

C(1) + C(3), 31.5, 29.0, 28.7 (2 $\times$ ), 22.5, 13.9 C(4)-C(9).

**1-Phenylundeca-1,2-diene (11):** bp 120 °C (0.4 mmHg);  $n_D^{20}$  1.5320; IR 1951 cm<sup>-1</sup>; mass,  $m/e$  228, M<sup>+</sup>; <sup>1</sup>H NMR (CCl<sub>4</sub>) see 9, with  $\delta$  1.15-1.60 (m, 12 H); <sup>13</sup>C NMR -.

**4-Methyl-1-phenylpenta-1,2-diene (12):** bp 102 °C (15 mmHg);  $n_D^{20}$  1.5395; IR 1945 cm<sup>-1</sup>; mass,  $m/e$  158, M<sup>+</sup>; <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  7.18 (br m, 5 H), 6.09 (dd, H<sub>A</sub>), 5.51 (dd, H<sub>B</sub>), 2.42 (ddsept, H<sub>X</sub>), 1.08 (br d, 6 H,  $J \approx 7$  Hz), simulated ABX system (90 MHz) <sup>3</sup>J<sub>BX</sub> = 5.75, <sup>4</sup>J<sub>AB</sub> = -6.35, <sup>5</sup>J<sub>AX</sub> = 3.07 Hz; <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  203.5 C(2), 135.1, 128.4, 126.5, 126.3 (arom C ipso, m, p, o), 102.3 C(3), 95.6 C(1), 28.3 C(4), 22.4 C(5).

**4-Methyl-1-phenylhexa-1,2-diene (13):** bp 112 °C (15 mmHg), 72 °C (0.5 mmHg);  $n_D^{20}$  1.5465; IR 1949 cm<sup>-1</sup>; mass,  $m/e$  172, M<sup>+</sup>; 200-MHz <sup>1</sup>H NMR (CDCl<sub>3</sub>), 2 diastereomer pairs (I)  $\delta$  7.07-7.31 (br m, 5 H), 6.15 (dd, H<sub>A</sub>), 5.53 (dd, H<sub>B</sub>), 2.19 (apparent septet, H<sub>M</sub>), 1.30-1.55 (m, H<sub>X</sub>), 1.07 (d, H<sub>Y</sub>), 0.95 (t, H<sub>Z</sub>), <sup>4</sup>J<sub>AB</sub> = -6.38, <sup>3</sup>J<sub>BM</sub> = 6.39, <sup>5</sup>J<sub>AM</sub> = 2.75, <sup>3</sup>J<sub>MY</sub> = 6.75, <sup>3</sup>J<sub>XZ</sub> = 7.30 Hz; (II)  $\delta$  7.07-7.31 (br m, 5 H), 6.14 (dd, H<sub>A</sub>), 5.52 (dd, H<sub>B</sub>), 2.18 (apparent septet, H<sub>M</sub>), 1.30-1.55 (m, H<sub>X</sub>), 1.06 (d, H<sub>Y</sub>), 0.94 (t, H<sub>Z</sub>), <sup>4</sup>J<sub>AB</sub> = 6.40, <sup>3</sup>J<sub>BM</sub> = 6.55, <sup>5</sup>J<sub>AM</sub> = 2.49, <sup>3</sup>J<sub>MY</sub> = 6.75, <sup>3</sup>J<sub>XZ</sub> = 7.30 Hz; <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  204.0 C(2), 135.1, 128.4, 126.4 (arom C ipso, m, p + o), 100.7 C(3), 95.2 C(1), 35.3/35.2, 29.9/29.7, 19.9/19.8, 11.6/11.6 diastereomer C(4)-C(7).

**4,4-Dimethyl-1-phenylpenta-1,2-diene (14):** bp 102 °C (15 mmHg);  $n_D^{20}$  1.5395; IR 1950 cm<sup>-1</sup>; mass,  $m/e$  172, M<sup>+</sup>; <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  7.18 (br m, 5 H), 6.09 (d, H<sub>A</sub>), 5.48 (d, H<sub>B</sub>), 1.10 (s, 9 H), <sup>4</sup>J<sub>AB</sub> = -6.45 Hz; <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  202.4 C(2), 135.2, 128.5, 126.5, 126.3 (arom C ipso, m, p, o), 106.7 C(3), 96.2 C(1), 32.6 C(4), 30.2 C(5).

**2,2-Dimethylhepta-3,4-diene (16):** bp 32 °C (15 mmHg);  $n_D^{20}$  1.4370; IR 1954 cm<sup>-1</sup>; mass,  $m/e$  124, M<sup>+</sup>; <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  4.95-5.25 (m, 2 H), 1.95 (m, 2 H), 1.01 (s, 9 H), 0.97 (br t, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  200.6 C(4), 103.6 C(3), 94.3 C(5), 31.5 C(2), 30.1 C(1), 22.0 C(6), 13.2 C(7).

**2,2-Dimethylocta-3,4-diene (17):** bp 48 °C (15 mmHg);  $n_D^{20}$  1.4390; IR 1958 cm<sup>-1</sup>; mass,  $m/e$  138, M<sup>+</sup>; <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  4.95-5.25 (m, 2 H), 1.95 (m, 2 H), 1.42 (m, 2 H), 1.01 (s, 9 H), 0.95 (br t, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  201.1 C(4), 102.8 C(3), 92.5 C(5), 31.6 C(2), 30.2 C(1), 31.3, 22.4, 13.7 C(6)-C(8).

**2,2-Dimethylnona-3,4-diene (18):** bp 62 °C (15 mmHg);  $n_D^{20}$  1.4402; IR 1958 cm<sup>-1</sup>; mass,  $m/e$  152, M<sup>+</sup>; <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  4.90-5.20 (m, 2 H), 1.93 (m, 2 H), 1.10-1.50 (m, 4 H), 1.01 (s, 9 H), 0.88 (unresolved t, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  201.0 C(4), 102.9 C(3), 92.6 C(5), 31.5 C(2), 30.1 C(1), 31.4, 28.8, 22.2, 13.8 C(6)-C(9).

**2,2-Dimethyldeca-3,4-diene (19):** bp 76 °C (15 mmHg);  $n_D^{20}$

1.4417; IR 1958 cm<sup>-1</sup>; mass,  $m/e$  166, M<sup>+</sup>; <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  4.90-5.20 (m, 2 H), 1.93 (m, 2 H), 1.10-1.50 (m, 6 H), 1.01 (s, 9 H), 0.87 (unresolved t, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  201.0 C(4), 102.9 C(3), 92.7 C(5), 31.5 C(2), 30.1 C(1), 31.4, 29.1, 28.9, 22.4, 13.9 C(6)-C(10).

**2,2,6-Trimethylhepta-3,4-diene (20):** bp 39 °C (15 mmHg);  $n_D^{20}$  1.4356; IR 1957 cm<sup>-1</sup>; mass,  $m/e$  138, M<sup>+</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) simulated ABMX<sub>3</sub>X'<sub>3</sub> (200 MHz)  $\delta$  5.17 (dd, H<sub>A</sub>), 5.12 (dd, H<sub>B</sub>), 2.26 (ddsept, H<sub>M</sub>), 1.02 (s, 9 H), 0.99 (d, 3 H<sub>X</sub>), 0.98 (d, 3 H<sub>X</sub>) diastereomer Me, <sup>3</sup>J<sub>XM</sub> = <sup>3</sup>J<sub>X'M</sub> = 6.76, <sup>3</sup>J<sub>BM</sub> = 5.31, <sup>4</sup>J<sub>AB</sub> = -6.22, <sup>5</sup>J<sub>AM</sub> = 3.36 Hz; <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  199.4 C(4), 104.1 C(3), 100.1 C(5), 31.5 C(2), 30.1 C(1), 27.9 C(6), 22.5, 22.3 diastereomer C(7).

**2,2,6,6-Tetramethylhepta-3,4-diene (21):** bp 52 °C (15 mmHg);  $n_D^{20}$  1.4375; IR 1958 cm<sup>-1</sup>; mass,  $m/e$  152, M<sup>+</sup>; <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  5.09 (s, 2 H), 1.00 (s, 18 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  198.1 C(4), 104.6 C(3) + C(5), 31.5 C(2) + C(6), 30.1 C(1) + C(7).

**Trideca-3,4-diene (22):** bp 98 °C (18 mmHg);  $n_D^{20}$  1.4545; IR 1959 cm<sup>-1</sup>; mass,  $m/e$  180, M<sup>+</sup>; <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  4.85-4.20 (m, 2 H), 1.75-2.20 (m, 4 H), 1.10-1.70 (m, 12 H), 0.98 (br t, 3 H), 0.87 (unresolved t, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  203.4 C(4), 92.5, 91.5 C(3) + C(5), 31.8, 29.3, 29.2 (2 $\times$ ), 29.0 (2 $\times$ ), 22.6, 14.0 C(6)-C(13), 22.0 C(2), 13.4 C(1).

**Tetradeca-4,5-diene (23):** bp 110 °C (18 mmHg);  $n_D^{20}$  1.4558; IR 1960 cm<sup>-1</sup>; mass,  $m/e$  194, M<sup>+</sup>; <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  4.85-5.15 (m, 2 H), 1.75-2.15 (m, 4 H), 1.10-1.65 (m, 14 H), 0.90 (br t, 3 H), 0.87 (unresolved t, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  203.9 C(5), 90.8, 90.6 C(4) + C(6), 31.8, 31.1, 29.3, 29.2 (2 $\times$ ), 29.0, 28.9, 22.6, 22.4, 14.0, 13.5 C(1)-C(3) + C(7)-C(14).

**Pentadeca-5,6-diene (24):** bp 125 °C (18 mmHg);  $n_D^{20}$  1.4563; IR 1960 cm<sup>-1</sup>; mass,  $m/e$  208, M<sup>+</sup>; <sup>1</sup>H NMR (CCl<sub>4</sub>) as 23, but  $\delta$  1.10-1.65 (m, 16 H), 0.88, 0.87 (2 unresolved t, 6 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  203.8 C(6), 90.8 C(5) + C(7), 31.8, 31.3, 29.4, 29.2 (2 $\times$ ), 29.0 (2 $\times$ ), 28.6, 22.6, 22.1, 14.0, 13.8 C(1)-C(4) + C(8)-C(15).

**2,2-Dimethyltrideca-3,4-diene (25):** bp 120 °C (18 mmHg);  $n_D^{20}$  1.4512; IR 1958 cm<sup>-1</sup>; mass,  $m/e$  208, M<sup>+</sup>; <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  4.93-5.20 (m, 2 H), 1.70-2.15 (m, 2 H), 1.10-1.60 (m, 10 H), 1.01 (s, 9 H), 0.87 (unresolved t, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  201.0 C(4), 102.9 C(3), 92.7 C(5), 31.5 C(2), 30.1 C(1), 31.8, 29.4, 29.2 (3 $\times$ ), 28.8, 22.6, 14.0 C(6)-C(13).

**Acknowledgment.** We thank Dr. G. Tadema and P. Wijkens for some of the chiral alcohols, A. V. E. George and S. Seijkens for NMR spectra, and Prof. H. J. T. Bos for his interest.

## Notes

### Ortho Substitution of *m*-Anisaldehyde via $\alpha$ -Amino Alkoxide Directed Lithiation

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Received February 7, 1989

The addition of aromatic aldehydes to certain lithium dialkylamides gives  $\alpha$ -amino alkoxides that can be ring-lithiated with alkyllithiums. Alkylation and hydrolysis on workup provides ortho-substituted aryl aldehydes via a one-pot reaction.<sup>2</sup> This methodology works well for the

one-pot substitution of heterocyclic aromatic aldehydes<sup>3</sup> as well as for benzaldehyde derivatives.<sup>2</sup> Several research groups have used this methodology with success;<sup>4</sup> however, two laboratories<sup>5</sup> have informed us that the substitution

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(3) Comins, D. L.; Killpack, M. O. *J. Org. Chem.* 1987, 52, 104.

(4) Liu, J.; Young, J.; Li, Y.; Sha, C. *J. Org. Chem.* 1986, 51, 1120. Uemura, M.; Kobayashi, T.; Isobe, K.; Minami, T.; Hayashi, Y. *Ibid.* 1986, 51, 2859. Thompson, A.; Lever, J. R.; Canella, K. A.; Miura, K.; Posner, G. H.; Seliger, H. H. *J. Am. Chem. Soc.* 1986, 108, 4498. Uemura, M.; Kobayashi, T.; Minami, T.; Hayashi, Y. *Tetrahedron Lett.* 1986, 27, 2479. Peet, N. P.; McCarthy, J. R.; Sunder, S.; McCowan, J. *Synth. Commun.* 1986, 16, 1551. McCarthy, J. R.; McCowan, J.; Zimmerman, M. B.; Wenger, M. A.; Emmert, L. W. *J. Med. Chem.* 1986, 29, 1586. Harvey, R. G.; Cortez, C.; Ananthanarayan, T. P.; Schmolka, S. *J. Org. Chem.* 1988, 53, 3936. Miller, R. B.; Tsang, T. *Tetrahedron Lett.* 1988, 29, 6715.

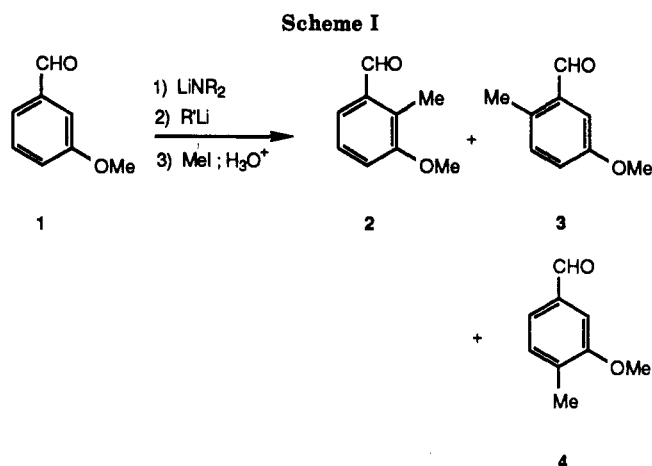
(5) See acknowledgment.

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Table I. Ortho Methylation of *m*-Anisaldehyde

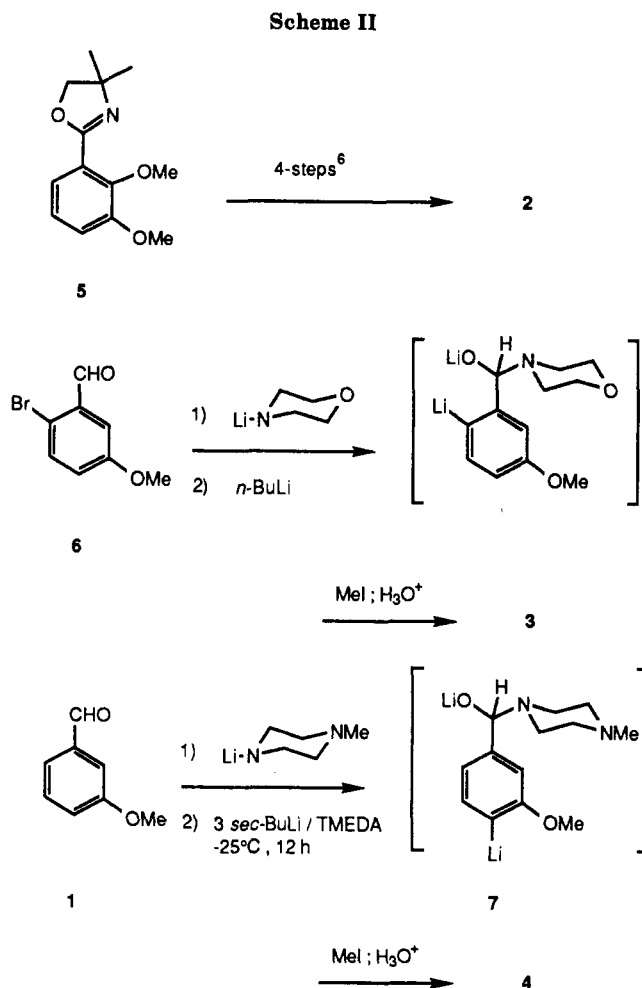
entry <sup>a</sup>	LiNR <sub>2</sub>	conditions <sup>b</sup>	yield <sup>c</sup> of 1, 2, 3 and 4, %	ratio <sup>d</sup> 2:3:4:1
a		3 <i>n</i> -BuLi, THF, -20 °C, 10 h	85	90:5:3:2
b		3 <i>n</i> -BuLi, benzene, rt, 8 h	90	88:1:10:1
c		3 <i>n</i> -BuLi, benzene, rt, 8 h	94	77:0:1:22
d		3 <i>n</i> -BuLi, benzene, rt, 2 h, reflux, 1 h	95	82:0:1:17
e		3 <i>n</i> -BuLi, THF, -20 °C, 10 h	75	16:0:14:70
f		3 <i>n</i> -BuLi, benzene, rt, 2 h	91	85:2:7:6
g		3 PhLi, <sup>e</sup> benzene, rt, 8 h	89	97.2:0.5:0.3:2
h		3 PhLi, toluene, rt, 4 h	86	98:0:0.1:1.9
i		3 PhLi, toluene, rt, 8 h	83	99:0:0:1
j		3 PhLi, benzene, rt, 8 h	91	96:0:0:4

<sup>a</sup>The reactions were performed on a 3-mmol scale in 8 mL of the indicated solvent. <sup>b</sup>After the indicated time, the mixture was cooled to -78 °C while 8 mL of THF was added. Methyl iodide (1.1 mL) was added slowly at -78 °C, and then the mixture was allowed to come to room temperature (rt) (30 min) and poured into cold, vigorously stirred 10% HCl. Extraction with ether provided the crude products. <sup>c</sup>Yield of isolated aldehydes 2, 3, 4, and 1 obtained as a mixture from radial preparative-layer chromatography. <sup>d</sup>The product ratios were determined by GC. <sup>e</sup>See ref 9.



of *m*-anisaldehyde is not as regioselective for the 2-position as we reported.<sup>2c</sup> Because of the popularity of this methodology and the fact that substituted anisaldehydes are useful starting materials for the synthesis of natural products, we decided to investigate the “*m*-anisaldehyde problem” in detail.

The lithiation-methylation of  $\alpha$ -amino alkoxides derived from 1 can lead to three possible ortho-methylated anisaldehydes 2, 3, and 4 (Scheme I). Authentic samples of these methylated anisaldehydes were prepared as shown in Scheme II. A sample of 2 was prepared from 2-(2,3-dimethoxyphenyl)-4,4-dimethyl-2-oxazoline (5).<sup>6</sup> Anisaldehyde derivative 3 was synthesized from 2-bromo-5-methoxybenzaldehyde (6) by in situ protection<sup>7</sup> followed by lithium-halogen exchange and methylation. Anisaldehyde derivative 4 was prepared by our published procedure.<sup>2c</sup> The  $\alpha$ -amino alkoxide formed from *m*-anisaldehyde (1) and lithium *N*-methylpiperazide (LNMP) in THF was treated with *sec*-butyllithium/TMEDA. Sub-



sequent methylation of the dianion 7 and workup with 10% HCl provided 4 in 60% yield. We performed several lithiation-methylation reactions of  $\alpha$ -amino alkoxides derived from *m*-anisaldehyde and analyzed (GC) the

(6) Leed, A. R.; Boettger, S. D.; Ganem, B. *J. Org. Chem.* 1980, 45, 1098.

(7) Comins, D. L.; Brown, J. D. *Tetrahedron Lett.* 1981, 22, 4213.

products for starting material (1) and methylated derivatives 2, 3, and 4. The results are given in Table I. When the reaction was run with *N*-lithio-*N,N,N'*-trimethylethylenediamine (LTMDA) by using our standard conditions,<sup>2c</sup> an oil was isolated in 85% yield, which contained 90% of the desired aldehyde 2, 8% of isomers 3 and 4, and 2% starting material (1). A similar reaction using benzene as the solvent (entry b) also failed to give the desired degree (>95%) of substitution at the 2-position. The use of lithium *N*-methylpiperazide (LNMP) as the amine component allowed for better regioselectivity, but incomplete metalation occurred (entries c and d).

In an attempt to find an  $\alpha$ -amino alkoxide with the desired ortho-directing power, we examined the reaction with *N*-lithio-*N,N,N'*-trimethylhydrazine<sup>9</sup> (LTMH) as the amine component. Interestingly, LTMH did form an effective ortho-directing  $\alpha$ -amino alkoxide of intermediate strength (entries e and f). When LTMH was the amine component, benzene the solvent, and phenyllithium<sup>9</sup> the base, a highly regioselective lithiation-methylation occurred in high yield (entry g). Phenyllithium also proved to be an effective base for metalations of LTMDA derived  $\alpha$ -amino alkoxides. In toluene or benzene, a highly regioselective methylation occurred to give the desired 2-methyl-3-methoxybenzaldehyde (2) in high yield (entries h-j).

Apparently, the lower basicity of phenyllithium, as compared to *n*-butyllithium, is responsible for the increased regioselectivity. The use of phenyllithium as a base allowed us to solve the "*m*-anisaldehyde problem". It is likely that phenyllithium would be effective in other directed lithiation reactions, and its potential as a base should not be overlooked.<sup>10</sup>

### Experimental Section

Reactions were performed in oven-dried glassware under a  $N_2$  atmosphere. Tetrahydrofuran (THF) was dried by distillation from sodium/benzophenone ketyl prior to use. Benzene, toluene, *N,N,N'*-trimethylethylenediamine, *N*-methylpiperazine, and *N,N,N'*-trimethylhydrazine<sup>9</sup> were distilled from calcium hydride and stored over 3-Å molecular sieves under  $N_2$ .

Gas-liquid chromatography (GC) was performed on a Hewlett-Packard Model 5890A gas chromatograph equipped with a 30 m  $\times$  0.25 mm FSOT column packed with OV-101. Radial preparative-layer chromatography (radial PLC) was carried out by using a Chromatotron (Harrison Assoc., Palo Alto, CA).

**Preparation of 2-Methyl-3-methoxybenzaldehyde from *m*-Anisaldehyde. General Procedure for the  $\alpha$ -Amino Alkoxide Directed Lithiation Reactions.** To a solution of 0.41 mL (3.2 mmol) of *N,N,N'*-trimethylethylenediamine in 8 mL of benzene was added 3.1 mmol of *n*-BuLi (2.3 M in hexane) dropwise with cooling (ice bath). After 15 min at room temperature, *m*-anisaldehyde (0.37 mL, 3.0 mmol) was added (0-5 °C) and the mixture was stirred at room temperature for 15 min. A solution of phenyllithium (4.5 mL, 9 mmol) in cyclohexane/ether<sup>9</sup> was added with cooling (ice bath). After the mixture was stirred at room temperature for 8 h, 8 mL of THF was added while the mixture was being cooled to -78 °C. Methyl iodide (1.1 mL, 18 mmol) was added slowly at -78 °C, the cooling bath was removed, and the mixture was allowed to come to room temperature (30 min). The mixture was poured into cold, vigorously stirred 10% HCl and extracted with ether. The combined organic layers were washed with brine, dried ( $MgSO_4$ ), and concentrated to give 510 mg of a dark oil. Purification by radial PLC ( $SiO_2$ , 5-20% Et-

OAc/hexanes) gave 410 mg (91%) of a light yellow oil. This oil consisted of 96% 3-methoxy-2-methylbenzaldehyde and 4% *m*-anisaldehyde as indicated by GC analysis.

**Acknowledgment.** We thank Larry Overman and Victor Snieckus for bringing the "*m*-anisaldehyde problem" to our attention.

### Dye-Sensitized Photooxygenation of the C=N Bond<sup>1</sup>

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Received November 7, 1988

Since the early 1970s, photooxygenations of a variety of compounds containing the C=N bond have been reported.<sup>2-12</sup> In some cases these reactions appear to use or-

(1) A preliminary account of this work was reported at the Pacific Conference on Chemistry and Spectroscopy, San Francisco, Oct 27, 1988.

(2) For a review of reactions of  $^1O_2$  with nitrogen-containing heterocycles, see: George, M. V.; Bhat, V. *Chem. Rev.* 1979, 79, 447-478. Also useful is the review by Boyer: Boyer, J. H. *Chem. Rev.* 1980, 80, 495-561.

(3) (a) Imines undergo photooxygenation and photooxidative cleavage via reaction of the triplet state with triplet oxygen: Toshima, N.; Hirai, H. *Tetrahedron Lett.* 1970, 433-436. (b) Schiff bases undergo cleavage of the C<sub>2</sub>-C= single bond subsequent to photooxidative C<sub>2</sub>-H cleavage by triplet oxygen: McCapra, F.; Burford, A. *J. Chem. Soc., Chem. Commun.* 1976, 607-608. (c) N-H hydrazones react with oxygen in an ene reaction giving C-hydroperoxyazo adducts, thence fragmentation products; singlet oxygen is not required: Yao, H. C.; Resnick, P. *J. Org. Chem.* 1965, 30, 2832-2834. Lewis, G. E.; Spencer, G. I. *Aust. J. Chem.* 1975, 28, 1733-1739.

(4) (a) Benzophenone oxime, its methyl ether, and its conjugate base are all cleaved to benzophenone by  $^1O_2$ : Wamser, C. C.; Herring, J. W. *J. Org. Chem.* 1976, 41, 1476-1477. (b) Oximes and oxime ethers are, in general, inert or almost so to  $^1O_2$ . Acetone oxime shows marginal reactivity.<sup>4a</sup> Valerophenone oxime *O*-methyl ether does not react: Ito, Y.; Konishi, M.; Matsuura, T. *Photochem. Photobiol.* 1979, 30, 53-57. Cyclohexanone oxime, its methyl ether, and acetophenone oxime react very sluggishly with  $^1O_2$ : Chawla, H. M.; Hassner, A. *Tetrahedron Lett.* 1986, 27, 4619-4622. Chawla and Hassner also showed that oxime carbamates react with  $^1O_2$  preferentially at the C-N center rather than the C=N center. The relative inertness of oximes to singlet oxygen is confirmed in the present study. C-Nitroso compounds (formally tautomeric with oximes and oxime ethers) have been shown to quench  $^1O_2$ , "...probably by an energy transfer mechanism": Singh, P.; Ullman, E. F. *J. Am. Chem. Soc.* 1976, 98, 3018-3019.

(5) Imidazoles give a variety of products depending on the substitution pattern. These reactions appear to begin by electrophilic addition (resembling the reaction of  $^1O_2$  with enamines<sup>9</sup>) and/or by 1,4-cycloaddition: Wasserman, H. H.; Stiller, K.; Floyd, M. B. *Tetrahedron Lett.* 1968, 3277-3280.

(6) (a) Foote, C. S.; Lin, J. W.-P. *Tetrahedron Lett.* 1968, 3267-3270. Foote, C. S.; Dzakpasu, A. A.; Lin, J. W.-P. *Tetrahedron Lett.* 1975, 1247-1250. (b) For a review, see: Schaap, A. P.; Zaklika, K. A. In *Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic: New York, 1979; p 180.

(7) (a) Sydnones are proposed to react with  $^1O_2$  by 1,3-cycloaddition with subsequent fragmentation: Bhat, V.; Dixit, V. M.; Ugarkar, B. G.; Trozzolo, A. M.; George, M. V. *J. Org. Chem.* 1979, 44, 2957-2961. (b) An azomethine imine was shown by the same workers to be cleaved by  $^1O_2$  to the parent ketone. This reaction too might begin with 1,3-cycloaddition. (c) Aziridines, via their azomethine ylide forms, afford products with  $^1O_2$  which can be rationalized by 1,3-cycloaddition followed by fragmentations: Bhat, V.; George, M. V. *J. Org. Chem.* 1979, 44, 3288-3292. Bhat, V.; George, M. V. *Tetrahedron Lett.* 1977, 4133-4136. (d) Diazoalkanes are cleaved by  $^1O_2$  to carbonyl compounds; in the presence of aldehydes, ozonides are also formed. The initial stage is probably 1,3-cycloaddition and/or electrophilic addition: Higley, D. P.; Murray, R. W. *J. Am. Chem. Soc.* 1974, 96, 3330-3332. Bethell, D.; McKeiver, R. *J. Chem. Soc., Perkin Trans. 2* 1977, 327-333.

(8) Trimethylhydrazine was prepared by a literature procedure, see: Class, J. B.; Aston, J. G.; Oakwood, T. S. *J. Am. Chem. Soc.* 1953, 75, 2937.

(9) Phenyllithium was purchased from Aldrich Chemical Co. as a 2.0 M solution in cyclohexane-ether.

(10) Phenyllithium is an effective base for the regioselective  $\alpha$ -lithiation of certain 1-(*tert*-butoxycarbonyl)-1,4-dihydropyridines. Comins, D. L.; Weglarz, M. A. *J. Org. Chem.* 1988, 53, 4437.