for 4 h. The solvent was removed under vacuum at low temperature, and the oily residue, consisting of a mixture of sulfur and amino derivatives, was purified through a Florisil column with *n*-pentane as an eluant.

After a first fraction, consisting of sulfur, 10% of diethyl ether in *n*-pentane was used as an eluant. The collected oil was composed of almost pure amino derivatives, and for compound **10** a distillation under vacuum was possible.

The acetylamino derivatives were prepared in a well-stirred diethyl ether mixture of acetyl chloride (1 equiv) and solid $K_2CO_3$ (1.5 equiv). After 4 h (TLC showed the absence of starting material), and the reaction mixture afforded a solid compound, which was crystallized from ligroin (bp 80–100 °C).

**2-(Acetylamino)-3,3′-bithienyl (15)** was obtained in 85% yield as a white solid, mp 113–115 °C (lit.[4] mp 110–115 °C).

**2-(Acetylamino)-2′,3-bithienyl (16)** was obtained in 83% yield as a white solid: mp 104–106 °C; NMR δ 8.04 (br s, 1, NH), 7.37–7.07 (m, 3, H-3′, H-4′, H-3′), 6.97 (d, 1, H-4 or H-5), 6.89 (d, 1, H-5 or H-4), 2.19 (s, 3, $CH_3$); $J(4,5)$ = 5.7 Hz; IR 3400 (NH), 1700 (>CO) $cm^{-1}$; mass spectrum, *m/e* 223 ($M^+$), 181. Anal. Calcd for $C_{10}H_9NOS_2$: C, 53.8; H, 4.06; S, 28.7. Found: C, 53.2; H, 4.24; S, 27.9.

**General Procedure for the Transformation of Azides 3–8 into Amino Derivatives 9–14. Reduction with Lithium Aluminum Hydride.** A suspension of hydride (1 g, 25 mmol) in dry ether (30 mL) was cooled to 0 °C, and the azidobithienyl (1 g, 5 mmol) in dry ether (20 mL) was added dropwise, maintaining the same temperature. The solution was stirred for 2 h after which it was allowed to warm to room temperature and was stirred at this temperature for 4 h (until TLC showed that no starting material was left). The mixture was cooled, and wet ether was added to destroy the excess of lithium aluminum hydride followed by cold distilled water to break up the complex. The resulting white solid was filtered off, and the filtrate was extracted with ether. The combined extracts were washed with water and dried, and the solvent was removed under vacuum. The oily residue was distilled under vacuum.

Yields and physical and IR data are collected in Table II.

**2-Amino-3,3′-bithienyl (10)** was prepared by the same procedure except that the suspension of hydride was cooled to 0 °C during the addition of a cooled (−20 °C) ethereal solution of azides. The reaction mixture was kept at this temperature for 2 h. The mixture was then allowed to warm slowly to room temperature and was stirred for an additional 2 h.

An attempt to reduce the 2-azido-2′,3-bithienyl (**8**) by the same procedure gave the corresponding amino compounds in low yield (32%).

**3-Amino-2,2′-bithienyl (9)**: NMR δ 7.19 (m, 1, H-5′), 7.11–6.97 (m, 2, H-3′, H-4′), 7.00 (d, 1, H-5), 6.57 (d, 1, H-4), 3.79 (br s, 2, $NH_2$); $J(4,5)$ = 5.3 Hz; mass spectrum, *m/e* 181 ($M^+$), 136. Anal. Calcd for $C_8H_7NS_2$: C, 53.00; H, 3.89; N, 7.72; S, 35.38. Found: C, 52.93; H, 3.86; N, 7.64; S, 35.28.

**2-Amino-3,3′-bithienyl (10)**: NMR δ 7.37–7.19 (m, 3, H-2′, H-4′, H-5′), 6.82 (d, 1, H-4), 6.47 (d, 1, H-5), 3.88 (br s, 2, $NH_2$); $J(4,5)$ = 5.4 Hz; mass spectrum, *m/e* 181 ($M^+$), 153, 136. Anal. Calcd for $C_8H_7NS_2$: C, 53.00; H, 3.89; N, 7.72; S, 35.38. Found: C, 52.98; H, 3.86; N, 7.69; S, 35.16.

**4-Amino-3,3′-bithienyl (11)**: NMR δ 7.40–7.18 (m, 3, H-2′, H-4′, H-5′), 7.09 (d, 1, H-5), 6.19 (d, 1, H-2), 3.80 (br s, 2, $NH_2$); $J(2,5)$ = 3.6 Hz; mass spectrum, *m/e* 181 ($M^+$), 136. Anal. Calcd for $C_8H_7NS_2$: C, 53.00; H, 3.89; N, 7.72; S, 35.38. Found: C, 53.22; H, 3.95; N, 7.58; S, 35.12.

**3-Amino-2,3′-bithienyl (12)**: NMR δ 7.40–7.20 (m, 3, H-2′, H-4′, H-5′), 7.01 (d, 1, H-5), 6.59 (d, 1, H-4), 3.53 (br s, 2, $NH_2$); $J(4,5)$ = 5.3 Hz; mass spectrum, *m/e* 181 ($M^+$), 136. Anal. Calcd for $C_8H_7NS_2$: C, 53.00; H, 3.89; N, 7.72; S, 35.38. Found: C, 52.91; H, 3.88; N, 7.69; S, 35.20.

**4-Amino-2′,3-bithienyl (13)**: NMR δ 7.30–6.97 (m, 3, H-2′, H-4′, H-5′), 7.15 (d, 1, H-5), 6.19 (d, 1, H-2), 3.65 (br s, 2, $NH_2$); $J(4',5')$ = 5.0 Hz, $J(3',4')$ = 3.6 Hz, $J(3',5')$ = 1.2 Hz, $J(2,5)$ = 3.3 Hz; mass spectrum, *m/e* 181 ($M^+$), 136. Anal. Calcd for $C_8H_7NS_2$: C, 53.00; H, 3.89; N, 7.72; S, 35.38. Found: C, 52.90; H, 3.85; N, 7.74; S, 35.16.

**2-Amino-2′,3-bithienyl (14)**: NMR δ 7.27–6.90 (m, 3, H-2′, H-4′, H-5′), 6.85 (d, 1, H-4), 6.49 (d, 1, H-5), 3.90 (br s, 2, $NH_2$). $J(4,5)$ = 5.6 Hz; mass spectrum, *m/e* 181 ($M^+$) 153, 136.

**Acknowledgment.** We thank Mrs. Ann Nordlund, Mrs. Kerstin Pettersson, and Mr. Einar Nilsson for technical assistance. Grants from the Swedish Natural Science Research Council to S.G. are gratefully acknowledged. P.Z. is grateful to CNR of Rome for a scholarship (No. 203.3.13), which made his stay in Lund possible.

**Registry No.** **1**, 82080-26-0; **2**, 82080-27-1; **3**, 82080-28-2; **4**, 82080-29-3; **5**, 82080-30-6; **6**, 82080-31-7; **7**, 82080-32-8; **8**, 82080-33-9; **9**, 82080-34-0; **10**, 74890-92-9; **11**, 82080-35-1; **12**, 82080-36-2; **13**, 82080-37-3; **14**, 60703-79-9; **15**, 74878-36-7; **16**, 82080-38-4; 3-bromo-4-iodothiophene, 73882-41-4; 3,4-dibromothiophene, 3141-26-2; (2-thienyl)copper, 5590-45-4; 2-bromo-3-iodothiophene, 24287-92-1; 4-bromo-3,3′-bithienyl, 28686-96-6; 2-bromo-3,3′-bithienyl, 82080-39-5; 3-bromo-2,3′-bithienyl, 28686-98-8; 3-bromo-2,2′-bithienyl, 19690-69-8; *p*-toluenesulfonyl azide, 941-55-9.

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# Behavior of *N*-*p*-Anisyl-*N*-*tert*-butylnitroxide in Nonaqueous Protic Acids

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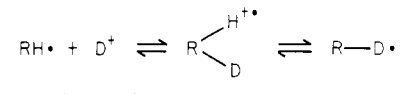
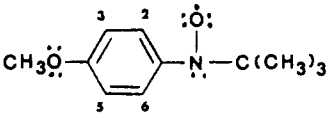
Recently, we[1] and others[2,3] have demonstrated that aryl carbocations will undergo an electrophilic substitution reaction with protons or deuterons in a nonaqueous acid medium. It occurred to us that aryl radicals should undergo a similar exchange reaction even more easily in these media. Clearly there are criteria which must be fulfilled before these reactions can be easily studied, especially by electron spin resonance (ESR) spectroscopy. First of all, the radical should be either long-lived (persistent) or, preferably, have an infinite lifetime. Secondly, the radical should be completely monomeric. If the radical were in equilibrium with a diamagnetic dimer, it would be difficult to tell which species is undergoing the substitution reaction. Finally, as many of the acids which are likely to be used in such a study are excellent oxidizing agents and many free radicals are easily oxidized, one must carefully match the radical with the acid.



We report at this time our work in this area on the radical *N*-*p*-anisyl-*N*-*tert*-butylnitroxide (**1**) which was



**1**

chosen for study because it possesses several desirable features. The nitroxide is monomeric and has an infinite lifetime.[4] The *tert*-butyl hydrogens yield a small or zero

(1) Pagni, R. M.; Smith, R. J. *J. Am. Chem. Soc.* **1979**, *101*, 506. (b) Smith, R. J.; Pagni, R. M *Ibid.* **1979**, *101*, 4769. (c) Pagni, R. M.; Smith, R. J.; Moore, T., Burnett, M. N. *Isr. J. Chem.* **1980**, *20*, 308.

(2) For reversible protonation of aryl cations, see: (a) Weiss, R.; Priesner, C. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 445. (b) Weiss, R.; Priesner, C.; Wolf, H. *Ibid.* **1978**, *17*, 446. (c) Olah, G. A.; Prakash, G. K. S.; Liang, G.; Westerman, P. W.; Kunde, K.; Chandrasekhar, J.; Scheyler, P. v. R. *J. Am. Chem. Soc.* **1980**, *102*, 4485. (d) Barltrop, J. A.; Barrett, J. C.; Carder, R. W.; Day, A. C.; Harding, J. R.; Long, W. E.; Samuel, C. J. *Ibid.* **1979**, *101*, 7510 and references cited therein.

(3) For irreversible protonation of carbocations, see: (a) Lammertsma, K.; Cerfontain, H. *J. Am. Chem. Soc.* **1980**, *102*, 3257. (b) Lammertsma, K. *Ibid.* **1981**, *103*, 1062.

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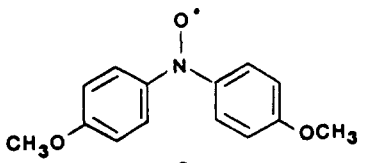
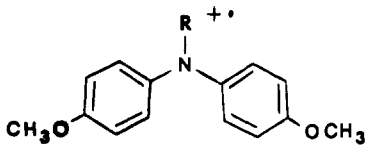
hyperfine coupling constant ($a_H$) which simplifies the compound's ESR spectrum. In the same vein, the placement of the two aryl substituents para to each other keeps the ESR spectrum simple. Placing the methoxyl group para to the nitroxide substituent also has two other advantages: (1) it prevents a destructive bimolecular reaction, which occurs so often for arylnitroxides lacking a para substituent;[4] (2) it activates the ring for electrophilic attack. Unfortunately, the activating ability of the nitroxide group is unknown. On the one hand, it might be activating because the substituent has a lone pair of electrons on the nitrogen while, on the other hand, it might be deactivating because of the electronegativity associated with its nitrogen and oxygen atoms. Thus, regardless of the effect of the nitroxide, the methoxy group should facilitate attack on the ring.

There are pitfalls in studying the chemistry of nitroxides by ESR spectroscopy. The chemistry of nitroxides is very complex and can take unexpected turns.[5] Identifying a reaction product by ESR spectroscopy should be done very cautiously. For example, treatment of bis(*p*-methoxyphenyl)nitroxide (2) with trifluoroacetic acid yields an ESR




2




3 (a) R=OH (b) R=H

spectrum which is consistent with the expected hydroxylamine radical cation **3a**,[6] The species is, in fact, the amine radical cation **3b**.[7] Note that both **3a** and **3b** have exactly the same number of ESR-active nuclei.

## Results and Discussion

Before description of the results it is pertinent at this time to discuss briefly what ESR will reveal about electrophilic protonation on 1 in nonaqueous protic acids. If no reaction occurs, of course, the ESR spectrum in the acid would be essentially the same as it is a neutral medium such as benzene or methylene chloride. If a very rapid exchange were to occur at C-3/5 or C-2/6, the ESR spectrum would simplify because the proton hyperfine coupling constants associated with the exchanging site(s) will disappear.[8] Irreversible protonation would likely result in a more complex spectrum because the new species will have one more ESR-active nucleus ($^1$H) than does 1, and the new species may have lower symmetry than 1. Finally, if the exchange reaction were slow, the ESR spectrum would not indicate this. Even here, ESR spectroscopy would be useful. If one now repeats the undetected reaction in the corresponding deuterio acid, 1 would incorporate deuterium onto the benzene ring. As deuterated 1 will have fewer $^1$H and more $^2$H than does undeuterated 1, the spectrum would change, hopefully in a predictable manner.

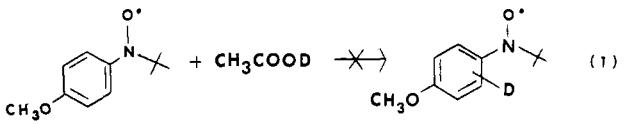
Table I. ESR Coupling Constants for 1 in Various Acids

| entry | solvent | coupling constants,[a] G $a_N$ | $a_{H\text{-}2/6}$ | $a_{H\text{-}3/5}$ |
|---|---|---|---|---|
| 1 | benzene | 13.2 | 1.8 | 0.9 |
| 2 | $CH_3COOH$ | 14.5 | 1.8 | 0.9 |
| 3 | $CH_3COOD$ | 14.5 | 1.8 | 0.9 |
| 4 | 1:1 $CHCl_2COOH$/ $CH_3COOH$ | 15.2 | 2.0 | 1.0 |
| 5 | 1:1 $CHCl_2COOD$/ $CH_3COOD$ | 15.2 | 2.0 | 1.0 |
| 6 | 1:10 $CF_3COOH$/ $CH_3COOH$ | 14.9 | 2.0 | 1.0 |
| 7 | 1:10 $CF_3COOD$/ $CH_3COOD$ | 14.8 | 2.0 | 0.9 |

[a] The coupling constants are accurate ±0.1 G.

The nitroxide 1 prepared in the standard way (see Experimental Section) in benzene yielded an ESR spectrum ($a_N$ = 13.2 G, $a_{H\text{-}2/6}$ = 1.8 G, $a_{H\text{-}3/5}$ = 0.9 G) in excellent agreement with that reported in the literature.[9] The spectrum of 1 dissolved in thoroughly degassed acetic acid ($pK_a$ = 4.75) was well resolved and unchanged in appearance from its spectrum in benzene. The only observed change was the increase in the $^{14}$N hyperfine coupling constant ($a_N$) from 13.2 G in benzene to 14.5 G in the acid (Table I). This increase is consistent with the observations of Hoffman and Eames[10] and of Malatesta and Ingold[11] and is generally attributed to the degree of hydrogen bonding between the nitroxide oxygen and hydrogen atoms on the solvent molecules.[4b]

The ESR spectrum of 1 in $CH_3COOH$ clearly shows no evidence for electrophilic aromatic substitution. If the reaction were occurring, it is very slow. To see if this slow exchange reaction were occurring, we repeated the above experiment in $CH_3COOD$ (eq 1). Even after 6 days at




1 1-d (1)

room temperature, there was no difference in the ESR spectrum when compared to the one in acid itself[12] (Table I). Thus, one can confidently say that electrophilic aromatic substitution does not occur in anhydrous acetic acid at room temperature.

Dissolution of 1 in the stronger acid $CHCl_2COOH$ ($pK_a$ = 1.36)[13] yielded only a very weak and broad ESR spectrum, even with high concentrations of 1. One explanation for this behavior is that 1 has been destroyed in dichloroacetic acid, while another explanation is that there

(4) (a) Nelsen, S. F. In "Free Radicals"; Wiley: New York, 1973; Vol. II, Chapter 21. (b) Forrester, A. R.; Hay, J. M.; Thomson, R. A. "Organic Chemistry of Stable Free Radicals"; Academic Press: New York, 1968.
(5) Aurich, H. G.; Weiss, W. *Top. Curr. Chem.* **1975**, *59*, 65.
(6) Hogeveen, H.; Gersmann, H. R.; Praat, A. P. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 1063.
(7) (a) Cauguis, G.; Serve, D. *Tetrahedron Lett.* **1970**, 17. (b) Neugebauer, F. A.; Bamberger, S. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 71.
(8) For a discussion of time-dependent phenomena and ESR, see: Wertz, J. E.; Bolton, J. R. "Electron Spin Resonance"; McGraw-Hill: New York, 1972; Chapter 9.
(9) (a) Petersen, J. A.; Torssell, K. *Acta Chem. Scand.* **1971**, *25*, 3151. (b) Goldman, J.; Petersen, T. E.; Torssell, K.; Becher, J. *Tetrahedron* **1973**, *29*, 3833.
(10) Hoffman, B. M.; Eames, T. B. *J. Am. Chem. Soc.* **1969**, *91*, 2169.
(11) Malatesta, V.; Ingold, K. U. *J. Am. Chem. Soc.* **1973**, *95*, 6404.
(12) Heating an acetic acid solution of 1 at 85 °C for 18 h destroyed the paramagnetic center. Thus, it was not possible to look for deuterium incorporation into 1 by heating the $CH_3COOD$ solution.
(13) The $pK_a$'s are ordinarily measured in $H_2O$. There should be a correlation between the acidity measured in $H_2O$ with that measured in the neat acid.

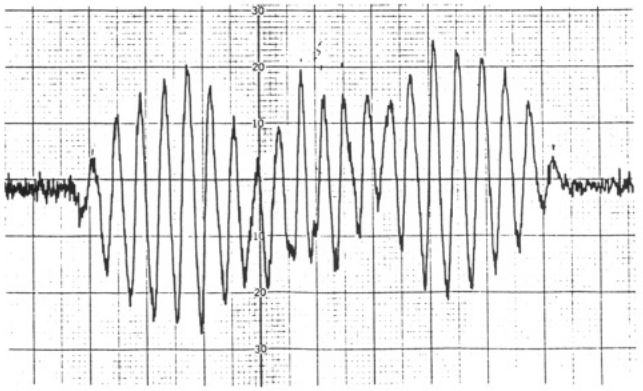
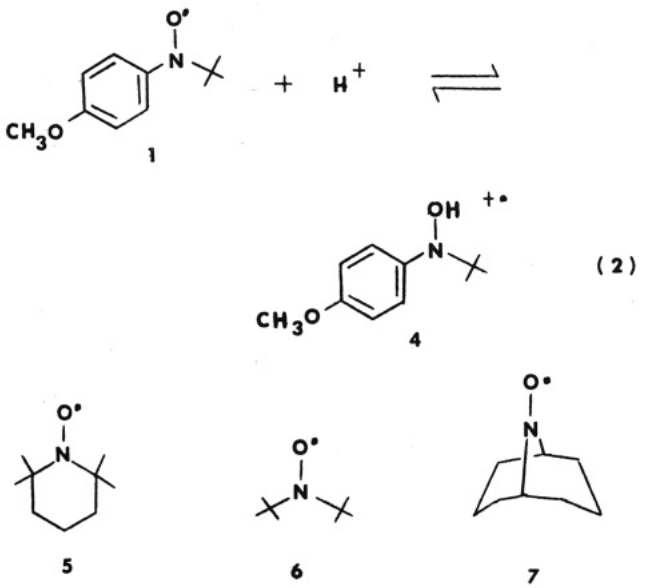


**Figure 1.** ESR spectrum of 1 in $CCl_2FCOOH$ immediately after sample preparation.

is excessive line broadening caused by a rapid exchange between 1 and a protonated form such as 4 (eq 2). Such



(2)

behavior has already been noted for 5–7.[11] If the latter explanation is correct, reduction of the acidity of the medium will shift the equilibrium in eq 2 to the left, and the ESR spectrum of 1 will reappear; increasing the acidity will shift the equilibrium to the right and yield the ESR spectrum of 4 or its equivalent. As shown below, this is what happened.

Dissolution of 1 in a 1:1 mixture of $CH_3COOH$ and $CHCl_2COOH$ which should have an acidity intermediate between the two carboxylic acids yielded a well-resolved spectrum of the neutral nitroxide (Table I). Dissolution of 1 in $CHCl_2COOD$ yielded, as with the solution in $CHCl_2COOH$, a very weak and broad ESR spectrum. When this solution was allowed to sit at room temperature for 2 h and then diluted 1:1 with $CH_3COOD$, the resulting ESR spectrum showed only the presence of 1 (Table I); there was also no evidence for the incorporation of deuterium onto 1. Thus, the nitroxide 1 survives, at least for 2 h, in dichloroacetic acid[14] and does not undergo electrophilic aromatic substitution.

A solution of 1 in $CCl_2FCOOH$ or $CF_3COOH$,[15] which

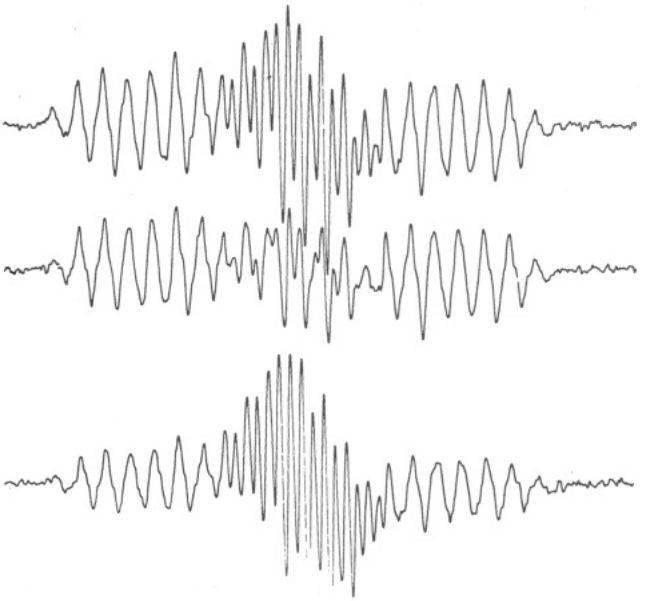


**Figure 2.** ESR spectra of 1 in $CF_3COOH$ as a function of time: middle spectrum, initial spectrum taken 15 min after sample preparation ($t$ = 15 min); top spectrum, $t$ = 26 min; bottom spectrum, $t$ = 38 min.

have $pK_a$ = 0.41 and 0.50, respectively, yielded an ESR spectrum consisting of 21 rather broad lines, with the smallest observable splitting being 2.2 G (Figure 1).[16] If the solution yielding this spectrum was immediately diluted 1:10 with $CH_3COOH$, the resulting solution yielded the ESR spectrum of 1 (Table I). Thus, whatever the new species is, the integrity of the molecular framework of 1 has been maintained.

The spectrum in $CF_3COOH$ was not static because within 10 min of sample preparation at room temperature; a new feature began to grow into the center of the spectrum. This new species appeared to have the same $g$ value as the original one but occupied approximately one-third its total width, and its smallest hyperfine coupling constant was close to 1 G. As this new feature began to grow in intensity, the original spectrum decreased until, after 3 days, only the new species could be detected (Figure 2).[17,18]

If the trifluoracetic acid solution was diluted with $CH_3COOH$ for periods up to 18 h after sample preparation, the spectrum of 1 could be regenerated; after 24 h, however, it could not. If 1 were dissolved in $CF_3COOD$[19] and

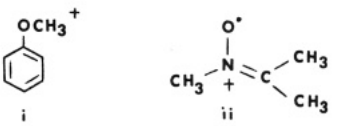
(14) When 1 is allowed to stand in $CHCl_2COOD$ for 24 h at room temperature and then diluted 1:1 with $CH_3COOD$, the ESR spectrum shows that 1 has been completely destroyed. A similar experiment in the protic acids yielded identical results.

(15) Most of the experiments were performed in the more readily available $CF_3COOH$. As best we could tell, the behavior of 1 in both acids was identical.

(16) The hyperfine coupling constants ($a_N$ = 13.6 G, $a_{H\text{-}2/6}$ = 4.2 G, $a_{H\text{-}3/5}$ = 2.1 G, and $a_H$ = 4.2 G) yield a spectrum which matches the experimental one nicely. As the lines are somewhat broad, we hardly claim that this solution is unique.

(17) A solution of 1 in triflic acid ($CF_3SO_3H$) yields an ESR spectrum which shows only this new feature, even at very short reaction times.

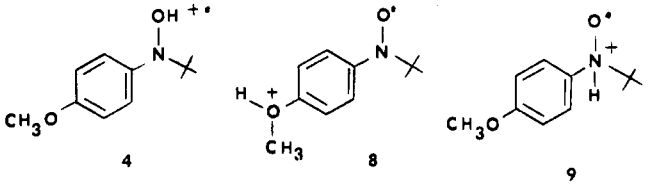
(18) We have been unable to identify the species produced in the irreversible reaction. Experiments suggest that it is a radical cation, but it is not either i or ii. See Smith, R. J., Ph.D. Dissertation, University of Tennessee, 1980, for details.



(19) The original spectrum in $CF_3COOD$ is more complex than it is in $CF_3COOH$. This clearly is due to the replacement of a unique H by a D. The smallest splitting in $CF_3COOD$ is ca. 0.6 G. If this is due to $a_D$, then $a_H$ for the unique hydrogen of the species in $CF_3COOH$ is ca. 4.2 G. The observed spectrum in $CF_3COOD$ matches closely that expected on the basis of the hyperfine coupling constants reported in ref 16, with the unique $a_H$ = 4.2 G being replaced by $a_D$ = 0.6 G.

then diluted 1:10 with $CH_3COOD$ after 2 and 18 h, the ESR spectrum of 1 was regenerated in both cases (Table I); there was no evidence of deuterium incorporated into 1. Thus, none of the phenomena observed in $CCl_2FCOOH$ and $CF_3COOH$ is associated with electrophilic aromatic substitution.

Clearly the original species in $CF_3COOH$ must be one of the three radical cations (**4**, **8**, or **10**) formed by pro-



tonation of one of the three heteroatoms belonging to **1**. Unfortunately, it is not possible with the present data to distinguish these possibilities unambiguously. The main point, however, is that the benzene ring of 1 is not protonated in $CF_3COOH$ or the weaker carboxylic acids.[20]

## Experimental Section

**Spectroscopy.** $^1H$ NMR spectra were recorded on a Varian T-60 spectrometer and IR spectra on a Perkin-Elmer 257 spectrometer.

Electron spin resonance spectra were recorded on a Varian 112 ESR spectrometer using 3-mm quartz tubes. The samples were degassed either by bubbling Ar or $N_2$ through the solution or by the freeze–pump–thaw technique.

Nitroxide samples were most often prepared by addition of a small amount (10–50 μL) of a concentrated solution in benzene to the solvent (ca. 2–3 mL) being used. Experiments demonstrated that traces of benzene made no difference in the ESR spectra.

***N*-(*p*-Methoxyphenyl)-*N*-*tert*-butylnitroxide (1).** *N*-(4-Methoxyphenyl)-*N*-*tert*-butylhydroylamine was prepared from (4-methoxyphenyl)magnesium bromide and 2-methyl-2-nitrosopropane[21] according to the procedure of Torssell and co-workers.[9b] The nitroxide was prepared by $Ag_2O$ oxidation of the hydroxylamine in benzene.[9b]

**Trifluoroacetic Acid-*d*.** Trifluoroacetic anhydride was prepared by cooling trifluoroacetic acid (50 mL) to 0 °C with stirring and adding $P_2O_5$ (50 g). The mixture was allowed to warm to room temperature, and the anhydride was removed by distillation through a short Vigreux column; bp 38–39 °C.

Trifluoroacetic acid-*d* was prepared in a flask equipped with a reflux condenser by cooling the anhydride (14.9 g, 0.07 mol) to 0 °C and adding (carefully!) $D_2O$ (1.4 g, 0.07 mol). **Caution**: this reaction is violent at room temperature. The mixture was allowed to warm to room temperature and then refluxed for 30 min. After the mixture cooled, the flask was equipped for distillation, and the acid was distilled through a short Vigreux column; bp 69.5–70 °C.

**Dichloroacetic Acid-*d*.** Dichloroacetic acid-*d* was prepared by the method of Greene and co-workers[22] (bp 97.5–98 °C/18 min). $^1H$ NMR showed 89% deuterium at the acid site.

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**Registry No.** 1, 3229-43-4; $CH_3CO_2H$, 64-19-7; $CH_3CO_2D$, 35223-87-1; $CHCl_2CO_2H$, 79-43-6; $CHCl_2CO_2D$, 82093-18-3; $CF_3CO_2H$, 76-05-1; $CF_3CO_2D$, 599-00-8; $CCl_2FCO_2H$, 354-19-8; $CF_3SO_3H$, 1493-13-6; *p*-methoxynitrosobenzene, 1516-21-8; *p*-nitrosophenol, 104-91-6.

(20) *p*-Methoxynitrosobenzene, a model for nitroxide 1, and *p*-nitrosophenol are not deuterated in $CF_3COOD$ at room temperature.
(21) Smith, R. J.; Pagni, R. M. *J. Org. Chem.* **1981**, *46*, 4307.
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# On the Lewis Acid Catalyzed Cyclocondensation of Silyloxy Dienes with α,β-Unsaturated Aldehydes

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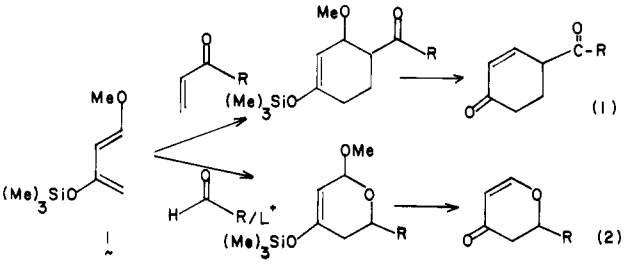
For some years we have investigated the thermal (i.e., noncatalyzed) Diels–Alder reactions of α,β-unsaturated carbonyl systems with siloxy dienes such as **1**.[1] Included among the dienophiles were α,β-unsaturated aldehydes (see eq 1).

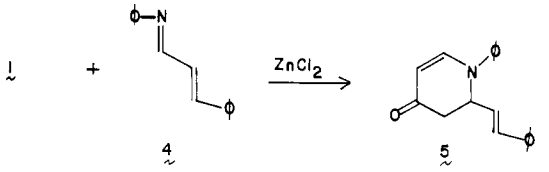


More recently we have discovered that a wide variety of aldehydes undergo "cyclocondensation" of the carbonyl linkage with diene 1 under very mild conditions under the influence of Lewis acid catalysis ($L^+$). Of the Lewis acid catalysts, the most extensively studied have been zinc chloride and boron trifluoride etherate (see eq 2).[2]

It was of interest to ascertain the effects of such catalysis on the reaction of diene 1 with α,β-unsaturated aldehydes. In particular we wanted to establish whether Lewis acid catalysis of "conventional" Diels–Alder reactions would now render the processes implied in eq 1 and 2 competitive.

A number of α,β-unsaturated aldehydes were subjected to Lewis Acid catalyzed reaction with diene 1 at -78 °C. The results are summarized in Scheme I. In no case could we discern product derived from addition to the carbon–carbon double bond (i.e., a classical Diels–Alder product).[3]

We have also extended the Lewis acid catalyzed cyclocondensation reaction of silyloxy diene 1 to include α,β-unsaturated imines.[5] Thus, reaction of imine **4** with diene 1 in the presence of zinc chloride gave adduct **5** in 41% yield. A new route to 2-vinyl-2,3-dihydro-4-pyridinones is thus opened. Further work in this area is continuing.



(1) Danishefsky, S.; Yan, C. F.; Singh, R. K.; Gammill, R. B.; McCurry, P. M., Jr.; Fritsch, N.; Clardy, J. *J. Am. Chem. Soc.* **1979**, *101*, 7001.
(2) Danishefsky, S.; Kerwin, J. F., Jr.; Kobayashi, S. *J. Am. Chem. Soc.* **1982**, *104*, 358. Danishefsky, S.; Kato, N.; Askin, D.; Kerwin, J. F., Jr. *Ibid.* **1982**, *104*, 360.
(3) Minor products from these reactions have been identified. They bear on the mechanism of the cyclocondensation reaction and will be discussed separately (Larson, Eric, unpublished results).
(4) A mixture of diasteromers in a 1:2 ratio (trans/cis) which was separated by HPLC on a Waters μ-Porasil column (7.8 mm i.d. × 30 cm) by using 5% ethyl acetate in hexane as elutant.
(5) We have also demonstrated the feasibility of this reaction with simple imines (Kerwin, J. F., Jr., unpublished results).

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