isomer, respectively, in the presence of hydroquinone scavenger. Curves were calculated from the kinetics of the mechanism of Chart II using the relative rate constants in Table I.

similar, but intracage, diffusion to reform the N-cage, would also be small and perhaps negligible so that $16k_{15} - 8.1k_9 = k_4 \simeq 0$ or $k_9 \simeq 2k_{15}$. This last relationship permits a comparison of the rate of an intracage diffusion process (k_5) with the rate of a diffusion out of the cage (k_9). Since $k_5 = 4k_{15}$ and $k_9 = 2k_{15}$, diffusion within the cage is somewhat faster, but of the same order of magnitude as diffusion from the cage. This result is not surprising in view of the fact that the aniline ring shields one side of the NO_2 radical from contact with the impeding solvent in the intracage diffusion.[11] It is also interesting to note that the rates of most of the intracage diffusion processes are faster than the rates of radical recombination at unit viscosity (e.g., $k_5 = 4k_{15}$ and $k_6 = 5k_{16}$).[11] Finally, the smallness of k_{11} (dissociation of the *p*-cage) may be due to the fact that the para position is sufficiently distant from the positive amino nitrogen so that the solvent structure making properties of the hydrophobic aromatic residue may become predominant.[12] This increase in solvent structure will strengthen the attractions between solvent molecules in this region and thus make it more difficult for the two radicals in the *p*-cage species to separate.

A set of experiments similar to those described above were carried out using water–glycerol mixtures. The findings are summarized in Figure 3 and Table I. The close correspondence of these results with those obtained in methanol–glycerol media indicates that solvent polarity is of little importance in determining the yields and isomer ratios in water, methanol, glycerol, or their mixtures.

This research yields two important conclusions. First, the influence of solvent viscosity on the composition of the product from the aromatic nitramine rearrangement is most readily interpreted in terms of a mechanism involving a solvent-caged intermediate. Therefore, the results support the previously proposed "cation radical" mechanism for this isomerization. Secondly, and more generally applicable, the effect of solvent viscosity on processes occurring within the solvent cage has been shown to be significant in determining the outcome of chemical reactions.

Experimental Section

***N*-, *o*-, and *p*-Nitro-*N*-methylanilines.** These substances were available from previous investigations.[2b]

Perchloric Acid Solutions. Sufficient 60% perchloric acid was added to pure methanol or pure glycerol to yield solutions approximately 0.5 M in acid. These solutions were titrated with standard sodium hydroxide solution to determine their exact concentrations.[13]

Rearrangement of *N*-Nitro-*N*-methylaniline in Methanol–Glycerol Solutions. Appropriate quantities of 0.481 M perchloric acid in glycerol and 0.485 M perchloric acid in methanol were combined to give a solution of the desired viscosity. About 49 ml of this methanol–glycerol solution was thermostated (40.0 ± 0.2 °C) in a 50.0-ml volumetric flask. The volume was adjusted to 50.0 ml by addition of the methanol–glycerol solution. A 1.00-ml aliquot of 0.0210 M *N*-nitro-*N*-methylaniline in dioxane was added and the mixture was shaken thoroughly and kept at 40.0 ± 0.2 °C for 2 h. It was then cooled and about 5 ml[14] of the solution was transferred to a 25.0-ml volumetric flask. A 5.0-ml aliquot of 5% sulfamic acid was added and the mixture was heated at 90 °C for 30 min to destroy nitrous acid. After the solution was cooled to room temperature, it was diluted to 25.0 ml with acetate buffer (15.0 g of sodium acetate trihydrate, 50.0 ml of water, and 50.0 ml of glacial acetic acid).

Aliquots (1 ml) of dioxane, 0.0130 M *n*-nitro-*N*-methylaniline in dioxane, and 0.00660 M *p*-nitro-*N*-methylaniline in dioxane were treated in a similar way. The final solution from the dioxane run was used as a spectral blank for the other three solutions. Absorbances were determined at 390, 410, 430, 450, and 470 nm and the method of least squares was used to calculate the concentrations of *o*- and *p*-nitro-*N*-methylanilines that best reproduced the optical densities at the five wavelengths.

Rearrangement solutions containing hydroquinone were prepared in the same way as described above except that 20 mg of hydroquinone was weighed into the reaction flask before addition of the methanol–glycerol solution. The nitramine, each of the standard substances, and dioxane alone were treated with the hydroquinone-containing solutions and the final absorbances were used to calculate the product distribution.

Rearrangement of *N*-Nitro-*N*-methylaniline in Water–Glycerol Solutions. Acid solutions of different viscosities were made up by combining 0.485 M aqueous perchloric acid with 0.489 M perchloric acid in glycerol. Aliquots of the *N*-, *o*-, and *p*-nitro-*N*-methylaniline solutions and of dioxane were heated at 40.0 ± 0.2 °C with these solutions as described above and then treated in the same way. Runs were also made in the presence of hydroquinone using the previous procedure.

Viscosity Measurements. The viscosities of the methanol–glycerol and water–glycerol reaction mixtures were determined using an Oswald viscometer and the falling sphere method. Both procedures were calibrated using distilled water and 60% aqueous sucrose solution at 40.0 °C (the temperature of all measurements).

Registry No.—*N*-Nitro-*N*-methylaniline, 7119-93-9; *o*-nitro-*N*-methylaniline, 612-28-2; *p*-nitro-*N*-methylaniline, 100-15-2.

References and Notes

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(2) Previous papers in this series: (a) W. N. White, J. R. Klink, D. Lazdins, C. Hathaway, J. T. Golden, and H. S. White, *J. Am. Chem. Soc.*, **83**, 2024 (1961); (b) W. N. White, D. Lazdins, and H. S. White, *ibid.*, **86**, 1517 (1964); (c) W. N. White, C. Hathaway, and D. Huston, *J. Org. Chem.*, **35**, 737 (1970); (d) W. N. White and J. R. Klink, *ibid.*, **35**, 965 (1970); (e) W. N. White, J. T. Golden, and D. Lazdins, *ibid.*, **35**, 2048 (1970); (f) W. N. White and H. S. White, *ibid.*, **35**, 1803 (1970); (g) W. N. White and J. T. Golden, *ibid.*, **35**, 2759 (1970).
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(9) The results reported in this study also yield a linear relation between the logarithm of the ortho/para ratio and the logarithm of viscosity for viscosities up to 25 cP.
(10) (a) An effect of medium rigidity (viscosity) on product distribution was postulated by J. M. McBride [cf. A. B. Jaffe, K. J. Skinner, and J. M. McBride, *J. Am. Chem. Soc.*, **94**, 8510 (1972); J. M. McBride, *ibid.*, **93**, 6302 (1971); and related papers] to explain the behavior of geminate radicals in various media. (b) R. C. Neuman, Jr. [*Acc. Chem. Res.*, **5**, 381 (1972)] has interpreted these results in terms of pressure effects on the rotational motions of radicals within the solvent cage.
(11) These findings are similar to those observed by F. D. Greene, M. A. Berwick, and J. C. Stowell, *J. Am. Chem. Soc.*, **92**, 867 (1970), and J. P. Engstrom and F. D. Greene, *J. Org. Chem.*, **37**, 968 (1972), for quite different systems

assuming that intracage rotation is similar to intracage diffusion.

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(13) The viscosity of the glycerol solution precluded volume measurements by pipetting. Instead, quantities of the solution were weighed out and the density (estimated by means of a pycnometer) was used to calculate the volume.

(14) The solution was weighed and its volume was determined using the density. A pycnometer was utilized to measure the density of the reaction mixture.

Chlorination of Anilines. Bimolecular Acid-Catalyzed Rearrangement of *N*-Chloroanilines

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N-Chloroanilines undergo an acid-catalyzed rearrangement in nonpolar solvents to yield a mixture of *o*-chloro-, *p*-chloro-, and 2,4-dichloroanilines. The ratio of the yield of the *o*- to that of the *p*-chloroaniline is much higher than would be predicted for a statistically controlled electrophilic aromatic substitution. Although current theories of electrophilic rearrangements attribute such high ortho:para ratios to intramolecular processes, our search could find no conclusive evidence for an intramolecular pathway in these rearrangements. On the contrary, our results show that the highest ortho:para ratios are observed only when the conditions are ideal for an intermolecular transfer of chlorine.

N-Chloroanilines have been shown in our earlier report to be intermediates in the chlorination of anilines.[2] Further, studies by Gassman and co-workers have also shown that these compounds are quite stable and can be isolated.[3] They also reported a detailed study of para-substituted *N*-chloroanilines in buffered ethanol solution which showed that 4-ethoxycyclohexadienone imines were formed with rates of solvolysis which correlated with Brown's σ^+ with ρ of -6.35.[4] This product and kinetic behavior indicated that in the absence of strong acid the rearrangement was proceeding by way of the electron-deficient nitrenium ion. With acid present, these authors found evidence for two competing mechanisms, one which proceeded through the nitrenium ion and another through the electron-deficient chloronium ion.

We observed in our earlier work[2] that the rearrangement of *N*-chloroanilines produced an unusually high ratio of ortho to para chlorinated products, and decided to search for an explanation for these unusual results. The literature shows that one other reaction, the acid-catalyzed rearrangement of *N*-nitroaniline, yields exclusively the ortho-substituted product, and there seems to be general agreement that this rearrangement takes place by an intramolecular mechanism.[5-7] There is much evidence in the literature which suggests that the rearrangement of a *N*-chloroaniline under acid catalysis should be similar to the rearrangement of *N*-nitroaniline. First, the most commonly accepted theory of the *N*-nitroaniline rearrangement is an intramolecular process proceeding by way of a π complex intermediate.[5,7] Evidence for the existence of π complexes[8] has been well established. Secondly, many similarities have been observed between chlorination and nitration.[10,11] Finally there are precedents in the literature for assuming that a high ortho:para ratio of products in the chlorination of anilines is evidence for an intramolecular process.[12,13] Neale and co-workers[12] have claimed that the higher than predicted yields of *o*-chloroaniline observed in the chlorination of aniline with *N*-chlorosuccinimide were caused by the formation of the *N*-chloroaniline which then rearranged by an intramolecular process to yield the ortho-substituted product. This view was accepted by Kovacic in his review on *N*-halo compounds.[13]

Because of these precedents our efforts were directed to determine whether there was any evidence other than the high selectivity for ortho substitution to support an intramolecular mechanism for the *N*-chloroaniline rearrangement. In the course of this study many new and interesting discoveries have been made about the chemistry of *N*-chloroanilines which are presented in this paper, but no evidence has been found to support an intramolecular mechanism for the acid-catalyzed rearrangement.

Results

The products of the rearrangement of *N*-chloroanilines in aprotic, nonpolar solvents were generally found to be *o*-chloro-, *p*-chloro-, 2,4-dichloroaniline, and appreciable quantities of the parent aniline. In samples in which the rearrangement was allowed to go to completion the ortho:para ratio was always much greater than 2.0. The results of some typical rearrangements are shown in Table I, which shows an ortho:para ratio of 7.1 for *N*-methylaniline and 19.3 for *N*-*tert*-butylaniline if the dichlorinated products are discounted. When the ortho:para ratio was determined at various points in the rearrangement of *N*-chloro-*N*-methylaniline (**1**), a steady increase was observed over the course of the rearrangement. These results are shown in Table II.

Kinetic studies of the rearrangement showed that it was an acid-catalyzed reaction. Solutions of both **1** and *N*-chloro-*N*-*tert*-butylaniline (**2**) behaved very erratically when no attempt was made to control the amount of acid with which they came in contact. Further, the rate of the rearrangement could be increased by the addition of small concentrations of acids or could be decreased by treatment of the glass containers to reduce the acidity of their surfaces. The kinetic behavior of **1** was also complicated by the spontaneous elimination of HCl to form the Schiff base $PhN{=}CH_2$. The HCl which was formed by this reaction caused an acceleration of the rate of rearrangement which could be eliminated by stirring the solution with finely powdered sodium carbonate as shown in Figure 1. No similar acceleration was observed for **2** which cannot undergo β-elimination of HCl.

A rapid exchange of chlorine was observed when a small