The reaction was repeated and analysis *via* gas chromatography on the same type of column (*vs.* ethyl *p*-aminobenzoate as the internal standard) yielded 58% of **43** and 26% of the starting amine **44**.

**Chlorination and Solvolysis of *p*-(*N*-*tert*-Butylamino)nitrobenzene.** To a solution of 1.0 g of *p*-(*N*-*tert*-butylamino)nitrobenzene in 50 ml of 1:1 carbon tetrachloride-pentane was added 10 g of powdered calcium hypochlorite. After the mixture was stirred for 4 hr at room temperature, the salts were removed by filtration and the solution was concentrated *in vacuo* to leave the neat chloramine **42**. Infrared analysis of **42** showed the complete absence of the N-H band of the starting amine. The sample was added to a solution of 3.42 g of silver trifluoroacetate in 50 ml of methanol. Silver chloride precipitated slowly. After the mixture was stirred overnight, an iodometric test for active chlorine was negative. Excess lithium chloride was added and the silver chloride was removed by filtration. The solvent was removed on the rotary evaporator and the residue was taken up in 100 ml of ether and stirred over sodium hydroxide pellets for 1 hr. The ethereal solution was decanted and the solvent evaporated to give yellow crystals. Chromatography on Activity I basic alumina separated two compounds. The first compound eluted (hexane-ether solvent) was 761 mg (65%) of 3-chloro-4-(*N*-*tert*-butyl)nitrobenzene (**45**): mp 113-115°; ir (KBr) 6.25, 7.52, 7.69, 8.20, and 8.85 $\mu$; nmr ($CDCl_3$) $\tau$ 8.49 (9 H, s), 7.00 (1 H, d), 1.72 (3 H, m).

*Anal.* Calcd for $C_{10}H_{13}N_2O_2Cl$: C, 52.52; H, 5.73; N, 12.25; Cl, 15.51. Found: C, 52.58; H, 5.75; N, 12.12; Cl, 15.50.

The second product to be eluted was starting *p*-(*N*-*tert*-butylamino)nitrobenzene (**46**).

**Acknowledgment.** We are indebted to the National Cancer Institute of the Public Health Service for a grant which supported this investigation.

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# Thermal Rearrangement of *N*-Chloroanilines. Evidence for the Intermediacy of Nitrenium Ions[1]

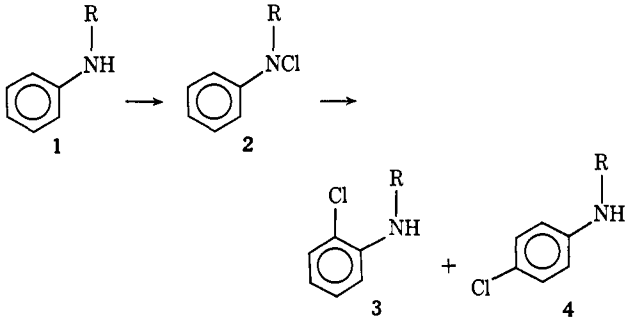
**Paul G. Gassman* and Gerald A. Campbell[2]**

*Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.*

*Received October 1, 1971*

**Abstract:** The mechanism of the thermal rearrangement of *N*-alkyl-*N*-chloroanilines has been studied in both ethanol buffered with 0.1 *N* sodium acetate and 0.1 *N* acetic acid and in unbuffered ethanol. Under buffered conditions, a series of six para-substituted *N*-*tert*-butyl-*N*-chloroanilines solvolyzed at rates which correlated excellently with Brown's $\sigma^+$. A $\sigma^+\rho$ plot gave a $\rho$ of $-6.35$. This showed that the mechanism involved the generation of an electron-deficient nitrogen species (anilenium ion) and chloride anion. In the presence of acid catalysis, two competing mechanisms seemed to be involved in the rearrangement of *N*-chloroanilines to *o*-chloroanilines, with one mechanism being favored by electron-donating substituents and the other mechanism being promoted by electron-withdrawing substituents.

The chlorination and bromination of the aromatic rings of anilines and related amines have been the subject of extensive discussion during the last 10 years. In general, sources of positive halogen, especially of positive chlorine, readily halogenate the aromatic nucleus when an amine function is attached to the aromatic ring. Much of the mechanistic thinking in this area has been fashioned by the careful investigations of Neale and coworkers[3] and by Haberfield and Paul.[4] These workers provided convincing evidence for the intermediacy of *N*-chloramines in the chlorination of aromatic amines by reagents such as *N*-chlorosuccinimide and calcium hypochlorite.[5,6] Experimental results already presented[1,4] leave little doubt about the validity of the hypothesis[3] that the first step involves *N*-chlorination. The major question which remained to be answered concerned the mechanism whereby **2** was converted into a mixture of **3** and **4**. We now wish to report the details of our studies which show that simple *N*-chloramines rearrange *via* heterolytic cleavage of the N-Cl bond of **2** to yield an electron-deficient divalent nitrogen species (anilenium ion) and chloride anion.[7]



1 2 3 4

Various mechanistic routes from **2** to **3** and **4** can be postulated. Of the many possibilities, the two most attractive alternates are shown in paths a and b.[8a]

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[1] Paper XXII in a series on The Chemistry of Nitrenium Ions. For the previous paper in this series, see P. G. Gassman, G. A. Campbell, and R. C. Frederick, *J. Amer. Chem. Soc.*, **94**, 3884 (1972).

[2] National Defense Education Act Fellow, 1967–1970; Stauffer Chemical Fellow, 1970–1971.

[3] R. S. Neale, R. G. Schepers, and M. R. Walsh, *J. Org. Chem.*, **29**, 3390 (1964).

[4] P. Haberfield and D. Paul, *J. Amer. Chem. Soc.*, **87**, 5502 (1965).

[5] Various other chlorinating agents have been used. For additional synthetic application and leading references, see T. A. Foglia and D. Swern, *J. Org. Chem.*, **33**, 4440 (1968); J. M. Muchowski, *Can. J. Chem.*, **48**, 422 (1970); A. M. Pinchuk, L. N. Markovskii, and I. M. Kosinskaya, *Zh. Obshch. Khim.*, **38**, 1008 (1968); and P. G. Gassman, G. A. Campbell, and G. Mehta, *Tetrahedron*, in press.

[6] For a detailed discussion of the initial *N*-chlorination of aromatic amines, see ref 1.

[7] For a preliminary report of part of this investigation, see P. G. Gassman and G. A. Campbell, *J. Amer. Chem. Soc.*, **93**, 2567 (1971).

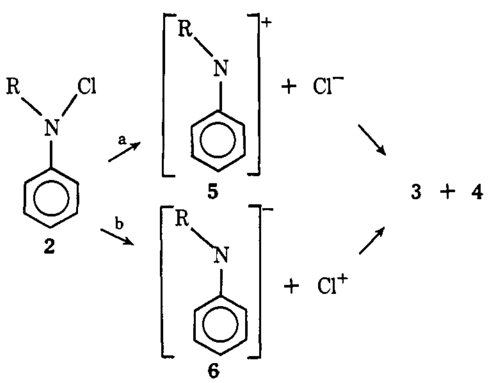
[8] (a) An alternate possibility would involve halogen exchange between halogenated aniline and protic solvent followed by direct transfer of positive halogen from the hypohalite to the aromatic nucleus in an electrophilic halogenation. This plausible mechanism is rendered

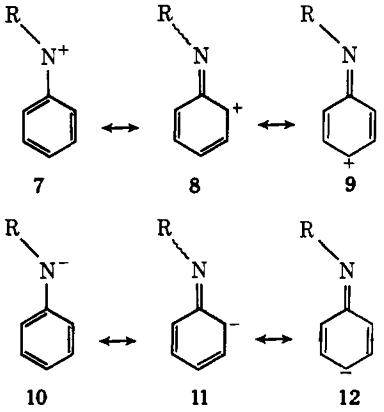
Table I. Rates of Rearrangement of *N*-Chloroanilines in Ethanol Buffered with 0.1 *N* Acetic Acid–0.1 *N* Sodium Acetate

| Compd | Temp, ±0.02°C | $k$, sec$^{-1\,b}$ | $k_{rel}$ | $\Delta H^{\ddagger}$, kcal/mol | $\Delta S^{\ddagger}$, eu |
|---|---|---|---|---|---|
| **13** | −10.0 | $(5.27 \pm 0.05) \times 10^{-5}$ | | | |
| | 0.0 | $(2.37 \pm 0.01) \times 10^{-4}$ | | 20.4 | −0.3 |
| | 10.0 | $(8.79 \pm 0.01) \times 10^{-4}$ | | | |
| | 25.00[a] | $5.85 \times 10^{-3}$ | 1,800,000 | | |
| **14** | 20.0 | $(7.47 \pm 0.01) \times 10^{-5}$ | | | |
| | 30.0 | $(2.60 \pm 0.01) \times 10^{-4}$ | | 21.2 | −5.0 |
| | 40.0 | $(8.18 \pm 0.04) \times 10^{-4}$ | | | |
| | 25.00[a] | $1.40 \times 10^{-4}$ | 44,000 | | |
| **15** | 30.0 | $(3.83 \pm 0.03) \times 10^{-5}$ | | | |
| | 40.0 | $(1.27 \pm 0.02) \times 10^{-4}$ | | 21.9 | −6.6 |
| | 50.0 | $(3.91 \pm 0.01) \times 10^{-4}$ | | | |
| | 25.00[a] | $2.06 \times 10^{-5}$ | 6,500 | | |
| **16** | 40.0 | $(1.12 \pm 0.02) \times 10^{-4}$ | | | |
| | 50.0 | $(3.60 \pm 0.02) \times 10^{-4}$ | | 23.0 | −3.1 |
| | 60.0 | $(1.09 \pm 0.01) \times 10^{-3}$ | | | |
| | 25.00[a] | $1.65 \times 10^{-5}$ | 5,200 | | |
| **17** | 70.0 | $(1.07 \pm 0.02) \times 10^{-5}$ | | | |
| | 80.0 | $(3.97 \pm 0.02) \times 10^{-5}$ | | 26.3 | −4.9 |
| | 90.0 | $(9.35 \pm 0.32) \times 10^{-5}$ | | | |
| | 25.00[a] | $2.96 \times 10^{-8}$ | 9 | | |
| **18** | 90.0 | $(2.04 \pm 0.08) \times 10^{-5}$ | | | |
| | 100.0 | $(6.10 \pm 0.04) \times 10^{-5}$ | | 28.4 | −2.2 |
| | 110.0 | $(1.68 \pm 0.04) \times 10^{-4}$ | | | |
| | 25.00[a] | $3.19 \times 10^{-9}$ | 1 | | |

[a] Extrapolated from other temperatures. [b] Rates were determined by iodometric titration of active chlorine. Unreacted *N*-chloroanilines were first treated with acidic potassium iodide followed by titration with thiosulfate using a dead-stop titration method.

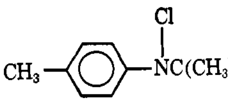
Path a involves heterolytic cleavage of the N–Cl bond of **2** to yield a phenylnitrenium ion[8b] and chloride anion. The alternate process shown by path b depicts the reverse type of heterolytic cleavage to yield an amide anion, **6**, and positive chlorine. The charges on the nitrogen atoms of both **5** and **6** would be expected to be extensively delocalized into the aromatic ring with **5** being represented by resonance structures **7**, **8**, and **9**, and **6** being depicted by the resonance structures **10**, **11**, and **12**. Nucleophilic attack by chloride anion on the anilenium ion, **5**, would be expected to yield the observed products. Similarly, electrophilic attack of positive chlorine on **6** should produce a mixture of *o*- and *p*-chloroanilines.



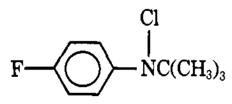


In order to distinguish between the two alternate mechanistic routes from **2** to **3** and **4**, we decided to study the thermal rearrangement of a series of para-substituted anilines. If an anilenium ion **5** was being generated in the rate-determining step, a decrease in the electron-withdrawing power of the substituent should result in an increase in the rate of thermal rearrangement. Conversely, if the transition state for thermal rearrangement led to **6**, a decrease in the electron-withdrawing power of the substituent would facilitate a decrease in the rate of thermal rearrangement. Table I lists the rates of solvolysis of a series of substituted *N*-*tert*-butyl-*N*-chloroanilines in ethanol buffered with 0.1 *N* acetic acid–0.1 *N* sodium acetate. Examination of Table I quickly shows that the rate of thermal rearrangement of the *N*-alkyl-*N*-chloroanilines is extremely dependent on the nature of the para substituent. The overall increase in rate in going from the *p*-cyano derivative **18** to the *p*-methyl case **13** was 1.8 × $10^6$. This very large change in rate in going from a strong electron-withdrawing substituent to an electron-donating group provides convincing evidence for the ionic nature of the rearrangement. Furthermore, the very large rate decrease in going from electron-donating substituents to electron-withdrawing substituents indicates that the heterolytic cleavage of the N–Cl bond occurs *via* a transition state which involves loss of chloride anion and the generation of positive charge on nitrogen. This process would lead to the intermediates indicated by path a. A more visual demonstration of this reasoning can be seen in Figure 1

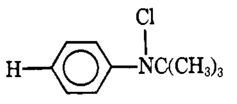
unlikely by the observation that the effect of substituents on the rate of rearrangement is qualitatively similar, in terms of this relative order of reactivity, in nonprotic solvents, such as pentane. (b) For a recent review of nitrenium ion chemistry, see P. G. Gassman, *Accounts Chem. Res.*, 3, 26 (1970).



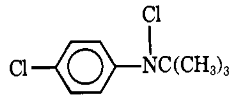
**13**



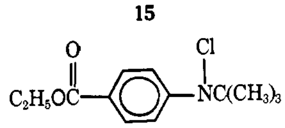
**14**



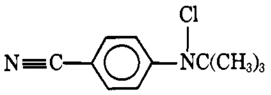
**15**



**16**



**17**



**18**

which shows a plot of log *K* *vs.* the Brown $\sigma^+$ substituent constants.[9] As shown, the correlation between the rates of rearrangement and $\sigma^+$ was excellent. The $\rho$ for the reaction was $-6.35$ and the correlation coefficient was 0.996. The relatively large value of $-6.35$ obtained for $\rho$ indicated that considerable delocalization of the charge into the aromatic ring must have been occurring. On the basis of electronegativities, it would be anticipated that the nitrogen nucleus should be much less able to bear a positive charge than should carbon. The closest analogy in the carbon system, of which we are aware, involves the solvolysis of 1-chloro-1-arylethanes in 20:80 water–dioxane.[10] The $\rho$ for this hydrolysis was reported to be $-4.50$. Thus, it would appear that the transition state for the solvolysis of a 1-chloro-1-arylethane to yield a trivalent carbon cation involved less charge delocalization into the aromatic ring than does the transition state for the solvolysis of *N*-alkyl-*N*-chloroanilines to produce a divalent nitrogen cation. This crude comparison[11] was consistent with expectations.

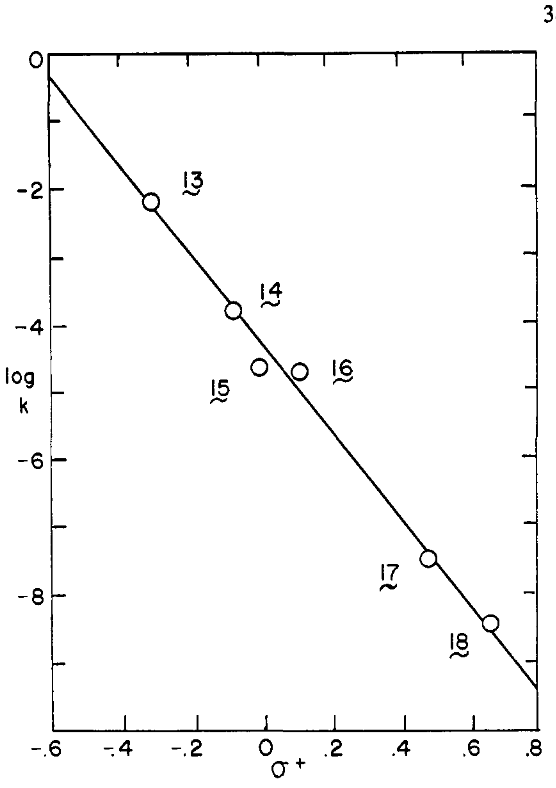
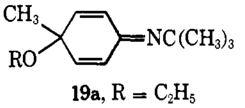


Figure 1. $\sigma^+\rho$ plot for the solvolysis of *N*-chloro-*N*-*tert*-butylanilines in ethanol buffered with 0.1 *N* sodium acetate–0.1 *N* acetic acid.

The products obtained from the solvolysis of the series of *N*-*tert*-butyl-*N*-chloroanilines in ethanol buffered with 0.1 *N* sodium acetate–0.1 *N* acetic acid are listed in Table II. Several aspects of this product study merit comment. First, all of the *N*-chloroanilines studied gave the corresponding *o*-chloroaniline as the major product. For **15**, where the para position was unsubstituted, we also observed some chlorination of the para carbon. Secondly, the formation of 4-ethoxy-4-methyl-2,5-cyclohexadienone *N*-*tert*-butylimine (**19a**) in the solvolysis of **13** indicated that the ionization of **13**, even in the absence of a chloride scavenger, such as silver ion, produced a cationic species which was susceptible to nucleophilic attack by solvent. When the solvent was changed from ethanol to the more nucleophilic solvent, methanol, we observed that the yield of 2,5-cyclohexadienone derivative **19b** was 32% (in addition to 61% of *o*-chloro-*p*-toluidine). This again supported the contention that the solvolytic ionization of **2** involved the initial formation of an anilenium ion.



**19a**, R = $C_2H_5$
**b**, R = $CH_3$

Table II. Products from the Solvolysis of Para-Substituted *N*-*tert*-Butyl-*N*-chloroanilines in Ethanol Buffered with 0.1 *N* Sodium Acetate–0.1 *N* Acetic Acid

| Para substituent | Compd | Yield of *o*-chloro-anilines, % | Yield of starting aniline, % | Other, % |
|---|---|---|---|---|
| $CH_3$ | **13** | 85 | 1 | 10[a] |
| F | **14** | 84 | 8 | |
| H | **15** | 64[b] | 16 | |
| Cl | **16** | 72 | 17 | |
| $CO_2C_2H_5$ | **17** | 78 | 19 | |
| C≡N | **18** | 64 | 29 | |

[a] 4-Ethoxy-4-methyl-2,5-cyclohexadienone *N*-*tert*-butylimine (**19a**) was produced in this reaction in 10% yield. [b] The yield of 64% includes 48% of *N*-*tert*-butyl-*o*-chloroaniline, 11% of *N*-*tert*-butyl-*p*-chloroaniline, and 5% of *N*-*tert*-butyl-*o*,*p*-dichloroaniline.

An interesting aspect of the data presented in Table II concerns the amount of parent anilines obtained from the *N*-chloroanilines **13**–**18**. As is obvious, the amount of aniline formed increased with the increasing electron-withdrawing power of the substituent. This phenomenon would appear to be related to the ability of the ring to stabilize the developing positive charge on nitrogen. As the electron-withdrawing power of the substituent increased, the amount of charge delocalized into the ring would decrease, and the nitrogen atom would attain greater positive character. The conversion of the resulting species into the parent amine could then follow either of two routes. One path would in-

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[9] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 80, 4979 (1958).

[10] C. Mechehynck-David and P. J. C. Fierens, *Tetrahedron*, 6, 232 (1959).

[11] The comparison made here is not rigorous since the substitution on nitrogen was not the same as on the analogous carbon, and the solvent system was different. Unfortunately, an exact comparison of nitrenium ions and carbenium ions cannot be made because the trivalent nature of nitrogen and the tetravalent nature of carbon exclude the possibility of having identical substitution and charge in both systems.

volve a hydride abstraction from solvent to yield the parent amine directly. An alternate, and somewhat more attractive postulate, is that, as the charge on nitrogen increases, the ability to spin invert from a singlet nitrenium ion to a triplet nitrenium ion becomes greater.[12] Since the triplet nitrenium ion should be the ground state of a simple, divalent, positively charged nitrogen species,[13] this type of spin inversion should occur with relative ease. The triplet nitrenium ion, being a type of diradical cation, should be an excellent hydrogen atom extractor. Removal of two hydrogens from the solvent would then give the protonated form of the parent amine. Unfortunately, present experiments do not allow us to distinguish between these two mechanistic possibilities.

The data discussed, thus far, have all been connected with the solvolysis of *N*-*tert*-butyl-*N*-chloroanilines in buffered ethanol. In unbuffered ethanol significant differences were noted. The solvolyses of **13**, **14**, **15**, and **16** still occurred with reasonable first-order kinetics at rates very similar to those observed under buffered conditions. The relative comparisons are given in Table III. However, compounds **17** and **18** failed to give acceptable first-order kinetic plots. Instead, rapidly accelerating rates were observed for these two *N*-chloroanilines. It was clear from the data that the rates of solvolysis of **17** and **18** were being catalyzed by the acid which was being generated in the solvolytic process.

**Table III.** Rates of Solvolysis of *N*-*tert*-Butyl-*N*-chloroanilines in Buffered and Unbuffered Ethanol

| Compd | Temp, °C | Rate in buffered ethanol, $sec^{-1}$ | Rate in unbuffered ethanol, $sec^{-1}$ |
|---|---|---|---|
| **13** | $25^a$ | $5.85 \times 10^{-3}$ | $4.17 \times 10^{-3}$ |
| **14** | $25^a$ | $1.40 \times 10^{-4}$ | $1.40 \times 10^{-4}$ |
| **15** | $25^a$ | $2.06 \times 10^{-5}$ | $1.29 \times 10^{-4}$ |
| **16** | $25^a$ | $1.65 \times 10^{-5}$ | $4.18 \times 10^{-5}$ |

[a] Extrapolated from other temperatures.

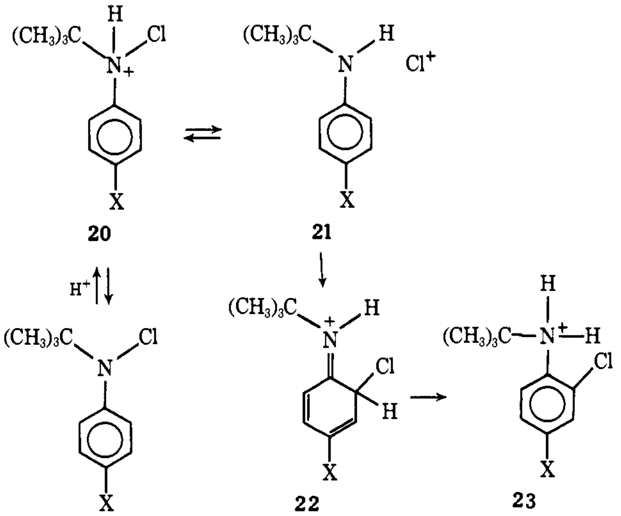
The products observed for the solvolysis of the series **13**–**18** in unbuffered solvent also indicated that acid catalysis was playing an important role in the thermal rearrangement of the *N*-chloroanilines. Table IV lists the yields of products formed from **13** to **18** in unbuffered ethanol. As can be seen from a comparison of Tables II and IV, the yield of products from **13**, **14**, and **15** changed little in going from buffered to unbuffered solvolytic conditions. However, for **16**, **17**, and **18**, considerable changes in the product composition occurred as a result of the removal of the buffer. These changes in product composition would again appear to be the result of protonation by acid.

The mechanism of this acid catalysis is open to debate. An attractive possibility would involve protonation on nitrogen to produce the chloroammonium type ion **20**. It is anticipated that **20** might be in equilibrium with the ion–molecule pair **21**. Electrophilic attack by positive chlorine would then produce **22** which on hydrogen shift and rearomatization would produce **23**.

**Table IV.** Products from the Solvolysis of Para-Substituted *N*-*tert*-Butyl-*N*-chloroanilines in Unbuffered Ethanol

| Substituent | Compd | Yield of *o*-chloroaniline, % | Yield of starting aniline, % | Other, % |
|---|---|---|---|---|
| $CH_3$ | **13** | 76 | 4 | $12^a$ |
| F | **14** | 61 | 11 | |
| H | **15** | $75^{b,c}$ | 9 | |
| Cl | **16** | 96 | 3 | |
| $CO_2C_2H_5$ | **17** | 99 | | |
| C≡N | **18** | 94 | | |

[a] 4-Ethoxy-4-methyl-2,5-cyclohexadienone *N*-*tert*-butylimine (**19a**) was the 12% product. [b] The 75% consisted of 51% of *N*-*tert*-butyl-*o*-chloroaniline and 24% of *N*-*tert*-butyl-*p*-chloroaniline. [c] In addition, 5% of *N*-*tert*-butyl-*o*,*p*-dichloroaniline was formed.



It would seem that electron-withdrawing substituents should facilitate the formation of **21** from **20**, making this route an important path for the rearrangement of **16**, **17**, and **18** in the presence of acid. Unfortunately, we can provide no definitive evidence in support of this mechanistic postulate.[14]

In summary, we have shown that the thermal rearrangement of *N*-chloroanilines in the absence of acid occurs *via* a mechanism which involves the generation of a phenylnitrenium ion (anilenium ion) and chloride anion. This would appear to be the mechanism of the ring chlorination of most aromatic amines. In the presence of acid, a mechanistic change occurs when strong electron-withdrawing substituents are present on the ring. However, the presence of catalytic amounts of acid has little effect on the mode of rearrangement of *N*-alkyl-*N*-chloroanilines which are substituted with electron-donating groups.

## Experimental Section

Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Melting and boiling points are uncorrected. Infrared spectra were taken on a Perkin-

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(12) For a discussion of the existence of singlet and triplet nitrenium ions, see P. G. Gassman and R. L. Cryberg, *J. Amer. Chem. Soc.*, **91**, 5176 (1969).

(13) The energy difference between the singlet and triplet forms of $NH_2^+$ has been calculated to be 45 kcal/mol (S. T. Lee and K. Morokuma, *J. Amer. Chem. Soc.*, **93**, 6863 (1971)). We wish to thank Professor Morokuma for informing us of his results prior to publication.

(14) The absence of the formation of parent amine in the acid-catalyzed rearrangement of **17** and **18** provides support for the suggestion that the acid-catalyzed process does not involve the intermediacy of a nitrenium ion. In the case of **16**, where a small amount of parent aniline was formed, it is thought that two competing mechanisms may be involved.

Elmer Model 137 Infracord as neat liquids, solutions in carbon tetrachloride, or powdered solids in potassium bromide disks. Nuclear magnetic resonance spectra were obtained on Varian Associates A-60-A and HA-100 spectrometers and reported in $\tau$ units relative to tetramethylsilane ($\tau = 10.00$) as the internal standard.

**_N-tert_-Butyl-_p_-fluoroaniline.** A mixture of 24 g of *p*-fluoroaniline hydrochloride and 100 ml of *tert*-butyl alcohol was sealed in a glass-lined steel bomb and heated at 155° for 13 hr. The bomb was cooled in a Dry Ice–2-propanol bath and opened. The contents were added to 200 ml of water and made basic with ammonium hydroxide solution, and the mixture was extracted with three 100-ml portions of ether. The combined ethereal extracts were dried over anhydrous magnesium sulfate and the desiccant was removed by filtration. The filtrate was concentrated *in vacuo* to leave a dark oil. The oil was added to 100 ml of water containing 4.6 g of acetic anhydride and the mixture was stirred for 3 hr. The solution was then made basic with excess sodium bicarbonate and steam distilled until the distillate was neutral to litmus. The distillate was extracted with two 100-ml portions of ether and the combined ethereal extracts were dried over anhydrous magnesium sulfate. The desiccant was removed by filtration and the filtrate was concentrated *in vacuo* to leave a clear oil. Distillation of the oil gave 11.1 g (40%) of *N-tert*-butyl-*p*-fluoroaniline: bp 48.5° (0.2 mm); $n^{25.1}\mathrm{D}$ 1.4992; ir (neat) 6.62, 8.13, 12.04, and 12.73 $\mu$; nmr ($CCl_4$) $\tau$ 8.73 (9 H, s), 3.25 (4 H, m).

*Anal.* Calcd for $C_{10}H_{14}NF$: C, 71.82; H, 8.44; N, 8.38. Found: C, 71.62; H, 8.34; N, 8.47.

**_p_-(_N-tert_-Butylamino)benzonitrile.** To a solution of 5.00 g (41.3 mmol) of *p*-fluorobenzonitrile in 50 ml of dry dimethyl sulfoxide was added 9.05 g (123.9 mmol) of *tert*-butylamine and the resulting solution was sealed in a glass-lined steel bomb. After heating at 150° for 5 days, the bomb was cooled to 0–5° and opened. The contents were added to 250 ml of water and extracted with two 100-ml portions of chloroform. The combined chloroform extracts were washed with two 100-ml portions of saturated sodium bicarbonate solution and 100 ml of saturated sodium chloride solution dried over anhydrous magnesium sulfate, filtered, and concentrated on the rotary evaporator to give a pale yellow oil which partially crystallized. The semisolid reaction mixture was washed with 100 ml of pentane to remove the unreacted starting material, which left a crystalline product. Recrystallization from hexane gave 3.50 g (49%) of *p*-(*N-tert*-butylamino)benzonitrile: mp 103–105°; ir (KBr) 2.82, 4.38, 6.16, and 12.00 $\mu$; nmr ($CCl_4$) $\tau$ 8.59 (9 H, s), 5.62 (1 H, s), 3.00 (4 H, q).

*Anal.* Calcd for $C_{11}H_{14}N_2$: C, 75.82; H, 8.10; N, 16.08. Found: C, 75.73; H, 8.13; N, 16.11.

**Thermal Rearrangement of _N_-Chloro-_N-tert_-butyl-_p_-toluidine (13).** A sample of **13**[1] was prepared from 0.509 g of *N-tert*-butyl-*p*-toluidine and 5.0 g of calcium hypochlorite and dissolved in 25 ml of ethanol buffered with 0.1 *N* acetic acid–0.1 *N* sodium acetate. After stirring the solution overnight at room temperature, the solvent was removed *in vacuo* and the residue was taken up in 50 ml of water and extracted with two 50-ml portions of ether. The combined ethereal extracts were dried over anhydrous magnesium sulfate and filtered, and the solvents removed on the rotary evaporator to leave an oil. The oil was separated into three components *via* preparative glpc on a 20% 4:1 Apiezon L–KOH on 60–80 Firebrick column to give 4-ethoxy-4-methyl-2,5-cyclohexadienone *N-tert*-butylimine (**19a**), *o*-chloro-*N-tert*-butyl-*p*-toluidine, and *N-tert*-butyl-*p*-toluidine. All compounds were identified by comparison with authentic samples.[1] The reaction was repeated and analysis by glpc on the same column gave (*vs.* *p*-chloro-*N-tert*-butylaniline as an internal standard) 10% of **19a**, 85% of the *o*-chloro derivative, and 1% of *N-tert*-butyl-*p*-toluidine.

The procedure was repeated using pure, unbuffered ethanol to yield 12% of **19a**, 76% of the *o*-chloro derivative, and 4% of *N-tert*-butyl-*p*-toluidine as indicated by analytical glpc.

**Thermal Rearrangement of _N_-Chloro-_p_-fluoro-_N-tert_-butylaniline (14).** To a solution of 516 mg (3.09 mmol) of *N-tert*-butyl-*p*-fluoroaniline in 25 ml of pentane was added 5.0 g of powdered calcium hypochlorite. After the mixture was stirred for 2 hr at room temperature, the salts were removed by filtration and the solvent was removed *in vacuo* to give the neat chloramine **14** which was dissolved in 25 ml of ethanol buffered with 0.1 *N* acetic acid–0.1 *N* sodium acetate. After the mixture was stirred for 14 hr at room temperature, the ethanol was evaporated to leave a residue which was taken up in 50 ml of water. The aqueous mixture was extracted with two 50-ml portions of ether and the combined ethereal extracts were dried over anhydrous magnesium sulfate. The desiccant was removed by filtration and removal of the solvent on the rotary evaporator left a brown oil which was separated into two components by preparative gas chromatography on 20% 4:1 Apiezon L–KOH on 60–80 Firebrick. The first component was *N-tert*-butyl-*p*-fluoroaniline which was identified by comparison with an authentic sample. The second component was *N-tert*-butyl-*o*-chloro-*p*-fluoroaniline: bp 70° (0.25 mm); $n^{25.6}\mathrm{D}$ 1.5104; ir (neat) 6.65, 8.20, 11.10, 11.62, and 12.40 $\mu$; nmr ($CCl_4$) $\tau$ 8.63 (9 H, s), 3.06 (3 H, m).

*Anal.* Calcd for $C_{10}H_{13}NClF$: C, 59.55; H, 6.50; N, 6.95; Cl, 17.58. Found: C, 59.65; H, 6.40; N, 6.88; Cl, 17.74.

The reaction was repeated and analysis *via* glpc on the same column yielded 84% of *N-tert*-butyl-*o*-chloro-*p*-fluoroaniline and 8% of *N-tert*-butyl-*p*-fluoroaniline. When the reaction was carried out in the same manner using pure, unbuffered ethanol as solvent, glpc analysis gave the same products in 61 and 11% yields, respectively.

**Thermal Rearrangement of _N_-Chloro-_N-tert_-butylaniline (15).** A sample of **15**[1] was prepared from 387 mg (2.60 mmol) of *N-tert*-butylaniline and 5.0 g of calcium hypochlorite and dissolved in 25 ml of ethanol buffered with 0.1 *N* acetic acid–0.1 *N* sodium acetate. The solution was stirred at room temperature for 5 hr and then worked up in the same manner as chloramine **13** to give an oil which was separated *via* preparative glpc on a 3% Amine 230 on 80–100 Diaport S column to give *N-tert*-butylaniline, *N-tert*-butyl-*o*-chloroaniline, *N-tert*-butyl-*p*-chloroaniline, and *N-tert*-butyl-*o*,*p*-dichloroaniline. The products were identified by comparison with authentic samples.[1] The reaction was repeated and analysis *via* glpc on the same column (*vs.* naphthalene as an internal standard) gave the above products in 16, 48, 11, and 5%, respectively. When the reaction was carried out in the same manner using pure unbuffered ethanol as solvent, analytical glpc yielded the same products in 9, 51, 24, and 5%, respectively.

**Thermal Rearrangement of _N-tert_-Butyl-_N,p_-dichloroaniline (16).** A sample of **16**[1] was prepared from 0.512 g of *N-tert*-butyl-*p*-chloroaniline and 5.0 g of calcium hypochlorite and dissolved in 25 ml of ethanol buffered with 0.1 *N* acetic acid–0.1 *N* sodium acetate. After stirring at room temperature for 48 hr, the reaction mixture was worked up in the manner used for chloramine **13**. This gave an oil which was separated by preparative glpc on a 10% Carbowax 20M-KOH on 60–80 Chromosorb W column to yield *N-tert*-butyl-*p*-chloroaniline and *N-tert*-butyl-*o*,*p*-dichloroaniline. The products were identified by comparison with authentic samples.[1] The reaction was repeated and analysis on the same column (*vs.* *N-tert*-butyl-*p*-toluidine as an internal standard) gave the above products in 17 and 72% yields, respectively. When the reaction was carried out in the same manner using unbuffered ethanol as the solvent, analytical glpc indicated that the above products were formed in 3 and 96% yields, respectively.

**Thermal Rearrangement of Ethyl _p_-(_N_-Chloro-_N-tert_-butylamino)benzoate (17).** A sample of **17**[1] was prepared from 505 mg of ethyl *p*-(*N-tert*-butylamino)benzoate and 5.0 g of calcium hypochlorite and dissolved in 25 ml of ethanol buffered with 0.1 *N* acetic acid–0.1 *N* sodium acetate. The solution was sealed in a glass tube and heated to 100° for 20 hr. The tube was then cooled and opened and the reaction mixture was worked up in the same manner as for chloramine **13** to give an oil which was separated on a 20% 4:1 Apiezon L–KOH on 60–80 Firebrick column. This yielded ethyl *p*-(*N-tert*-butylamino)benzoate and ethyl 3-chloro-4-(*N-tert*-butylamino)benzoate.[1] The reaction was repeated and analyzed on the same column (*vs.* benzocaine as an internal standard) to yield the above products in 19 and 76% yields, respectively. When the reaction was carried out in unbuffered ethanol the yield of ethyl 3-chloro-4-(*N-tert*-butylamino)benzoate was 99% as indicated by analytical glpc. No parent amine could be detected in the unbuffered solvent.

**Thermal Rearrangement of _p_-(_N_-Chloro-_N-tert_-butylamino)benzonitrile (18).** To a solution of 0.452 g of *p*-(*N-tert*-butylamino)benzonitrile in 25 ml of 1:1 ether–pentane was added 10 g of powdered calcium hypochlorite and the mixture was stirred at room temperature for 3 hr. The salts were removed by filtration and the solvents evaporated *in vacuo* at 0–5° to give the neat chloramine. Infrared analysis showed the complete absence of the N–H band of the starting amine. The neat chloramine was then dissolved in 25 ml of ethanol buffered 0.1 *N* in sodium acetate and 0.1 *N* in acetic acid and the solution was sealed in a glass tube and heated at 100° for 24 hr. The tube was cooled and opened and the ethanol was removed on the rotary evaporator. The residue was taken up in 25 ml of water and excess sodium bicarbonate was added. The mixture was then extracted with three 25-ml portions of ether. The combined ethereal extracts were dried over anhydrous magnesium sulfate and filtered, and the solvent was evaporated to leave a yellow oil. The oil was triturated with 25 ml of pentane which brought about the precipitation of white crystals. Cooling to 0–5° and filtration yielded

133 mg (29%) of *p*-(*N*-*tert*-butylamino)benzonitrile. The filtrate was concentrated to leave another crystalline solid which was recrystallized from hexane to yield 264 mg (64%) of 3-chloro-4-(*N*-*tert*-butylamino)benzonitrile: mp 81–83.5°; ir (KBr) 4.54, 6.24, 6.56, 11.34, and 12.05 $\mu$; nmr ($CCl_4$) $\tau$ 8.53 (9 H, s), 3.08 (1 H, d), 2.50 (2 H, m).

*Anal.* Calcd for $C_{11}H_{13}N_2Cl$: C, 63.31; H, 6.28; N, 13.42; Cl, 16.99. Found: C, 63.39; H, 6.26; N, 13.22; Cl, 16.88.

When the reaction was carried out in pure, unbuffered ethanol the *o*-chloro derivative was isolated in 94% yield. No parent amine was detected in unbuffered ethanol.

**Kinetics. Reagents.** Commercial absolute ethanol was dried by the reaction with magnesium turnings followed by distillation.[15] Standard sodium thiosulfate solution (*ca.* 0.020 *N*) was used to titrate the liberated iodine.

**Procedure.** Stock solutions of the *N*-chloramines in a nonpolar solvent were prepared as indicated above for each compound. For each kinetic run, an aliquot of the stock solution was taken and the solvent was evaporated *in vacuo* to leave the neat chloramine. The chloramine was then dissolved in ethanol buffered 0.1 *N* in anhydrous sodium acetate and 0.1 *N* in acetic acid or in pure ethanol without buffer. The ethanolic solution was quickly thermostated to the desired temperature and aliquots were withdrawn at the desired time intervals. The aliquots were quickly added to 1.0 *N* methanolic potassium iodide solution and acidified with a few drops of 0.1 *N* hydrochloric acid solution to liberate the iodine. The iodometric titrations were quickly done *via* sodium thiosulfate solution using a dead-stop technique employing two platinum electrodes and a Fisher Accumet Model 310 pH meter.

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# Reactions of the Nitrosonium Ion. II. Reactions of Triphenylmethyl, Benzhydryl, and Benzyl Azides with Nitrosonium Compounds[1a]

**Michael P. Doyle* and Wendell Wierenga[1b]**

*Contribution from the Department of Chemistry, Hope College, Holland, Michigan 49423. Received August 4, 1971*

**Abstract:** Triphenylmethyl azide reacts with $NO^+BF_4^-$ in acetonitrile to produce, quantitatively, triphenylmethyl tetrafluoroborate, nitrogen, and nitrous oxide. In acetonitrile benzhydryl azide produces the corresponding cation in equilibrium with the *N*-benzhydrylacetonitrilium ion. Side reactions, including phenyl migration to electron-deficient nitrogen and hydrogen abstraction, are also observed and account for as much as 32% of the reaction products at room temperature. Control over these side reactions has been achieved by variation of the reaction temperature. Benzyl azide reacts with $NO^+BF_4^-$ in acetonitrile to give 1% benzaldehyde and 99% *N*-benzylacetonitrilium tetrafluoroborate. The reactions of alkyl azides with nitrosonium salts are compared with the corresponding reactions of isothiocyanates, sulfinylamines, and amines. These results are discussed in relation to a general mechanism for alkyl azide reactions with the nitrosonium ion.

The reaction between hydrazoic acid and nitrous acid produces an equivalent amount of both nitrogen and nitrous oxide.[2] In aqueous solution the rate of this reaction is found to be dependent on temperature and ionic strength[3a] and, under certain conditions, independent of azide concentration. The mechanism can be viewed as an electrophilic attack by the nitrosonium ion on the azide ion to form nitrosyl azide, followed by decomposition to the observed products (eq 1). In this regard, Lucien has obtained evidence,

$$NO^+ + N_3^- \longrightarrow N_4O \longrightarrow N_2 + N_2O \qquad (1)$$

including physical properties, for the formation of nitrosyl azide from a variety of nitrosonium compounds and either sodium azide or hydrazoic acid.[4] The yellow nitrosyl azide decomposes to nitrogen and nitrous oxide even at temperatures as low as −50°. The structure of nitrosyl azide is predicted to be linear, NNNNO, on the basis of $^{15}N$-labeling experiments.[5]

Considering the instability of nitrosyl azide, the rate of reaction of nitrosonium compounds with substituted azides should depend only on how readily the substituted nitrosyl azide is formed. Reactions of azidopentaaminecobalt(III)[6] and azidopentaaquochromium(III)[7] ions with sodium nitrite, for example, are easily effected in aqueous acid solutions to give both nitrogen and nitrous oxide in equal amounts. Use of stable nitrosonium salts such as $NO^+BF_4^-$, $NO^+SbF_6^-$, and $NO^+PF_6^-$ in anhydrous nonhydroxylic media would certainly be expected to effect similar reactions with aliphatic azides.

With substituted azides ($A{-}N_3$), unlike the azide ion which has two equivalent sites for attack, reaction with

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