assuming that intracage rotation is similar to intracage diffusion.
(12) W. P. Jencks, "Catalysis in Chemistry and Enzymology", McGraw-Hill, New York, N.Y., 1969, Chapter 7; J. L. Kavanau, "Water and Solute-Water Interactions", Holden-Day, San Francisco, Calif., 1964; R. W. Gurney, "Ionic Processes in Solution", McGraw-Hill, New York, N.Y., 1953.
(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

Denis F. Paul*[1] and Paul Haberfield

Division of Natural Science and Mathematics, Medgar Evers College, The City University of New York, Brooklyn, New York 11225, and Department of Chemistry, Brooklyn College, The City University of New York, Brooklyn, New York 11210

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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

Table I. Products of the Rearrangement of *N*-Chloroanilines in Carbon Tetrachloride Solution at 25.0 °C

	Yield, %			
N-Chloroaniline	PhNHR	*o*-Cl	*p*-Cl	2,4-Di-Cl
N-Methyl-[a]	10.9	66.4	9.4	10.3
N-*tert*-Butyl-[b]	5.0	83.2	6.9	5.0
N-*tert*-Butyl-[c]	3.2	89.0	4.6	2.8
N-*tert*-Butyl-[d]	2.6	84.0	5.3	3.1

[a] 0.020 M in untreated glass vessel at 25 °C. [b] Catalyzed by glass surface at 43 °C (in a polyethylene bottle no reaction took place within minutes). [c] Catalyzed by HCl (0.01 M) at 43 °C. [d] Catalyzed by trichloroacetic acid (0.01 M) at 43 °C.

Table II. Ortho:Para Ratios and Yields of Dichloro Product in the Rearrangement of 1 in Carbon Tetrachloride Solution at 25 °C

N-Chloroaniline Rearranged, %	2,4-Dichloro-aniline, %	Ortho:para ratio[a]
43	4.5	3.3
56	5.9	4.6
87	10.1	5.5
100	10.3	7.0

[a] This ratio contains no correction for the disubstituted product.

quantity of trichloroacetic acid was added to a solution of **2** and *p*-chloro-*N*-*tert*-butylaniline (**3**) in carbon tetrachloride. Table III shows that in the absence of acid no exchange took place, and that after the addition of the acid, equilibrium was established before 1% of the rearrangement had taken place. This experiment also showed that *p,N*-dichloro-*N*-*tert*-butylaniline was formed readily under the conditions of the rearrangement, but in a similar experiment with **2** and *o*-chloro-*N*-*tert*-butylaniline no evidence could be found for *o,N*-dichloro-*N*-*tert*-butylaniline.

In Table IV are shown the results of an experiment in which **2** was allowed to rearrange in a solution containing *N,N*-dimethylaniline (**5**). As can be seen, **5** was readily chlorinated to yield the *o*-chloro product but no measurable quantity of the *p*-chloro product of either of the anilines was observed.

The rates of rearrangement of chloroanilines **1** and **2** were increased by the addition of their corresponding anilines. Plots of the log of concentration of these chloroanilines against time gave straight lines which are shown in Figures 2 and 3. From

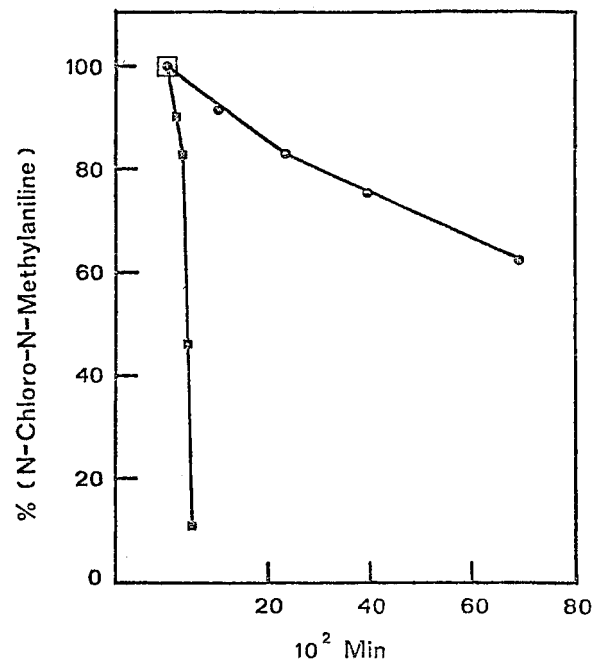

Figure 1. Percent of *N*-Chloro-*N*-methylaniline, 0.020 M in carbon tetrachloride, vs. time (■) in a glass vessel (●) stirred with sodium carbonate in a glass vessel.

the slopes of these lines first-order rate constants for the initial rates were calculated using the rate law, rate = k_1[PhNHR][PhNClR]. These pseudo-first-order rate constants, shown in Table V, appear from the analysis of columns A and B to be proportional to the total concentration of aromatic molecules and not to the concentration of the added anilines. The products of these rearrangements are also presented in Table V which shows a very large range in the ortho:para ratio for *N*-methylaniline while the ratio for the *tert*-butylaniline is always very high.

Discussion

Two outstanding features of the rearrangement of *N*-chloroanilines in the absence of added anilines are the formation of dichlorinated anilines and an ortho:para ratio which is always greater than 2.0. Such high ortho:para ratios have been assumed to be evidence for an intramolecular rearrangement.[5,6,7,12] Yet the formation of dichlorinated product requires the presence of some type of intermolecular process. Therefore, it seemed necessary to examine the nature of the rearrangement more closely.

Evidence that the rearrangement was not a simple intra-

Table III. The Chlorine Exchange Reaction (1). Products and Reactants (%) in the Chlorination of *p*-Chloro-*N*-*tert*-Butylaniline by *N*-Chloro-*N*-*tert*-butylaniline (0.95 M in Carbon Tetrachloride at 43 °C)

Time, 10^3 s	PhNClR[a]	PhNHR	*o*-ClPhNHR	*p*-ClPhNClR	*p*-ClPhNHR	2,4-Cl_2PhNHR	K_{eq}[b]
0.00	74.0	0.0	1.0	0.0	24.0	0.0	
1.74[c]	74.0	0.0	1.0	0.0	24.0	0.0	
3.24	62.0	11.0	1.0	11.0	15.0	0.0	0.13
5.28	57.0	16.0	2.0	16.0	9.0	0.0	0.50
6.48	56.0	16.0	3.0	16.0	9.0	0.0	0.51
8.70	54.0	16.0	4.0	16.0	9.0	0.0	0.53
14.58	51.0	16.0	7.0	16.0	9.0	0.0	0.56
72.18	31.0	15.0	29.0	12.0	11.0	3.4	0.53
97.98	26.0	15.0	34.0	10.0	10.0	4.0	0.58
116.70	20.0	15.0	38.0	11.0	12.0	4.0	0.69
185.40	16.0	13.0	44.0	8.0	14.0	5.0	0.46

[a] R = *tert*-butyl. [b] K_{eq} = [*p*-ClPhNClR][PhNHR]/[PhNClR][*p*-ClPhNHR]. [c] Trichloroacetic acid, 20 μl of 0.2 M, was added after this point.

Table IV. Molar Quantities of Products and Reactants at Intervals in the Trichloroacetic Acid (0.0025 M) Catalyzed Reaction of *N*-Chloro-*N*-*tert*-butylaniline (0.25 M) and *N,N*-Dimethylaniline (0.34 M) at 43 °C in Carbon Tetrachloride

Time, s × 10^{-3}	Ph-NHR′[a]	*o*-ClPh-NHR′	Ph-NClR′	Ph-NR_2[b]	*o*-ClPh-NR_2
0.00	0.63	0.44	8.89	12.1	0.45
0.30	0.89	0.48	8.63	14.2	0.89
1.02	1.17	0.67	8.10	12.9	1.23
1.38	1.17	0.68	8.15	12.5	1.24
1.98	1.34	0.77	7.88	12.5	1.34
2.82	1.64	0.93	7.50	12.4	1.67
3.54	1.67	0.92	7.45	12.1	1.64
4.98	1.79	1.00	7.13	11.7	1.75
5.76	1.94	1.14	6.92	11.8	1.90
8.52	2.22	1.38	6.40	11.4	2.14
10.08	2.28	1.53	6.20	11.0	2.24
11.04	2.35	1.65	6.00	11.2	2.35
12.84	2.62	1.85	5.51	10.6	2.53
15.90	2.86	2.16	4.97	10.6	2.74
18.12	3.06	2.41	4.50	10.4	2.86
21.96	3.22	2.83	3.87	10.2	3.05
25.68	3.46	3.20	3.32	10.4	3.36
28.62	3.58	3.54	2.88	9.9	3.40
Final	4.40	5.63	0	9.3	4.27

[a] R′ = *tert*-butyl. [b] R = methyl.

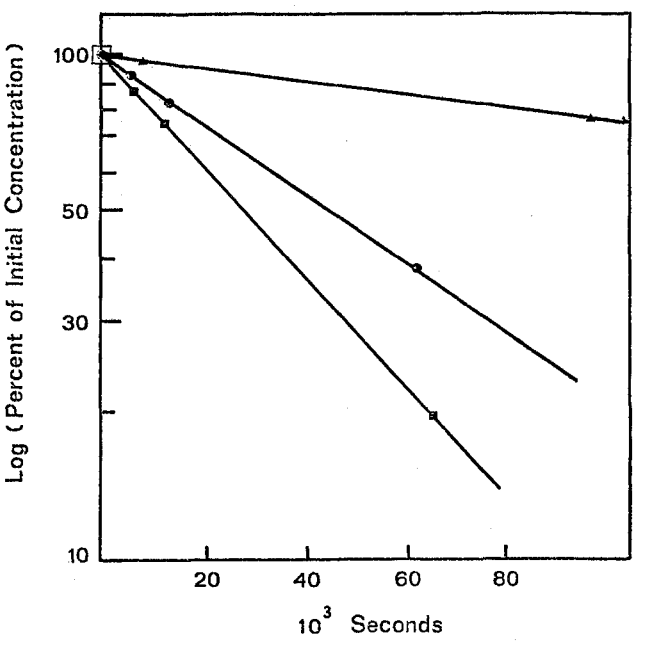

Figure 2. Log of percent of initial concentration of *N*-chloroaniline vs. time in the rearrangement of *N*-chloro-*N*-methylaniline in hexane at 25 °C with the ratio of parent aniline to *N*-chloroaniline as indicated: (▲) zero, (●) 8.0, (■) 16.0.

Table V. First-Order Rate Constants[a] (k_1) and Ortho:Para Ratios for the Rearrangement of *N*-Chloroanilines with Added Anilines in Carbon Tetrachloride and Their Dependence on the Concentration of Anilines

PhNHR[b]	PhNClR[b]	R	$k_1 \times 10^6$, s	*A*[c]	*B*[d]	*o*-/*p*-
0	0.02	CH_3	1.1		55	2.9
0.16	0.02	CH_3	5.6	35	31	3.9
0.32	0.02	CH_3	9.6	30	28	11.5
0	0.40	$C(CH_3)_3$	4.8		12	16.0
0.04	0.40	$C(CH_3)_3$	4.2	105	9.5	16.0
0.10	0.40	$C(CH_3)_3$	5.5	55	11	13.0
0.59	0.40	$C(CH_3)_3$	12.2	21	12.3	13.0

[a] 25 °C for *N*-chloro-*N*-methylaniline and 43 °C for *N*-chloro-*N*-*tert*-butylaniline. [b] Concentration in moles per liter as determined by NMR anaalysis of the reaction mixture. [c] $10^6 k_1/[\text{PhNHR}] = A$. [d] $10^6 k_1/([\text{PhNClR}] + [\text{PhNHR}]) = B$.

molecular process was provided by the changing ortho:para ratio shown in Table II. If the rearrangement was a clean intramolecular process of the type proposed for *N*-nitroaniline,[5] one would expect the product ratio to be constant at all stages of the rearrangement. This was not observed. There was a steady increase in the ortho:para ratio as the rearrangement progressed which is shown in Table II. A unimolecular process involving only a protonated *N*-chloroaniline could not yield this result.

The data discussed thus far do not rule out the possibility that the transfer of chlorine from the nitrogen to the carbon of the aromatic ring is an intramolecular process. Such a transfer could account for the products in Table I if the rearrangement were preceded by an exchange of chlorine between the anilines in solution such as

$$\text{PhNClR} + \text{Ph′NHR} \rightleftharpoons \text{PhNHR} + \text{Ph′NClR} \quad (1)$$

Since this exchange reaction takes place as is shown in Table III, the presence of dichlorinated products and the increasing ortho:para ratio in Table II cannot be used as conclusive evidence for either the intra- or the intermolecular pathway.

If there was an intramolecular mechanism, it might be detected by carrying out the rearrangement in the presence of an aniline which would not be expected undergo the nitrogen chlorination shown in eq 1. Since **5** is at least as reactive as **3** to electrophilic aromatic substitution, the absence of its chlorinated products in a rearranging sample of **2** would be evidence for an intramolecular process. The data in Table IV show, however, that **5** is readily chlorinated by **2** and that the ortho:para ratios for both the chlorinating and substrate anilines are very much higher than would have been predicted for a statistically controlled process. The unusually high selectivity for the ortho position in both anilines strongly suggests that the carbon chlorination took place by the same mechanism. And although this result does not prove an intermolecular transfer from nitrogen to carbon, it makes speculation about this possibility quite plausible.

Evidence that the nitrogen to carbon transfer of chlorine might be an intermolecular process is provided in Figures 2 and 3, and by Table V. They show that the rate of rearrangement is increased by the added anilines and that the ortho:para ratio increases for *N*-methylaniline whenever there is a significant quantity of free aniline present. As can be seen in eq 2, the chlorine exchange reaction can produce no change in the composition of an aniline and its *N*-chloro derivative because the products are identical with the reactants.

$$\text{PhNHR} + \text{PhNClR} \rightleftharpoons \text{PhNClR} + \text{PhNHR} \quad (2)$$

If the rearrangement were intramolecular its rate would depend on the concentration of PhNClR and should not be affected by the addition of PhNHR. Thus the increase in the rate is most probably caused by an intermolecular transfer of chlorine from nitrogen to carbon, since it is under these conditions that unusually high yields of ortho chloroanilines are observed.

The increase in rate discussed above could also have been caused by an increase in the polarity of the medium. Two pieces of data would seem to contradict this proposition. The first is that at the end of the rearrangement shown in Table II the ortho:para ratio was higher than at the beginning. The experimental data show that the last 13% of the rearrangement yielded almost exclusively the ortho product. Since the

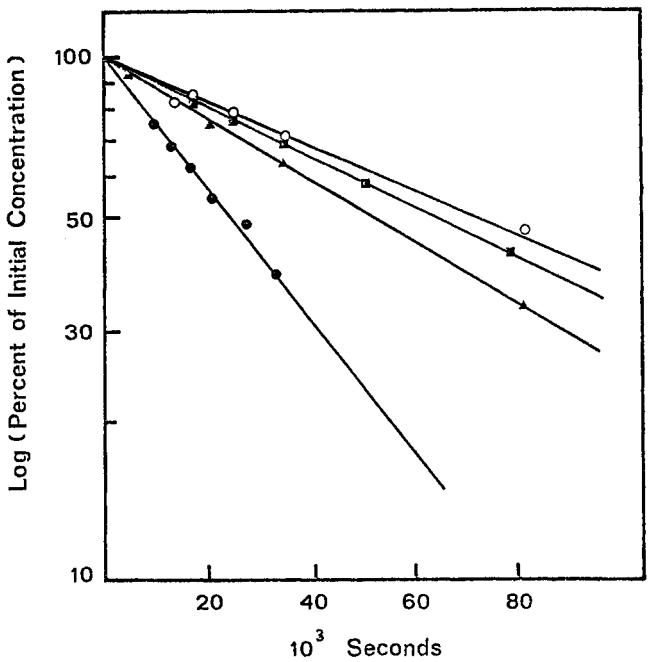

Figure 3. Log of percent of initial concentration of N-chloro-*tert*-butylaniline vs. time in the rearrangement of N-chloro-N-*tert*-butylaniline in carbon tetrachloride at 42 °C with the ratio of parent aniline to N-chloroaniline as indicated: (■) zero, (○) 0.10, (▲) 0.25, (●) 1.48.

number of aromatic molecules remained constant over the course of the rearrangement, it is unlikely that there was a significant change in the polarity of the medium yet a change in the product ratio took place. This change in the ortho:para ratio could be caused by the increase in the concentration of the parent aniline which was generated by the formation of dichlorinated products. Secondly, the results of the chlorination of dimethylaniline presented in Table IV show that both anilines are chlorinated and that in the completely rearranged mixture there are no p-chloroanilines. This essentially infinite ortho:para ratio for *tert*-butylaniline should be contrasted to the data in Table I which show that in the absence of added aniline a significant quantity of para product is always formed. The similarity of product ratio between added dimethyl- and parent aniline also suggests that the rate enhancement produced by the parent aniline could have been caused by an intermolecular transfer of chlorine from nitrogen to carbon.

Summary and Conclusion

We have shown that the rearrangement of N-chloroanilines is a complex mixture of reactions and not a single reaction as that proposed for the rearrangement of N-nitroaniline.[5] We have shown also that the high ortho:para ratios observed in the rearrangement are enhanced by the addition of dimethylaniline, and when there is a significant quantity of the parent aniline the product formed is almost exclusively ortho. These experiments were designed primarily to find evidence to support the proposition that the high ortho:para ratios were produced by an intramolecular reaction. We had expected that if the rearrangement were intramolecular, the product ratio over the course of the rearrangement would be reasonably constant, but the ortho product became increasingly favored as the rearrangement progressed. We had expected that if there was a clean intramolecular pathway that none or only very little of the dimethylaniline would have been chlorinated. This was not observed. We had expected to find no change in rate or product distribution on the addition of the parent aniline, but both an increase in rate and an increase in the ortho:para ratio were observed. This absence of any clear-cut

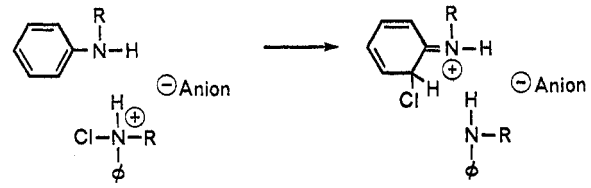

Figure 4. Reactants and σ complex intermediate in the ortho chlorination of an aniline molecule by a N-chloroanilinium ion.

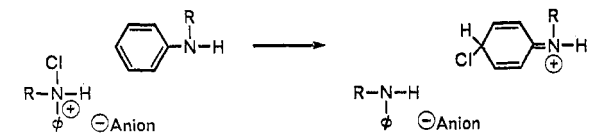

Figure 5. Reactants and σ complex intermediate in the para chlorination of an aniline molecule by a N-chloroanilinium ion.

evidence for the intramolecular reaction prompted us to examine whether a plausible explanation could be presented in terms of an intermolecular transfer of chlorine from the nitrogen of a chloroaniline to the aromatic carbon of an aniline molecule.

First, the changing ortho:para ratios as the rearrangement progresses could have been caused by chlorination of one chloroaniline molecule by another at the very early stages of the rearrangement. This chlorination should take place predominantly in the para position because, as we have shown, p,N-dichloroanilines form very readily whereas there is no evidence for the o,N-dichloroaniline. This is further supported by the data in Table V which show that the rate of rearrangement shows a better dependence on the total aromatic than on the free aniline concentration.

Second, the data from the dimethylamiline experiment and the added aniline experiment could be explained by an intermolecular transfer which favors ortho substitution because of differences in the charge separation in the intermediates leading to ortho and para substitution. It has been shown that for reactions which require varying degrees of charge separation in the transition state the one which can proceed with the minimum separation of charge would be favored in solvents of low polarity.[14,15] Figures 4 and 5 show possible arrangements of the reactants for the intermolecular transfer of chlorine to the ortho and para positions of aniline molecules. Since the reaction is acid catalyzed, the most likely chlorinating agent would be a protonated N-chloroaniline closely associated with the anion of the acid. It can be seen that the developing charge in para substitution would be much further removed from the anion than would be the case in ortho substitution. An alternate explanation could be provided by an expansion of Kovacic's concept of a linear coordination mechanism. In such a mechanism, the protonated N-chloroaniline would be positioned by this coordination effect near the most basic site of an aniline molecule, i.e., near the nitrogen atom, as shown in Figure 4. The geometry of such a complex would be ideal for the transfer of the chlorine to the ortho position of the aniline molecule. This explanation focuses on the greater stability of the ortho chlorination transition state by using a reactant-like transition state model, whereas the charge separation explanation uses a product-like transition state model. It is possible that a combination of both of these effects operate in this case.

Finally, although there is no clear-cut evidence in any one of the experiments to say that the rearrangement is unambiguously intermolecular, it seems fair to say that the grounds for the speculation that it is intramolecular are the high ortho:para ratios which could equally be explained by an intermolecular process as described above. Further, it seems that

taken as a group the data provide good circumstantial evidence for an intermolecular process.

Experimental Section

***N*-Methylaniline (6).** The commercially available yellow oil was mixed with 1% by weight of lithium aluminum hydride and distilled under a nitrogen atmosphere to give an almost colorless product better than 99% pure by vapor phase chromatography.

***p*-Chloro-*N*-methylaniline (7).** A 38.3-g sample of *p*-chloroaniline (Eastman Yellow Label) mixed with 47.7 g of trimethyl orthoformate (Fischer Scientific, practical) and with 1.2 g of concentrated sulfuric acid was heated under reflux for 0.5 h. The mixture was distilled to yield 42 g of *p*-chloro-*N*-formyl-*N*-methylaniline, bp 166–170 °C (20 mm), lit.[16] 165–170 °C (20 mm). The amide was hydrolyzed by heating under reflux with 120 ml of 3 M sulfuric acid for 4 h. The reaction mixture was extracted with ether, made basic with NaOH, and extracted again with ether. The second ether extract was dried over sodium carbonate and distilled to yield 22.2 g (53%) of **7**: bp 120 °C (20 mm), lit.[4] bp 120 °C (20 mm); n^{20}D 1.5816, lit.[2] n^{25}D 1.5779; NMR (CCl_4) τ 7.30 (s, 3), 6.50 (s, 1), 2.73–3.80 (symmetrical m, 4).

***o*-Chloro-*N*-methylaniline (8).** *N*-Formyl-*N*-methyl-*o*-chloroaniline was prepared as described for aniline **7**. The reaction product was dissolved in ether and extracted with two 50-ml portions of 1 M sulfuric acid. The ether was evaporated and the residue was hydrolyzed as described for aniline **7** to yield 32.0 g of **8** (76%): bp 106 °C (20 mm); n^{24}D 1.5784, lit.[4] n^{25}D 1.5784; NMR (CCl_4) τ 7.65 (s, 3), 6.06 (s, 1), 2.66–3.66 (m, 4).

2,4-Dichloro-*N*-methylaniline (9). A 4.05-g sample of 2,4-dichloroaniline (Eastman White Label) was heated under reflux for 0.5 h with 2.55 g of 90% formic acid. The mixture was dissolved in 50 ml of ether, stirred over sodium carbonate, filtered, and concentrated to 15 ml. On standing, it crystallized to give 4.0 g (86%) of *N*-formyl-2,4-dichloroaniline (mp 159–160 °C). This was dissolved in 50 ml of tetrahydrofuran and heated under reflux for 4 h with 1.0 g of lithium aluminum hydride. After evaporation of the solvent, the residue was dissolved in hydrochloric acid and extracted with ether. The aqueous layer was made basic and extracted with ether which was then dried over sodium carbonate and distilled to yield 2.4 g of a product which was found to be a 1:5 mixture of **7** and **9** by vapor phase chromatography. A pure sample of **9** was obtained by vapor phase chromatography: n^{20}D 1.5945; NMR (CCl_4) τ 7.20 (s, 3), 5.80 (s, 1), 2.20–3.70 (m, 3).

Anal. Calcd for $C_7H_7Cl_2N$: C, 47.74; H, 4.01. Found: C, 47.74; H, 4.12.

Attempts to prepare **8** by a similar reduction of the formyl derivative gave **6** as the principle product.

***N*-*tert*-Butylaniline (10).** To 175 g of *tert*-butylamine (Eastman Yellow Label) and 7.8 g of sodamide which had been heated under reflux for 24 h was added 32 g of bromobenzene, and the mixture was heated again for another 72 h. Unreacted butylamine was removed by distillation. The residue, dissolved in 100 ml of 6 N hydrochloric acid, was extracted with ether which was dried over sodium carbonate and distilled to yield 11.0 g (40%) of **10**: bp 105 °C (22 mm); lit.[17] bp 97 °C (19 mm); n(^{24}D 1.5250, lit.[17] n^{24}D 1.5246; NMR (0.2 M, CCl_4) τ 8.78 (s, 9), 6.65 (s, 1), 2.80–3.66 (m, 5).

***p*-Chloro-*N*-*tert*-butylaniline (3).** A 2.98-g sample of **10** was heated under reflux for 1 h with 2.66 g of *N*-chlorosuccinimide in 50 ml of benzene. The solution was extracted with water, dried over sodium carbonate, add concentrated to a volume of 5.0 ml. The products were separated by vapor phase chromatography to give 1.2 g (32%) of **3**: n^{24}D 1.5425, lit.[16] n^{24}D 1.5416; NMR (1.2 M, CCl_4) τ 8.70 (s, 9), 6.68 (s, 1), 3.22 (symmetrical m, 4).

***o*-Chloro-*N*-*tert*-butylaniline (4).** The chlorination mixture from which **3** was extracted gave also by preparative gas chromatography 1.8 g (50%) of **4**: n^{24}D 1.5350, lit.[16] n^{24}D 1.5346; NMR (0.80 M, CCl_4) τ 8.66 (s, 9), 5.83 (s, 1), 2.80–3.70 (m, 4) [lit.[16] NMR τ 8.63 (s, 9), 5.83 (s, 1), 2.70–3.60 (m, 4)].

2,4-Dichloro-*N*-*tert*-butylaniline (11). In 50 ml of benzene, 0.92 g of **3** was stirred for 0.5 h at 25 °C with 5.0 g of calcium hypochlorite which had been moistened with 0.5 ml of water. The mixture was filtered. The filtrate was mixed with 1.0 ml of 0.1 N trichloroacetic acid in benzene and held at 43 °C for 48 h. Evaporation of the benzene left **11**, better than 98% pure. It was purified further by gas chromatography: n^{20}D 1.5524; NMR (2.0 M CCl_4) τ 8.60 (s, 9), 5.90 (s, 1), 2.72–3.33 (m, 3).

Anal. Calcd for $C_{10}H_{13}Cl_2N$: C, 55.07; H, 5.95. Found: C, 55.36; H, 6.05.

***N*-Chloro-*N*-methylaniline (1). Method A.** A 1.075-g sample of **6** in 500 ml of carbon tetrachloride at 0 °C was mixed with 10.0 g of calcium hypochlorite which had been moistened with 1.0 ml of water. The mixture was stirred for 15 min, vacuum filtered on a Buchner funnel with genuine Whatman filter paper no. 1, and readjusted to 500 ml with carbon tetrachloride. Titration[2] of an aliquot immediately after filtering showed a 99% yield of **1**.

Method B. A 0.268-g sample of **6** was mixed with 0.58 g of *N*-chlorobenzanilide and 2.0 g of finely powdered sodium carbonate in 125 ml of benzene at 25 °C. The mixture was stirred for 25 h, filtered as in method A, and titrated to give a 99% yield of **1**. The residue, dissolved in water and filtered, gave 0.48 g (96%) of benzanilide (mp 161–162 °C).

***N*-Chloro-*N*-*tert*-butylaniline (2).** A 1.49-g sample of **10** was chlorinated by method A of *N*-chloro-*N*-methylaniline to give a 99+% yield by titration of **2**: NMR (0.40 M, CCl_4) τ 8.80 (s, 9), 2.50–3.00 (m, 5).

Method C. To a 1.49-g sample of **10** in 25 ml of carbon tetrachloride were added 1.362 g of *N*-chlorosuccinimide (Aldrich, 98+% purity) and 2.0 g of finely powdered sodium carbonate. The mixture was stirred for 18 h at 25 °C in a polyethylene flask and filtered to give a 99+% yield of **2** having the same NMR spectrum as the sample obtained by method A.

Rearrangement of 1 in an Untreated Glass Vessel at 25 °C. A 0.020 M solution of **1** in carbon tetrachloride was kept in a glass vessel at 0 °C, and 5.00-ml aliquots were removed at intervals for titration. The titrated samples were made basic with sodium hydroxide and the anilines were extracted from them with hexane and analyzed by vapor phase chromatography. The products obtained from these samples are shown below. A plot of percent of positive chlorine vs. time is shown in Figure 1.

	Yield of products, %			
Sample no.	6	7	8	9
1		7.9	25.8	4.5
2	44.7	8.9	41.3	5.9
3	22.1	10.3	56.5	10.1
4	10.9	9.4	66.4	10.3

Rearrangement of 1 over Sodium Carbonate in an Untreated Glass Vessel at 25 °C. A 200-ml sample of a 0.02 M solution of **1** in carbon tetrachloride at 25 °C was placed in a 500-ml glass flask and stirred very vigorously with 10 g of finely powdered sodium carbonate. Aliquots of the solution were removed at intervals and titrated for positive chlorine.[2] A plot of the data is shown in Figure 1. A sample, titrated at the end of 115 h of stirring, was made basic with sodium hydroxide, and the anilines were extracted with hexane and analyzed by vapor phase chromatography. The products observed were aniline, 6.2%; **6**, 60.4%; **7**, 3.6%; **8**, 12.9%; **9**, 1.2%.

Rearrangement of 2 in Carbon Tetrachloride at 43 °C Catalyzed by Glass Surface. Samples (1.00 ml) of a 0.40 M solution of **2** in carbon tetrachloride (calcium hypochlorite preparation) were placed in glass tubes which were prepared by soaking in a chromic acid bath for 1 h, then washing with water and baking at 180 °C for 12 h. They were degassed by repeatedly freezing and thawing at 0.01 mm pressure, sealed, and placed in constant-temperature baths at 43 °C. Samples were removed at intervals and titrated for positive halogen with standard thiosulfate.[2] A 20% decrease in concentration was observed in 5.90×10^3 s.

The products obtained by NMR analysis of the samples after all of the **2** had reacted were as follows.

Products	Water-washed glass vessels	Catalyzed	Trichloroacetic acid catalyzed
10	5.0	3.2	2.6
4	83.2	89.0	84.0
3	6.9	4.6	5.3
11	5.0	2.8	3.1

Rearrangement of 2 in Carbon Tetrachloride Solution at 43 °C Catalyzed by Hydrochloric and Trichloroacetic Acids. Samples of 3.33 M solution of **2** in carbon tetrachloride, 0.20 ml each, were placed in NMR sample tubes. To one tube was added 0.2 ml of 0.19 N HCl in carbon tetrachloride; to the other tube was added 0.2 ml of 0.019 N trichloroacetic acid in carbon tetrachloride. Spectra were taken at intervals in the course of the rearrangement from which the concentrations of reactants and products were determined. The rates of rearrangements were quite similar with both samples showing a

change to 50% in approximately 25×10^3 s.

Reaction of 2 with 3 in Carbon Tetrachloride at 43 °C. To a 0.40-ml sample of a 0.40 M solution of **2** in carbon tetrachloride, 12 μl of **3** was added. The sample was placed in an NMR sample tube which had been washed with water and baked dry. It was then placed in a constant-temperature bath at 43 °C. The products were identified by the position of the *tert*-butyl resonance signal of the various anilines and were determined quantitatively by peak height analysis. The results are presented in Table III.

Reaction of 2 with 5 at 43 °C Catalyzed by Trichloroacetic Acid. To 1.0 ml of a 0.40 M solution of *N*-chloro-*N*-*tert*-butylaniline in carbon tetrachloride was added 0.654 g (0.540 mmol) of **5**. The sample was placed in NMR sample tubes which had been washed with a dilute (ca. 0.5%) solution of sodium carbonate and baked dry. To the tube was added 20 μl of 0.2 M trichloroacetic acid in carbon tetrachloride. Spectra of the mixtures were taken at intervals, and the relative molar ratio of products and reactants were calculated. The results are recorded in Table IV. Para-chlorinated anilines accounted for less than 2% of the total product.

Rearrangement of 1 with 6 over Sodium Carbonate at 25 °C. An 0.02 M solution of **1** was prepared in hexane by method A. Three samples, 200 ml each, of this solution were stirred over 4.0 g of finely powdered sodium carbonate. To sample A was added 3.43 g (32.0 mmol) of **6**, and to sample B was added 6.86 g (64.0 mmol) of the same. Sample C was an 0.02 M solution of **1** and sodium carbonate. Aliquots of A, B, and C, 10.14 ml each, were transferred to a solution of potassium iodide in 50% acetic acid and titrated with standard sodium thiosulfate solution. The results are shown in Figure 2.

Effect of Glass Surfaces on the Rate of Rearrangement of 2. Samples of a 0.10 M solution of **2**, 1.00 ml each, in carbon tetrachloride were placed in glass tubes which were prepared in the following manner: 8-mm o.d. Pyrex tubing was sealed off in 6-in. lengths and constricted 4 in. from the bottom. They were kept in a chromic acid bath for 1 h, then washed exhaustively with water, and finally with a 5% sodium carbonate solution. Some of the tubes were washed with distilled water to remove all sodium carbonate. Both sets of tubes were then baked for 12 h at 180 °C. The samples of this solution of **2** were degassed by freezing and thawing four times at 0.01 mm pressure; they were then sealed at the same pressure and placed in a 43 °C constant-temperature bath. Tubes were removed at intervals, and their contents were transferred to a mixture of potassium iodide in 50% acetic acid, for titration with standard sodium thiosulfate solution. The results are shown below.

Water-washed tubes		Sodium carbonate washed tubes	
Time, h	Concn, %	Time, h	Concn, %
0.0	100	0.0	100
3.5	85	3.5	98
14.0	30	29.0	99
23.0	18	52.0	99

Rearrangement of 2 with 10 in Carbon Tetrachloride at 43 °C. A 4.0-ml sample of a 0.40 M solution of **2** and 40 μl of 0.2 M trichloroacetic acid was prepared in carbon tetrachloride. Aliquots, 1.00 ml each, were added to NMR sample tubes which had been washed with 20% nitric acid in sulfuric acid, then with water, and finally with a dilute solution of sodium carbonate (ca. 0.2% solution) and baked for 12 h at 180 °C. Samples of **10** were added to these tubes in the following order: tube A, none; tube B, approximately 5.0 μl; tube C, approximately 12.0 μl; tube D, approximately 30.0 μl. The exact quantities were determined by integration of the NMR spectra of the mixtures and are shown in Table V. The course of the rearrangement was followed by scanning the region of the spectrum between 0 and 100 Hz downfield from Me_4Si. The results are shown in Figure 3. First-order rate constants calculated from the results of this experiment are shown in Table V.

Rearrangement of 2 with 4 in Carbon Tetrachloride at 43 °C. A sample of **4**, 0.0524 g (0.350 mmol), was added to 0.20 ml of 1.90 M solution of **2** in carbon tetrachloride and the volume made up to 0.40 ml with the solvent. The sample was placed in an NMR sample tube which had been washed with water and baked dry. It was kept in a constant-temperature bath at 43 °C and removed at intervals for NMR spectra to be taken. Resonance signals were observed for *tert*-butyl protons at −1.6, 3.0, 5.0, 7.4, and 9.4 Hz from that of the *tert*-butyl resonance of **2** indicating the presence of these anilines, respectively: *p*,*N*-dichloro-*N*-*tert*-butylaniline, **3**, **4**, **10**, and **11**. There were no other peaks present which could be attributed to *o*,*N*-dichloro-*N*-*tert*-butylaniline. After all positive chlorine had been used up the products observed on analysis by NMR were **4**, 85.5%; **3**, 6.3%; **11**, 4.0%; 10, 4.0%. Under the conditions of the analysis, an absorption corresponding to less than 0.5% of the total mixture could have been identified.

Registry No.—**1**, 4707-14-6; **2**, 22020-91-3; **3**, 48131-06-2; **4**, 939-36-6; **5**, 121-69-7; **6**, 100-61-8; **7**, 932-96-7; **8**, 57218-02-7; **9**, 35113-88-3; **10**, 937-33-7; **11**, 38370-52-4; *p*-chloroaniline, 106-47-8; trimethyl orthoformate, 149-73-5; *p*-chloro-*N*-formyl-*N*-methylaniline, 26772-93-0; *o*-chloroaniline, 95-51-2; *N*-formyl-*N*-methyl-*o*-chloroaniline, 14924-76-6; 2,4-dichloroaniline, 554-00-7; *N*-formyl-2,4-dichloroaniline, 22923-00-8; *tert*-butylamine, 75-64-9; bromobenzene, 108-86-1; *N*-chlorobenzanilide, 5014-47-1; benzanilide, 93-98-1; *N*-chlorosuccinimide, 128-09-6; *N*-chloroaniline, 24613-03-4.

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