and

$$\frac{1}{T_{1C}(\mathrm{LEH})} = \frac{1}{T_{1CL}} + \frac{1}{T_{1CE}} + \frac{1}{T_{1CH}} + \frac{\alpha'}{T_{1HE}} \qquad (6)$$

where α' describes the efficiency with which the electrons relax C *via* H (*i.e.*, the so-called three-spin effect[4]). T_{1CH} thus refers to C–H relaxation in the absence of electrons. Substituting eq 5 and 6 into eq 3 and writing[4] $1/T_{1CE} = k[\mathrm{E}]$ and $\alpha'/T_{1HE} = \alpha[\mathrm{E}]$, eq 4 becomes

$$\frac{C_z - C_0}{C_0} = \rho_{CH} S_H \frac{\gamma_H}{\gamma_C} \left[\frac{\dfrac{1}{T_{1CH}} + \alpha[\mathrm{E}]}{\dfrac{1}{T_{1C}(\mathrm{LH})} + (k + \alpha)[\mathrm{E}]} \right] \qquad (7)$$

[E] is the concentration of electron spins and

$$\frac{1}{T_{1C}(\mathrm{LH})} = \frac{1}{T_{1CL}} + \frac{1}{T_{1CH}}$$

Equation 7 thus describes the effect of electron spins on the ^{13}C Overhauser enhancement factor during proton irradiation.

The effect of electron spins on the observed ^{13}C line width $(\Delta\nu_{1/2})$ is given by $\Delta\nu_{1/2} = [\pi T_{2C}(\mathrm{LEH})]^{-1}$ where

$$\frac{1}{T_{2C}(\mathrm{LEH})} = \frac{1}{T_{2CL}} + \frac{1}{T_{2CH}} + \delta k[\mathrm{E}] + \alpha[\mathrm{E}] \qquad (8)$$

δ is the ratio T_1/T_2 for the C–E coupling and is normally a little greater than unity[6] since dynamic scalar coupling operates between ^{13}C nuclei and electrons.[7]

Substitution of the condition $4\gamma_H{}^2 H_2{}^2 \gg \pi^2 J_{CH}{}^2$ for complete proton decoupling[8] into eq 2 and evaluation of $(T_1T_2)_H$ *via* eq 6 and 8 as outlined for ^{13}C shows that decoupling always implies $S_H \approx 1$ unless J_{CH} is very small ($\sim$3 Hz).

Equations 7 and 8 predict the following significant points. (1) Addition of increasing amounts of a paramagnetic species reduces (or increases) the ^{13}C Overhauser enhancement to a constant value before significant broadening of the ^{13}C line occurs. This is true for a wide range of k values. (2) When $(k + \alpha)T_{1C}\cdot(\mathrm{LH})[\mathrm{E}] \gg 1$ the enhancement factor is $1.988 S_H \alpha/(k + \alpha)$. Thus, when $\alpha = 0$ (which commonly occurs[3,4]), the Overhauser effect is completely eliminated. (3) The initial enhancement factor ([E] = 0) is $1.988 S_H T_{1C}\cdot(\mathrm{LH})/T_{1CH}$ as for the two-spin case.[4] (4) Absolute values of k, α, $T_{1C}(\mathrm{LH})$, and T_{1CH} (and thus T_{1CL}) can be obtained by fitting eq 7 to a plot of $(C_z - C_0)/C_0$ *vs.* [E] unless $T_{1CH} \approx T_{1C}(\mathrm{LH})$ or $k = 0$. (5) $k \propto r_{CE}{}^{-3}$, where r_{CE} is the ^{13}C–E distance. For a given value of [E], therefore, the Overhauser enhancements of those ^{13}C nuclei closest to the paramagnetic species will, in general, be preferentially reduced. This effect is observed at values of [E] at least two orders of magnitude lower than the observation of preferential line broadening.[9]

The validity of the theory is indicated by the fact that La Mar's esperimental results for *p*-dioxane[3] are described quantitatively by eq 7 and 8 if account is taken of the oxygen dissolved in his samples. The effects of dissolved oxygen, complex formation, and radical dimerization will be discussed elsewhere.

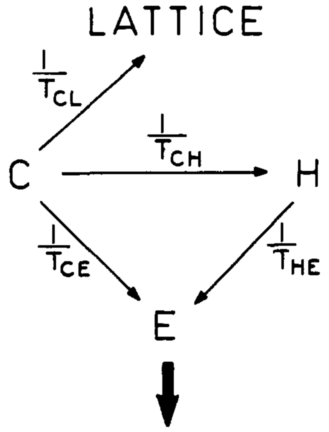

Figure 1. ^{13}C relaxation processes in a three-spin system.

The theory suggests that any soluble, nonreactive paramagnetic species will reduce the Overhauser enhancement almost to zero when α is small. Preference can therefore be given to readily available, stable, easily handled materials. In cases where α is appreciable its value (and thus C_0) can be obtained by curve fitting. It appears feasible, therefore, to obtain the number of ^{13}C nuclei contributing to a given resonance by addition of a paramagnetic species to the sample. In addition the preferential reduction of ^{13}C Overhauser enhancements can be used to establish the binding sites of paramagnetic metal ions and spin labels in labile complexes.

Acknowledgment. The author wishes to thank Dr. G. N. La Mar for suggesting the problem and Professor H. S. Gutowsky and Dr. D. K. Dalling for helpful discussions. The support of the National Science Foundation and the U. S. Office of Naval Research is gratefully acknowledged.

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(7) D. F. S. Natusch and R. E. Richards, *Chem. Commun.*, 579 (1966).

(8) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959.

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The Mechanism of the Chlorination of Anilines and Related Aromatic Amines. The Involvement of Nitrenium Ions[1]

Sir:

The careful work of Neale and coworkers[2] and of Haberfield and Paul[3] has firmly established the intermediacy of *N*-chloramines in the chlorination of aromatic amines by reagents such as *N*-chlorosuccinimide and calcium hypochlorite.[4] Although there is little doubt about the initial step in the reaction being N-

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(1) Paper XVI in a series on the Chemistry of Nitrenium Ions. For previous papers in this series, see P. G. Gassman and A. Carrasquillo, *Tetrahedron Lett.*, 109 (1971), and P. G. Gassman and J. H. Dygos, *ibid.*, 4749 (1970), and references therein.

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

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

(4) Various other chlorinating agents have been used. For additional synthetic applications, see T. A. Foglia and D. Swern, *J. Org. Chem.*, 33, 4440 (1968); J. M. Muchowski, *Can. J. Chem.*, 48, 422 (1970); and A. M. Pinchuk, L. N. Markovskii, and I. M. Kosinskaya, *Zh. Obshch. Khim.*, 38, 1008 (1968).

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
5	−10.0	$(5.27 \pm 0.05) \times 10^{-5}$		20.4	−0.3
	0.0	$(2.37 \pm 0.01) \times 10^{-4}$			
	10.0	$(8.79 \pm 0.01) \times 10^{-4}$			
	25.00[a]	5.85×10^{-3}	1,800,000		
6	20.0	$(7.47 \pm 0.01) \times 10^{-5}$		21.2	−5.0
	30.0	$(2.60 \pm 0.01) \times 10^{-4}$			
	40.0	$(8.18 \pm 0.04) \times 10^{-4}$			
	25.00[a]	1.40×10^{-4}	44,000		
7	30.0	$(3.83 \pm 0.03) \times 10^{-5}$		21.9	−6.6
	40.0	$(1.27 \pm 0.02) \times 10^{-4}$			
	50.0	$(3.91 \pm 0.01) \times 10^{-4}$			
	25.00[a]	2.06×10^{-5}	6,500		
8	40.0	$(1.12 \pm 0.02) \times 10^{-4}$		23.0	−3.1
	50.0	$(3.60 \pm 0.02) \times 10^{-4}$			
	60.0	$(1.09 \pm 0.01) \times 10^{-3}$			
	25.00[a]	1.65×10^{-5}	5,200		
9	70.0	$(1.07 \pm 0.02) \times 10^{-5}$		26.3	−4.9
	80.0	$(3.97 \pm 0.02) \times 10^{-5}$			
	90.0	$(9.35 \pm 0.32) \times 10^{-5}$			
	25.00[a]	2.96×10^{-8}	9		
10	90.0	$(2.04 \pm 0.08) \times 10^{-5}$		28.4	−2.2
	100.0	$(6.10 \pm 0.04) \times 10^{-5}$			
	110.0	$(1.68 \pm 0.04) \times 10^{-4}$			
	25.00[a]	3.19×10^{-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.

chlorination, the mechanistic pathway from the *N*-chloramine to the halogenated aromatic ring remained a mystery. We now wish to report that this chlorination proceeds *via* heterolytic cleavage of the N–Cl bond to yield a nitrenium ion and chloride anion.

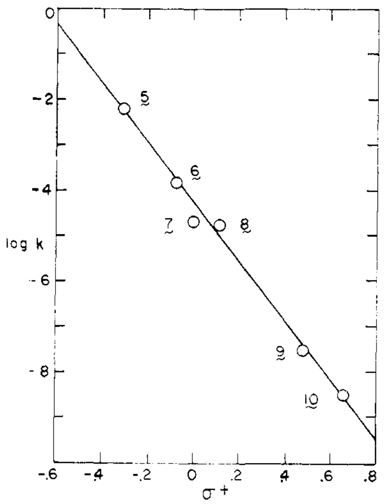
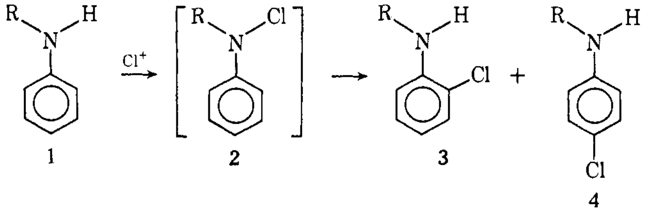
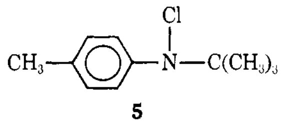


Figure 1. $\sigma^{+}\rho$ plot for the solvolysis of *N*-chloro-*N*-*tert*-butylanilines in buffered ethanol.

In general, the reaction of aromatic amines with sources of positive halogen proceeds to give mixtures of ring-chlorinated products. As shown below for aniline derivatives, the ortho:para ratio is normally *ca.* 2 and the *N*-chloroaniline intermediate is generally not isolated or observed.[2] Several mechanistic schemes could be suggested for the conversion of **2** into **3** and **4**. Of the various possibilities, the most likely choices are heterolytic cleavage of the N–Cl bond to yield amide anion and positive chlorine, or heterolytic cleavage of the chloramine to produce divalent electron-deficient nitrogen (nitrenium ion) and chloride anion. In order to distinguish between these divergent concepts, we have studied the kinetics of the facile rearrangement of substituted *N*-chloroanilines in ethanol buffered with 0.1 *N* acetic acid–0.1 *N* sodium acetate.[5,6]



1 2 3 4



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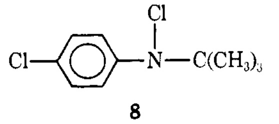

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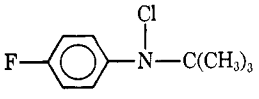

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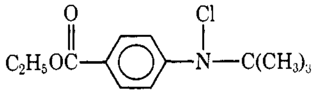

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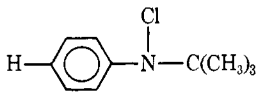

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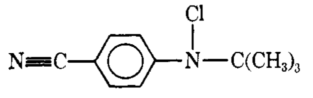

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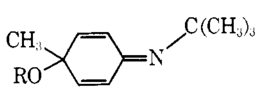
Table I lists the rates of solvolysis of a series of substituted *N*-chloroanilines in buffered ethanol. Inspection of Table I shows that the presence of electron-with-

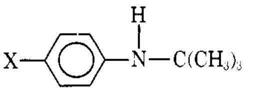
[5] All rates were followed to at least 65% reaction. All of the rates measured in buffered ethanol showed excellent pseudo-first-order kinetics.

[6] Investigation of the solvolyses of **5–10** in unbuffered ethanol showed that the buffer was unimportant for **5–8** since these four *N*-chloramines showed essentially the same rates and same products, irrespective of the presence of buffer. However, in the absence of buffer, **9** and **10** gave kinetic data indicative of a rapidly increasing rate of reaction. In view of the excellent pseudo-first-order rates obtained for **9** and **10** in buffered ethanol, the observations for the unbuffered solvolyses indicated that a change of mechanism was occurring. Clearly, the solvolysis of **9** and **10** could be acid catalyzed, while the solvolysis of **5–8** was not sensitive to small amounts of acid. Ortho-chlorinated products were obtained from **9** and **10** in 99 and 96% yields, respectively, under the unbuffered conditions.

drawing substituents results in a marked decrease in the rate of rearrangement of the six anilines studied. The overall rate decrease in going from the para methyl derivative, **5**, to the para cyano case, **10**, was 1.8×10^6. This decrease in rate indicated that the transition state for the rearrangement of **2** involved the generation of a positive center adjacent to the aromatic ring. Confirmation of this concept was provided by Figure 1 which shows a plot of log K *vs.* the Brown σ^+ substituent constants.[7] For the six compounds studied, we obtained an excellent correlation with σ^+. The ρ for the reaction was -6.35 and the correlation coefficient was 0.996. Each of the compounds listed gave ortho chlorinated anilines as the major product. When the para position of the aniline was blocked the yields of ortho chlorinated products ranged from 65% for **10** to 85% for **5**. As previously noted,[2,3] **7** gave a mixture of ortho and para substitution. Two interesting facets of the product studies merit discussion. First, solvolysis of **5** in buffered ethanol gave 10% of **11a**, indicating the presence of positive charge on the ring. When the solvolysis of **5** was carried out in pure unbuffered methanol, we obtained 32% of **11b** and 61% of the normal ortho chlorinated aniline. The increased amount of 2,5-cyclohexadienone derivative,[8] **11**, formed in methanol was consistent with the difference in solvolytic properties between ethanol and methanol. The second interesting feature of the product studies was the amount of starting aniline, **12**, which was formed in the reaction. The amount of this amine gradually increased as the substituents became more electron withdrawing, going from 1% when X was methyl to 29% when X was cyano. This indicated that the presence of electron-withdrawing substituents decreased the amount of charge delocalized into the aromatic nucleus. Increased positive charge on nitrogen appeared to result in increased amounts of **12**.[9]



11a, R = CH_2CH_3
b, R = CH_3



12

Investigation of the solvolysis of **5**–**10** in buffered ethanol showed that the mode of heterolytic cleavage involved the formation of an aryl nitrenium ion (anilenium ion) and chloride anion. The large ρ of -6.35 indicated that considerable delocalization of the charge onto the aromatic nucleus must have been present. This is consistent with the relative abilities of divalent nitrogen and trivalent carbon to bear a positive charge.[10] The solvolysis of *N*-chloroanilines to give anilenium ions adds still another category to the growing list of reactions which occur *via* nitrenium ion intermediates.[11]

Acknowledgment. We are indebted to the National Cancer Institute of the Public Health Service for a grant in support of this investigation.

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

[8] We have recently shown that the reaction of **5** with silver ion in methanol produces **11b** in a 70% yield in a useful synthesis of 2,5-cyclohexadienone derivatives: P. G. Gassman and G. A. Campbell, *Chem. Commun.*, 427 (1970).

[9] In these cases it is unknown whether **12** arises *via* a hydride abstraction mechanism or *via* spin inversion of the singlet nitrenium ion to a hydrogen-abstracting triplet nitrenium ion. For an example of the latter see P. G. Gassman and R. L. Cryberg, *J. Amer. Chem. Soc.*, **91**, 5176 (1969).

[10] It is interesting to compare the solvolysis of derivatives of **2** with that of substituted 1-chloro-1-arylethanes. The ρ for the latter in 20:80 water–dioxane has been reported to be -4.50 (C. Mechelynck-David and P. J. C. Fierens, *Tetrahedron*, **6**, 232 (1959)). It would appear that the nitrogen cation was much more dependent on charge delocalization into the aromatic ring than was the analogous carbonium ion.

[11] For a recent review see P. G. Gassman, *Accounts Chem. Res.*, **3**, 26 (1970).

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

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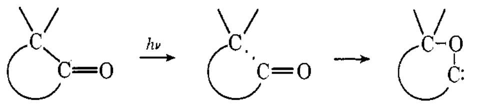
Received March 6, 1971

Mechanism of Photochemical Ring Expansion Reactions of Cyclic Ketones[1]

Sir:

A number of publications have appeared concerning the photochemical ring expansion reactions of selected cyclic ketones.[2–9] In most cases, the rearrangement was proposed to involve homolysis of a carbon–carbon bond α to the excited carbonyl function, followed by electronic rearrangement and rebonding to form an oxacarbene intermediate (eq 1). Evidence for intermediate **3** derives from its trapping by alcoholic solvents to yield acetals as isolable products. Yates has suggested[9] that ring expansion is associated with certain structural features which inhibit other competing intramolecular rearrangements; *i.e.*, ring expansion only occurs from **2** when other reactions of this species are disfavored. We present results here which demonstrate that while certain structural features are necessary for observation of photochemical ring expansion, the reaction can compete favorably with other common fates of **2**.[10]



1 **2** **3** (1)

Key compounds in this study are cyclopentanones **4**, **6**, **9**, and **11**, and cyclobutanones **15** and **17**. The photoproducts, efficiencies, and reactivities of the former set are listed in Table I. Photochemical ring expansion of **6** is in itself a rather unusual reaction[6,11]

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[1] Molecular Photochemistry. XLIV. Paper XLIII: K. Dawes, N. J. Turro, and J. M. Conia, *Tetrahedron Lett.*, in press. The authors are pleased to acknowledge the generous support of this research by the Air Force Office of Scientific Research (Grant No. AFOSR-70-1848).

[2] P. Yates and L. Kilmurry, *Tetrahedron Lett.*, 1739 (1964).

[3] P. Yates and L. Kilmurry, *J. Amer. Chem. Soc.*, **88**, 1563 (1966).

[4] (a) H. U. Hostettler, *Tetrahedron Lett.*, 687 (1965); (b) H. U. Hostettler, *Helv. Chim. Acta*, **49**, 2417 (1966).

[5] N. J. Turro and R. M. Southam, *Tetrahedron Lett.*, 545 (1967).

[6] D. R. Morton, E. Lee-Ruff, R. M. Southam, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 4349 (1970).

[7] G. Quinkert, G. Cimbollek, and G. Buhr, *Tetrahedron Lett.*, 4573 (1966).

[8] N. J. Turro and D. M. McDaniel, *J. Amer. Chem. Soc.*, **92**, 5727 (1970), and unpublished results.

[9] P. Yates, *Pure Appl. Chem.*, **16**, 93 (1968).

[10] It should be emphasized that our results do not necessarily invalidate the original suggestion made by Yates. That ring expansion is an inherently inefficient reaction in the bicyclo[2.2.1]heptan-2-one system is still quite plausible.

[11] J. K. Crandall and R. J. Seidewand, *J. Org. Chem.*, **35**, 697 (1970).