ESR STUDIES OF GROUP IV SUBSTITUTED ANILINES

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ESR STUDIES OF GROUP IV SUBSTITUTED ANILINES

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By

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TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>LIST OF TABLES</th>
<th>iv</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF ILLUSTRATIONS</td>
<td>vi</td>
</tr>
<tr>
<td>Chapter</td>
<td></td>
</tr>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. EXPERIMENTAL</td>
<td>28</td>
</tr>
<tr>
<td>Preparation of \text{Para-Trimethylsilyl-N,N-Dimethylaniline}</td>
<td></td>
</tr>
<tr>
<td>Preparation of \text{Para-Tert-Butyl N,N-Dimethylaniline}</td>
<td></td>
</tr>
<tr>
<td>Solvent and Electrolytes</td>
<td></td>
</tr>
<tr>
<td>ESR Spectra</td>
<td></td>
</tr>
<tr>
<td>III. DISCUSSION</td>
<td>34</td>
</tr>
<tr>
<td>APPENDIX</td>
<td>48</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>58</td>
</tr>
<tr>
<td>Table</td>
<td>Page</td>
</tr>
<tr>
<td>-------</td>
<td>------</td>
</tr>
<tr>
<td>I. Cleavage of Trimethylsilyl-N,N-Dimethyl-aniline by Aqueous-Methanolic Per-chloric Acid at 51.2°</td>
<td>5</td>
</tr>
<tr>
<td>II. The Dipole Moments of Trimethyltin- and Trimethylsilyl-N,N-Dimethylaniline in Benzene Solution at 25°</td>
<td>9</td>
</tr>
<tr>
<td>III. Values of $\lambda_{\text{max}}$ ($\mu$) for the Principal Electronic Bands of Anilines and Dimethylanilines</td>
<td>15</td>
</tr>
<tr>
<td>IV. Values of $\nu_{\text{max}}$ (cm$^{-1}$), $\epsilon_{\text{max}} x 10^{-3}$ and Transition Moment Length, $q$(Å) for Para-RC$_6$H$_4$NM$_2$ at 25° in Heptane</td>
<td>15</td>
</tr>
<tr>
<td>V. Ionization Potentials of Some Substituted Benzene from the Charge Transfer Energy of Their TCNE Complexes in Chloroform at 24 ± 0.2°</td>
<td>17</td>
</tr>
<tr>
<td>VI. Experimental Hyperfine Coupling Constants of Para-, Meta-Trimethylsilylnitro Benzenes and Nitrobenzene</td>
<td>20</td>
</tr>
<tr>
<td>VII. Experimental Proton Hyperfine Splitting Constants of Tert-Butyl-, Trimethylsilyl-, Trimethylgermyl-Benzenes</td>
<td>21</td>
</tr>
<tr>
<td>VIII. Value of $\lambda_{\text{max}}$ ($\mu$) for the Principal Electronic Band of N,N-Dimethylaniline, Para-Methyl, Para-Tert-Butyl, and Para-Trimethylsilyl-N,N-Dimethylanilines</td>
<td>34</td>
</tr>
<tr>
<td>IX. Coupling Constants of Cation Radicals of Para-Substituted N,N-Dimethylanilines</td>
<td>38</td>
</tr>
<tr>
<td>Table</td>
<td>Page</td>
</tr>
<tr>
<td>----------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>X. Coupling Constants of Some <em>Para</em>-Substituted Anilines and Their Electrophilic Substituent Constants</td>
<td>40</td>
</tr>
</tbody>
</table>
## LIST OF ILLUSTRATIONS

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Energy Level Diagram for Aromatic Chromophore Showing the Effect of Metalloid Substitution. Both the Inductive and the Resonance Effect of the Substituent Are Diagrammatically indicated</td>
<td>35</td>
</tr>
<tr>
<td>2.</td>
<td>Relationship Between $A_{\text{CH}_3}$, and $\sigma^+$</td>
<td>41</td>
</tr>
<tr>
<td>3.</td>
<td>Relationship Between $A_N$ and $\sigma^+$</td>
<td>42</td>
</tr>
<tr>
<td>4.</td>
<td>ESR Spectra</td>
<td>49</td>
</tr>
<tr>
<td>5.</td>
<td>Infrared Spectra</td>
<td>54</td>
</tr>
</tbody>
</table>
CHAPTER I

INTRODUCTION

The earliest study of p-trimethylsilyl N,N-dimethylaniline was the cleavage of some organosilanes by hydrogen chloride (17). The purpose of the work was to investigate the general applicability of hydrogen chloride cleavage to organosilanes, and to see if, in that sense at least, silicon could be considered metallic. It has been shown that cleavage by hydrogen chloride is characteristic of carbon-metal bonds (16). Para-trimethylsilyl-N,N-dimethylaniline, in refluxing acetic acid, is cleaved by treatment with dry gaseous hydrogen chloride in 7-15 hours. The yields of chlorotrimethylsilane and N,N-dimethylaniline were 67 per cent and 73.5 per cent respectively. The order of ease of removal from trimethylsilyl groups in this series, 2-thienyl > p-anisyl and p-dimethylaminophenyl > p-tolyl > phenyl > p-chlorophenyl > benzyl and phenylethyl, is in essential agreement with that established with mercury (22) and lead derivatives (18).

In 1953, Benkesker et al. (2) reported the hydrogen chloride cleavage of some trimethylarylsilanes by acidic reagents. The ease of cleavage by acidic reagent appears to
be facilitated when the trimethylarylsilane contains substituents capable of furnishing high electron density to the aryl C-Si bond. One would expect that the ease of cleavage of trimethylarylsilane with ortho, para directors substituted meta to the trimethylsilyl group would be less than if these groups were substituted para. Since the electron density at the aryl C-Si bond is less in the former than in the latter, electrophilic attack is less likely on the carbon atom holding the silicon (see I, II).

\[
\begin{align*}
\text{I} & : \quad \text{R} = \text{H}^+ \\
\text{SiMe}_3 \\
\text{II} & : \quad \text{R} = \text{H}^+ \\
\text{SiMe}_3
\end{align*}
\]

Also, one might expect that the relative difference in ease of cleavage between meta and para compounds containing strong ortho-, para- directors would be less than in the cleavage of weaker ortho-, para- director under the same conditions, because the aromatic ring as a whole would be much richer in electrons in the former case and thus more susceptible to attack by electrophilic reagents. The yield of trimethylchlorosilane by cleavage of meta, and para trimethylsilyl-N,N-dimethylaniline are 80 per cent and 94 per cent
respectively. It has been shown that the $\sigma_p$ value for the trimethylsilyl group in dimethylaniline is positive, whereas $\sigma_m$ is negative (3). Consequently, the salt of the $p$-amine would be more highly dissociated than that of the $m$-amine. If both amines existed largely in the salt form, consideration of transition states such as III to VIII for the cleavages analogous to those proposed for nitration of phenyltrimethylammonium salts would lead to a conclusion contrary to that found experimentally, i.e., the meta isomer would be cleaved more readily than would the para.

![Diagram](image)

(lesser contribution for adjacent charge)
On the other hand, if both isomers existed largely as the free amines, one might expect the difference in ease of cleavage to amount to perhaps 10-20 per cent and thus be comparable to that observed in the case of the methoxyphenytrimethylysilane. To account for the large cleavage of the silyl group from amine, one has to assume that the equilibrium between the free m-amine and its salt lies largely in the direction of the salt form, while that of the p-amine lies principally in the direction of free base.

The acid-catalyzed cleavage of some substituted phentrimethylysilanes in aqueous methanolic perchloric acid has been studied spectrophotometrically for a range of activating and weakly deactivating substituents by Eaborn (10) in 1956. The acid catalyzed solvolytic cleavage of the aryl-Si bond is an electrophilic aromatic substitution in which a proton, initially solvated, is the attacking species (11). Since removal of a trimethylsilyl group from a benzene ring shifts the ultraviolet absorption spectrum about 3-15 μ to the blue, with little change of shape, the reaction is easily followed spectrophotometrically and may be conveniently used to study the effects of nuclear substituents on aromatic reactivity. Because of the opposition of +σ and −π effects, the trimethylsilyl group supplies electrons to the
ring or withdraws them according to the demand (3, 6, 12). Nitration studies have shown the trimethylsilyl- group to be slightly activating and weakly ortho-, para- directing (34); results also show the trimethylsilyl- group to activate slightly more from the para position than does the methyl group from the meta position.

The very great activating power of the p-dimethylamino group is shown by cleavage of substituted phenyltrimethylsilane by aqueous-methanolic perchloric acid at 51.2° (10). The p-dimethylaminophenyltrimethylsilane is at least 430 times as reactive as mesityltrimethylsilane, and > 2.3 x 10^7 times as reactive as phenyltrimethylsilane. Para-dimethylaminophenyltrimethylsilane reacts at a maximum rate with ca. 0.1 M (added) acid, as shown in Table I.

TABLE I

CLEAVAGE OF TRIMETHYLSILYL-N,N-DIMETHYLANILINE BY AQUEOUS-METHANOLIC PERCHLORIC ACID AT 51.2°

<table>
<thead>
<tr>
<th>HClO₄(M)</th>
<th>Relative Rate 10³k(min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001056</td>
<td>46</td>
</tr>
<tr>
<td>0.01056</td>
<td>105</td>
</tr>
<tr>
<td>0.1056</td>
<td>116</td>
</tr>
<tr>
<td>0.832</td>
<td>105</td>
</tr>
<tr>
<td>9.22</td>
<td>53.5</td>
</tr>
</tbody>
</table>
This behavior is to be expected as the rate of desilylation is proportional to the proton-donating power of the medium as measured by the indicator ratio, \((BH^+)/(B)\), for a neutral base, \(B\) (para-nitroaniline being the base employed). Since with acid concentration at least 0.1M (added), the \(p\)-dimethylaminophenyltrimethylsilane is almost all in the protonated form (which reacts at a negligible rate), the concentration of the latter changes inappreciably, and increasing the acid strength to double the indicator ratio for this base doubles the rate at which the free amine reacts but halves its concentration. At a given indicator ratio for a particular base, the rate of desilylation falls as the proportion of water in the medium decreases. Comparison of effects of substituents in desilylation with those in halogenation and nitration reveal no special features arising from the fact that in the former reaction a C-Si bond is being broken instead of a C-H bond.

H. Soffer and T. De Vries (33) in 1951 measured the dipole moment of aromatic derivative of trimethylsilane in benzene solutions at 25°C and 752 mm pressure. The dipole moment was calculated by both the Gugghein (20) and Hedestrand (25) equation. The values were respectively, 1.84 and 1.83 Debyes. The value of dipole moment of the
unmethylated \textit{p}-trimethylsilylaniline was 1.66. It was found that electron supplying group para to the trimethylsilyl group produce a marked decrease in the algebraic value of the moment of this group. Such a decrease seems to be proportional to the ease with which the para groups give up electrons to the ring. The structure which must be postulated to account for this decrease is one which involves a double bond between the carbon and silicon atoms and places ten electrons around the silicon as below.

![Image of structure IX]

The trimethylsilyl groups attached to benzene rings have been shown by dipole moment studies to be slightly electron releasing (27). Three possible electrical effects due to the trimethylsilyl group can be represented by resonance forms XI, XII, XIII.

The electropositive nature of silicon relative to carbon is reflected by XI, while XII represents hyperconjugative
resonance of the type postulated for alkylbenzene. XIII depicts the tendency for silicon to expand its valence shell by interaction of the 3d orbital of silicon with the unsaturation electrons of the benzene ring. It is expected that XI should be somewhat more important than the corresponding resonance forms involving the Si-C bonds of the methyl group, since the phenyl group is more electron attracting than is the trimethylsilyl group.

Huang and Hui (21) made a measurement of the electric dipole moments of some trimethylphenyltin derivatives, the moments of the analogous silicon compounds are included for comparison as shown in Table II.
TABLE II
THE DIPOLE MOMENTS OF TRIMETHYLTLN- AND TRIMETHYLSILYL
N,N-DIMETHYLANILINE IN BENZENE SOLUTION AT 25°

<table>
<thead>
<tr>
<th></th>
<th>p-Me₂NC₆H₄SiMe₃</th>
<th>p-Me₂NC₆H₄SnMe₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>obs(D)</td>
<td>1.84</td>
<td>1.83</td>
</tr>
<tr>
<td>cal(D)</td>
<td>1.58</td>
<td>1.54</td>
</tr>
<tr>
<td>(D)</td>
<td>0.26</td>
<td>0.29</td>
</tr>
</tbody>
</table>

Their results confirmed that tin, like silicon and other group IV b elements, has vacant d-orbitals in its valence shell available for dative bonding with suitable electron donors, but that silicon in the Si(CH₃)₃ group is more effective in delocalizing aromatic pi electrons than is tin.

Benkesker et al. (3), in 1953, made a further study of the conjugative ability of the trimethylsilyl group upon the ionization constants of aniline, dimethylaniline, phenols and benzoic acid. Their data indicate that the m-Me₃Si group exerts mainly an electron releasing effect in all these reactions. The same is true of the p-Me₃Si group in benzoic acids and, further, the silyl group is capable of limited conjugation involving an expansion of the silicon valence shell in the reaction of phenols, aniline and dimethylaniline.
Their pH data clearly indicate that $p$-trimethylsilyl- 
$N,N$-dimethylaniline is a weaker base than is $N,N$-dimethylaniline. It would appear that there are small but significant 
interactions in $p$-amines in which the trimethylsilyl group 
is capable of conjugation to a limited extent, possibly in-
volving contribution of a structure such as IX. This 
conclusion is further substantiated by the $\sigma_p$ value.

In 1950, Sunthankar and Gilman (36) studied the silicon 
containing azo dyes. The silicon containing azo dyes were 
prepared by coupling organosilicon compounds with selected 
diazonium salts. A convenient method for the preparation 
of organosilicon compounds is by the action of chlorosilanes 
upon organolithium compounds (35). The lithium compounds of 
dimethylaniline were prepared by direct action of lithium on 
the corresponding bromo-$N,N$-dimethylaniline (20).

A notable difference was observed in the behavior of 
ortho, meta, and para substituted dimethylanilines toward 
diazonium salts. Para-trimethylsilyl- and $p$-triphenylsilyl-
$N,N$-dimethylaniline coupled readily with $p$-nitro benzene-
diazonium salts; but the dye isolated was $N,N$-dimethyl-4-
($p$-nitrophenyl azo) aniline in about 80 per cent yield. The 
latter is evidently formed by the replacement of the tri-
methlysilyl group by the diazonium cation, during the
diazo-coupling reaction (9). In contrast \( p-\text{t-butyl} \) N,N-dimethylaniline does not couple with diazonium salts.

Meta-trimethyldisilyl- and \( m \)-triphenylsilyl N,N-dimethylaniline, however, showed normal behavior towards diazonium salts and gave a series of azo dyes in very good yields (see IX to XI).

\[
\text{(CH}_3\text{)}_2\text{N} + \text{N}=\text{N} \longrightarrow (\text{CH}_3\text{)}_2\text{N} \text{N} = \text{N} \text{NO}_2
\]

IX \hspace{2cm} X \hspace{2cm} XI

The color of the dyes obtained from these two compounds and the respective diazonium salts were almost the same, but a comparison of the visual color of some of these dyes with that of unsubstituted dyes shows that the substitution of trimethyldisilyl and triphenylsilyl- group in azo dyes has a general bathochromic effect on the color. In general, the trimethyldisilyl derivative coupled more readily than did the triphenylsilyl compound, and this may be attributed to steric effects. A notable difference was observed in their reaction with certain diazonium salts containing functional groups in the ortho position to the diazo group. For example:
the diazonium sulfates obtained from 2-hydroxy-4-nitroaniline, 
2,4-dinitro-5-chloroaniline, and 2-trifluoromethyl-4-nitro-
aniline coupled readily with the trimethylsilyl compounds 
but failed to react with the triphenyl derivatives, even 
though the reaction was carried out for a prolonged time.

Ortho trimethylsilyl- and o-triphenylsilyl-dimethyl-
aniline did not couple with p-nitrobenzenediazonium salt, 
even though the reaction was carried out for several hours. 
It has been reported that dimethylaniline substituted with
nitro, methyl, and chloro- groups in the ortho position does 
not show any tendency to couple with the diazonium salt. The 
low reactivity of the above anilines is also exhibited in 
the difficulty of their coupling reactions with benzaldehyde 
and formaldehyde (5).

An important result of this study was the observation 
that dyes which were quite resistant to cleavage by dry 
hydrogen chloride in glacial acetic acid were quite suscep-
tible to acid reducing agents. By the action of tin or
stannous chloride and hydrochloric acid, reduction of the 
azo linkage to amino groups and simultaneous cleavage of 
the C-Si bond took place.

In 1970, Bock and Alt (4) studied the charge transfer 
spectra of some silyl- and alkyl- benzenes. Data indicated
the charge transfer bands of SiR₃-substituted benzenes appear at even shorter wavelengths than do those of the corresponding alkyl derivatives. The SiH₃ group shows no donor property at all. The substituent effects on the benzene eₘ molecular orbitals can be rationalized in terms of inductive polarization -I_{SiR₃} + I_{CR₃}, as well as strong electron back-donation Si<−Cπ from the benzene π system into empty silicon atomic orbitals of π symmetry. At the same time, the ionization energy of some silyl derivatives of benzene were determined by mass spectrometry; the value of p-trimethylsilyl-N,N-dimethylaniline is 6.73 ev.

Only a few studies of p-t-butyl N,N-dimethylaniline have been reported; the earliest study of p-t-butyl N,N-dimethylaniline was the preparation by Davis and Hubert (8) in 1938.

Electron donor and acceptor properties of alkyl groups were studied by Schuber et al. (29, 30) with a view to the nature of electronic transitions. Their results imply that alkyl groups are better electron acceptors than is hydrogen, when called upon strongly to accept electrons. Such a transition is the "principal" electronic transition of phenol, anisole, aniline and dimethylaniline, represented approximately by the following:
Table III shows that the excitation energies of para-methyl and para-\textsuperscript{t}-butyl compounds lie below those of the para hydrogen compound in each case. No significance should be attached to the relative $\lambda_{\text{max}}$ values of the principal band of methyl and \textsuperscript{t}-butyl compounds, since the principal bands are somewhat asymmetric, owing evidently to a near-lying lower wavelength transition. However, the principal band for each alkyl compound clearly lies at longer wavelengths than that of the corresponding hydrogen compound. In view of the nature of the transition, these results imply that alkyl groups are better electron acceptors than is hydrogen when called upon strongly to accept electrons. This suggests that an alkyl group is more readily polarized than is hydrogen when attached to a highly electron-rich system, as well as when attached to an electron-deficient system (29, 31).
TABLE III
VALUES OF $\lambda_{\text{max}}(\text{m} \mu)$ FOR THE PRINCIPAL ELECTRONIC BANDS OF ANILINES AND DIMETHYLANILINES

<table>
<thead>
<tr>
<th></th>
<th>H</th>
<th>Me</th>
<th>But</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Z=\text{NH}_2$</td>
<td>229.4</td>
<td>233.7</td>
<td>232.7</td>
</tr>
<tr>
<td>$Z=\text{NMe}_2$</td>
<td>241.8</td>
<td>243.5</td>
<td>244.5</td>
</tr>
</tbody>
</table>

The energy order for the nucleophilic electronic transitions is Neo-$p<\text{CH}_3$, $t$-Bu$<H$, with the $p$-methyl and $p$-$t$-butyl groups having comparable effects. The energy order in electronic transition is Neo-$p<t$-Bu$<\text{CH}_3<H$, as shown in Table IV.

TABLE IV
VALUES OF $\nu_{\text{max}}(\text{cm}^{-1})$, $\epsilon_{\text{max}} \times 10^{-3}$ AND TRANSITION MOMENT LENGTH, $q(A^\circ)$ FOR $p$-$\text{RC}_6\text{H}_4\text{NMe}_2$ AT 25°C IN HEPTANE

<table>
<thead>
<tr>
<th>R</th>
<th>H</th>
<th>Me</th>
<th>T-bu</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_{\text{max}}$</td>
<td>39380</td>
<td>39490</td>
<td>39600</td>
</tr>
<tr>
<td>$\epsilon_{\text{max}} \times 10^{-3}$</td>
<td>14.9</td>
<td>15.9</td>
<td>16.3</td>
</tr>
<tr>
<td>$q$</td>
<td>0.87</td>
<td>0.91</td>
<td>0.94</td>
</tr>
</tbody>
</table>
The value of the transition moment length \( q \) in heptane is a quantity which was determined from the area of the absorption band, \( Q^2 = 1.09 \times 10^{-19} \text{ cm} \cdot \text{dG ln} \lambda \). It is considered to measure the extent of oscillation of the solute dipole during the interaction with the electronic vector of light being absorbed and takes exactly the same order for nucleophilic excitation of nitrobenzene. The order of \( q \) is neo-p > t-bu > CH\(_3\) > H and is considered to correspond to the order of "substituent polarizability."

Shroygin et al. (32) in 1959 studied the mutual effect of t-butyl N,N-dimethylaniline in raman and ultraviolet spectra. The electron acceptor properties of the C\(_6\)H\(_4\)NO\(_2\) group was stronger than that of Ph; the reverse order was true for the C\(_6\)H\(_4\)NR\(_2\) group. The electron-donor ability of the substituents depended on the specific mutual effect of the attached groups, which can not be expressed by any independent increments quantitatively.

In 1965, ionization potentials of p-t-butyl N,N-dimethylaniline were detected (13) from charge transfer spectra of complexes formed by (N\(_5\))\(_2\)C:C(CN)\(_2\) with the anilines. The energy of the charge transfer transition may be expressed as follows:

\[ h\nu_T = aI_D + b \]
Where a and b are constants for a given acceptor, b contains terms such as the electron affinity of the acceptor, coulombic interaction between the no bond and dative states, and any solvent effects. Thus, from the long wave length, the charge transfer absorption maximum of an electron donor may be calculated if the constants a and b for a system are known. (See Table V.)

**TABLE V**

IONIZATION POTENTIALS OF SOME SUBSTITUTED BENZENES FROM THE CHARGE TRANSFER ENERGIES OF THEIR TCNE COMPLEXES IN CHLOROFORM AT 24 ± 0.2°

<table>
<thead>
<tr>
<th>Substituent Group of Benzene</th>
<th>$h\nu$</th>
<th>$I_d$ (ev)</th>
<th>$I_d$ (ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_2$</td>
<td>2.097</td>
<td>7.76</td>
<td>7.76</td>
</tr>
<tr>
<td>NHMe</td>
<td>1.946</td>
<td>7.58</td>
<td>7.60</td>
</tr>
<tr>
<td>NHEt</td>
<td>1.931</td>
<td>7.56</td>
<td>7.50</td>
</tr>
<tr>
<td>NH-n-Pr</td>
<td>1.916</td>
<td>7.54</td>
<td>7.50</td>
</tr>
<tr>
<td>NH-n-Br</td>
<td>1.910</td>
<td>7.53</td>
<td>7.50</td>
</tr>
<tr>
<td>NMe$_2$</td>
<td>1.839</td>
<td>7.44</td>
<td>7.30</td>
</tr>
<tr>
<td>NMe$_2$-p-isopPr</td>
<td>1.813</td>
<td>7.41</td>
<td></td>
</tr>
<tr>
<td>NMe$_2$-p-t-Bu</td>
<td>1.831</td>
<td>7.43</td>
<td></td>
</tr>
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</table>
Analysis of the data by the least-squares method, assuming the error to be in measurement of $h\nu_{cT}$, gives $a$ and $b$ values shown in the equation as follows:

$$h\nu_{cT} = 0.82 I_d - 4.28\text{eV}$$

The anion and cation radicals of some $p$-substituted $N,N$-dimethylanilines were reported (15, 24, 26). However, they do not include substituents with a silicon atom. In general, the number of radicals of organosilicon compounds studied is extremely limited, apparently because of the difficulties of their production, as well as their frequently low stability under experimental conditions in chemical methods of reduction.

A few ESR measurements of radical anions of some trimethylsilyl-substituents were made. They show that the trimethylsilyl group acts as a stronger electron acceptor in spite of its strong $+I$ effect relative to $t$-butyl group (14).

The radical anion of XIV is more stable than is the radical anion of $t$-butyl benzene.

Anion radicals of para- and meta-trimethylsilylnitro-benzene were studied (23). Their results show that the introduction of the trimethylsilyl group into the para
position of nitrobenzene reduces the coupling constant of nitrogen by 0.6 gauss in comparison with the anion radical of nitrobenzene (7). Such an appreciable decrease in $A_N$ can be explained only by the fact that silicon attracts part of the spin density of the unpaired electron away from the nitro-group, i.e., there is a substantial contribution of structure of the following type:

*$A_{Si I'}$ is the coupling constant of $^{29}Si$. 
Experimental hyperfine coupling constants of para-, meta-trimethylsilylnitrobenzenes and nitrobenzene are summarized in Table VI.

### TABLE VI

**EXPERIMENTAL HYPERFINE SPLITTING CONSTANTS OF PARA-, META-TRIMETHYLSILYLNITROBENZENES AND NITROBENZENE**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Method of Prod. AR</th>
<th>Solvent</th>
<th>Nature of Splitting</th>
<th>Hyperfine Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Structure 1" /></td>
<td>EC</td>
<td>Acetonitrile</td>
<td>3x3x3</td>
<td>$A_N=9.7$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$A_2, 6=3.3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$A_3, 5=0.9$</td>
</tr>
<tr>
<td><img src="image2.png" alt="Structure 2" /></td>
<td>EC</td>
<td>Acetonitrile</td>
<td>3x2x3x2</td>
<td>$A_N=10.0$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$A_4=3.8$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$A_2, 6=3.4$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$A_3=1.0$</td>
</tr>
<tr>
<td><img src="image3.png" alt="Structure 3" /></td>
<td>EC</td>
<td>Acetonitrile</td>
<td>3x2x3x3</td>
<td>$A_1=10.32$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$A_2=A_6=3.39$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$A_3=A_5=1.09$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$A_4=3.97$</td>
</tr>
</tbody>
</table>
In the meta isomer, the nitro group is brought out of resonance with the trimethylsilyl group, therefore, the constants of nitrogen splitting in the anion radical of this compound in acetonitrile are very close to the corresponding constants of the anion radical of nitrobenzene and its meta-alkyl derivative. This once again confirms the correctness of the hypotheses advanced above on the electron-acceptor properties of the trimethylsilyl groups.

The electron spin resonance spectra of the phenyltrimethyl-silane and -germane anions were studied by Carrington et al. (29). Data (see Table VII) indicated that the ring proton hyperfine constants are quite different from those of the t-butyl benzene anion and demonstrated that relative to -CMe₃, the -SiMe₃ and -GeMe₃ groups are electron attracting.

### Table VII

**Experimental Proton Hyperfine Splitting Constants**

<table>
<thead>
<tr>
<th></th>
<th>Ortho</th>
<th>Meta</th>
<th>Para</th>
<th>Methyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-Butyl Benzene</td>
<td>4.66</td>
<td>4.66</td>
<td>1.74</td>
<td>0.10</td>
</tr>
<tr>
<td>Trimethylsilyl Benzene</td>
<td>2.66</td>
<td>1.06</td>
<td>8.13</td>
<td>0.40</td>
</tr>
<tr>
<td>Trimethylgermyl Benzene</td>
<td>2.33</td>
<td>1.46</td>
<td>7.61</td>
<td>0.10</td>
</tr>
</tbody>
</table>
The \textit{t}-butyl benzene anion exhibits a very simple five-line spectrum due to hyperfine splitting by four equivalent ring protons, and each of the five main lines is further split into two lines by the para ring proton. The spectrum of the phenyltrimethylsilane anion arises from a large doublet splitting due to the para ring proton, two fairly small triplet splittings from the ortho- and meta-ring protons, and a still smaller splitting from the nine methyl protons. The spectrum of the phenyltrimethylgermane anion is very similar to that of the silicon compound, except that no methyl hyperfine structure is resolved.

Comparison of the data for the silicon and germanium derivatives shows that the \textit{-GeMe}_3\ group has the smaller electron-withdrawing power, and the ortho-, meta-, and para-splittings are actually smaller in the germanium derivative. A further indication that the electron-withdrawing power of the substituent decreases from silicon to germanium is given by the resolved methyl hyperfine structure (0.4 gauss) in the silicon compound and not resolved in the germanium derivative.

The vacant 3d and 4d orbitals of silicon and germanium respectively may fulfill a bonding function in two ways: in the formation of \(\sigma\)-bonds and the formation of \(\pi\)-bonds of the
\((p \leftrightarrow d)\) type (7). In connection with the ESR spectra of phenyltrimethyl-silane and -germane anions, silicon in the trimethylsilyl group is more efficient than is germanium in delocalizing aromatic pi electrons. Furthermore, studies on hydrogen-bond formation of the compounds \((\text{C}_6\text{H}_5)_3\text{MOH}\) (where \(M = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}\)), with ether and phenol, suggest that the pi bonding from oxygen to \(M\) decreases markedly in the order \(\text{Si} > \text{Ge} > \text{Sn} > \text{Pb}\), being neglectable for Sn and Pb.

Radical cations of silicon compounds have not been reported.

The substituent effect of \(\text{MR}_3\) groups, where \(M\) is a group IV B element, is a subject of some current interest, and we have investigated the electron spin resonance spectra of the \(p\)-\(t\)-butyl- and \(p\)-trimethylsilyl-\(N,N\)-dimethylaniline radical cations.

The purpose of the investigation described herein was to investigate the degree of delocalization of the unpaired electron in ion radicals formed in the oxidation process of compounds with aromatic rings connected by means of various groups and atoms not entering the ring; then, to establish the relationship of coupling constants in radical cations with substituent \(\sigma\) values. The parent cation radical, in which the co-planar ion was derived from \(N,N\)-dimethylaniline
(see XVI), was selected in order to maximize the substituent effects on coupling constants and to obtain couplings at several positions (specifically, \( \text{CH}_3 \), N, and ring protons).

In an attempt to ensure the greatest possible extent of generality of the results, \( \text{t-butyl} \)- and trimethylsilyl-group substituted in the para position were used.
CHAPTER BIBLIOGRAPHY


CHAPTER II

EXPERIMENTAL

All melting points were determined on a Thomas Hoover Capillary Melting Apparatus. The infrared spectra were obtained by using a Perkin-Elmer 237 Grating Infrared Spectrophotometer, and the thin-film technique was used. The nuclear magnetic resonance (nmr) spectra were recorded on a Janpan Electron Optics Laboratory JNM-MH-6011, with deuterochloroform as solvent and tetramethyilsilane as an internal standard. Chemical shifts were recorded in ppm (δ). The mass spectra were obtained by using a Hitachi Perkin-Elmer RMU-6E mass spectrometer. Ultraviolet spectra were obtained from a Cary 14 Recording Spectrophotometer with isooctane as solvent. Elemental analyses for carbon, hydrogen, and nitrogen were obtained by using a F & M Scientific 185 CHN Analyzer.

Preparation of Para-Trimethylsilyl-N,N-Dimethylaniline

Para-Trimethylsilyl-N,N-dimethylaniline was prepared according to the method outlined by Gilman and Marshall (5).
About 25 ml (40 m mole) of n-butyl lithium (Foote Mineral Company) was put into a dry, three-necked, 500-ml reaction flask equipped with a Hirschberg Stirrer, Friedrichs condenser, and a dropping funnel, under nitrogen atmosphere. To this was added 8 grams (40 m mole) of p-bromo-N,N-dimethyl-aniline which was dissolved in 20 ml dry benzene, then the mixture was refluxed for two hours. About 5.8 ml of trimethylchlorosilane was added slowly; the mixture was refluxed two hours longer and stirred overnight. After hydrolysis with 20 ml of distilled water and one drop of concentrated hydrochloric acid, the water layer was separated; the aqueous layer was extracted three times with ether. The combined ether and organic layer was dried over anhydrous calcium sulfate, filtered, and distilled to give 6.2 gram (70.1%) of p-trimethylsilyl-N,N-dimethylaniline, b.p 101°C.

The pure compound was obtained by vpc collection using a Varian Aerograph Series 1800 Chromatograph with a 20' x 3/8" aluminum column, packed with 30 per cent carbowax on 40-60 mesh Chromosorb-P, operating at 240°C with a carrier gas flow of 150 cc He/min. Under these conditions, its retention time is 36 min. Infrared spectrum: 3080 cm⁻¹(w), 2970(m), 2800(m), 1825(w), 1600(s), 1545(m), 1520(s), 1480(m), 1450(m), 1300(m), 1250(m), 1225(m), 1115(s),
1060(w), 1010(w), 945(w), 860(s), 840(s), 810(m), 760(m), 725(w); nmr spectrum: 0.26 -Si(CH_3)_3 singlet, 2.98 -N(CH_3)_3 singlet, and two doublets centered at 7.25 and 6.58 with approximately the same coupling constants 9 cps due to the two pairs of equivalent aromatic ring protons; mass spectrum: parent peak (M^+) = 193 and base peak (M - SiMe_3)^+ = 120 which indicated the carbon-silicon bond to be the weakest bond; ultraviolet spectrum: \( \lambda_{\max} = 2625\text{A}^0 (\varepsilon = 19307) \) and \( \lambda_{\max} = 2950 \ (\varepsilon = 2500) \).

Anal. Calc. for C_{11}H_{19}NSi: C, 67.01; H, 9.84; N, 7.25. Found: C, 68.33; H, 10.23; N, 7.14.

Preparation of Para-tert-Butyl N,N-Dimethylaniline

Para-tert-butyl benzene (bp 125) was prepared by using the procedure outlined by Davis and Hubert (2). The pure compound was obtained by vpc collection using a 20' x 3/8" aluminum column, packed with 30 per cent carbowax on 40-60 mesh Chromosorb-P, operating at 200°C with a carrier gas flow of 160 cc He/min. Under these conditions, its retention time is 35 min. Infrared spectrum: 2940 cm\(^{-1}\)(s), 2850(m), 2820(m), 2780(m), 1710(w), 1615(s), 1520(s), 1475(m), 1380(w), 1350(m), 1330(m), 1225(w), 1215(m), 1200(m), 1165(m), 1125(w), 1050(w), 940(m), 830(m); nmr spectrum: 1.306 -C(CH_3)_3 singlet,
2.9\delta-N(CH_3)_2 singlet, and two doublets centered at 7.24 and 6.70\delta with approximately the same coupling constants 4.3 cps due to the two pairs of equivalent aromatic ring protons; mass spectrum: parent peak (M^+) m/e = 177, base peak ((CH_3)_2C_6H_4N(CH_3)_2^+) m/e = 162; ultraviolet spectrum: \lambda_{max} = 2510\AA\ (\epsilon = 14620), \lambda_{max} = 3000 (\epsilon = 1940).

Anal. Calc. for C_{12}H_{19}N: C, 81.35, H, 10.73, N, 7.91. Found: C, 82.36, H, 11.08, N, 8.12.

Solvent and Electrolytes

Tetrabutylammonium perchlorate.—Using the procedure outlined by Geski and Maki (4), this compound was prepared in 85 per cent yield. mp 211.5-212°C (lit mp, 213°C).

Sodium perchlorate.—This was obtained from the G. Fredrick Smith Chemical Co., and recrystallized from absolute ethanol by ordinary procedure (6).

Acetonitrile.—This was obtained from Millickrodt Chemical Works and further purified by the method outlined by Cunningham et al. (1).

ESR Spectra

The ESR spectra were determined on a Varian Model V 4502-13 Spectrometer equipped with a 9-inch magnet, 100 kc
field modulation, dual cavity and electrolytic accessories. Radical cations of both anilines were generated by electrolytic method. Both sodium perchlorate and tetrabutylammonium perchlorate were used as electrolytes; acetonitrile was used as solvent. Samples were prepared at about $1 \times 10^{-3}$ M in the anilines, and 0.1 M in the electrolyte. The V-4556 electrolytic cell was used as the sample cell. The cell and the solutions were purged for 3-5 min with purified nitrogen to remove oxygen, and after filling the cell, the solutions were purged another two min before electrolysis was begun. The nitrogen purge was continued during the electrolysis.

Cation radicals of the aniline were generated in situ using a platinum gauze anode and mercury cathod. The voltages were 3.5 volt and 7 volt for p-trimethylsilyl-N,N-dimethylaniline and p-t-butyl-N,N-dimethylaniline respectively. All of the g values and coupling constants were measured using Fremy's salt ($A = 13.00$ gauss, $g = 2.00550 \pm 0.00005$) as a standard in the reference cavity.

The electrolysis of the silyl compound gave a secondary spectrum which is identical to the N,N,N',N'-tetramethylbenzidine spectrum (3, 4), and this phenomenon was not observed in tert-butyl compound.
CHAPTER BIBLIOGRAPHY


CHAPTER III

DISCUSSION

The ultraviolet spectrum of p-trimethylsilyl-N,N-dimethylaniline shows the bathochromic shift for the $\pi \rightarrow \pi^*$ transition and the hypsochromic shift for the $n \rightarrow \pi^*$ transition when compared to the corresponding transition for its carbon analog, p-t-butyl N,N-dimethylaniline. The data of their ultraviolet spectra are shown in Table VIII.

TABLE VIII

VALUE OF $\lambda_{\text{max}}$ (mu) FOR THE PRINCIPAL ELECTRONIC BAND OF N,N-DIMETHYLANILINE, p-METHYL-, p-t-BUTYL, AND p-TRIMETHYLSILYL-N,N-DIMETHYLANILINES

<table>
<thead>
<tr>
<th></th>
<th>CH$_3$</th>
<th>H$_3$C</th>
<th>t-Bu</th>
<th>Si</th>
<th>CH$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\pi \rightarrow \pi^*$</td>
<td>241.8*</td>
<td>243.5*</td>
<td>244.5*</td>
<td>262.5</td>
<td></td>
</tr>
<tr>
<td>$n \rightarrow \pi^*$</td>
<td>...</td>
<td>...</td>
<td>300.0</td>
<td>295.0</td>
<td></td>
</tr>
</tbody>
</table>

In terms of $\pi \rightarrow \pi^*$ transition, alkyl substitution of the parent aniline moves the absorption to longer wavelengths. The bathochromic effect is progressive as the number of alkyl groups increases. The bathochromic shift, accompanying alkyl substitution, may be explained by hyperconjugation, in which the $\sigma$ electrons (9) of the alkyl group are mobile enough to interact with the chromophoric group. We can rationalize the bathochromic shift of $p$-trimethylsilyl-N,N-dimethylaniline in the following way (Fig. 1 10):

![Energy level diagram for aromatic chromophore showing the effect of metalloid substitution. Both the inductive and the resonance effect of the substituent are diagrammatically indicated.](image)

Both inductive and resonance interaction can take place between the metalloid substituent M and aromatic chromophore. The inductive effect of the electropositive substituent is
to raise both $\pi$ and $\pi^*$ by a small amount, while the vacant pi-type orbital of the metal will be lowered by a similar small amount. Resonance interaction will also take place between the vacant metal orbital and both $\pi$ and $\pi^*$, to generate three new levels, $\pi_1$, $\pi_2^*$ and $\pi_3^*$. However, because of better energy matching, interaction of the metal orbital is expected to be substantially stronger with antibonding $\pi^*$ level than with bonding $\pi$ level. The aromatic electronic absorption must be only of the $\pi \rightarrow \pi^*$ type, in which an electron moves from the bonding to antibonding $\pi$ levels. $\pi_1$ and $\pi_2^*$ should be closer in energy than the corresponding levels ($\pi$ and $\pi^*$) were in the original aromatic chromophore, and a bathochromic (red shift) is observed for the transition. On the other hand, evidence which suggests that the trimethylsilyl group acts as a strong electron acceptor in spite of its strong +I effect relative to the t-butyl group is that a small blue shift for the $n \rightarrow \pi^*$ transition of the $p$-trimethylsilyl-$N,N$-dimethylaniline was observed in comparison with its carbon analog. This can be attributed to a significant contribution of resonance structure of the type

$$(-)\text{Me}_3\text{Si}=-\text{NMe}2^+ \quad \text{XVII}$$
involving significant interaction of the nitrogen lone pair with the $\pi$ system. This results in a decrease of the electron density on nitrogen, or a stabilization of the nitrogen $n$ level, and is evidenced by the hypsochromic shift for the $n \to \pi^*$ transition.

Either $p$-trimethylsilyl-$N,N$-dimethylaniline or its carbon analog was oxidized to the radical cation by electrolytic method in acetonitrile with 0.1 M electrolyte. The ESR spectra consist of a septet of lines with relative intensities 1:6:15:20:15:6:1; each line was split into a triplet of lines with relative intensities 1:1:1, then further split into a triplet with relative intensities 1:2:1. Further splitting of each line into a triplet with relative intensities 1:2:1 was observed in the silyl compound but not in the corresponding carbon analog. The septet is attributed to the interaction of the unpaired electron with the six equivalent protons on the methyl groups of the nitrogens, the triplet with relative intensities 1:1:1 is due to the interaction of the unpaired electron with the nitrogen atom, and the other triplets with relative intensities 1:2:1 are attributed to the interaction of the unpaired electron with the ortho or meta protons to the $-\text{N}(\text{CH}_3)_2$ group. The interaction of the unpaired electron with the trimethylsilyl- or $t$-butyl-group
is not observed in either case. (See Appendix Fig. 4-1, 4-2, 4-3).

McConnell (5, 6) suggested that the relationship between coupling constant and electron density is as follows:

\[ A_H = Q \rho \]

where \( \rho \) is the unpaired electron density at a given carbon atom and can be calculated from valence theory; \( A_H \) is the hyperfine splitting due to the adjacent ring proton, and one can measure it from the experimental spectrum; \( Q \) is a constant, usually taken to have a value between 22.5 and 30 gauss. The magnitude of the coupling constants are directly related to the spin density at the atom in question.

The coupling constants for these radical cations are given in Table IX.

| TABLE IX |
| COUPLING CONSTANTS OF CATION RADICALS OF PARA-SUBSTITUTED-N,N-DIMETHYLANILINES |

<table>
<thead>
<tr>
<th></th>
<th>( A_{CH_3} )</th>
<th>( A_N )</th>
<th>( A_H^0 )</th>
<th>( A_H^m )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me(_3)Si—( \text{NMe}_2 )</td>
<td>12.50</td>
<td>11.50</td>
<td>5.30</td>
<td>1.50</td>
</tr>
<tr>
<td>t-Bu—( \text{NMe}_2 )</td>
<td>12.31</td>
<td>11.35</td>
<td>5.75</td>
<td>( \ldots )</td>
</tr>
</tbody>
</table>
The coupling constants for the nitrogen and for the N,N-dimethyl protons are larger for the silicon compound than for the t-butyl compound. This is consistent with the shifts observed in the ultraviolet spectra. Since, in a radical cation we are observing the unpaired electron in a bonding orbital, the larger coupling constants indicate a greater interaction of the n levels of the molecule with the \( \pi \) system of the aniline.

The coupling constants of some para-substituted anilines and their electrophilic substituent constants are shown in Table X.

The data available in Table X show that the trimethylsilyl group has an electron-withdrawing resonance effect and electron-donating inductive effect. On the other hand, the t-butyl group acts as an electron-donating group in both resonance and inductive effects.

The data from Table X were plotted against the available variety of \( \sigma \) parameters (see Figures II and III). Since the coupling constant of a particular atom in the molecule is taken to be a measure of the electron density around the atom, linear relationships between \( \sigma^+ \) and \( A_N \) or \( \sigma^+ \) and \( A_{\text{CH}_3} \) were expected within the precision of the analysis.
One can see that the trimethylsilyl group, like fluorine, does not fall in the line. It is probably due to its resonance effect with the π ring.

**TABLE X**

**COUPLING CONSTANTS OF SOME PARA-SUBSTITUTED ANILINES AND THEIR ELECTROPHILIC SUBSTITUENT CONSTANTS**

<table>
<thead>
<tr>
<th>Substituent</th>
<th>$A_{CH_3}$</th>
<th>$A_N$</th>
<th>$\sigma^+_{R}$**</th>
<th>$\sigma^1_*$</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(CH$_3$)$_2$</td>
<td>6.83</td>
<td>7.01</td>
<td>-1.97</td>
<td>0.10</td>
<td>Taft</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>10.40</td>
<td>10.00</td>
<td>-1.03</td>
<td>0.25</td>
<td>Adams</td>
</tr>
<tr>
<td>NH$_2$</td>
<td>7.75</td>
<td>7.62</td>
<td>-1.67</td>
<td>0.10</td>
<td>Taft</td>
</tr>
<tr>
<td>NHCOCH$_3$</td>
<td>10.70</td>
<td>10.24</td>
<td>-0.84</td>
<td>0.24</td>
<td>Taft</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>12.22</td>
<td>11.17</td>
<td>-0.26</td>
<td>-0.05</td>
<td>Taft</td>
</tr>
<tr>
<td>F</td>
<td>12.95</td>
<td>11.68</td>
<td>-0.59</td>
<td>0.52</td>
<td>Taft</td>
</tr>
<tr>
<td>CHO</td>
<td>14.00</td>
<td>12.10</td>
<td>0.11</td>
<td>0.31</td>
<td>Taft</td>
</tr>
<tr>
<td>Si(CH$_3$)$_3$</td>
<td>12.50</td>
<td>11.50</td>
<td>0.141***</td>
<td>-0.12</td>
<td>This work</td>
</tr>
<tr>
<td>C(CH$_3$)$_3$</td>
<td>12.31</td>
<td>11.35</td>
<td>-0.186</td>
<td>-0.07</td>
<td>This work</td>
</tr>
</tbody>
</table>


**$\sigma^+_{R} = \sigma^+ - \sigma_1$**

Fig. 2--Relationship between $A_{CH_3}$, and $\sigma^+$: ordinate, $A_{CH_3}$, gauss; abscissa, $\sigma^+$. 

$\cdot$ CH$_2$C(CH$_3$)$_3$  
$\cdot$ Si(CH$_3$)$_3$  
$\cdot$ NHCOCH$_3$  
$\cdot$ OCH$_3$  
$\cdot$ NH$_2$  
$\cdot$ N(CH$_3$)$_2$
Fig. 3—Relationship between $A_N$ and $\sigma^+$: ordinate, $A_N$, gauss; abscissa, $\sigma^+$. 
During the electrolysis of the silyl compound, the solution turned from colorless to Wurster blue (1) as a secondary spectrum was generated and developed, and the Wurster blue cation was identical to the one of N,N,N',N-tetramethylbenzidine (7). Three compounds, N,N-dimethylaniline, p-bromo-N,N-dimethylaniline and sodium p-N,N-dimethyl-aminobenzoate, all gave identical spectra when oxidized, which were reported by Adams (3) and Taft (4). The spectrum of the Wurster blue cation was not observed from the electrolysis of p-t-butyl N,N-dimethylaniline, showing that the bond between the t-butyl group and the aromatic ring is not cleaved as easily as the silyl compound by oxidation.

The anodic oxidation of Ph₃N in various nonaqueous solvents proceeds via formation of the triarylamine cation radicals Ph₃N⁺ which couple readily to give the corresponding substituted N,N,N',N-tetraphenylbenzidine (TPB). The cation radical TPB⁺ is quite stable, and it is this radical ion species which accumulates in solution on oxidation of Ph₃N (2).

Adams et al. (1) proposed that the overall reaction scheme is as follows:
Generally speaking, this process is of the electron transfer-chemical reaction-electron transfer (ece) type. By similar means, we propose the N,N,N',N'-tetramethylbenzidine was formed by the following mechanism:
The cation dimerizes (couples) or reacts with the parent rapidly to form N,N,N',N'-tetramethylbenzidine. This is accompanied by the loss of two trimethylsilyl groups per dimer, but it has not been ascertained if the silyl group loss occurs before or after coupling. The fate of the trimethylsilyl group is not presently known. The chemical follow-up reaction product, tetramethylbenzidine, is more easily oxidized than the starting material, trimethylsilyl-N,N-dimethylaniline, and undergoes further oxidation at the applied potential.

Summary

The ESR spectra of the radical cations of p-trimethylsilyl-N,N-dimethylanilene and p-tert-butyl-N,N-dimethylaniline were obtained and interpreted. The spin densities, related to the hyperfine coupling constants using the McConnell relationship, give the first example in which a resonance effect involving interaction between a silicon d orbital and the aromatic π system appears to be more important than the inductive effect of silicon. The results are consistent with the ultraviolet spectra of the compounds which show a hypsochromic shift for the n → π* transition and a bathochromic shift for the π → π* transition for the silyl compound in comparison with its carbon analog.
The silyl radical cation was found to give rise to a secondary ESR spectrum, identified as the radical cation of N,N,N',N'-tetramethylbenzidine, and a path is proposed for its formation.


Fig. 4-1--Experimental ESR spectrum of the radical cation of \( p \)-trimethylsilyl-
N,N-dimethylaniline.
Fig. 4-2—Simulated ESR spectrum of the radical cation of \( p \)-trimethylsilyl-\( N,N \)-dimethylaniline.
Fig. 4-3---Secondary ESR spectrum of the radical cation of p-trimethylsilyl-N,N-dimethylaniline.
Fig. 4-4--Simulated ESR spectrum of the radical cation of N,N,N',N'-tetramethylbenzidine.
Fig. 4-5--Experimental ESR spectrum of the radical cation of para-tert-butyl N,N-dimethylaniline.
Fig. 5-1—Infrared red spectrum of p-trimethylsilyl-N,N-dimethylaniline.
Fig. 5-2. Infrared red spectrum of Para-tert-butyl N,N-dimethylaniline.
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