(*E*)-1-[(1-(Phenylthio)cyclopropyl)methylene]-3,3-dimethyl-2-butanone (10). To a solution of 3.97 mL (27.6 mmol) of cyclopropyl phenyl sulfide in 10 mL of dry THF at 0 °C under Ar was added 20.0 mL (28.0 mmol) of 1.4 M *n*-butyllithium, and the resulting mixture was stirred for 2.5 h. A solution of 5.00 g (27.6 mmol) of **8** in 30 mL of benzene was distilled under N_2 until 15 mL of solvent was displaced. The remaining benzene solution of **8** was added via syringe to the THF solution of 1-lithio-1-(phenylthio)cyclopropane. The resulting mixture was stirred for 18 h at room temperature. The reaction was quenched with 125 mL of water, and the separated aqueous layer was saturated with NaCl and then extracted with hexane (5 × 100 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and evaporated to give 8.27 g of gold solid, which was recrystallized from methanol to afford 3.90 g (54%) of **10** as very pale orange crystals: mp 66–67 °C. An additional 0.81 g was obtained by flash chromatography (hexane, $CHCl_3$) for a total yield of 4.71 g (65%) of **10**. Four recrystallizations from methanol:water with hot filtration provided a colorless analytical sample of **10**: mp 65–66 °C; IR (KBr) 3020, 2990, 1690, 1620, 1588, 1480, 1443, 1420 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.07 (9 H, s), 1.33–1.54 (4 H, m), 6.47 (1 H, d, J = 14 Hz), 6.85 (1 H, d, J = 14 Hz), 7.23 (5 H, br s); ^{13}C NMR ($CDCl_3$) δ 20.4, 26.0, 26.9, 42.9, 124.2, 125.3, 127.0, 128.7, 136.2, 150.0, 203.9. Anal. Calcd for $C_{16}H_{20}OS$: C, 73.80; H, 7.74; S, 12.31. Found: C, 73.76; H, 7.78; S, 12.26.

2-(2-Oxo-1-cyclobutyl)cyclohexanone (11). A solution of 1.56 g (6.03 mmol) of **6** in 50 mL of 1:1 trifluoroacetic acid:water was heated at reflux for 18 h. The mixture was then cooled to room temperature and combined with 400 mL of ether. The separated organic layer was treated with 2 L of 10% NaOH, washed with brine (2 × 50 mL), dried over anhydrous $MgSO_4$, filtered, and evaporated to afford an orange oil, which was purified by flash chromatography (gradient, hexane to 1:1 hexane:ether) to give 0.75 g (75%) of **11** as an orange oil. Further purification by bulb-to-bulb distillation gave 0.73 g (73%) of clear, colorless **11** as a 3:2 mixture of diastereomers which were inseparable by TLC: bp 109–117 °C (0.37 mmHg). MPLC (1:1 hexane:ether) of a different batch of **11** obtained in 90% yield afforded an analytical sample of **11**: IR (film) 2940, 2875, 1780, 1715, 1450, 1130, 1080 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.80–2.60 (10 H, m), 2.60–3.80 (4 H, m); ^{13}C NMR ($CDCl_3$) δ 13.9, 14.5, 24.0, 24.5, 27.0, 27.1, 30.8, 31.4, 41.0, 41.2, 43.8, 43.9, 50.7, 50.8, 59.0, 59.3, 209.6, 209.9, 210.3, 210.5. Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.14; H, 8.50.

2-(2-Oxo-1-cyclobutyl)cycloheptanone (12). A solution of 0.81 g (2.8 mmol) of **9** in 75 mL of 3:1 trifluoroacetic acid:water was heated at reflux for 18 h. The mixture was cooled to room temperature and combined with 250 mL of ether. The separated organic layer was washed with water (2 × 75 mL) treated with 500 mL of 10% NaOH, washed with brine (2 × 50 mL), dried over anhydrous $MgSO_4$, filtered, and evaporated to afford 0.62 g of brown oil, which was subjected to flash chromatography (gradient, hexane to 1:1 hexane:ether) to give 0.34 g (67%) of gold oily **12**. Further purification by bulb-to-bulb distillation yielded 0.21 g (42%) of clear colorless **12** as a 5:4 mixture of diastereomers which were inseparable by TLC: bp 100–110 °C (0.05 mmHg); IR (film) 2930, 2860, 1780, 1705, 1460, 1200, 1080, 940 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90–2.30 (10 H, m), 2.30–2.71 (2 H, m), 2.79–3.26 (3 H, m), 3.30–4.00 (1 H, m); ^{13}C NMR ($CDCl_3$) δ 14.6, 15.7, 23.4, 23.7, 28.9, 28.9, 29.1, 29.3, 29.3, 29.4, 43.1, 43.2, 44.4, 44.4, 51.0, 52.6, 61.2, 61.5, 210.4, 211.1, 213.1, 213.2. Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.34; H, 8.95.

1-(2-Oxo-1-cyclobutyl)-3,3-dimethyl-2-butanone (13). A solution of 3.01 g (11.6 mmol) of **10** in 150 mL of 1:1 trifluoroacetic acid:water was heated at reflux for 18 h. The mixture was then cooled to room temperature, and 300 mL of ether was added. The organic layer was separated, washed successively with 100 mL of water, 400 mL of 10% NaOH, 100 mL of water, and 50 mL of brine, dried over $MgSO_4$, filtered, and evaporated to give 1.75 g of yellow oil, which was subjected to flash chromatography (hexane, 25% ether in hexane) to afford 1.65 g (85%) of yellow oily **13**. Further purification by bulb-to-bulb distillation yielded 1.44 g (74%) of **13** as a pale yellow oil: bp 90–110 °C (0.45 mmHg). MPLC (1:1 hexane:ether) afforded an analytical sample of **13**: IR (film) 2970, 2920, 2880, 1787, 1710, 1485, 1400, 1370, 1070 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10 (9 H, s), 1.24–2.60 (2 H, m), 2.60–3.34 (4 H, m), 3.34–3.94 (1 H, m); ^{13}C NMR ($CDCl_3$) δ 16.4, 25.7, 35.8, 43.2, 44.4, 54.4, 210.0, 212.3. Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.41; H, 9.59. Found: C, 71.45; H, 9.62.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Oxidation of 3- or 4-Substituted *N,N*-Dimethylanilines with Molecular Oxygen in the Presence of either $FeCl_3$ or [Fe(salen)]OAc

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Received March 31, 1989

Iron-catalyzed oxidation of amines is of considerable interest because of the relevance to enzymatic degradation of N-containing compounds in biological systems.[1-3] We have recently reported that *N,N*-dimethylaniline (**1a**) is oxidized by molecular oxygen in the presence of various iron complexes and salts, the product composition being remarkably influenced by the identity of the iron species employed:[4] The reaction of **1a** using $FeCl_3$ is considered to proceed via initial one-electron oxidation and subsequent dimerization to give 4,4′-methylenebis(*N,N*-dimethylaniline) (**5a**) along with *N*-methylaniline (**2a**), whereas with [Fe(salen)]OAc (salen = *N,N*′-ethylenebis(salicylidenaminato)] *N*-methylformanilide (**3a**) is obtained as the predominant product together with **2a** in a free-radical chain process.

We report herein the results for the oxidation of a series of 3- (**1b,c**) and 4-substituted *N,N*-dimethylanilines (**1d–f**) in the presence of either $FeCl_3$ or [Fe(salen)]OAc; the position of the substituents also appeared to be an important factor determining the course of the reaction.

When **1a** (1.0 M) in acetonitrile was treated with $FeCl_3$ (3 mM) under oxygen (1 atm) at 60 °C for 20 h, a mixture of **2a** and **5a** was favored (eq 1 and Table I). Similar results were also obtained in the reactions of 3-substituted *N,N*-dimethylanilines **1b** and **1c**. The order of reactivity for **1a–c** was found to be **1b** (3-Me) > **1a** (H) > **1c** (3-Cl)

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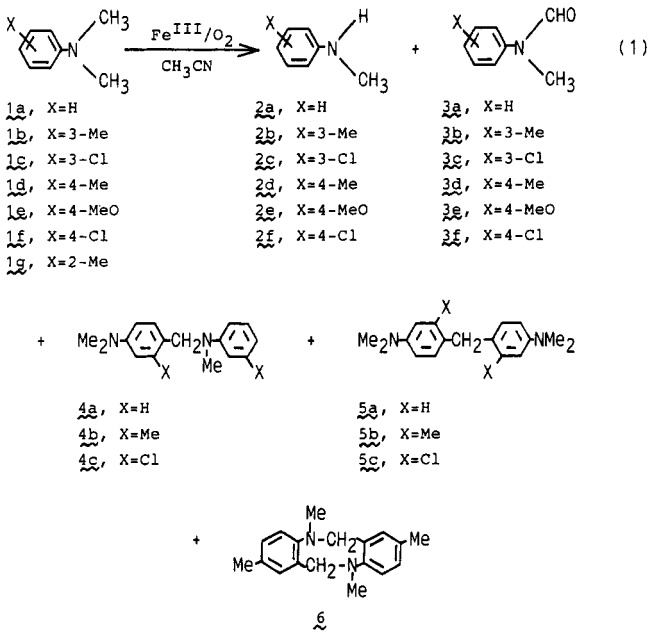
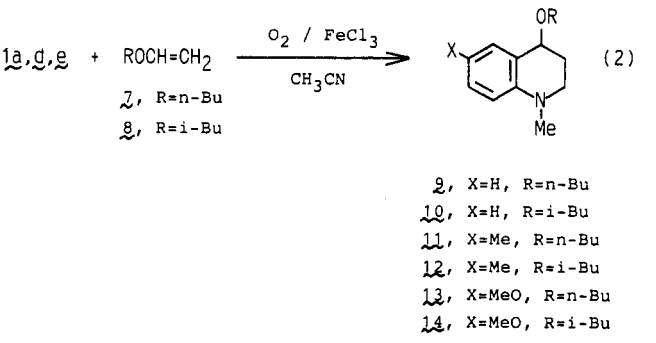


(1)

in agreement with the initial one-electron oxidation mechanism (Figure 1). In contrast, the reaction of *N,N*-dimethyl-*p*-toluidine (**1d**) gave the formanilide **3d** in a fairly high yield together with **2d** and a dimerized product, **6**. This reaction was remarkably affected by addition of BHT (50 mM) to afford a mixture of **2d** and **6**, suggesting that **3d** is formed by a radical chain process. The reaction of 4-substituted substrates **1e** and **1f** also gave the corresponding mixture of **2e,f** and **3e,f**. Conversion of *N,N*-dimethyl-*o*-toluidine (**1g**) was extremely low.

On the other hand, the reactions of the 4-substituted substrates **1d,e** (1.0 M) in the presence of *n*-butyl (**7**) and isobutyl vinyl ethers (**8**) (2.0 M) using $FeCl_3$ (3 mM) selectively gave the corresponding 4-butoxy-1-methyl-1,2,3,4-tetrahydroquinolines (**11–14**) as well as those with **1a** to afford **9** and **10**;[4] 26–40 equiv of product was produced per equivalent of catalyst used (eq 2 and Table II).[5,6]



(2)

The oxidation of both 3- and 4-substituted *N,N*-dimethylanilines **1** using [Fe(salen)]OAc favorably afforded the corresponding mixture of the *N*-methylanilines **2** and the formanilides **3**. The order of reactivity for **1a,d–f** was **1d** (4-Me) > **1a** (H) ≃ **1e** (4-MeO) > **1f** (4-Cl) (Figure 2), suggesting that the reaction using this complex may also involve one-electron oxidation as the initiation reaction.[7,8]

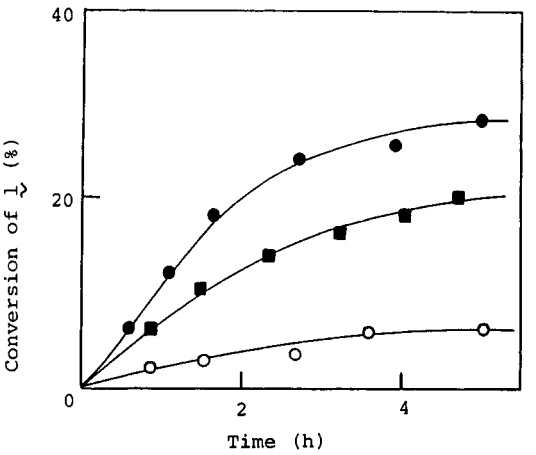


Figure 1. Oxidation of *N,N*-dimethylanilines **1a–c** (0.50 M) with oxygen in the presence of $FeCl_3$ (3.0 mM) in acetonitrile at 20 °C: ■, **1a**; ●, **1b**; ○, **1c**.

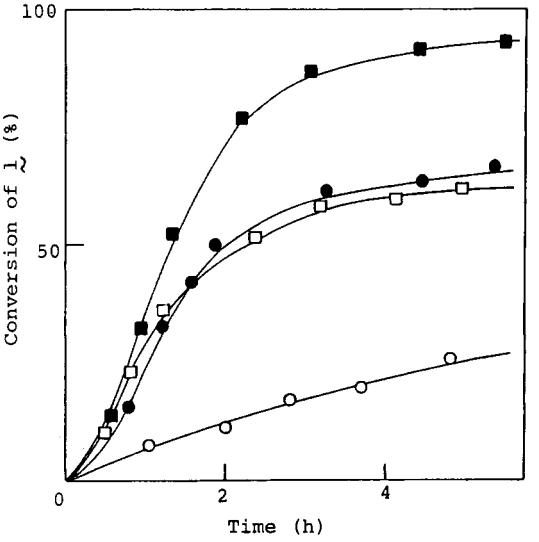


Figure 2. Oxidation of *N,N*-dimethylanilines **1a,d–f** (0.50 M) with oxygen in the presence of [Fe(salen)]OAc (3.0 mM) in acetonitrile at 60 °C: ●, **1a**; ■, **1d**; □, **1e**; ○, **1f**.

Experimental Section

^1H NMR spectra were obtained with a JEOL JNM-PS-100 spectrometer (100 MHz) and a JEOL JNM-GSX-400 spectrometer (400 MHz) in $CDCl_3$. ^{13}C NMR spectra were obtained with a JEOL JNM-GSX-400 spectrometer in $CDCl_3$. GC-MS spectra were obtained with a JEOL JMS-DX-303 spectrometer. GC analysis was carried out on a Shimadzu GC-8A gas chromatograph.

Monosubstituted *N,N*-dimethylanilines (**1b–g**)[10] and [Fe(salen)]OAc[11] were prepared by the methods reported previously. The other chemicals used were commercially available.

Oxidation of *N,N*-Dimethylanilines 1 with Oxygen in the Presence of an Iron Species. A solution of **1** (10 mmol) in acetonitrile (10 ml) containing $FeCl_3$ or [Fe(salen)]OAc (0.03 mmol) was stirred under oxygen (1 atm) at 60 °C for 20 h. Analysis of the products was carried out by GC and GC-MS after addition of an appropriate internal standard. The products were

(5) While the conversion of **1** also increased by increasing the concentration of $FeCl_3$, the selectivity of the tetrahydroquinolines remarkably decreased, several unidentified byproducts being formed.

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(7) The reaction of **1a** (1.0 M) with $FeCl_3$ or [Fe(salen)]OAc (0.1 M) under nitrogen gave no detectable amount of products, suggesting that oxygen is also required for the initiation reaction.

(8) The unexpectedly low reactivity of **1e** (Table I and Figure 2) may be attributable to the fact that the proton loss from the corresponding aminium cation radical is relatively slow. A similar trend has also been reported in the photooxidation of 4-substituted benzyl alcohols with oxygen involving initial one-electron oxidation.[9]

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Table I. Iron-Catalyzed Oxidation of *N,N*-Dimethylanilines with Oxygen[a]

aniline (subst)	cat.[b]	product,[c] mM 2	3	4	5	6	concn of 1 after rctn,[c] mM
1a (H)	A	28			69		793
1b (3-Me)	A	77			109		595
1c (3-Cl)	A	53			52		811
1d (4-Me)	A	203	266			46	293
1d (4-Me)[d]	A	22				20	885
1e (4-MeO)	A	169	18				696
1f (4-Cl)	A	357	124				331
1a (H)	B	208	231	12	5		197
1b (3-Me)	B	222	262	6	10		106
1c (3-Cl)	B	90	100	18	5		647
1d (4-Me)	B	364	275				75
1e (4-MeO)	B	407	254				351
1f (4-Cl)	B	223	168				495

[a] The reaction was carried out in acetonitrile under oxygen at 60 °C for 20 h; 1, 1.0 M; catalyst, 3.0 mM. [b] A, $FeCl_3$; B, [Fe(salen)]OAc. [c] Determined by GC analysis. [d] The reaction in the presence of BHT (50 mM).

Table II. Reaction of *N,N*-Dimethylanilines with Butyl Vinyl Ethers[a]

aniline (subst)	vinyl ether	product,[b] mM tetrahydroquinoline	2	3	concn of 1 after rctn,[b] mM
1a (H)	7[c]	105	10		855
1a (H)	8	136	8	18	827
1d (4-Me)	7	108	12	14	861
1d (4-Me)	8	99	10	13	848
1e (4-MeO)	7	86	14		900
1e (4-MeO)	8	78	10		902

[a] The reaction was carried out in acetonitrile under oxygen at 60 °C for 20 h; 1, 1.0 M; vinyl ether, 2.0 M; $FeCl_3$, 3.0 mM. [b] Determined by GC analysis. [c] Reaction for 10 h. Taken from the data in ref 4.

also isolated by column chromatography on silica gel using hexane–ethyl acetate as eluant.

Oxidative Coupling of *N,N*-Dimethylanilines 1 with Vinyl Ethers 7 and 8. A mixture of 1 (10 mmol) and a vinyl ether 7 or 8 (20 mmol) was stirred in the presence of $FeCl_3$ (0.03 mmol) under oxygen at 60 °C for 20 h. Then the mixture was poured into water, and the products were extracted with ether. After removal of the solvent and excess of 1 and the vinyl ether in vacuo, the coupling product was isolated by column chromatography on silica gel using hexane–ethyl acetate as eluant.

Products. The purity of the following products isolated was judged to be ≥90% by GC and/or ^1H and ^{13}C NMR analyses. The dimerized products **4a**,[12a,b] **4b**,[12d] **5a**,[12b,c] **5b**,[12d] and **6**[12d] are known and compared with authentic specimens. The dimer **4c** was an oil; MS *m/e* 308, 310, and 312 (M^+); ^1H NMR (100 MHz) δ 2.87 (s, 6 H), 2.98 (s, 3 H), 4.46 (s, 2 H), 6.40–7.20 (m, 7 H). The dimer **5c** was a solid: mp 106–109 °C (from benzene–hexane); MS *m/e* 322, 324, and 326 (M^+); ^1H NMR (100 MHz) δ 2.90 (s, 12 H), 4.00 (s, 2 H), 6.44–6.96 (m, 6 H). Anal. Calcd for $C_{17}H_{20}N_2Cl_2$: C, 63.2; H, 6.2; N, 8.7; Cl, 21.9. Found: C, 63.0; H, 6.2; N, 8.7; Cl 21.9. The tetrahydroquinoline **9** was an oil: MS *m/e* 219 (M^+); ^1H NMR (400 MHz) δ 0.91 (t, *J* = 7.6 Hz, 3 H), 1.29–1.43 (m, 2 H), 1.52–1.62 (m, 2 H), 1.87–1.95 (m, 1 H), 2.08–2.14 (m, 1 H), 2.91 (s, 3 H), 3.08–3.13 (m, 1 H), 3.36–3.43 (m, 1 H), 3.45–3.65 (m, 2 H), 4.31 (t, *J* = 3.7 Hz, 1 H), 6.61–6.65 (m, 2 H), 7.14–7.26 (m, 2 H); ^{13}C NMR δ 13.94, 19.50, 27.32, 32.17, 38.95, 46.36, 67.60, 73.10, 111.36, 115.60, 121.63, 129.21, 130.34, 146.34. The tetrahydroquinoline **10** was an oil: MS *m/e* 219 (M^+); ^1H NMR (400 MHz) δ 0.905 (d, *J* = 6.8 Hz, 3 H), 0.915 (d, *J* = 6.8 Hz, 3 H), 1.83–1.95 (m, 2 H), 2.07–2.14 (m, 1 H), 2.91 (s, 3 H), 3.08–3.13 (m, 1 H), 3.23–3.35 (m, 2 H), 3.35–3.42 (m, 1 H), 4.29 (t, *J* = 3.7 Hz, 1 H), 6.62–6.65 (m, 2 H) 7.14–7.26 (m, 2 H); ^{13}C NMR δ 19.51, 19.62, 27.29, 28.70, 38.95, 46.42, 73.24, 74.89, 111.34, 115.62, 121.78, 129.13, 130.28, 146.34. The tetrahydroquinoline **11** was an oil: MS *m/e* 233 (M^+); ^1H NMR (400 MHz) δ 0.91 (t, *J* = 7.3 Hz, 3 H), 1.35–1.44 (m, 2 H), 1.55–1.62 (m, 2 H), 1.87–1.95 (m, 1 H), 2.07–2.13 (m, 1 H), 2.23 (s, 3 H), 2.88 (s, 3 H), 3.04–3.09 (m, 1 H), 3.28–3.35 (m, 1 H), 3.46–3.60 (m, 2 H), 4.28 (t, *J* = 3.7 Hz, 1 H), 6.55–6.57 (m, 1 H), 6.96–6.97 (m, 2 H); ^{13}C NMR δ 13.95, 19.51, 20.28, 27.49, 32.21, 39.25, 46.60, 67.67, 73.15, 111.74, 121.93, 124.93, 129.74, 130.81, 144.38. The tetrahydroquinoline **12** was an oil: MS *m/e* 233 (M^+); ^1H NMR (400 MHz) δ 0.918 (d, *J* = 6.8 Hz, 3 H), 0.923 (d, *J* = 6.4 Hz, 3 H), 1.84–1.95 (m, 2 H), 2.06–2.27 (m, 1 H), 2.23 (s, 3 H), 2.88 (s, 3 H), 3.04–3.09 (m, 1 H), 3.25–3.35 (m, 3 H), 4.26 (t, *J* = 4.3 Hz, 1 H), 6.55–6.57 (m, 1 H), 6.95–6.98 (m, 2 H); ^{13}C NMR δ 19.55, 19.66, 20.28, 27.43, 28.71, 39.26, 46.65, 73.30, 75.00, 111.74, 122.07, 124.93, 129.68, 130.78, 144.40. The tetrahydroquinoline **13** was an oil: MS *m/e* 249 (M^+); ^1H NMR (400 MHz) δ 0.92 (t, *J* = 7.3 Hz, 3 H), 1.32–1.45 (m, 2 H), 1.56–1.63 (m, 2 H), 1.92–1.99 (m, 1 H), 2.07–2.17 (m, 1 H), 2.86 (s, 3 H), 3.03–3.08 (m, 1 H), 3.22–3.29 (m, 1 H), 3.48–3.65 (m, 2 H), 3.75 (s, 3 H), 4.30 (t, *J* = 4.2 Hz, 1 H), 6.59–6.62 (m, 1 H), 6.77–6.81 (m, 2 H); ^{13}C δ 13.94, 19.51, 27.67, 32.19, 39.69, 47.02, 55.89, 67.83, 73.30, 112.87, 115.05, 115.76, 123.39, 141.31, 150.95. The tetrahydroquinoline **14** was an oil: MS *m/e* 249 (M^+); ^1H NMR (400 MHz) δ 0.849 (d, *J* = 6.8 Hz, 3 H), 0.857 (d, *J* = 6.7 Hz, 3 H), 1.70–1.92 (m, 2 H), 2.1 (m, 1 H), 2.79 (s, 3 H), 2.97–3.00 (m, 1 H), 3.15–3.34 (m, 3 H), 3.68 (s, 3 H), 4.22 (t, *J* = 4.2 Hz, 1 H), 6.52–6.55 (m, 1 H), 6.69–6.75 (m, 2 H); ^{13}C NMR δ 19.55, 19.62, 27.63, 28.73, 39.70, 47.09, 55.87, 73.46, 75.13, 112.87, 115.00, 115.69, 123.54, 141.33, 150.95.

Supplementary Material Available: NMR and mass spectra for **9**–**14** and mass spectrum for **4c** (13 pages). Ordering information is given on any current masthead page.

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A New Entry into C7-Oxygenated Tetrahydro-1*H*-3-benzazepines: Efficient Labeling with Carbon-14 in the Benzo Ring

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Received March 31, 1989

Derivatives of 2,3,4,5-tetrahydro-1*H*-3-benzazepine ("3-benzazepine") constitute a large class of pharmacologically important compounds. A number of compounds in this group have agonist activity at peripheral and/or central nervous system dopamine receptor systems[1] and have

(1) Calne, D. B.; Larsen, T. A. Potential therapeutic uses of dopamine receptor agonists and antagonists In *Dopamine Receptors*; Kaiser, C., Kebabian, J. W., Eds.; Am. Chem. Soc. Symp. Series; American Chemical Society: Washington, DC, 1983, Vol. 224, p 147.

0022-3263/89/1954-4702$01.50/0