The Journal of Organic Chemistry

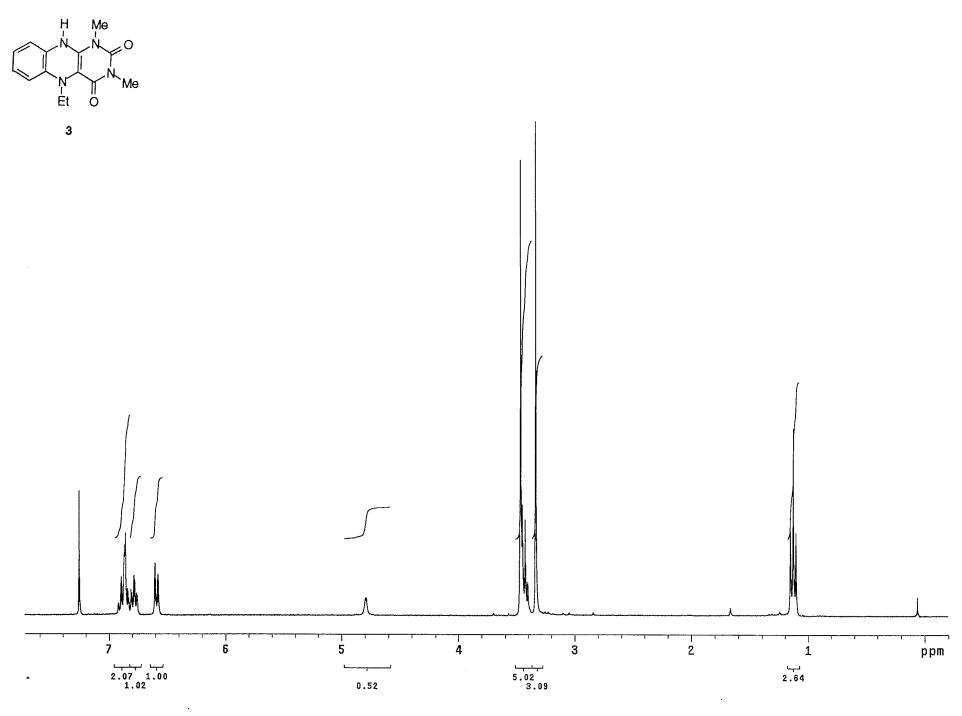
J. Org. Chem., 1998, 63(19), 6650-6655, DOI:10.1021/jo980926d

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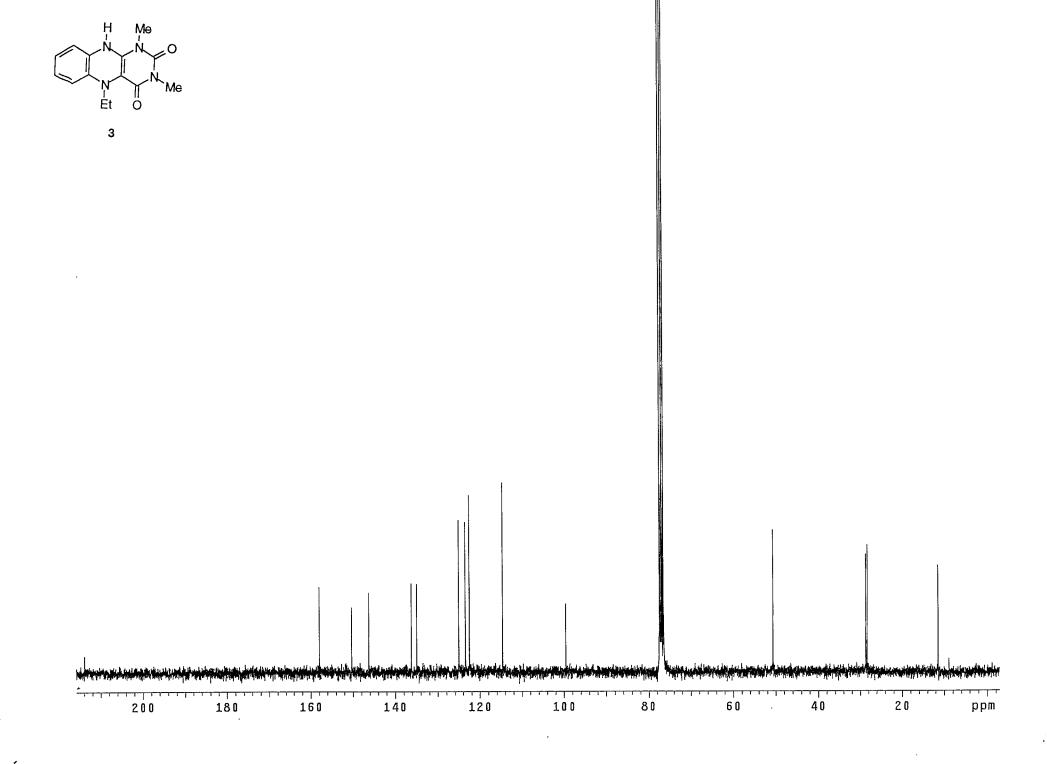


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Procedure Preparation of Tertiary Amines. N,N-General for Dimethylbenzylamine (15). A mixture of benzylbromide (3.50 mL, 29.4 mmol) and dimethylamine (19 mL of a 40% aqueous solution, 150 mmol) in EtOH (39 mL) were refluxed for 1 h 15 min. After acidification of the solution to pH 1 with concentrated HCl, most of the solvents were evaporated. 2M NaOH was added to the resulting oil until the pH was 14. The phases were separated, and the aqueous phase was extracted with ether. The combined organic phases were washed with saturated aqueous NaCl and dried (MgSO₄). Concentration under reduced pressure followed by distillation of the crude product (3.47 g) yielded 15 as a colorless oil (2.76 g, 69%) (bp 35-37 °C/4 mmHg). The ¹H and ¹³C NMR spectra of the product were in accordance with those previously reported.¹

N,N-Dimethyldodecylamine (9). Dodecylbromide (10.0 g, 40.1 mmol) and dimethylamine (26 mL of a 40% aqueous solution, 206 mmol) in EtOH were refluxed for 1 h 30 min. 9 was obtained as a colorless oil (5.43 g, 63%) (bp 104-106 °C/4 mmHg). The ¹H and ¹³C NMR spectra of the product were identical to data reported in the literature.², ³

N,N-Dimethyl-2-Octylamine (11). 2-Octylbromide (2.0 g, 10.4 mmol) and dimethylamine (7.1 mL of a 40% aqueous solution, 56 mmol) in EtOH were refluxed for 4 h. 11 was obtained as a colorless oil (1.02 g, 62%) (bp 46-48 °C/4 mmHg). ¹H NMR⁴ (CDCl₃, 400 MHz) δ 2.45 (tq, 1H, J= 1.3, 6.5 Hz), 2.21 (s, 6H), 1.48 (m, 1H), 1.38-1.16 (br s, 9H), 0.93 (d, 3H, J= 6.5 Hz), 0.89 (t, 3H, J= 6.9 Hz). ¹³C NMR (CDCl₃, 100.6 MHz) δ 59.1, 40.6, 33.5, 31.9, 29.6, 26.8, 22.7, 14.1, 13.6.

N,N-Dimethylcycloheptylamine (17). Cycloheptylbromide (5.02 g, 28.3 mmol) and dimethylamine (18 mL of a 40% aqueous solution, 142 mmol) in EtOH were refluxed for 4 h 30 min. 17 was obtained as a colorless oil (2.10 g, 52%) (bp 40-41 °C/4 mmHg). The ¹H and ¹³C NMR spectra of the product were identical to data reported in the literature.^{5, 6}

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N,N-Dimethyl-2-Octylamine N-Oxide (12). ¹H NMR (MeOH-d₄, 400 MHz) δ 3.20 (m, 1H), 3.08 (s, 3H), 3.06 (s, 3H), 2.14 (m, 1H), 1.51-1.17 (d (J=6.7 Hz) overlapped by m, 12H), 0.89 (t, 3H, *J*= 6.8Hz). ¹³C NMR (MeOH-d₄, 100.6 MHz) δ 76.6, 55.6, 54.5, 32.7, 31.7, 30.1, 28.0, 23.5, 14.9, 14.3.

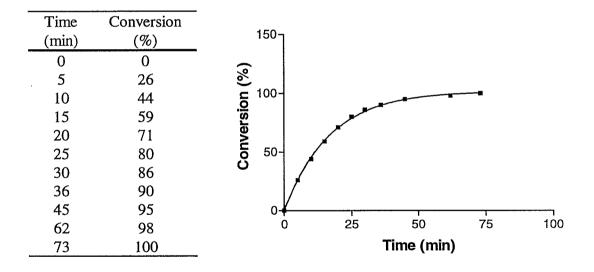
N,N-Dimethylcyclohexylmethylamine N-Oxide (14). ¹H NMR (CDCl₃, 400 MHz) δ 3.16 (s, 6H), 3.10 (d, 2H, *J*= 4.6 Hz), 2.03 (tt, 1H, *J*= 4.0, 11.2 Hz), 1.92 (br d, 2H, *J*= 12.8 Hz), 1.75-1.58 (m, 3H), 1.34 (tq, 2H, *J*= 3.3, 12.5 Hz), 1.22-1.03 (m, 3H) ¹³C NMR (CDCl₃, 100.6 MHz) δ 78.0, 58.9, 33.1, 33.0, 25.5, 25.3.

N,N-Dimethylcycloheptylamine N-Oxide (18). ¹H NMR (CDCl₃, 400 MHz) δ 3.18 (tt, 1H, *J*= 3.8, 9.7 Hz), 3.06 (s, 6H), 2.46 (m, 2H), 1.78 (m, 2H), 1.67-1.46 (m, 8H). ¹³C NMR (CDCl₃, 100.6 MHz) δ 80.4, 54.7, 28.3, 27.2, 24.8.

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Oxidation of N-Methylmorpholine (7):

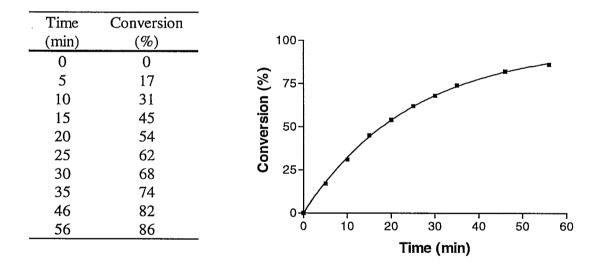
Oxidation of N,N-Dimethyldodecylamine (9):



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Oxidation of N,N-Dimethyl-2-Octylamine (11):

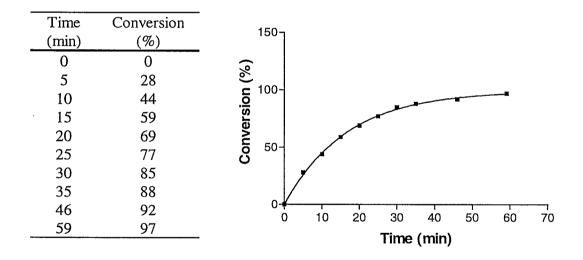
Oxidation of N,N-Dimethylcyclohexylmethylamine (13):



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Oxidation of N,N-Dimethylbenzylamine (15):

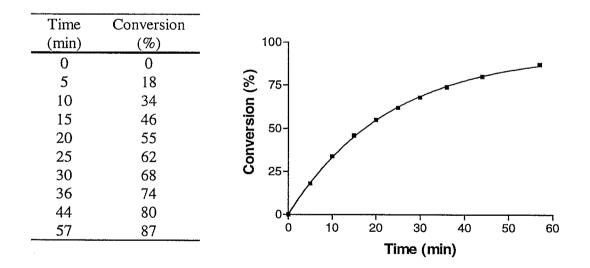
Oxidation of N,N-Dimethylcycloheptylamine (17):



Time (min)	Conversion (%)	100
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30	67	1
35	73	
45	80	0 10 20 30 40 50 60 70
55	85	Time (min)
65	89	

Oxidation of N-Methylpiperidine (19):

Oxidation of Triethylamine (21):



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