# Lewis Acid Catalyzed Rearrangements of Nitroxide Radicals

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The interaction of nitroxide radicals with the Lewis acids, aluminum chloride and boron trifluoride has been investigated using e.s.r. and n.m.r. techniques. Three types of reaction have been demonstrated. Initially a paramagnetic complex with the nitroxide group is formed. This can then dimerize or polymerize to a diamagnetic complex. Concurrently rearrangement of *t*-butyl groups to *s*-butyl groups can occur giving a further series of radicals and complexes. The rearrangements are analogous to the well known carbonium ion rearrangements induced by Lewis acid catalysts. Relative equilibrium constants and rates for the various reactions are discussed in a qualitative manner.

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On a examiné, utilisant les techniques de la r.p.e. et de la r.m.n. les interactions entre les radicaux nitroxydes et des acides de Lewis tels que le chlorure d'aluminium et le trifluorure de bore. On a mis en évidence trois types de réactions. Au début un complexe paramagnétique se forme avec le groupe nitroxyde. Celui-ci peut alors se dimériser ou se polymériser pour former un complexe diamagnétique. Concurremment des réarrangements des groupes *tertio*-butyles en groupes butyles secondaires peuvent se produire donnant naissance à une nouvelle série de radicaux et de complexes. Les réarrangements sont semblables à ceux, bien connus, que subissent les carbocations sous l'influence de catalyseurs acide de Lewis. On discute, d'une façon qualitative, des constantes d'équilibre et des vitesses relatives des diverses réactions.

[Traduit par le journal]

## Results

In a previous paper (1) we reported the synthesis and use of certain radicals as spin labelled ligands. In particular, interactions of a molecule in which a pyridine moiety acted as the Lewis base and a *t*-butyl nitroxide group provided the spin label were studied with a variety of metal compounds. In the large majority of cases the resulting e.s.r. spectrum could be interpreted in terms of complexing of the pyridine nitrogen with the metal. In the case of the strong Lewis acids  $AlCl_3$  and  $BF_3$  we obtained e.s.r. spectra which could not be readily interpreted along these lines. It seemed possible that with strong Lewis acids interaction with the oxygen of the nitroxide group was occurring. Electron spin resonance studies of such complexes have indeed been reported (2-4) but their relevance to the interpretation of the spectra mentioned above was not clear. We have therefore further investigated the reactions of several nitroxide radicals with strong Lewis acids. In the course of these studies it became apparent that some of the e.s.r. spectra observed did not arise from the nitroxide radical introduced into the system. The present paper therefore presents evidence for Lewis acid catalyzed rearrangements of nitroxide radicals.

Introduction

The radical initially used in these studies has the structure  $\mathbf{1}$ 

# $N = N - C(CH_3)_3$

In the presence of AlCl<sub>3</sub> an e.s.r. spectrum consisting of 14 broad lines is obtained. In the presence of BF<sub>3</sub> the spectrum is essentially similar except that an additional quartet splitting with intensity ratios 1:3:3:1 is observed. This can be reasonably assigned to the fluorine atoms. This latter spectrum is shown in Fig. 1 and the former in Fig. 5A. These spectra are anomalous in two respects: (a) we were unable to find a reasonable combination of coupling constants which, allowing for overlapping lines, would reproduce the observed spectrum. The basic problem is that radical 1 should give a spectrum with an odd number of lines whereas the observed spectra clearly have an even number of lines; (b) the e.s.r. spectra are much weaker than those obtained with other metal complexes and the spectrum decays with time. Other complexes seem quite stable. In order to clarify these results the



FIG. 1. Electron spin resonance spectrum of 4-pyridyl-*t*-butyl nitroxide radical in 1,4-dioxane/THF mixture in the presence of excess  $(C_2H_5)_2OBF_3$ .

spectrum of the simpler radical 2 was investigated in the presence of BF<sub>3</sub> and AlCl<sub>3</sub>. In this case only complexing with the oxygen of the nitroxide group is possible

$$(CH_3)_3 C - N - C (CH_3)_3$$

$$| O$$
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The e.s.r. spectrum comprises a simple triplet which is shown in Fig. 2A. Eames and Hoffman (4) have described the preparation of complexes of this radical with BF<sub>3</sub> using a technique of distilling excess BF<sub>3</sub> into a solution of the radical in toluene. In order to duplicate the conditions used to obtain the spectrum of Fig. 1 a rather different approach was adopted. Initially a solution of the diethyl ether addition compound of boron trifluoride in 1,4-dioxane was added incrementally to a solution of radical 2 in the same solvent. It was observed that the e.s.r. spectrum of radical 2 decreased in intensity with the addition of  $BF_3$ but that a new weaker spectrum appeared. This second spectrum consists of three triplets and is shown in Fig. 2B. With a large excess of  $BF_3$  this latter spectrum also disappeared. The original spectrum with approximately its original intensity can be regenerated by adding triethylamine to the final solution. Presumably triethylamine, a strong base, preferentially complexes with the BF<sub>3</sub> and restores the status quo. The rate of reaction of di-t-butyl nitroxide with BF<sub>3</sub> appears to be relatively slow since the intensity of the e.s.r. signal



FIG. 2. (A) Electron spin resonance spectrum of di-*t*butyl nitroxide radical in 1,4-dioxane. (B) Electron spin resonance spectrum obtained by adding excess  $(C_2H_5)_2OBF_3$  to di-*t*-butyl nitroxide in 1,4-dioxane.

continues to fall for some time after an aliquot of the  $BF_3$ /ether solution is added. In the experiments in which triethylamine was added to the solution with excess BF<sub>3</sub> no regeneration of the second e.s.r. spectra was observed but since radical 2 is much more intense than the second spectrum the latter may still be present. It seemed likely that the solution with excess BF<sub>3</sub> was diamagnetic. This was confirmed by measuring the magnetic susceptibility using the n.m.r. method. The susceptibility falls from  $\sim 1.45$  B.M. to zero on adding  $BF_3$ /ether solution. As expected this solution also gave a sharp line n.m.r. spectrum shown in Fig. 3A. This proton spectrum shows the CH<sub>2</sub> and CH<sub>3</sub> groups of the diethyl ether and an additional intense peak assigned to the *t*-butyl protons originating from radical 2. A number of weaker peaks in the methyl region are also apparent indicating that a mixture of diamagnetic species is probably formed. The ether chemical shifts have reverted from their positions in the  $BF_3$ /ether complex (Fig. 3B) towards the positions found for free ether (Fig. 3C) confirming that the reaction proceeds by displacement of the ether of the  $BF_3$ /ether complex.

Similar experiments were carried out with AlCl<sub>3</sub>. In this case it proved more convenient to use tetrahydrofuran as a solvent. The e.s.r. results were exactly analogous to those with BF<sub>3</sub> including the observation of the spectrum of Fig. 2B. However some further information resulted from an attempt to examine the e.s.r. spectra in  $CCl_4$ . An excess of  $AlCl_3$  was added to a solution of the radical in  $CCl_4$ . A yellow precipitate appeared immediately. After decanting the CCl<sub>4</sub> this precipitate was found to be soluble in benzene. On standing the solution separated into two layers the upper layer being yellow in color and the lower layer deep red. The yellow solution was found to be diamagnetic but the red solution gave the e.s.r. spectrum shown in Fig. 4. This spectrum has 18 lines of equal intensity and can be readily analyzed on the basis of a <sup>14</sup>N hyperfine coupling constant of 20.1 G and a  ${}^{27}Al(I =$ 5/2) hyperfine coupling constant of 11.5 G. It is

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FIG. 3. 100 MHz n.m.r. spectra of benzene solutions containing (A) di-t-butyl nitroxide and excess  $(C_2H_5)_2$ -OBF<sub>3</sub>; (B)  $(C_2H_5)_2$ OBF<sub>3</sub>; (C)  $(C_2H_5)_2$ O.

in fact the spectrum of the AlCl<sub>3</sub> complex reported by Eames and Hoffman (4). The significant observation is that reaction with AlCl<sub>3</sub> leads to two products only one of which is paramag-

netic. It is reasonable to assume the formation of a complex between the Lewis acid and the free radical is the initial reaction and that rapid precipitation from  $CCl_4$  has enabled us to isolate this intermediate. The  $AlCl_3$  complex has only limited stability in benzene since the spectrum disappears in 45–60 min.

There remains the question of the assignment of the spectra shown in Figs. 1 and 2B. The possibilities in the second case are quite limited. It is obviously a nitroxide radical showing hyperfine coupling with the nitrogen and two additional nuclei of spin 1/2. The latter can only be protons. Protonation of di-t-butyl nitroxide has been reported (5). The proton is located on the oxygen atom and gives rise to a hyperfine coupling of 3.3 G. However this would only account for coupling with one proton and it is accompanied by a large increase in the <sup>14</sup>N coupling constant. We observe coupling with two protons and a decrease in the <sup>14</sup>N coupling. Coupling to protons on the carbon adjacent to the nitrogen is therefore suggested. The observed couplings to a  $CH_2R_1$ group in this position vary from 8-10 G (6) whereas those for CHR<sub>2</sub> groups are in the range 3-4 G (6). A value of 3.6 G is found in this case. These arguments suggest the di-s-butyl nitroxide radical 3.



The e.s.r. spectrum of this radical has been reported in the literature (7). The reported coupling constants  $a_N = 13.4$  G and  $a_H = 3.8$  G (obtained in benzene) agree satisfactorily with those found in the present experiments,  $a_N = 13.2$  G and  $a_H = 3.62$  G (obtained in dioxane). No other assignment of the radical seems plausible.

By analogy the spectra obtained with the pyridine nitroxide radical 1 might be expected to be derived from 4.



This radical has not been reported previously and it was therefore synthesized by the reaction of  $\gamma$ -nitropyridine with *s*-butyl magnesium chloride. It was obtained only in low yield and the in-

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FIG. 4. Electron spin resonance spectrum of di-t-butyl nitroxide AlCl<sub>3</sub> complex in benzene.



FIG. 5. (A) Electron spin resonance spectrum of 4-pyridyl-*t*-butyl nitroxide in the presence of excess  $AlCl_3$  in 1,4-dioxane. (B) Electron spin resonance spectrum of 4-pyridyl-*s*-butyl nitroxide in the presence of  $ZnCl_2$  in 1,4-dioxane.

completely resolved spectrum cannot be analyzed in detail. The nitrogen coupling constant of 9.4 G can however be readily picked out and assigned to the nitroxide group. Some difficulty was experienced obtaining reasonable spectra of this radical in the presence of metal compounds since the initial radical spectrum is relatively weak. A fairly well resolved spectrum was however obtained with zinc chloride. This spectrum proved to be virtually identical to that obtained initially with radical 1 and AlCl<sub>3</sub>. The two are shown together in Fig. 5. In both cases the nitrogen hyperfine coupling constant has been reduced to 8.3 G as expected for metal complexing on the pyridine nitrogen. We therefore assign spectrum 5A to

and spectrum 1 to the analogous  $BF_3$  adduct with some confidence. Both spectra can be reasonably analyzed on this basis since an even number of lines is predicted. The coupling constants obtained from the various spectra discussed in this section are gathered together in Table 1.

### Discussion

It is apparent that strong Lewis acids can interact with nitroxide radicals in several ways. The present studies provide evidence for three different reactions namely: (1) the formation of paramagnetic adducts of the type reported by Eames and Hoffman (4); (2) the formation of diamagnetic adducts presumably involving dimers or polymers of the radical;<sup>1</sup> (3) rearrangement of the alkyl groups to give different radicals.

The third type of reaction is established by the identification of e.s.r. spectra arising from radicals containing s-butyl groups. We considered the possibility that such radicals might have been present as impurities in the original t-butyl radicals. Samples of di-t-butyl nitroxide were examined very carefully to check this possibility. Several of the lines of the s-butyl radical occur in positions well away from the e.s.r. lines of the tbutyl radical. No signs of absorption at these frequencies could be observed. In the spectra used the <sup>15</sup>N satellites of di-*t*-butyl nitroxide were observed with a signal-to-noise ratio better than  $10:1.^{15}$ N has a spin of 1/2 and an isotopic abundance of 0.365%. Each line therefore corresponds to an abundance of 0.18%. We deduce therefore

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<sup>&</sup>lt;sup>1</sup>It has been reported that 2,2,6,6-tetramethylpiperidine nitroxide can be oxidized to give a diamagnetic compound  $[TMPN^+ \equiv O]_2 SnX_6^{2-}$  by reaction with Sn(IV) halides (14). Since neither BF<sub>3</sub> nor AlCl<sub>3</sub> is an oxidizing agent an analogous explanation of the diamagnetism observed in the present reactions seems unlikely.

|                   |                              |                   |                              |                               |                   |                             |                 | -R.  | \$\$\$ \$\$\$ \$\$\$ \$\$\$ \$\$\$ \$\$\$ \$\$\$ \$\$\$ \$\$\$ \$ |
|-------------------|------------------------------|-------------------|------------------------------|-------------------------------|-------------------|-----------------------------|-----------------|--|---|
|                   |                              |                   |                              |                               |                   |                             |                 |  | *In benzene.<br>†Reference 7.                                     |
|                   |                              |                   |                              | olved                         | Not reso          | -                           | 9.4             |  | (Py)—N—(s-Bu) + —<br>—<br>O·                                      |
| l                 |                              | l                 | _2<br>∕                      | Not<br>observed               | ∕                 | $\widetilde{}$              | 8.5             | $Cl_2Zn \leftarrow N \xrightarrow{(n-1)} N^{(s-Bu)}$ | $(Py) - N - (s-Bu) + ZnCl_2$<br>O                                 |
| ~0.5              | Not<br>observed              | ł                 | _2<br>∕                      | Not<br>observed               | <sup>7</sup><br>∕ | 27<br>22                    | 8.3             | $F_3 B \leftarrow N $                                | $(Py)-N-(l-Bu) + BF_3$  |
| 1                 | I                            | Not<br>observed   | <sup>2</sup>                 | Not<br>observed               | 2                 | <b>5</b><br>∽               | 8.3             | $CI_3AI \leftarrow N \swarrow N (s-Bu) O$            | $(Py)-N-(t-Bu) + AICI_3$  |
| $a^{\mathrm{F}}$  | a <sup>B</sup>               | a <sup>AI</sup>   | a <sub>ch</sub> <sup>H</sup> | a <sub>5,7</sub> <sup>H</sup> | $a_{4,8}^{H}$     | a <sub>6</sub> <sup>N</sup> | a2 <sup>N</sup> | Radical<br>product                                   | Original + Lewis<br>radical + acid                                |
|                   |                              | nstants (G)‡      | upling co                    | Hyperfine cou                 | н                 |                             |                 | Dadical  | Original Lewis  |
|                   | 1                            | 15.2              |                              |                               |                   |                             |                 |  | (t-Bu) <sub>2</sub> NO <sup>·</sup> +                             |
|                   | 3.84†                        | $13.39_{1}^{+}$   |                              |                               |                   |                             |                 | -  | $(s-Bu)_2NO' +$   |
| 11.5              |                              | 20.1              |                              |                               |                   |                             |                 | $(t-Bu)_2 N\dot{O} \rightarrow AlCl_3^*$             | $(t-Bu)_2NO^{-} + AICI_3$   |
| ł                 | 3.62                         | 13.2              |                              |                               |                   |                             |                 | (s-Bu) <sub>2</sub> NO                               | $(t-Bu)_2NO^{-1} + AICI_3$  |
|                   | 3.62                         | 13.2              |                              |                               |                   |                             |                 | (s-Bu) <sub>2</sub> NO                               | $(t-Bu)_2NO^\circ + BF_3$   |
| $a^{\mathrm{AI}}$ | a <sub>CH</sub> <sup>H</sup> | a <sub>NO</sub> N |                              |                               |                   |                             |                 | product  | Original radical + MX <sub>3</sub>                                |
| stants (G)        | oupling cons                 | Hyperfine co      |                              |                               |                   |                             |                 | Radical  |   |
|                   |                              |                   |                              |                               |                   |                             |                 | •  |   |

TABLE 1. Radicals produced by the reaction of nitroxides with AlCl<sub>3</sub> and BF<sub>3</sub> in 1,4-dioxane

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that any s-butyl impurity is present in a concentration of less than 0.03%. This is insufficient to account for the observed spectra.

It is reasonable that the initial reaction in each case is formation of an adduct with the Lewis acid, *e.g.* 

$$R_2NO + AlCl_3 \rightarrow R_2NO \rightarrow AlCl_3$$

Abakumov *et al.* (2) suggested that such adducts involved  $\pi$  bonding to the N—O bond but Hoffman and Eames (3, 4) and other authors (8) prefer a  $\sigma$  donor bond. The latter seems more reasonable. The electronic structure of such adducts can be discussed either in terms of valence bond or molecular orbital theory. In the former terms the radical has two principal contributing structures:

$$\begin{array}{cccc} \mathbf{R} - \mathbf{N} - \mathbf{R} & \mathbf{R} - \mathbf{N} - \mathbf{R} \\ & | & \text{and} & | \\ \mathbf{O} & \mathbf{O}^{-} \\ \boldsymbol{a} & \boldsymbol{b} \end{array}$$

Complexation with a Lewis acid greatly increases the contribution of **b**. This is manifested by a large increase in the <sup>14</sup>N hyperfine coupling constant, *e.g.*, from 15.2 to 20.1 G in the case of the aluminum chloride adduct with di-*t*-butyl nitroxide. In molecular orbital terms the effect of complexation may be represented by an increase in the coulomb integral of the oxygen and a Hückel calculation reproduces the increase in the N spin density quite satisfactorily. Eames and Hoffman (4) have considered the molecular orbital diagram in more detail and have calculated N spin densities from the equation

$$[1] a_{\rm N} = Q \rho_{\rm N}^{\ \pi} + q$$

where Q = 16.0 G and q = 7.2 G. We wish to suggest that the increased polarity of the N—O

bond provides a rationale for the subsequent reactions.

A possible reaction to give a diamagnetic species is

The Lewis acid must be involved in the diamagnetic complex since the n.m.r. experiments show that ether is no longer bound to  $BF_3$ . More than one radical could be complexed to  $AlCl_3$  but not to  $BF_3$ . The n.m.r. shows a single intense peak for the *t*-butyl group but this observation does not necessarily have structural significance since there may be exchange processes operative which are fast on the n.m.r. time scale. The weaker peaks could arise from higher polymers. Since nitroxide radicals show little or no tendency to dimerize in the absence of Lewis acids it seems reasonable to attribute the process to the enhanced dipole of the N—O bond which results from complexation.

Rearrangements of alkyl groups catalyzed by strong Lewis acids are well known. They frequently occur for example during the alkylation of benzene using the Friedel Crafts reaction with  $AlCl_3$  as a catalyst. Perhaps the most pertinent report is that of Roberts *et al.* (9) who observed the isotope position rearrangement of *t*-butyl chloride on treatment with  $AlCl_3$ . They proposed a carbonium ion mechanism with the secondary butyl carbonium ion acting as an intermediate, *i.e.* 

$$CH_{3} \xrightarrow{CH_{3}} CH_{3} \xrightarrow{CH_{3}} CH_{3} \xrightarrow{CH_{3}} CH_{3} \xrightarrow{CH_{3}} CH_{3} \xrightarrow{CH_{3}} CH_{2}CH_{2}CH_{3}$$

$$\Rightarrow CH_{3}CH_{2}CHCH_{3} \Rightarrow CH_{3} \xrightarrow{CH_{3}} CH_{3} \xrightarrow{$$

The existence of carbonium ions in solutions of alkyl halides with  $AlCl_3$  or  $BF_3$  seems to be uncertain. Thus Olah and Olah (10) referring to studies with *t*-butyl chloride comment on the basis of n.m.r. evidence that the shifts "could be

attributed only to weak-donor-acceptor complexes and not to carbonium ions." Alkyl fluorides and very strong Lewis acids such as SbF<sub>5</sub> unambiguously produce carbonium ions and the rearrangements of these ions have been directly studied by n.m.r. (11). In any event whether  $AlCl_3$  produces discrete carbonium ions or not it seems clear that its key function in catalyzing alkyl rearrangements is to withdraw charge from the carbon atom.

In the present case the e.s.r. data clearly show that complexation with AlCl<sub>3</sub> withdraws a substantial amount of charge from the nitrogen. The change in spin density calculated from eq. 1 suggests that this withdrawal amounts to approximately 1/3 of an electron. This effect will certainly be reflected in a more positive charge on the adjacent carbon. Rearrangement of the alkyl group can then proceed in a manner exactly analogous to that suggested by Roberts et al. (9) for *t*-butyl chloride except that only the first two steps are necessary. The present results do not provide any further evidence as to whether there is any carbonium ion intermediate. Any mechanism which suffices to explain the AlCl<sub>3</sub> catalyzed rearrangement of alkyl halides will suffice to explain the present rearrangement.

We therefore postulate the following reaction scheme to describe the interactions of Lewis acids with nitroxide radicals.

$$R_{2}NO + MX_{3} \stackrel{f}{\rightleftharpoons} R_{2}NOMX_{3} \stackrel{2}{\rightleftharpoons} (R_{2}NO)_{2n}(MX_{3})_{m}$$

$$\int 5$$

$$R_{2}'NO + MX_{3} \stackrel{3}{\rightrightarrows} R_{2}'NOMX_{3} \stackrel{4}{\rightleftharpoons} (R_{2}'NO)_{2n}(MX_{3})_{m}$$

The species observed depend on the equilibrium constants for these various reactions and the rates at which equilibrium is attained. The observations are consistent with the equilibrium constant for complex formation (reaction 1) being smaller in polar solvents such as dioxane than in nonpolar solvents such as benzene or toluene. The dependence of this equilibrium constant on solvent is demonstrated by the observation that the addition of DMSO to a diamagnetic di-t-butyl nitroxide/AlCl<sub>3</sub> solution in benzene leads to the regeneration of the di-t-butyl nitroxide e.s.r. spectrum. It also appears that reactions 1, 3, and 5 are fast but 2 and 4 are relatively slow and solvent dependent. Thus in 1,4dioxane the dimerization reaction is fairly fast and this factor, combined with the smaller equilibrium constant for complex formation, does not allow sufficient buildup of the intermediate paramagnetic complex to permit observation by e.s.r. In the less polar solvents the equilibrium is more favorable and dimerization is apparently much slower so that e.s.r. spectra of complexed radicals

are observed although they decay slowly with time. The same considerations apply to the isomeric s-butyl compounds. The latter differ however in the important respect that the overall equilibrium of reactions 3 and 4 is significantly further to the left than that of reactions 1 and 2. Thus under conditions in which sufficient AICl<sub>3</sub> has been added to convert di-t-butyl nitroxide completely to the diamagnetic dimer there is still sufficient di-s-butyl nitroxide present to give a reasonably intense e.s.r. spectrum. It is this latter factor which allows the isomerization to be observed in spite of the fact that the equilibrium concentration of the s-butyl-isomer is considerably less than that of the t-butyl isomer. We also infer that the isomer with one *t*-butyl and one s-butyl group has equilibrium constants similar to those of the di-t-butyl compound and is not observed for this reason.

Finally we turn to the original observations involving the pyridyl radical 1. The considerations here are similar but with the additional complication that complexing to the pyridine nitrogen can also occur. Apparently the addition to radical 1 of sufficient AlCl<sub>3</sub> or BF<sub>3</sub> to form the pyridine complex also suffices to completely dimerize the compound. The e.s.r. spectrum of the expected complex was therefore not observed. However a smaller amount of the s-butyl isomer has been formed by rearrangement, this is less susceptible to dimerization, and sufficient free radical is present to form a pyridyl complex. It is interesting to note that the e.s.r. characteristics of the radicals obtained by interaction of the Lewis acid with the pyridine nitrogen mirror those of complexes involving the nitroxide group. Thus with the BF<sub>3</sub> pyridine complex the coupling constant of the nitroxide nitrogen is reduced, <sup>19</sup>F coupling is observed but no <sup>11</sup>B coupling occurs. For the nitroxide complex the <sup>14</sup>N coupling is enhanced, <sup>11</sup>B coupling is quite large but <sup>19</sup>F coupling is absent. Assignment of the Lewis base site is therefore unambiguous.

# Experimental

The preparation of radical 1 has been described previously (1). Di-*t*-butyl nitroxide was obtained by a standard method (12) and purified by distillation (b.p.  $52-54^{\circ}$ C at 11 mm Hg pressure). Radical samples were degassed on a vacuum line before measuring the e.s.r. spectra. Aluminum trichloride was purchased from Baker and Adamson and boron trifluoride etherate from Matheson Coleman and Bell. Electron spin resonance spectra were obtained using a JEOL spectrometer operating at 9K MHz. It

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proved convenient to use di-*t*-butyl nitroxide as a calibration standard based on the line separations given by Faber *et al.* (13).

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