positive charge (electron deficient) on the C_4 position and a significant negative charge (electron sufficient) on the O_1 position.[12] The good correspondence of $(E_x - E_\phi)_{exptl}$ with $(E_x - E_\phi)_{calcd}$ ascertains the presence of the zwitterionic transition state.

The solvent effect on the rate constant is discussed. Mulzer and Zippel determined the decarboxylation rates of 1_{iii} in several solvents, for example, decalin, anisole, and formanilide.[3d] They obtained a satisfactory correlation of the rate constants with polarities of the solvents. The rate constant is large in polar solvents. Figure 6 shows the large localization of the positive and negative charges on the C_4 and O_1 positions, respectively, in the transition state. The transition state is stabilized by the Coulombic attraction between the cationic site of a polar solvent and the O_1 atom of the reactant. In addition, the zwitterionic nature of the transition state gives the large polarity of the reactant. Figure 5 shows the dipole moment of 2-oxetanone and the reacting system. The calculated dipole moment of 2-oxetanone at point A (3.862 D) is in good agreement with the observed one (4.174 D).[6] The dipole moment is found to be largest at the transition state (8.183 D). Therefore, the transition state is most stabilized by the long-range dipole–dipole interaction between solvent molecules and the reactant. Consequently, polar solvents make the activation energy small and the rate constant large by the Coulombic and dipole–dipole interactions. This analysis supports the finding by Mulzer and Zippel. Therefore, the solvent effect also ascertains the presence of the zwitterionic transition state.

Thus, the present calculation demonstrates that the reactivity of the thermal decarboxylation is determined by the extent of the $O_1 \cdots C_4$ polarity. The reaction rate is enhanced by the lowering of the activation barrier through the polarized transition state···solvent interaction.

Concluding Remarks

In this paper, the thermal decarboxylation mechanism for 2-oxetanones is investigated by the MNDO method. Although the energetics of the decarboxylation is not so accurate, the significant feature of this reaction is obtained. It is found that five heavy atoms of 2-oxetanones, three carbons and two oxygens, are preserved on the same plane in the essential part of the reaction. The decarboxylation is a one-step reaction with successive bond fission. First, the O_1–C_4 bond is broken at the transition state, and then the C_2–C_3 bond is broken. The transition state of the reaction has a largely polarized character, the extent of which is a crucial factor of the reactivity. The electron-donating substituent on the aryl of C_4 position enhances this polarity, which deserves both intramolecular ($O_1^{\delta-} \cdots C_4^{\delta+}$) Coulombic attraction and reactant–solvent interaction. The state correlation diagram demonstrates that the triplet spin state does not concern the thermal decarboxylation.

Acknowledgment. We thank the Computer Center, Institute for Molecular Science, for the use of the HITAC M-200H computer. We also express our gratitude to Miss Minako Hirata for her assistance in the MO calculation.

Registry No. 3i, 85005-04-5; **3ii**, 85005-05-6; **3iii**, 4287-98-3; **3iv**, 85005-06-7; **3v**, 85005-07-8; **3vi**, 35202-08-5; **4i**, 85005-08-9; **4ii**, 85027-94-7; **4iii**, 27150-91-0; **4iv**, 85005-09-0; **4v**, 85005-10-3; **4vi**, 85005-11-4.

(12) The charge distribution of 2-aminoethanoic acid ($NH_3^+CH_2COO^-$) is calculated by the MNDO method as an example of the ion-pair species. The calculated result shows that the electronic charge on the carboxylic oxygen is −0.57 and that on amino group is +0.63 (the charge on the nitrogen is only +0.05). In view of these values for the typical ion-pair molecule, we may say analogously that the transition state of the decarboxylation obtained here has a zwitterionic nature.

Reaction of *N*,*N*-Dimethylaniline Derivatives with Cumene Hydroperoxide. Oxazolidine Formation via Addition of α-Aminomethyl Radicals to Formaldehyde

Robert W. R. Humphreys

Loctite Corporation, Newington, Connecticut 06111

Received July 1, 1982

The reactions of *N*,*N*-dimethylaniline derivatives (**1**) with cumene hydroperoxide in acetonitrile at 100 °C produce significant amounts of the corresponding *N*-aryloxazolidine (**6**). Oxazolidine formation occurs by addition of α-aminomethyl radicals (**7**) to formaldehyde to give the alkoxy radical (**8**), followed by intramolecular 1,6 H-atom abstraction, oxidation, and cyclization. The results of labeling experiments and the dependence of the oxazolidine yield on the formaldehyde concentration support this mechanism. Alkoxy radical **8** was generated by an alternative route and does give the oxazolidine. Radical addition to the carbonyl carbon of formaldehyde is a reflection of the electron-rich, nucleophilic nature of the α-aminomethyl radical **7** and rapid trapping of the resulting alkoxy radical **8** via intramolecular H-atom abstraction through a six-membered transition state.

One of the characteristic reactions of alkoxy radicals is the β-scission to give a carbonyl compound and a new, usually carbon-centered radical.[1] The reverse of this process, addition of a radical to a carbonyl group to give an alkoxy radical, is rare and only a few examples can be found in the literature.[2] We now report that α-aminomethyl radicals, generated in the reaction of *N*,*N*-dimethylaniline derivatives with cumene hydroperoxide (CHP), add to formaldehyde at the carbonyl carbon to give

(1) (a) Walling, C. *Pure Appl. Chem.* **1967**, *15*, 69. (b) Kochi, J. K. In "Free Radicals"; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. 2, Chapter 3, p 683.

(2) (a) Rust, F. F.; Seubold, F. H.; Vaughan, W. E. *J. Am. Chem. Soc.* **1948**, *70*, 4253. (b) Fuller, G.; Rust, F. F. *J. Am. Chem. Soc.* **1958**, *80*, 6148. (c) Oyama, M. *J. Org. Chem.* **1965**, *30*, 2429. (d) Urry, W. H.; Nishihara, A.; Niu, J. H. Y. *Ibid.* **1967**, *32*, 347. (e) Bentrude, W. G.; Darnell, K. R. *J. Am. Chem. Soc.* **1968**, *90*, 3588. (f) Maruyama, K.; Taniuchi, M.; Oka, S. *Bull Chem. Soc. Jpn.* **1974**, *47*, 712. (g) Petryaev, E. P.; Skadyro, O. I.; Davidovich, P. N. *Zh. Org. Khim.* **1978**, *14*, 2488.

0022-3263/83/1948-1483$01.50/0

Table I. Product Yields (%) for Reaction of 1a-c with CHP

starting amine	1[a]	2	3	4	5	6
1a	45.8 ± 2.3[b]	19.1 ± 1.4	76.8 ± 3.0	19.7 ± 0.8	13.4 ± 1.0	4.6 ± 0.6
1b	36.2 ± 0.7	15.1 ± 1.3	85.3 ± 2.6	24.5 ± 1.4	10.9 ± 0.1	4.9 ± 1.0
1c	35.9	13.1	82.4	24.9	11.8	5.09

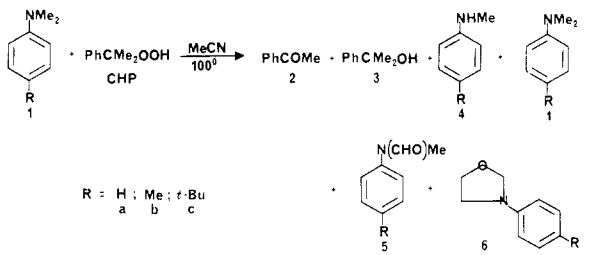
[a] Unreacted starting material. [b] Range of two or more individual experiments.

Table II. Product Yields (%) for Reaction of 1a-c with CHP, Paraformaldehyde Added

starting amine	1[a]	2	3	4	5	6
1a	53.5 ± 1.2[b]	19.9 ± 0.3	76.0 ± 0.1	3.2 ± 0.1	5.8 ± 0.3	11.0 ± 0.1
1b	45.3	13.9	77.5	5.96	5.82	10.2
1c	49.8	13.1	82.9	1.76	4.91	13.3

[a] Unreacted starting material. [b] Range of two or more individual experiments.

Scheme I



eventually the corresponding oxazolidine.

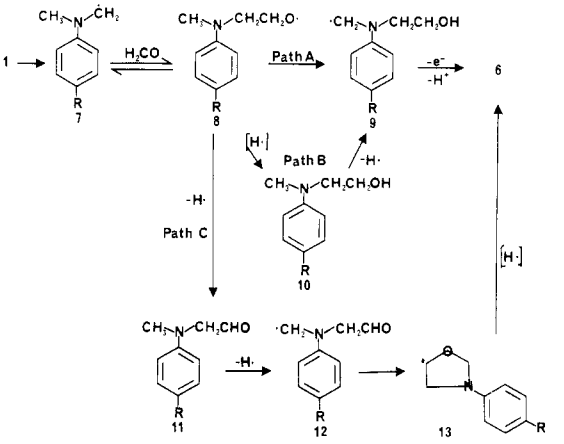
Reactions between **1a–c** and CHP were carried out in dilute (1 and CHP, 0.2 M each) acetonitrile solution in sealed tubes at 100 °C. In every case, the results of product analysis could be described by Scheme I. Product yields are listed in Table I. Of particular interest is the formation of significant amounts of the *N*-aryloxazolidine (**6**).

Oxazolidines **6** are produced in approximately the same yield from **1a–c**. The reaction appears to be sensitive to reagent purity; consistent yields of **6** could be obtained only with carefully purified reagents and treated glassware. (see Experimental Section for details).

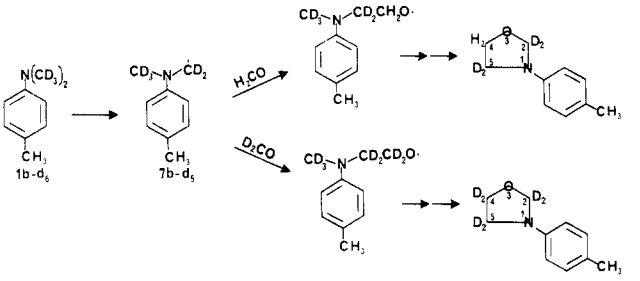
A mechanism that explains the formation of **6** and is consistent with previously reported chemistry of amines and hydroperoxides (vide infra) involves the addition of the α-aminomethyl radical **7** to formaldehyde to give **8** (Scheme II). Both **7** and formaldehyde are expected to be present during the reaction of **1** and CHP. Aldehydes are formed as coproducts during the dealkylation of amines by hydroperoxides.[3] The reactions of tertiary amines with hydroperoxides clearly involve a radical-chain mechanism[3c] and radicals such as **7** are expected under such conditions from good H-atom donors such as **1**.[4]

Oxazolidine formation from alkoxy radical **8** could take several paths. Path A could involve intramolecular H-atom abstraction through a six-membered transition state, a reaction for which there is ample precedent; oxidation and cyclization would give **6** directly. Path B could involve intermolecular H-atom abstraction by **8** to afford the amino alcohol **10**. H-atom abstraction from **10** would produce **9**, which gives **6** as in path A. Path C could lead to **6** via aldehyde **11**, generated from **8** by loss of an H atom. H-atom abstraction from **11** could furnish **12**; generalizations developed by Beckwith et al.[5] for radical cyclizations

Scheme II



Scheme III



allow one to predict the closure of **12** to **13**. H-atom abstraction would then furnish oxazolidine **6**.

When formaldehyde is deliberately added to the reaction mixture as paraformaldehyde (equivalent to 0.2 M formaldehyde) before thermolysis, the oxazolidine yield rises to ca. 10% (see Table II); an oxazolidine yield of 21% was obtained on addition of paraformaldehyde equivalent to 0.4 M formaldehyde. These results are consistent with more efficient trapping of radicals **7** by formaldehyde at higher concentration.

A small amount of amino alcohol **10** was identified in reaction mixtures by GC retention time and by GC/MS, while no evidence was found for the formation of aldehyde **11**. Amino alcohol **10b** does give oxazolidine **6b** on reaction with CHP in acetonitrile. However, competition experiments indicate that the reactivities of **10b** and **1b** with CHP are comparable. Therefore, the rate of oxazolidine formation by path A must be much greater than by path B under these conditions.

The results of labeling experiments supply further support for path A as the major route for oxazolidine formation. The thermolysis of a mixture of **1b**-d_6 and CHP

(3) (a) Capp, C. W.; Hawkins, E. G. E. *J. Chem. Soc.* **1953**, 4106. (b) De La Mare, H. E. *J. Org. Chem.* **1960**, *25*, 2114. (c) Hiatt, R. In "Organic Peroxides"; Swern, D., Ed.; Wiley-Interscience: New York, 1971; Vol. 2, Chapter 1, p 74–77.

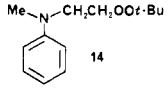
(4) Howard, J. A.; Yamada, T. *J. Am. Chem. Soc.* **1981**, *103*, 7102.

(5) Beckwith, A. L. J.; Easton, C. J.; Serlis, A. K. *J. Chem. Soc., Chem. Commun.* **1980**, 482.

under the usual conditions in the presence of protioparaformaldehyde should give a mixture of oxazolidines resulting from addition of **7**-d_5 to formaldehyde and formaldehyde-d_2 (produced in the reaction of **1b**-d_6 with CHP; see Scheme III). This experiment was carried out and the oxazolidine was isolated by preparative GC and analyzed by ^{1}H NMR, ^{13}C NMR, and GC/MS. GC/MS (chemical ionization) results indicated that several deuteriooxazolidines were present, with M + 1 peaks of 166, 168, and 170 amu. The ^{1}H NMR spectrum (60 MHz) of the isolated sample clearly showed that all oxazolidines were fully deuterated at position 5, and either D_2 or H_2 at positions 2 and 4. These results were confirmed by ^{13}C NMR spectroscopy; no evidence was found for mixed isotopic substitution at ring positions 2, 4, or 5.[6] Since the last step in the formation of **6** from **11** involves H abstraction by **13** (Scheme II), aldehyde **11** is effectively ruled out as a source of **6**. In the presence of **1b**-d_6 and protioformaldehyde, the step **13** → **6** should occur by deuterium-atom abstraction, leading to mixed isotopic substitution at position 4 of the oxazolidine ring.

The loss of deuterium from position 2 of **6b**-d_6 to give **6b**-2,2-H_2 occurs by a formaldehyde exchange process with protioparaformaldehyde and water, a product of hydroperoxide decomposition. Thus, it was shown in a separate experiment that *N*-phenyloxazolidine-2,2-d_2 readily exchanges formaldehyde at 100 °C in wet acetonitrile containing protioparaformaldehyde. Therefore, all of the labeling results are consistent with the addition of α-aminomethyl radical **7b**-d_5 to formaldehyde and formaldehyde-d_2 and subsequent reaction via Scheme II, path A, to give labeled **6b**.[7]

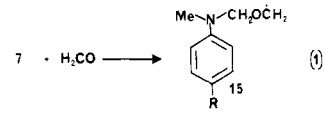
An important step in oxazolidine formation via path A involves the trapping of alkoxy radical **8** via intramolecular H-atom abstraction to give **9** (Scheme II). We have prepared peroxide **14**, which should give alkoxy radical **8a**



14

directly upon thermolysis. When **14** was thermalized in acetonitrile at 100 °C, only a small amount (5%) of oxazolidine **6a** was formed. However, the thermolysis of **14** is complicated by the formation of a caged radical pair that includes the *tert*-butoxy radical. Cage reaction is indicated by the formation of substantial amounts of aldehyde **11a**. Also, since oxazolidines are excellent H-atom donors,[8] it is possible that some of the initially formed **6a**, as well as **14**, undergo further reaction with *tert*-butoxy radicals under these conditions. In agreement with this hypothesis, thermolysis of **14** in acetonitrile containing **1b** or in toluene gave **6a** in 14% and 18% yields, respectively. Presumably, reaction of good H-atom donors **1b** or toluene with *tert*-butoxy radicals gives less reactive radicals, leading to higher yields of **6a** and less induced decomposition of **14**.

The addition of α-aminomethyl radical **7** to formaldehyde at the carbonyl carbon is exactly the reverse of the well-known alkoxy radical β-scission.[1] An alternative mode of addition of **7** to formaldehyde is shown in eq 1.



(1)

One might expect this mode of addition to predominate since radical **15** should be more stable than alkoxy radical **8**. However, there is clear precedent in the literature for addition of radicals to formaldehyde and other carbonyl groups at the carbonyl carbon.[2] Cyclohexyl and cyclopentyl radicals add to formaldehyde to give the corresponding carbinols.[2b] Urry et al.[2d] have reported that acyl radicals add to hexafluoroacetone at the carbonyl oxygen, while alkyl radicals add at the carbonyl carbon. Bentrude et al.[2e] have reported the addition of alkyl radicals at the carbonyl carbon of biacetyl and point out that the mode of addition to the carbonyl group may depend strongly on several factors, including the electronic character of the attacking radical and the reactivity of the radical resulting from addition. The latter is particularly important in determining the product distribution since both modes of addition may be reversible. In our case, rapid trapping of radical **8** via intramolecular 1,6 H abstraction undoubtedly accounts for significant yields of **6**.

The addition of **7** to formaldehyde at the carbonyl carbon is also a reflection of the nucleophilicity of this electron-rich α-aminomethyl radical. Indeed, it is now well-established that the electronic nature of a radical profoundly affects its reactivity toward H abstraction and addition to double bonds. Thus, while H abstraction from ring-substituted toluenes by alkoxy radicals exhibits large negative Hammett ρ values,[9] the analogous treatment of alkyl radicals results in positive ρ values.[10] The formation of alternating copolymers in the radical polymerization of mixtures of electron-rich and electron-poor olefins is at least partially a reflection of preferred attack of electron-rich, nucleophilic radicals on electrophilic olefins, and visa versa.[11] Similar constraints presumably apply to free-radical addition to the carbonyl group.

The other products derived from the reactions of **1a–c** with CHP (**2–4**) are consistent with the results of previous studies of reactions between hydroperoxides and tertiary amines.[3] The principal hydroperoxide-derived product is the corresponding alcohol, usually obtained in greater than 80% yield. Alkoxy radical products are also found, consistent with our observation of significant amounts of acetophenone from β-scission of the cumyloxy radical. The principal product from tertiary amines is that resulting from monodealkylation to give the dialkylamine and a carbonyl compound, which accounts for the formation of **4** and formaldehyde from **1**. We have little to add to the controversy that still surrounds the initiation mechanism for the reaction of amines with hydroperoxides.

About 20% of **1** could not be accounted for and probably involves the formation of products too nonvolatile to be observed under our GC conditions. The recovery of 35–40% unreacted **1** after complete consumption of CHP suggests the formation of amine products in higher oxidation states than that of **4**. Two such products are **5** and **6**. The formation of formamide **5** is interesting in that it apparently arises from the thermal decomposition of α-peroxy amine **16**. Thus, when reaction of **1b** with CHP

(6) For an excellent discussion of the application of ^{13}C NMR to the determination of the extent of deuteration of organic compounds, see: Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectrometric Identification of Organic Compounds", 4th ed.; Wiley: New York, 1981; Chapter 5, p 257.

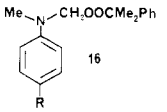
(7) Radical **9** could give amino alcohol **10** by H-atom abstraction from CHP or **1**. However, one-electron transfer from **9** to CHP apparently competes successfully to give the cumyloxy radical, hydroxide ion, and the anilinium ion, which should rapidly cyclize to **6**·H$^+$ (or **6** and H$^+$).

(8) Latypova, F. N.; Aleksandrov, A. L.; Zlot-skii, S. S.; Rakhmankulov, D. L. *Izv. Akad. Nauk., Ser. Khim.* **1970**, 1780.

(9) (a) Walling, C.; McGuinness, J. A. *J. Am. Chem. Soc.* **1969**, *91*, 2053. (b) Sakurai, H.; Hosomi, A. *Ibid.* **1967**, *89*, 458.

(10) Pryor, W. A.; Tang, F. Y.; Tang, R. H.; Church, D. F. *J. Am. Chem. Soc.* **1982**, *104*, 2885.

(11) (a) Walling, C. "Free Radicals in Solution"; Wiley: New York, 1957; Chapter 4, p 132. (b) Lenz, R. W. "Organic Chemistry of Synthetic High Polymers"; Wiley-Interscience: New York, 1967; Chapter 10, p 285.



16

was carried out in acetonitrile in a sealed NMR tube at 100 °C, the formation and subsequent disappearance of peroxide **16b** could clearly be observed. Addition of authentic **16b**[12a] to the reaction mixture after partial thermolysis caused an increase in intensity for all appropriate NMR peaks, confirming its formation. It has been reported previously that thermolysis of peroxides analogous to **16b** gives substantial amounts of the corresponding formamides.[12b] We suggest that **16** is formed by addition of CHP to the formaldehyde *N*-methylanilinium ion, generated from radical **7** by one-electron oxidation.

In conclusion, we have provided evidence for the addition of α-aminomethyl radicals of structure **7** to formaldehyde to give the alkoxy radical **8**. The addition is presumably reversible, but **8** is trapped by intramolecular 1,6 H abstraction to give, eventually, the corresponding oxazolidine. The addition is a reflection of the reactivity of formaldehyde and the nucleophilic nature of the electron-rich α-aminomethyl radical.

Experimental Section

GC analyses were performed with a Perkin-Elmer 3920B FID instrument modified with a capillary attachment. A 50-m OV-17 glass capillary column was used for all GC analyses. HPLC analyses were carried out with a Perkin-Elmer Series 3B LC equipped with both refractive index and UV detection. All chromatographic data (GC and HPLC) were analyzed with a Perkin-Elmer Sigma 10 Data Station. Most ^{1}H NMR spectra were recorded on a Varian EM-360 60-MHz spectrometer. A Bruker WM-250 spectrometer was used for some ^{1}H NMR spectra and all ^{13}C NMR spectra (62.8 MHz). All NMR spectra were obtained in chloroform-*d* containing Me_4Si as an internal standard. Infrared spectra were recorded on a Nicolet MX-1 FT-IR spectrometer. GC/MS data were obtained with a Hewlett-Packard 5985 GC/MS system.

Purification of Materials. Most compounds used in this study were commercial materials or were prepared by standard synthetic methods, unless noted otherwise.

N,N-Dimethylaniline derivatives were purified by a procedure described elsewhere[13] and were >99% pure as determined by GC. HPLC-grade acetonitrile was distilled from calcium hydride under argon. Cumene hydroperoxide was purified by very careful fractional vacuum distillation; the best fraction from a preliminary distillation was redistilled. The best fraction from the second distillation was usually >97% pure with cumyl alcohol as the only impurity. Cumene hydroperoxide purity was determined by HPLC with a 10-μm RP CN Waters 30 cm × 0.46 cm column run in reverse phase with gradient elution (10–90% acetonitrile–water, 10 min, slope 2, 2 mL/min, back pressure 8.2 mPa, 254-nm detection).

All glassware used in the distillations described above and in the thermolysis experiments was treated beforehand with 0.25 M aqueous Na_4EDTA, followed by repeated rinsing with deionized water and oven drying. Such treatment of distillation and thermolysis glassware should reduce the chance of metal contamination.

Thermolysis Experiments. Thermolysis experiments were carried out in sealed glass (Carius) tubes in a thermostatically controlled oil bath at 100 °C for at least 48 h unless noted otherwise. Thermolysis solutions were usually 0.2 M in amine and hydroperoxide. Formaldehyde was added as solid paraformaldehyde. Typically, a reaction mixture was prepared in the appropriate volumetric flask and transferred to a Carius tube. The solution was purged with argon for 15 min and was then sealed and placed in the oil bath.

Products were analyzed by quantitative GC (50-m OV-17 capillary column, 150 or 200 °C, 1 mL/min), using the internal standard technique with response factors calibrated against authentic reference compounds. Products from *N,N*-dimethyl-*p*-toluidine (**1b**) were identified by ^{1}H NMR, IR, and MS after isolation by preparative GC (10 ft × 0.25 in. 15% OV-17 on Chromosorb W, 200 °C, 60 mL/min).

N,N-Dimethyl-*p*-toluidine-d_6 (1b-d_6). A solution of *p*-toluidine (10.0 g, 0.0933 mol) in methanol-d_4 (10.0 g, 0.277 mol) was placed in a Carius tube. Hydriodic acid (57%, 52.3 g, 0.233 mol) was added and the tube was sealed and heated in an oil bath at 125 °C for 40 h. After cooling, the tube was opened and the reaction mixture was carefully added to saturated aqueous sodium bicarbonate (600 mL) in a separatory funnel. The amine product was extracted with hexanes (2 × 200 mL), and the combined organic layers were dried over $MgSO_4$. Filtration and evaporation gave a yellow liquid. The product was added to acetic anhydride (20 g) and the mixture was heated at reflux for 1 h. Most of the acetic anhydride was removed by distillation (atm) and the remainder of the reaction mixture was poured into 7% hydrochloric acid (100 mL). After two hexane extractions, the acid solution was neutralized with ammonium hydroxide solution. The amine was extracted with hexanes (2 × 100 mL). After drying ($MgSO_4$) and filtration, evaporation gave a light-orange liquid, which was distilled under reduced pressure to give 1.90 g (14.4%) **1b**-d_6, which was >99% pure by GC: IR (film) 3096, 2919, 2188, 2051, 1614, 1519, 1497, 1337, 1206, 1193, 1136, 803 cm^{-1}.

2-(Methylphenylamino)ethyl *tert*-Butyl Peroxide (14). Potassium *tert*-butoxide (17.9 g, 0.160 mol) was added to water (80 mL) in a 250-mL, round-bottom flask equipped with a magnetic stirring bar. After complete solution was attained, *tert*-butyl hydroperoxide (90%, 16.0 g, 0.160 mol) was added and the mixture was stirred for 10 min. Methylene chloride (80 mL), 2-(methylphenylamino)ethanol tosylate (12.2 g, 0.0400 mol; prepared from 2-(methylphenylamino)ethanol by a standard procedure[14]) and 18-crown-6 (0.56 g, 0.0022 mol) were added, and the reaction mixture was stirred vigorously for 4 days at room temperature, at which point the ^{1}H NMR spectrum of the methylene chloride layer showed that virtually all of the tosylate had been consumed. The layers were separated, the aqueous layer was extracted with methylene chloride (50 mL), and the combined organic layers were dried over magnesium sulfate. After gravity filtration, solvent and unreacted *tert*-butyl hydroperoxide were evaporated; care was taken to keep the rotary evaporator bath temperature at ≤40 °C. The ^{1}H NMR spectrum of the crude product indicated that only the desired peroxide and 18-crown-6 were present. The product was carefully distilled under high vacuum to give 2.44 g (20.0%) pure (by NMR) 2-(methylphenylamino)ethyl *tert*-butyl peroxide (**14**): considerable decomposition accompanied the distillation; ^{1}H NMR ($CDCl_3$) δ 6.92 (m, 5 H), 4.00 (t, 2 H), 3.64 (t, 2 H), 2.90 (s, 3 H), 1.20 (s, 9 H); IR (film) 2977, 2931, 1600, 1506, 1362, 1196, 991, 747, 692 cm^{-1}.

2-(Methylphenylamino)acetaldehyde (11a) and 2-[Methyl(4-methylphenyl)amino]acetaldehyde (11b). These compounds were prepared by Swern oxidation[15] of the corresponding 2-(methylarylamino)ethanols (**10a,b**). Aldehydes **11a** and **11b** were isolated as crude products and proved to be too unstable to store for any length of time. The crude products were adequate to identify any of the corresponding compounds in the amino–hydroperoxide reactions. **11a**: ^{1}H NMR ($CDCl_3$) δ 9.58 (t, 1 H), 6.91 (m, 5 H), 3.86 (d, 2 H), 2.91 (s, 3 H). **11b**: ^{1}H NMR ($CDCl_3$) δ 9.56 (t, 1 H), 6.77 (m, 4 H), 3.87 (d, 2 H), 2.92 (s, 3 H), 2.20 (s, 3 H).

***N*-Phenyloxazolidine-2,2-d_2 (6a-2,2-d_2) and Formaldehyde Exchange Reactions.** Compound **6a**-2,2-d_2 was prepared by reacting 2-(phenylamino)ethanol with deuterioparaformaldehyde in benzene with *p*-toluenesulfonic acid as a catalyst. The poor quality of the deuterioparaformaldehyde led to a poor yield of **6a**-2,2-d_2 and, thus, the crude product (identified unambiguously

(12) (a) Kharasch, M.; Fono, A. *J. Org. Chem.* **1959**, *24*, 72. (b) Hawkins, E. G. E. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 783.

(13) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. "Purification of Laboratory Chemicals", 2nd ed.; Pergamon Press: New York, 1980; p 221.

(14) Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis", Wiley: New York, 1967; Vol. 1, p 1180.

(15) (a) Mancuso, A.; Brownfain, D.; Swern D. *J. Org. Chem.* **1979**, *44*, 4148. (b) Mancuso, A. J.; Huang, S-L; Swern, D. *Ibid.* **1978**, *43*, 2480.

by GC and ^1H NMR) was used in the formaldehyde exchange experiment. A reaction mixture consisting of **6a**-2,2-d_2 (0.0350 g, 2.34×10^{-4} mol), protioparaformaldehyde (0.0120 g), water (0.010 g, 5.88×10^{-4} mol), and acetonitrile (2.00 mL) was sealed in a Carius tube and heated at 100 °C for 40 h. After cooling, the tube was opened and the acetonitrile was evaporated. Analysis of the product by ^1H NMR indicated that the major product was **6a**-2,2-H_2, thus verifying that formaldehyde exchange does occur under these reaction conditions.

***N*-[(Cumylperoxy)methyl]-*N*-methyl-*p*-toluidine (16b).** This compound was prepared by a modification of the procedure of Kharasch and Fono.[8a] Benzene (15 mL), *N*,*N*-dimethyl-*p*-toluidine (2.57 g, 0.0190 mol), cumene hydroperoxide (8.10 g, 0.0380 mol, based on 60% pure reagent), cuprous chloride (6 mg, 6×10^{-5} mol), and four drops of water were placed in a 50-mL, round-bottom flask equipped with a reflux condenser and stirring bar. The contents were stirred vigorously at 35 °C for 15 h, giving a dark-brown solution. The benzene was removed on a rotary evaporator, and the flask contents were taken up in hexanes. The hexane solution was placed in a freezer until crystallization occurred. The crystals were collected, washed with cold hexanes, and recrystallized from hexanes after filtration of the warm hexane solution (care should be taken not to heat the hexane solution near boiling). A total of four recrystallizations gave colorless crystals, mp 64–65.5 °C, in 42% yield: ^1H NMR ($CDCl_3$) δ 7.4 (m, 5 H), 6.86 (m, 4 H), 5.1 (s, 2 H), 3.07 (s, 3 H), 2.26 (s, 3 H), 1.57 (s, 6 H); IR ($CHCl_3$) 2984, 2924, 1616, 1518, 1448, 1362 cm^{-1}.

Proof of Formation of *N*-[(Cumylperoxy)methyl]-*N*-methyl-*p*-toluidine (16b) in Thermal Reaction of 1b with CHP. An acetonitrile solution containing 0.2 M each of **1b** and CHP was placed in a NMR tube. After the solution was purged with argon for 5 min, the tube was sealed and placed in a 100 °C oil bath. The reaction was monitored by NMR; after 1.5 h, signals corresponding to **16b** were of significant intensity. Heating was stopped, the NMR tube was opened and authentic **16b** was added. The ^1H NMR spectrum was then obtained. All of the appropriate signals corresponding to **16b** increased in intensity, thus verifying its presence in the reaction mixture.

Thermolysis of 2-(Methylphenylamino)ethyl *tert*-Butyl Peroxide (14). In a typical experiment, a 0.1 M acetonitrile solution of **14** was prepared in a volumetric flask. After transfer to a Carius tube, the solution was purged with argon for 10 min. The tube was sealed and placed in a 100 °C oil bath. After heating for 40 h, the tube was opened and the reaction mixture was analyzed by GC and NMR. In variations of this procedure, thermolysis was carried out in acetonitrile containing 0.1 M **1b** or in toluene.

Acknowledgment. I express my gratitude to Dr. William Rastetter and Dr. Rick Danheiser for many helpful discussions as this work progressed. I also thank Mr. David Glaser for carrying out LC analysis and Mr. Robert Trottier for providing GC/MS analysis.

Registry No. **1a**, 121-69-7; **1b**, 99-97-8; **1b**-d_6, 84895-10-3; **1c**, 2909-79-7; **6a**-2,2-d_2, 84877-51-0; **10a** tosylate, 84877-52-1; **11a**, 84877-53-2; **11b**, 84877-54-3; **14**, 84877-55-4; **16b**, 84877-56-5; cumene hydroperoxide, 80-15-9; formaldehyde, 50-00-0; *p*-toluidine, 106-49-0; methanol-d_4, 811-98-3; potassium *tert*-butoxide, 865-47-4.

Oxidation of *m*-Phenoxytoluene with Ceric Trifluoroacetate

Matt Marrocco* and George Brilmyer

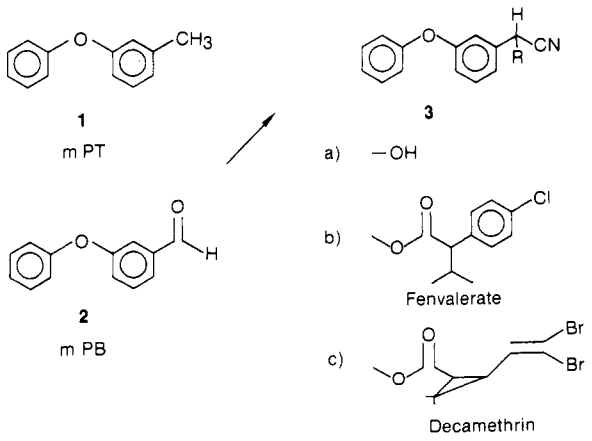
Occidental Research Corporation, Irvine, California 92713

Received May 14, 1982

Ceric trifluoroacetate in aqueous trifluoroacetic acid has been found to be especially effective for the oxidation of activated toluenes to the corresponding aldehydes. Ceric ion is consumed in stoichiometric amounts but can be regenerated electrochemically at high current efficiencies (95%). A detailed study of the oxidation of *m*-phenoxytoluene to *m*-phenoxybenzaldehyde is presented. A study of the reaction mechanism, which involves both cations and radical cations, led to a choice of cosolvents which stabilize these intermediates and thus increase the yield of aldehyde formation.

The most potent of the pyrethroid insecticides[1] are based on esters of *m*-phenoxybenzaldehyde cyanohydrin (**3**). Efficient routes to **3** are thus in great demand. The majority of the reported syntheses rely on partial oxidation of *m*-phenoxytoluene (mPT, **1**) to *m*-phenoxybenzaldehyde (mPB, **2**, Scheme I). The most heavily investigated route involves bromination of mPT followed by hydrolysis.[2] Direct aerial oxidation of mPT has received some attention in the patent literature,[3] but like the bromination route it lacks selectivity to mPB. A third approach,[1,4] wherein

Scheme I



mPT is oxidized to *m*-phenoxybenzoic acid (**4**), reduced to *m*-phenoxybenzyl alcohol (**5**), and finally oxidized to mPB, is impractically long. In a recent paper, good yields of **5** as its propionate and butyrate esters were obtained from mPT by using a novel manganic oxidant; however, only 4% mPB was formed.[5] Synthesis of the ether linkage

(1) (a) M. Elliot and N. F. Janes, *Chem. Soc. Rev.*, **7**, 473 (1978). (b) D. Arlt, M. Jautelat, and R. Lantzsch, *Angew. Chem., Int. Ed. Engl.*, **20**, 703 (1981).

(2) (a) E. J. Smutny, T. H. Colby, and E. E. Ryder, Jr., Japanese Patent 54 112 829; *Chem. Abstr.*, **92**, 58429 (1980); (b) P. A. M. Grotenhuis and L. Menninga, Eur. Pat. Appl. 3066; *Chem. Abstr.*, **91**, 211088 (1978); (c) J. warnant and J. Jolly, German (West) Patent 2 810 305; *Chem. Abstr.*, **90**, 6064 (1979); (d) D. G. Brown and W. W. Brand, German (West) Patent 2 741 764; *Chem. Abstr.*, **89**, 59785 (1979).

(3) (a) J. Imamura, *Yuki Gusei Kagaku Kyokaishi*, **37**, 667 (1979); *Chem. Abstr.*, **92**, 6158 (1980); (b) H. Imamura, K. Onisawa, and T. Yoshimoto, Japanese Patent 7 882 734; *Chem. Abstr.*, **90**, 22596 (1979); (c) T. Matsuda, T. Shirafuji, and T. Murata, Japanese Patent 7 959 242; *Chem. Abstr.*, **91**, 211086 (1979).

(4) A. Chaintreau, G. Adrian, and D. Couturier, *Synth. Commun.*, 11, 439 (1981).

0022-3263/83/1948-1487$01.50/0