

**Synthesis of 1,4-Diphenylbutadiyne (3). Method A.** Benzyltrimethylammonium methoxide (20 mmol, as a 40% w/w MeOH solution) was slowly added to the phosphonium salt (1.85 g, 3 mmol) and benzaldehyde (450 mg, 4 mmol) in methanol (5 mL) with stirring under argon at  $-60^{\circ}\text{C}$ . The solution was gradually (1 h) warmed to  $20^{\circ}\text{C}$  and then stirred for 2 h more. The product was isolated after an aqueous workup ( $\text{Et}_2\text{O}$ ) and flash silica gel column chromatography (hexane) as 550 mg (91%) of colorless solid. All entries of Table I were prepared by this method.

**Synthesis of *E/Z* Mixtures of 1-Bromo-1,4-diphenylbutatriene (2a). Method B.** Lithium bis(trimethylsilyl)amide (6 mmol as a 1 M THF solution) was added dropwise to a THF suspension (10 mL) of the phosphonium salt **1a** (1.85 g, 3 mmol) at  $-70^{\circ}\text{C}$  under argon. The deep red solution was stirred for 15 min followed by the single-portion addition of benzaldehyde (448 mg, 4 mmol). The reaction was warmed to  $-25^{\circ}\text{C}$  (30 min) and then diluted with  $\text{Et}_2\text{O}$  (50 mL) and filtered through a plug of Florisil. The filtrate was adsorbed onto 20 g of Florisil by removing the solvent at  $0-20^{\circ}\text{C}$  in vacuo. The product was isolated via flash column chromatography on Florisil (hexane). The product **2a**, a yellow oil, rapidly decomposed in the presence of air at room temperature and was best stored in argon degassed  $\text{CCl}_4$  solutions at  $-20^{\circ}\text{C}$  or below:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ) *E/Z* mixtures  $\delta$  6.65, 6.83 (2 s, 1, vinyl, ratio 2:1), 7.2-7.6 (m, 9, Ar), 7.75 (m, 1, Ar);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3/\text{CCl}_4$ ) isomers  $\delta$  101.0, 101.4, 109.4, 109.6 (CPh), 127.7, 127.85, 128.1, 128.2, 128.3, 128.4, 128.5, 128.8, 128.9, 129.1, 132.4, 135.8, 136.2, 136.4 (Ar), 152.5, 152.7, 154.6, 154.7 (cumulene carbons); IR ( $\text{CCl}_4$ )  $\nu_{\text{max}}$   $\text{cm}^{-1}$  3040, 3010, 2010, 1600, 1480, 1435; MS (EI), *m/e* (relative intensity) 284, 282 ( $\text{M}^+$ , 4, 4), 202 ( $\text{M}^+ - \text{HBr}$ , 60), 105 (88), 82 (100).

The yellow oil **2a** was diluted with THF (10 mL) under argon at  $-30^{\circ}\text{C}$ . To this was slowly added (7 mmol, as a 40% w/w MeOH solution) benzyltrimethylammonium methoxide. The resultant solution was warmed to  $0^{\circ}\text{C}$  (1.5 h) and then quenched ( $\text{H}_2\text{O}$ ). The product diphenylbutadiyne, 275 mg (47%), was isolated as in method A.

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**Registry No.** **1a**, 105836-22-4; (*Z*)-**1b**, 105836-23-5; (*E*)-**2a**, 105836-26-8; (*Z*)-**2a**, 105836-27-9; **3a**, 886-66-8; **3b**, 51624-43-2; **3c**, 23429-36-9; **3d**, 105836-24-6; **3e**, 77093-14-2; **3f**, 105836-25-7; **3g**, 54334-99-5; **3h**, 13641-39-9; **3i**, 58672-84-7; **4a**, 105836-20-2; **4b**, 105836-21-3; PhCHO, 100-52-7; 4- $\text{ClC}_6\text{H}_4\text{CHO}$ , 104-88-1; 4- $\text{MeOC}_6\text{H}_4\text{CHO}$ , 123-11-5; (*E*)- $\text{CH}_3\text{CH}=\text{CHCHO}$ , 123-73-9;  $\text{CH}_3(\text{CH}_2)_5\text{CHO}$ , 111-71-7; 3-phenyl-2-propyn-1-ol, 1504-58-1; *trans*-2,3-dibromo-3-phenyl-2-propen-1-ol, 105836-18-8; *cis*-2,3-dibromo-3-phenyl-2-propen-1-ol, 105836-19-9; benzyltrimethylammonium methoxide, 122-08-7; 1-naphthylencarboxaldehyde, 66-77-3; 2-thiophenecarboxaldehyde, 98-03-3; 3-thiophenecarboxaldehyde, 498-62-4; 3-pyridinecarboxaldehyde, 500-22-1; lithium bis(trimethylsilyl)amide, 4039-32-1.

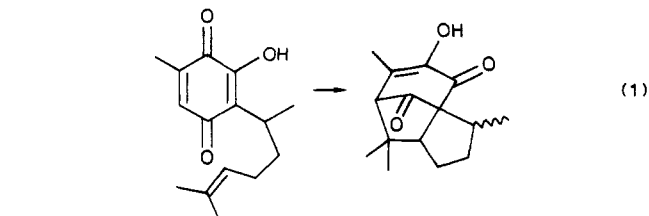
## Reaction of 5-Substituted 2-Methoxy 1,4-Quinones with Boron Tribromide

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During a study designed to examine the perezone to pipitzol cyclization,<sup>2</sup> (eq 1), we prepared several 2-methoxybenzoquinones containing olefins. Attempted cleavage of the methyl ether moiety with boron tribromide ( $\text{BBr}_3$ ) afforded unprecedented products, the nature of which we report here (Table I).



A methylene chloride solution of quinone **1**, **3**, **6**, or **9** was treated with  $\text{BBr}_3$  at  $-78^{\circ}\text{C}$  for 4 h. The crude products were acetylated to facilitate purification. From literature reports with naphthoquinones,<sup>3</sup> we anticipated little difficulty with this reaction and therefore initially examined quinones **6** and **9**. We were surprised to isolate cyclic ethers **7a** and **7b** in 41% and 46% yields, respectively. Ether **7a** was accompanied by diacetate **8** in 36% yield. Quinone **1** gave a complex mixture containing diacetate **2** in 22% yield. Under these same reaction conditions, about half of quinone **3** was reduced and all of the olefin was brominated, resulting in products **4** and **5**.

The structures have been characterized by routine spectral techniques. The identification of all of the products except **7a** and **7b** requires no comment. Compounds **7a** and **7b** exhibited the expected mass spectral fragment losses of  $\text{CH}_2\text{Br}$  and  $\text{CHBrCH}_3$ , respectively. The carbon and proton magnetic resonance data are consistent with the assigned structures.

Previous reports about  $\text{BBr}_3$  or quinone reactions do not suggest a mechanism. After completion of this work,  $\text{BBr}_3$  has been shown to reduce sulfoxides to mercaptans<sup>4</sup> and borobrominate alkynes.<sup>5</sup> Neither of these reaction pathways can be invoked in this study. Moore<sup>6</sup> observed that  $\text{HBr}$  in acetic acid and some quinones yield hydroquinones and molecular bromine.

Moore's<sup>6</sup> report provides a basis for a mechanistic rationalization of our observations (Scheme I). The formation of ether **7** requires quinone reduction and the presence of a bromonium ion. We suggest that  $\text{BBr}_3$  coordinates with the quinone carbonyl and that this complex loses bromide ion. Bromide can transfer an electron to the complex, generating a quinone radical and a bromide radical. A second bromide anion can combine with this radical pair to form molecular bromine and a hydroquinone anion complexed to  $\text{BBr}_2$ . Molecular bromine reacts with the olefinic side chain to provide the observed products.

Three experiments are forthcoming from this mechanism: First, the involvement of bromide anion suggests that added bromide might improve yields or increase reaction rates. Added  $\text{LiBr}$  did not affect the product mixture from **6**. Second, the analogy with Moore's report<sup>6</sup> implies that  $\text{HBr}/\text{HOAc}$  should give similar results. Quinones **3** and **6** gave the same product mixtures with

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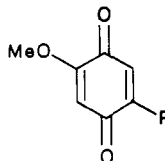
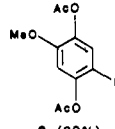
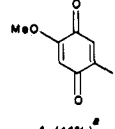
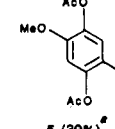
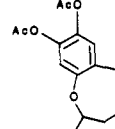
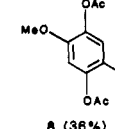
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Table I. Reaction of Quinones and BBr<sub>3</sub>

quinone (R)	products (% yield)
	 2 (22%)
3 (CH <sub>2</sub> ) <sub>3</sub> CH=CH <sub>2</sub>	 4 (41%) <sup>a</sup>  5 (39%) <sup>a</sup>
6 (CH <sub>2</sub> ) <sub>2</sub> CH-(CH <sub>2</sub> CH=CH <sub>2</sub> )-CO <sub>2</sub> Me	 7a (41%) <sup>b</sup>  7b (46%) <sup>c</sup>
9 (CH <sub>2</sub> ) <sub>2</sub> CH-(CH <sub>2</sub> CH=CH <sub>2</sub> )-CH(CH <sub>3</sub> )CO <sub>2</sub> Me	7b (46%) <sup>c</sup>

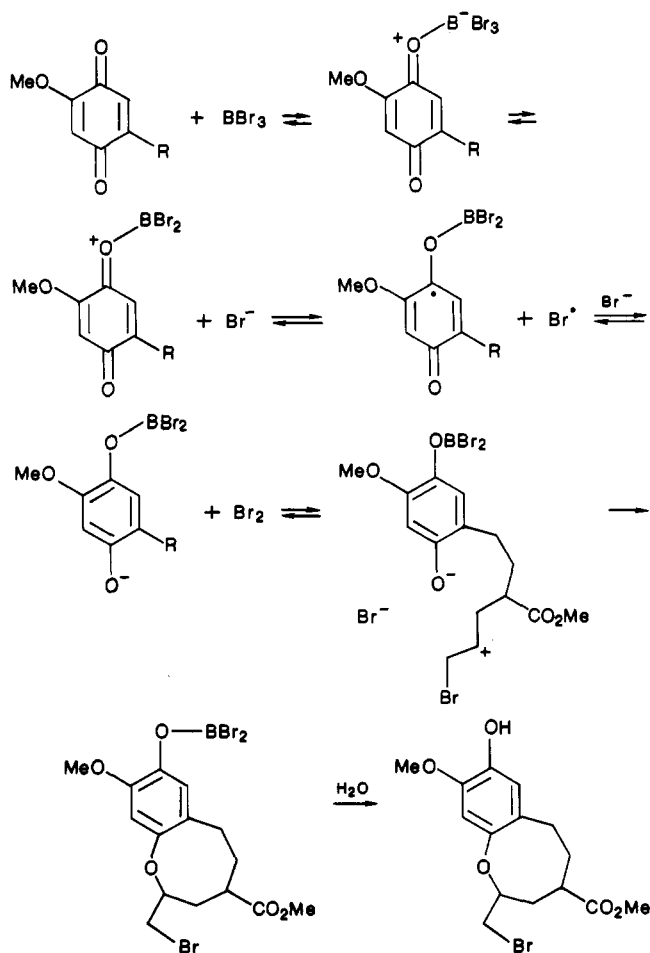
<sup>a</sup> R' = (CH<sub>2</sub>)<sub>3</sub>CHBrCH<sub>2</sub>Br. <sup>b</sup> R'' = CH<sub>2</sub>Br. <sup>c</sup> R'' = CHBrCH<sub>3</sub>.

BBr<sub>3</sub> or with HBr/HOAc treatment. Finally, we examined BBr<sub>3</sub> as a potential method for the bromination of quinones. Treatment of benzoquinone with BBr<sub>3</sub> followed by acetylation yielded 2-bromo-1,4-diacetoxybenzene (41%) and 1,4-diacetoxybenzene (16%). Added lithium bromide did not improve these yields.

Other reagents also failed to effect the cleavage of the methyl ether of these quinones. These reagents included Me<sub>3</sub>SiI, LiI/collidine, and aqueous base.<sup>7,8</sup>

The quinones 1, 3, 6, and 9 were synthesized by a standard sequence of reactions. 4-(2,4,5-Trimethoxyphenyl)butanoic acid was prepared by Friedel-Crafts acylation of trimethoxybenzene with succinic anhydride followed by reduction with Zn/HCl.<sup>9-11</sup> The dianion of this acid was alkylated,<sup>12</sup> and the product was esterified with diazomethane. Ceric ammonium nitrate (CAN) oxidation of these aryl esters gave quinones 1, 6, and 9.<sup>13</sup> Quinone 3 was prepared by conversion of the butanoic acid into the corresponding aldehyde,<sup>14</sup> Wittig olefination, and CAN oxidation.

The reaction of these benzoquinones with boron tribromide clearly gives unexpected reaction products. This work and Guindon's report<sup>4</sup> suggest that boron tribromide may act as a mild reducing agent. In certain systems the reduction utilizing boron tribromide is faster than the

Scheme I. Reaction of Quinones with BBr<sub>3</sub>

addition of it to sites of unsaturation.<sup>5</sup>

### Experimental Section

**General Procedures.** Infrared spectra (IR) were recorded as thin films on a Beckman IR 18-AX spectrophotometer; bands yielding structural information are reported in reciprocal centimeters (cm<sup>-1</sup>), with polystyrene calibration. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian EM 390 spectrometer at 35 °C in deuteriochloroform, unless noted, and peak positions are reported in parts per million (δ) from tetramethylsilane internal standard as multiplet (m), pentet (p), quartet (q), triplet (t), doublet (d), or singlet (s). Decoupling experiments were completed on a Varian HR-220 spectrometer or a Nicolet 360-MHz spectrometer. <sup>13</sup>C NMR were recorded on a Varian CFT-20 spectrometer or on a Nicolet 200-MHz multinuclear, wide-bore spectrometer. Low-resolution mass spectra were obtained from a Finnigan 4021 GCMSDS at 70-eV ionizing voltage. Samples were introduced by GC using a DEXSIL column or an SE 30 column (vide infra) or by direct inlet (DI). Relative percentages of the base peak are in parentheses. High-resolution spectra (HRMS) were performed at the Midwest Center for Mass Spectrometry. GLPC analysis was performed on a Varian 3700 gas chromatograph with fid detector outfitted with a 6 ft × 0.25 in. glass column containing 3% SE 30 or 3% DEXSIL on 100/120 Gas Chrom Q (Applied Science). Column chromatography was done on E. Merck silica gel 60, particle size 0.063–0.200 mm, or Florisil, 100–200 mesh. Preparative HPLC was completed on a Waters analytical instrument using a 4 ft × 3/8 column packed with Li Chrosorb SI 100 of 5-μm particle size (EM reagents). Thin-layer chromatography (TLC) was completed on 0.10-mm-thick silica gel with a fluorescent indicator and visualized with UV light and/or iodine.

**General Method for the BBr<sub>3</sub> Reaction.** The published methods were adapted to this system.<sup>3</sup> The methoxyquinone was dissolved in freshly distilled CH<sub>2</sub>Cl<sub>2</sub> to make a 0.1 M solution and the resultant cooled to -78 °C; 1–2 equiv of BBr<sub>3</sub> (1 M in CH<sub>2</sub>Cl<sub>2</sub>)

(7) For the details of these experiments, see: Frazier, J. D. Ph.D. Thesis, UCSD, 1984.

(8) We are grateful to Dr. F. Vellaccio for completing some of these experiments.

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was then added. The brownish solution was stirred 4 h at  $-78^{\circ}\text{C}$ . The reaction was quenched with 10 mL of a saturated  $\text{KH}_2\text{PO}_4$  solution and brought to ambient temperature. The aqueous layer was extracted with  $3 \times 20$  mL of  $\text{CH}_2\text{Cl}_2$ , and the organic layer was 3 dried with  $\text{MgSO}_4$ . Removal of the solvent yielded a brown residue with higher than theoretical yields.

The residue from the  $\text{BBr}_3$  reaction was dissolved in 1 mL of  $\text{Ac}_2\text{O}$  and 0.1 mL of pyridine/mmol of quinone and stirred overnight at ambient temperature. The excess reagents were removed under reduced pressure, and the residue was passed through a short Florisil column using 3:1 hexane/ $\text{EtOAc}$  as solvent. The solvent was removed to afford a yellow residue for purification.

**$\text{BBr}_3$  Reaction with 1.** From 0.31 g (1.3 mmol) of 1 and 1.5 mL (1.5 mmol) of  $\text{BBr}_3$  was isolated 0.41 g of a red solid: IR 3400, 3070, 2995, 2950, 1740, 1710, 1670, 1610, 1520, 1450, 1370  $\text{cm}^{-1}$ ; NMR  $\delta$  1.85 (m, 4), 2.35, 2.47 (each m, 7.4), 3.7 (s, 6), 3.8 (s, 3), 3.88 (s, 3), 4.92 (s, 1), 5.5 (br s, 2), 5.85 (s, 1), 6.42 (s, 1), 6.6 (s, 1). Acetylation with 10 mL of acetic anhydride and 4 mL of pyridine, followed by filtration through Florisil, yielded 0.41 g of a yellow oil.

This mixture resisted purification. Several fractions were obtained by HPLC, the purist of which accounted for 30% of the crude mixture and possessed two components by GC: (SE-30  $t_r$  130  $^{\circ}\text{C}$  for 2 min, 40  $^{\circ}\text{C}/\text{min}$ ,  $t_r$  280  $^{\circ}\text{C}$ ) rt 6.2 (73%), 7 min (27%); IR 2950, 1760, 1730, 1610, 1510, 1440, 1360, 1200, 1160, 1000, 910  $\text{cm}^{-1}$ ; NMR  $\delta$  1.8 (m, 2.5 H), 2.25 (s), 2.27 (s, 3.8 H), 2.3 (s, 3.8 H), 2.4 (m, 2.5 H), 2.5-2.8 (m, 2.5 H), 3.65 (s, 1 H), 3.75 (s, 3.8 H), 3.82 (s, 3 H), 5.9 (s, 0.5 H), 6.67 (s, 1 H), 6.9 (s, 1 H); mass spectrum (GC SE-30) rt 6.2 min,  $m/z$  324 ( $\text{M}^+$ ), 282 ( $\text{M}^+ - \text{C}_2\text{H}_2\text{O}$ ), 240 ( $\text{M}^+ - 2 \text{C}_2\text{H}_2\text{O}$ ), 208, 180, 153 (100); mass spectrum (GE SE-30) rt 7 min,  $m/z$  404, 402 ( $\text{M}^+$ ), 362, 360 ( $\text{M}^+ - \text{C}_2\text{H}_2\text{O}$ ), 320, 318 ( $\text{M}^+ - 2 \text{C}_2\text{H}_2\text{O}$ ), (320, 94% of 318), 288, 286 ( $\text{M}^+ - 2 \text{C}_2\text{H}_2\text{O} + \text{CH}_2\text{OH}$ ), 233, 231, 207 (100), 153. The compound with GC retention time of 6.2 min has been assigned to structure 2. Many of the other HPLC fractions included bromine adducts as determined by GCMS.

**2-(4,5-Dibromopentyl)-5-methoxy-2,5-cyclohexadiene-1,4-dione (4) and 2-(4,5-Dibromopentyl)-5-methoxy-1,4-benzenediol Diacetate (5).** From the reaction of 0.059 g (0.029 mmol) of quinone 3 and  $\text{BBr}_3$  followed by acetylation was obtained 0.12 g (92%) of 4 and 5. These compounds were in a 1:1 ratio and separated by HPLC. From 0.025 g was isolated 0.011 g of quinone 4: IR 3030, 2915, 2860, 1760, 1720, 1670, 1650, 1605, 1440, 1370, 1220, 1200, 1170, 990, 895, 855  $\text{cm}^{-1}$ ; NMR  $\delta$  1.7 (m, 1 H, coupled to  $\delta$  2.5), 1.83 (m, 2 H, coupled to  $\delta$  4.18, 2.5, 2.22), 2.22 (m, 1 H), 2.5 (m, 2 H), 3.62 [dd, 1 H, coupled to  $\delta$  3.85 (d), 4.18], 3.83 (s, 3 H), 3.85 [dd, 1 H, coupled to  $\delta$  3.62 (d) and 4.18], 4.18 [m, 1 H, coupled to  $\delta$  1.85, 3.62 (d), 3.85 (d)], 5.9 (s, 1 H), 6.55 (s, 1 H); HRMS for  $\text{C}_{12}\text{H}_{18}\text{O}_3\text{Br}_2$  ( $\text{M}^+ + 2$ ) obsd  $m/z$  369.9433, 367.9400, 365.9311, calcd 369.94258, 367.94458, 365.94658; LRMS  $m/z$  370 ( $\text{M}^+ + 2$ ), 368, 366, 287, 285, 277, 260, 248, 153 (100). Benzenediacetate 5 was isolated as an oil (0.010 g): IR 2930, 2860, 1760, 1630, 1510, 1445, 1370, 1200, 1100, 1015, 925  $\text{cm}^{-1}$ ; NMR  $\delta$  1.65 (m, 1 H), 1.79 (m, 2 H, coupled to  $\delta$  2.47, 4.15), 2.15 (m, 1 H, coupled to  $\delta$  1.79, 1.65), 2.3 (s, 3 H), 2.34 (s, 3 H), 2.47 (m, 2 H, coupled to  $\delta$  1.79, 1.65), 3.6 [dd, 1 H,  $J = 10$  Hz, coupled to  $\delta$  3.8 (d), 4.15], 3.79 (s, 3 H), 3.81 [dd, 1 H,  $J = 4.5$  and 10 Hz, coupled to  $\delta$  3.6 (d), 4.15 (br t)] 4.15 [m, 1 H, coupled to  $\delta$  3.6 (d), 3.8 (d), 2.15, 1.79], 6.67 (s, 1 H), 6.92 (s, 1 H); HRMS for  $\text{C}_{16}\text{H}_{20}\text{O}_5\text{Br}_2$ , obsd  $m/z$  452.11587, 412.16771, 410.1185, 408.12539 ( $\text{M}^+ - \text{C}_2\text{H}_2\text{O}$ ), 370.40789, 368.38688 (100), 366.43804, calcd 452.1546, 412.1166 ( $\text{M}^+ - \text{C}_2\text{H}_2\text{O}$ ), 410.1186, 412.1166.

**Methyl 8,9-Diacetoxy-2-(bromomethyl)-3,4,5,6-tetrahydro-2H-1-benzoxocin-4-carboxylate (7a) and Methyl 2-(2-Propenyl)-4-(2,5-diacetoxy-4-methoxyphenyl)butanoate (8).** From the reaction of 0.25 g (0.9 mmol) of quinone 6 followed by column chromatography on 10 g of silica gel using 8:2 hexane/ $\text{EtOAc}$  was isolated 0.12 g (41% yield) of 7a: IR 3010, 2940, 2865, 1760, 1630, 1510, 1450, 1360, 1200, 1160, 1100, 1020, 930, 910  $\text{cm}^{-1}$ ; NMR  $\delta$  1.72 (m, 2 H), 2.02 (m, 1 H), 2.28 (s, 3 H), 2.32 (s, 3 H), 2.58 (m, 4 H), 3.5 (dd, 2 H,  $J = 6, 6$  Hz), 3.75 (s, 3 H), 4.52 (m, 1 H), 6.62 (s, 1 H), 6.87 (s, 1 H);  $^{13}\text{C}$  NMR  $\delta$  177.2 (s), 169.2 (s), 168.6 (s), 149.8 (s), 146.6 (s), 137.1 (s), 124.2 (s), 123.4 (d), 107.1 (d), 75.6 (d), 55.9 (q), 39.4 (d),  $2 \times 33.3$  (t), 30.2 (t), 26.5 (t), 20.7 (q), 20.4 (q); MS,  $m/z$  388 ( $\text{M}^+ - 42$ ), 346 (94% of 344),

344 ( $\text{M}^+ - 2 \text{CH}_2\text{CO}$ ), 293, 248, 195, 166, 153 (100); HMRS for  $\text{C}_{16}\text{H}_{19}\text{O}_6\text{Br}$ , obsd  $m/z$  388.2203, 386.2313, calcd 388.2283, 386.2303. Continued elution yielded 0.11 g (36%) of an oil containing 90% 8: GC (SE-30,  $t_r$  130  $^{\circ}\text{C}$  for 2 min, 40  $^{\circ}\text{C}/\text{min}$ ,  $t_r$  280  $^{\circ}\text{C}$ ) rt 6.2, 6.7 min (1:9 ratio); IR 2950, 2820, 1765, 1730, 1510, 1370, 1200, 1160, 910  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  1.8 (m), 2.28 (s), 2.35 (s), 2.45 (m), 2.7 (m), 3.65 (s), 3.7 (s), 3.78 (s), 4.9-5.15 (m), 5.7 (m), 6.65 (s), and 6.9 ppm (s); MS (70 eV, GC SE-30; rt 6.7 min)  $m/z$  364, 322, ( $\text{M}^+ - \text{C}_2\text{H}_2\text{O}$ ), 280 ( $\text{M}^+ - 2 \text{C}_2\text{H}_2\text{O}$ ), 248 ( $\text{M}^+ - 2 \text{C}_2\text{H}_2\text{O} \& \text{HOCH}_3$ ), 153 (100).

**Methyl 8,9-Diacetoxy-2-(1-bromoethyl)-3,4,5,6-tetrahydro-2H-1-benzoxocin-4-carboxylate (7b).** From reaction of 0.47 g (1.91 mmol) of 9 was obtained 0.35 g of crude product. From 0.05 g was isolated 0.03 g of 10 (40%) by HPLC: IR 3000, 2940, 2860, 1765, 1610, 1505, 1445, 1370, 1200, 1010, 920  $\text{cm}^{-1}$ ; NMR  $\delta$  1.70 (m, 2 H), 1.76 (d, 3 H,  $J = 7$  Hz), 2.10 (m, 1 H), 2.3 (s, 3 H), 2.34 (s, 3 H), 2.60 [m, 4 H, coupled to  $\delta$  4.28, 2.28 (d), 1.70], 3.79 (s, 3 H), 4.07 [m, 1 H,  $J = 7$  Hz coupled to  $\delta$  4.28, 1.76 (s)], 4.28 [m, 1 H, coupled to  $\delta$  4.07 (q) 2.60, 1.70], 6.68 (s, 1 H), 6.91 (s, 1 H); HRMS for  $\text{C}_{17}\text{H}_{21}\text{O}_6\text{Br}$  obsd  $m/z$  402.0479, 400.0509 ( $\text{M}^+ - \text{C}_2\text{H}_2\text{O}$ ), calcd 402.05013, 400.05213; MS,  $m/z$  444, 442, 402 ( $\text{M}^+ - \text{C}_2\text{H}_2\text{O}$ ), 400 (equal intensity to 402), 360 ( $\text{M}^+ - 2 \text{C}_2\text{H}_2\text{O}$ ), 358 (equal intensity to 360), 335 ( $\text{M}^+ - \text{C}_2\text{H}_4\text{Br}$ ), 279, 195, 177, 166, 153 (100), 125, 110.

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**Registry No.** 1, 105563-73-3; 2, 105563-74-4; 3, 105597-48-6; 4, 105563-75-5; 5, 105563-76-6; 6, 105563-77-7; 7a, 105563-78-8; 7b, 105563-79-9; 8, 105563-80-2; 9, 105563-81-3;  $\text{BBr}_3$ , 10294-33-4.

**Supplementary Material Available:** Spectral data for 1, 3, 6, and 9 as well as all synthetic precursors (4 pages). Ordering information is given on any current masthead page.

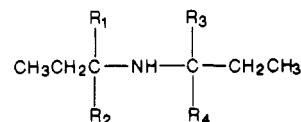
## Preparation of Hindered Lithium Amide Bases and Rates of Their Reaction with Ether Solvents

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We previously described<sup>2</sup> methods for the preparation of a series of highly branched secondary amines (1a-f).



- 1a:  $\text{R}_1, \text{R}_2 = \text{R}_3, \text{R}_4 = -(\text{CH}_2)_5-$   
 b:  $\text{R}_1 = \text{R}_2 = \text{R}_3 = \text{R}_4 = \text{CH}_3$   
 c:  $\text{R}_1 = \text{R}_2 = \text{R}_3 = \text{CH}_3, \text{R}_4 = \text{CH}_2\text{CH}_3$   
 d:  $\text{R}_1 = \text{R}_3 = \text{CH}_3, \text{R}_2 = \text{R}_4 = \text{CH}_2\text{CH}_3$   
 e:  $\text{R}_1 = \text{CH}_3, \text{R}_2 = \text{R}_3 = \text{R}_4 = \text{CH}_2\text{CH}_3$   
 f:  $\text{R}_1 = \text{R}_2 = \text{R}_3 = \text{R}_4 = \text{CH}_2\text{CH}_3$

We report here our observations on the preparation and ether stability of the lithium amide bases derived from this series and from other commercially available, secondary amines.

## Results and Discussion

**Preparation of Lithium Amides.** The commonly used metal amides, lithium diisopropylamide (LDA) and

(1) Dow Summer Fellow, 1980.

(2) Kopka, I. E.; Fataftah, Z. A.; Rathke, M. W. *J. Org. Chem.* 1980, 45, 4616.