modification of the Howk and Sauer method gave ready access to acetal **2** and was successfully applied to the formation of other alkynal acetals. The $NiCl_2/NaBH_4$ reducing systems allowed the stereoselective formation of (*Z*)-alkenal acetal **3** on a large scale independent of autoclaves or hydrogenators.

Experimental Section

The IR spectra were recorded on a Perkin-Elmer Model 782 spectrophotometer. ^1H NMR spectra were obtained with a Varian EM-360A spectrometer with Me_4Si as the internal standard. GLC analyses were carried out on Hewlett-Packard 5840H and 5710A gas chromatographs with 15% Carbowax-20M on 80/100 Chromasorb W ($^1/_8$ in. × 6 ft) columns. A standard program of 100–210 °C and 8 deg/min was used for all analyses. Samples of 1-heptyne, 1-hexyne, and 1-octyne were graciously provided by Heico Division, Whittaker Corp. All were used without further purification.

1,1-Diethoxy-2-octyne (2). 1-Heptyne (1100 g, 11.46 mol), triethyl orthoformate (1100 g, 7.5 mol), sodium iodide (73.9 g, 0.49 mol), and zinc chloride (44.9 g, 0.33 mol) were heated to reflux, removing the ethanol/1-heptyne azeotrope by distillation. When the reaction was complete by GC, heating was stopped (pot temperature 195 °C, 4 h). The cooled reaction mixture was washed with a 2.4% sodium bicarbonate solution (1400 g) and the aqueous phase extracted with hexane (350 g). The organic phases were combined and the hexane removed in vacuo. The crude product was distilled through a 1-ft Goodloe column to give a 70.2% yield (1052.6 g) of **2**: bp 87 °C (2.8 torr); IR (neat, film) 2975, 2930, 2870, 1122, 1052 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (m, 3 H), 1.22 (t, *J* = 7 Hz, 6 H) [superimposed on δ 1.40 (m, 6 H)], 2.18 (m, 2 H), 3.62 (m, 4 H), 5.22 (m, 1 H).

1,1-Diethoxy-2-heptyne (11). **11** was synthesized as above. The reaction was quenched after 4.5 h, pot temperature 120 °C, to give a 42.8% yield of **11**: bp 50 °C (0.5 torr); IR (neat, film) 2975, 2030, 1151, 1052 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92 (m, 3 H), 1.27 (t, *J* = 7 Hz, 6 H) [superimposed on δ 1.45 (m, 4 H)], 2.21 (m, 2 H), 3.65 (m, 4 H), 5.23 (m, 1 H).

1,1-Diethoxy-2-nonyne (10). **10** was synthesized as above. The reaction was quenched after 5 h, pot temperature 180 °C, to give a 74.3% yield of **10**: bp 85 °C (1 torr); IR (neat, film) 2940, 1156, 1048 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (m, 3 H), 1.23 (t, *J* = 7 Hz, 6 H) [superimposed on δ 1.35 (m, 8 H)], 2.22 (m, 2 H), 3.68 (m, 4 H), 5.25 (m, 1 H).

1,1-Diethoxy-2(*Z*)-octene (3). To anhydrous denatured ethanol (210 g) at 0 °C and under nitrogen atmosphere were added sodium borohydride (5.2 g, 0.14 mol) and nickel(II) chloride (2.4 g, 0.019 mol). A solution of **1** (60 g, 0.30 mol) in 30 g of methanol was added over 20 min, keeping the reaction temperature below 5 °C. Methanol (189.0 g) was then added over 1 h, keeping the temperature below 5 °C. The reaction mixture was stirred at 0 °C and the progress followed by GLC. When the reaction was 95% complete (approximately 3 h), the catalyst was deactivated by stirring air into the system for 5 min. Water (750.0 g) was added, and the reaction mixture was extracted twice with hexane (150 mL). The organic layer was filtered through diatomaceous earth and the hexane removed in vacuo. The crude was distilled through a 6-in. Goodloe column to give a 64.3% yield (39.0 g) of **3** (alkane/*Z*/*E* ratio, 0.1/97.1/1.1): bp 45 °C (0.07 torr); IR (neat, film) 2972, 2922, 2870, 1122, 1055, 995 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, *J* = 5 Hz, 3 H), 1.2 (t, *J* = 8 Hz, 6 H), 1.35 (m, 6 H), 2.21 (m, 2 H), 3.6 (m, 4 H), 5.25 (m, 1 H), 5.60 (m, 1 H), 5.65 (m, 1 H).

1,1-Diethoxy-2(*Z*)-heptene (12). **12** was synthesized as above: IR (neat, film) 2972, 2922, 2870, 1122, 1055, 995 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, *J* = 5 Hz, 3 H), 1.2 (t, *J* = 8 Hz, 6 H), 1.35 (m, 4 H), 2.21 (m, 2 H), 3.6 (m, 4 H), 5.25 (m, 1 H), 5.60 (m, 1 H), 5.65 (m, 1 H).

1,1-Diethoxy-2(*Z*)-nonene (13). **13** was synthesized as above: IR (neat, film) 2972, 2922, 2870, 1122, 1055, 995 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, *J* = 5 Hz, 3 H), 1.2 (t, *J* = 8 Hz, 6 H), 1.35 (m, 8 H), 2.21 (m, 2 H), 3.6 (m, 4 H), 5.25 (m, 1 H), 5.60 (m, 1 H), 5.65 (m, 1 H).

2(*Z*)-Octenal (4). To a solution of acetone (1000 g, 17.22 mol), water (500 g, 27.76 mol), and *p*-toluenesulfonic acid (4.0 g, 0.023 mol) at 0 °C was added **3** (300 g, 1.50 mol). The reaction mixture was stirred at 0 °C for 15 min and then neutralized with sodium bicarbonate (5.0 g, 0.059 mol). It was then extracted five times with hexane (150 mL) at 0 °C, concentrated in vacuo, and distilled through a short-path still to yield 93.1% (176.2 g) of **4** (97.6% *Z* isomer): bp 51 °C (1.8 torr); IR (neat, film) 1678, 1621, 1609 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91 (t, *J* = 8 Hz, 3 H), 1.41 (m, 6 H), 2.62 (m, 3 H), 5.98 (ddt, *J* = 11, 8, 1 Hz, 1 H), 6.68 (dt, *J* = 11, 8 Hz, 1 H), 10.12 (d, *J* = 8 Hz, 1 H).

Ethyl 2(*E*),4(*Z*)-Decadienoate (6). To toluene (1500 g) at 0 °C was added with mechanical stirring sodium hydride (32.8 g, 0.68 mol) as a 50% mineral oil dispersion. Under nitrogen, ethyl (diethoxyphosphinyl)acetate[8] (150 g, 0.67 mol) was added dropwise over 30 min, maintaining 0 °C during the addition. Aldehyde **4** (80.1 g, 0.63 mol) was then added over 75 min at 0 °C. After being stirred for 30 min, the reaction mixture was washed with water (350 g). The crude product was distilled through a 1-ft Goodloe column to give a 76.9% yield (94.9 g) of ester **6** (purity; 88% 2*E*,4*Z* and 12% 2*E*,4*E*): bp 86 °C (0.9 torr); IR (neat, film) 2940, 2860, 1710, 1635, 1605, 1270, 1175, 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91 (m, 3 H), 1.31 (br t, *J* = 7 Hz, 9 H), 2.28 (m, 2 H), 4.24 (q, *J* = 7 Hz, 2 H), 5 .66–6.35 (m, 2 H), 5.82 (d, *J* = 11 Hz, 1 H) 7.61 (dd, *J* = 11, 15 Hz, 1 H).

Registry No. **1**, 628-71-7; **2**, 16387-55-6; **3**, 16387-56-7; **4**, 20664-46-4; (2*E*,4*Z*)-**6**, 3025-30-7; (2*E*,4*E*)-**6**, 7328-34-9; **8**, 629-05-0; **9**, 693-02-7; **10**, 79496-57-4; **11**, 18232-30-9; **12**, 81149-92-0; **13**, 91043-38-8; $(EtO)_2P(O)CH_2CO_2Et$, 867-13-0.

Stereodivergent Syntheses of *threo*- and *erythro*-6-Amino-6-deoxyheptosulose Derivatives via an Optically Active Oxazolidine Aldehyde

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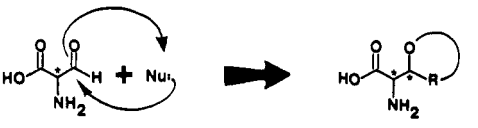
The stereocontrolled assembly of complex amino sugars is today an area of intense research effort. Introduction of nitrogen onto a pyranose or furanose ring can often be done specifically but similar control of acyclic side chain stereochemistry remains a less secure issue. Furthermore, it is desirable to form optically pure products—i.e., to exert *absolute* as well as relative stereocontrol.[1]

We began investigating nucleophilic (cyclo)additions to penaldic acid equivalents (vis., I → II) in connection with a projected synthesis of amipurimycin (1) and related amino sugar antibiotics.[2] One requirement of such a



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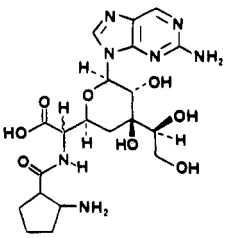

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(1) For a review of carbohydrate syntheses with an emphasis on acyclic stereocontrol, see: McGarvey, G. J.; Kimura, M.; Oh, T.; Williams, J. M. *J. Carbohydr. Chem.* **1984**, *3*, 125.

0022-3263/86/1951-2609$01.50/0

Table I. Cyclocondensation of Aldehyde 2 with Siloxy Dienes 3

entry	diene	conditions[a]	5:6[b]	yield, %
1	**3a** (X = H)	5% $ZnCl_2/CH_2Cl_2$, 0 °C	16.9:1.0	86
2	**3a**	2% $ZnCl_2/CH_2Cl_2$, RT	1.0:1.3	94
3	**3a**	7% $ZnCl_2/CH_2Cl_2$, RT	18.0:1.0	89
4	**3a**	70% $ZnCl_2/CH_2Cl_2$, RT	60.0:1.0	57
5	**3a**	5% $ZnCl_2$/THF, RT	1.0:1.0	74
6	**3a**	5% $ZnCl_2$/THF, reflux	1.0:1.2	95
7	**3a**	15% $ZnCl_2$/DMF	*e*	*e*
8	**3b** (X = OAc)[c]	5% $ZnCl_2/CH_2Cl_2$, RT	19.0:1.0	83
9	**3b**	70% $ZnCl_2/CH_2Cl_2$, RT	77.4:1.0	76
10	**3b**	9% $ZnCl_2$/DME, RT	3.0:1.0	68
11	**3b**	7% $ZnCl_2$/THF, RT	1.2:1.0	72
12	**3b**	15% $ZnCl_2$/DMF, RT	1.0:4.5	8[d]
13	**3b**	toluene reflux	1.0:2.0	17

[a] Reactions were run with 1–2 equiv of diene **3** at the indicated temperature until no aldehyde remained then stirred with 1 N HCl–Et_2O at room temperature (RT) until **4** → **5** + **6** was complete. [b] Diastereomer ratios were determined by HPLC on 10μ SiO_2 (25 cm × 4.5 mm) eluting with 3:1 hexanes–EtOAc at 1.0 mL/min and employing UV detection at 250 nm: **5a**, t_r 18 min; **6a**, t_r 21 min; **5b**, t_r 22 min; **6b**, t_r 25 min. [c] Prepared according to: Danishefsky, S.; Craig, T. *Tetrahedron* **1981**, *37*, 4081. [d] Recovered aldehyde **2** showed considerable racemization (see text). [e] No reaction.

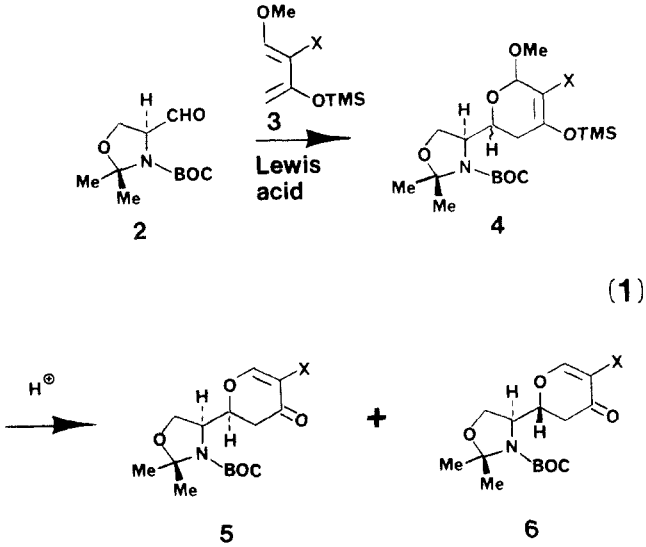
Table II. Aldol/Cyclization Route to Dihydropyrans 5 and 6

entry	enolate	aldol conditions[a]	5:6[b]	overall yield, %
1	**7a** (X = H)	THF–5% HMPA, −100 °C	1.0:5.7	51%
2	**7a**	THF–5% HMPA, −78 °C	1.0:7.0	53%
3	**7a**	THF–5% HMPA, −78 °C, RT	*c*	*c*
4	**7b** (X = OAc)	THF–HMPA	*d*	*d*

[a] A chilled solution of aldehyde **2** was added to the orange enolate solution at the indicated temperature via cannula. The reaction was stirred at this temperature until judged complete by TLC when it was worked up to give crude **8** + **9** which was cyclized to **5**–**6** with hot PPTS in C_6H_6 (see text) RT = room temperature. [b] Ratio determined by HPLC as described in Table I. [c] Decomposition. [d] No reaction.

strategy was that it should be possible to selectively form either the *threo* or *erythro* modifications of II at will and in optically pure form. Herein we report a conceptually simple solution to this problem that allows the asymmetric preparation of either title compound from a common amino acid precursor.

As we have previously reported,[3] the penaldic acid equivalent **2** reacts with electron-rich diene **3a** (X = H) in the presence of Lewis acids to give good yields of diastereomeric dihydropyrones **5** and **6** via the intermediate silyl enol ethers **4** (eq 1).[4] Systematic variation of pertinent reaction parameters led to the results shown in Table I. It can be seen that the degree of *threo* selectivity observed is directly proportional to the amount of zinc chloride used (cf. entries 2–4, 8, and 9) but inversely proportional to the solvent polarity (entries 3, 5, 8, and 10–12).



Thus, analytically pure *threo*-**5a** (X = H), mp 85–86 °C, $[\alpha]_D$ +5.3° (*c* 0.93, $CHCl_3$), and *threo*-**5b** (X = OAc), mp 85–87 °C, $[\alpha]_D$ +4.5° (*c* 1.1, $CHCl_3$),[5] are both available on a preparative scale by simply applying the optimum conditions described followed by one recrystallization. Production of the latter compound **5b** was of particular interest since the target **1** requires an oxygen substituent at C(2). In spite of the low specific rotations observed for these substances, dihydropyrone **5b** was shown to be optically pure by a chiral LSR ^1H NMR experiment.[6]

These data are consistent with chelation-controlled addition to conformer A from the least hindered *si* face to give the *threo*-product **5**. Solvents that compete effectively with the *N*-BOC group for coordination to the CHO···Zn(II) species might be expected to favor addition from the *re* face via the (zinc-coordinated) extended conformer B and lead to a reversal of the diastereoselectivity. Unfortunately the solvent that showed the most potential for such an *erythro*-selective process, *N*,*N*-dimethylformamide, also led to inactivation of the aldehyde **2** possibly via silyl enol ether formation (see entries 7 and 12). Pure

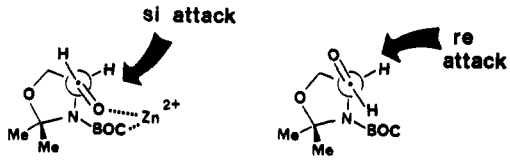
(2) Goto, T.; Toya, Y.; Ohgi, T.; Kondo, T. *Tetrahedron Lett.* **1982**, 1271. Unambiguous assignment of the relative stereochemistry at C(6) or the absolute configuration of amipurimycin (**1**) was not possible.

(3) Garner, P. *Tetrahedron Lett.* **1984**, 5855. The oxazolidine aldehyde **2** and its antipode *ent*-**2** are readily prepared on a large scale from L-serine and D-serine, respectively.

(4) Details concerning the development and several applications of this approach to sugar synthesis by Danishefsky and his co-workers has recently appeared: Danishefsky, S. J.; Larson, E.; Askin, D.; Kato, N. *J. Am. Chem. Soc.* **1985**, *107*, 1246. Danishefsky, S. J.; Pearson, W. H.; Harvey, D. F.; Maring, C. J.; Springer, J. P. *Ibid.* **1985**, *107*, 1256. Danishefsky, S. J.; Maring, C. J. *Ibid.* **1985**, *107*, 1269. Danishefsky, S. J.; Larson, E.; Springer, J. P. *Ibid.* **1985**, *107*, 1274.

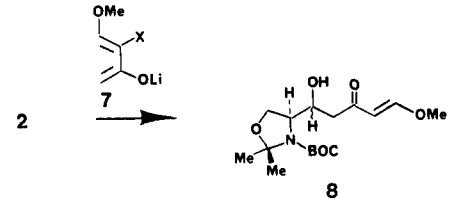
(5) The *threo* stereochemistry of **5b** was confirmed in a manner analogous to that used for **5a**—see ref 3.

(6) Enantiomeric resolution of the C(1)H signal was observed in the presence of 20 mol % $Eu(hfc)_3/CDCl_3$, 55 °C. $Eu(hfc)_3$ is the trade name (Aldrich Chemical Co.) for tris[3-(heptafluoropropyl)hydroxymethylene)-*d*-camphorato]europium(III).

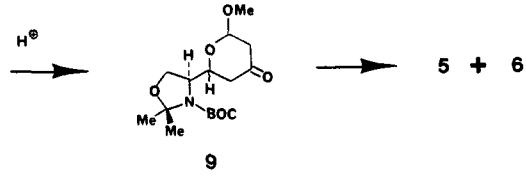


erythro-**6b**, $[\alpha]_D$ −114° (*c* 0.63, $CHCl_3$), could be isolated—albeit in low yield—from the $ZnCl_2$/DMF reaction using preparative HPLC.

At this point we decided to examine the addition of lithium enolate **7** to the aldehyde **2** reasoning that a Felkin–Anh transition-state conformation similar to B should predominate[7] and that the resulting aldols **8** would be easily converted to the dihydropyrones **5** and **6** (eq 2). In



(2)



the event, enolate **7a** (X = H) reacted smoothly with aldehyde **2** at −78 °C in THF–5% HMPA to give a mixture of aldols **8** and isomeric glycosides **9** after a buffered extractive workup. These two compounds could be isolated in 51% and 32% yield, respectively, by flash chromatography or treated directly with PPTS in hot benzene (MeOH removal) to give the desired dihydropyrones **5a** and **6a** in 53% overall yield.[8] HPLC analysis of this mixture showed a reversal of the diastereoselectivity as expected with the *erythro*-isomer **6a** making up 88% of the mixture. Preparative HPLC again allowed isolation of pure (noncrystalline) **6a**, $[\alpha]_D$ −146° (*c* 0.42, $CHCl_3$), which like **6b** showed a comparatively high specific rotation compared to the *threo*-diastereomers **5** (vide supra). Conducting the reaction at −100 °C did not improve the *erythro* selectivity of the process (entry 1, Table II) and attempted equilibration by warming to room temperature led to extensive decomposition (entry 3). The analogous reaction with substituted enolate **7b** (X = OAc) failed to give any noticeable addition products under a variety of conditions.[9] Nonetheless an efficient route to the *erythro*-dihydropyrone **6a** was achieved by using this two-step procedure.

Though addition reactions to various serine-derived aldehydes have been investigated sporadically over the years, the method has been plagued by either poor yields or no diastereoselectivity.[10] Our work illustrates that complete stereochemical control is possible with these systems and underscores the usefulness of the oxazolidine aldehyde **2** in this context.

Experimental Section

All reactions were performed under a nitrogen atmosphere. Melting points were taken on a Mel-Temp Capillary melting point apparatus and are uncorrected. Optical rotations were determined with a Perkin-Elmer 141 polarimeter and are the average of at least four measurements. IR spectra were recorded on a Perkin-Elmer 1420 spectrophotometer. NMR spectra were recorded at 200 MHz with a Varian XL-200 spectrometer using ca. 0.25% Me_4Si as an internal standard. Combustion analyses were performed by Galbraith Labs, Inc., and high-resolution mass spectra were obtained at 70 eV with a Kratos MS30 instrument.

***threo*-Selective Cyclocondensation Procedure.** To a suspension of anhydrous $ZnCl_2$ (70 mol %) in CH_2Cl_2 (1.5 mL/mmol of **2**) was added aldehyde **2** followed by 1–2 equiv of siloxy diene **3** (**a** or **b**). The suspension was stirred at ambient temperature until no aldehyde remained as judged by TLC (ca. 1 h). To this was added Et_2O (4 mL/mmol of **2**) and 1 N HCl (2 mL/mmol of **2**), and the two-phase mixture was stirred vigorously at room temperature until the conversion of **4** into **5** + **6** was complete (ca. 1 h). The reaction mixture was partitioned between saturated $NaHCO_3$ solution and Et_2O. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated to an amber residue. Flash chromatography on SiO_2 eluting with 7:3 hexanes–EtOAc gave the crude *threo*-pyranone **5** as an oily solid, R_f 0.5 in 1:1 EtOAc–hexanes. HPLC analysis showed <2% of the *erythro*-diastereomer **6** to be present. Final purification of **5a** (and **5b**) was achieved by recrystallization from Et_2O–hexanes.

***erythro*-Selective Aldol/Cyclization Procedure.** To a −78 °C solution of LDA, prepared from 1.35 equiv each of 2.5 M *n*-BuLi/hexanes and diisopropylamine in THF (3.0 mL/mmol of **2**) at 0 °C, was added HMPA (0.3 mL/mmol of **2**) followed by 4-methoxy-3-buten-2-one (1.71 equiv). The resulting orange solution was stirred at this temperature for 2 h when a chilled (−78 °C) solution of aldehyde **2** in THF (3.0 mL/mmol of **2**) was added to it via cannula. The reaction mixture was stirred at −78 °C until no aldehyde remained as judged by TLC (ca. 1 h). The cold mixture was poured into pH 7 buffer (KH_2PO_4 + NaOH) and extracted with Et_2O. The organic phase was washed with brine, dried over $MgSO_4$, filtered, and concentrated to give a mixture of **8** + **9** as a pale yellow oil.

The mixture **8** + **9** was dissolved in benzene (30 mL/mmol of **2**) and treated with PPTS (0.12 mmol/mmol of **2**). The mixture was slowly distilled (bath temperature ca. 120–130 °C) through a 20-cm Vigreaux column until the original volume was reduced by $^1/_3$. The procedure was repeated four more times—fresh benzene being added to the pot each time. The cooled reaction mixture was partitioned between saturated $NaHCO_3$ solution and Et_2O. The ether was washed with brine, dried over $MgSO_4$, filtered, and concentrated to give a mixture of pyranones as a pale yellow oil. NMR analysis showed ca. 5% of remaining methyl glycoside **9**. Flash chromatography on SiO_2 eluting with 7:3 hexanes–EtOAc gave pyranones **6** + **5** as an oil, R_f 0.5 in 1:1 EtOAc–hexanes. HPLC analysis showed an (88:12) ratio of *erythro*-pyranone **6** to *threo*-**5**.

5a: IR ($CHCl_3$) 1686, 1599 cm^{-1}; NMR (C_6D_6, 60 °C) δ 1.33 (s, 9 H), 1.37 (br s, 3 H), 1.54 (br s, 3 H), 2.35–2.60 (m, 2 H), 3.56 (dd, *J* = 9.8 and 6.3 Hz, H), 3.69 (dd, *J* = 9.8 and 1.7 Hz, H), 4.08 (br m, H), 4.68 (br m, H), 5.19 (d, *J* = 5.9 Hz, H), 6.62 (d, *J* = 5.9 Hz, H).

Anal. Calcd for $C_{15}H_{23}NO_5$: C, 60.58; H, 7.81. Found: C, 60.46; H, 7.56.

5b: IR ($CHCl_3$) 1760, 1684, 1626 cm^{-1}; NMR (C_6D_6, 60 °C) δ 1.32 (s, 9 H), 1.35 (br s, 3 H), 1.50 (br s, 3 H), 1.81 (s, 3 H), 2.47

(7) Cf.: Uenishi, J.; Tomozane, H.; Yamoto, M. *J. Chem. Soc., Chem. Commun.* **1985**, 717. For a comparative discussion of the Felkin–Anh model see: Anh, N. T. *Top Curr. Chem.* **1980**, *88*, 145.

(8) Compare: Crimmins, M. T.; Bankaitis, D. M. *Tetrahedron Lett.* **1983**, 5303. A related route to γ-pyrones based on C-acylation of **7** had been reported: Koreeda, M.; Akagi, H. *Ibid.* **1980**, 1197. Morgen, T. A.; Ganem, B. *Ibid.* **1980**, 2773.

(9) Attempted quenching of the presumed enolate **7b** with D_2O at −78 °C followed by buffered workup and chromatography led to a 20% recovery of the starting 1-methoxy-2-acetoxybutene-3-one with ca. 7% deuterium incorporation as determined by mass spectrometry.

(10) Mori, K.; Funaki, Y. *Tetrahedron* **1985**, *41*, 2379. Tkaczuk, P.; Thornton, E. R. *J. Org. Chem.* **1981**, *46*, 4393. Saitoh, H.; Moriyama, Y.; Takahashi, T.; Khuong-Huu, Q. *Tetrahedron Lett.* **1980**, 75. Newman, H. *J. Am. Chem. Soc.* **1973**, *95*, 4098.

(dd, J = 16.9 and 4.7 Hz, H), 2.61 (d, J = 16.9 Hz, H), 3.52 (dd, J = 9.8 and 6.3 Hz, H), 3.62 (dd, J = 9.8 and 1.7 Hz, H), 4.02 (m, H), 4.68 (m, H), 6.86 (s, H).

Anal. Calcd for $C_{17}H_{25}NO_7$: C, 57.46; H, 7.10. Found: C, 57.95; H, 7.16.

6a: IR (neat) 1685, 1592 cm^{-1}; NMR (C_6D_6, 60 °C) δ 1.35 (s, 9 H), 1.46 (br s, 3 H), 1.55 (br s, 3 H), 2.3–2.5 (m, 2 H), 3.50 (dd, J = 9.2 and 5.9 Hz, H), 3.79 (dd, J = 9.2 and 1.3 Hz, H), 3.84 (m, H), 4.40 (m, H), 5.18 (d, J = 5.9 Hz, H), 6.59 (d, J = 5.9 Hz, H); MS, calcd for $C_{15}H_{23}NO_5$ 297.1576, found 297.1568.

6b: IR (neat) 1779, 1690, 1630 cm^{-1}; NMR (C_6D_6, 60 °C) δ 1.33 (s, 9 H), 1.44 (br s, 3 H), 1.51 (br s, 3 H), 1.81 (s, 3 H), 2.43 (dd, J = 17.0 and 4.5 Hz, H), 2.56 (dd, J = 17.0 and 13.2 Hz, H), 3.46 (dd, J = 9.3 and 5.6 Hz, H), 3.76 (dd, J = 9.3 and 1.4 Hz, H), 3.85 (m, H), 4.46 (m, H), 6.80 (s, H); MS, calcd for $C_{17}H_{25}NO_7$ 355.1631, found 355.1615.

8 (major): IR (neat) 3460, 1690, 1620, 1592 cm^{-1}; NMR (C_6D_6, 60 °C) 1.38 (s, 9 H), 1.46 (br s, 3 H), 1.61 (br s, 3 H), 2.64 (br d, J = 4.9 Hz, 2 H), 2.95 (s, 3 H), 3.66 (dd, J = 8.1 and 5.7 Hz, H), 3.99 (m, H), 4.12 (dd, J = 8.1 and 2.1 Hz, H), 4.31 (m, H), 5.44 (d, J = 12.9 Hz, H), 7.45 (d, J = 12.9 Hz, H); MS, calcd for $C_{16}H_{28}NO_6$ (M + 1) 330.1916, found 330.1912.

9 (major): IR ($CHCl_3$) 1715, 1686 cm^{-1}; NMR (C_6D_6, 60 °C) δ 1.36 (s, 9 H), 1.49 (br s, 3 H), 1.58 (br s, 3 H), 2.13 (dd, J = 16.3 and 4.6 Hz, H), 2.30 (d, J = 16.3 Hz, H), 2.36 (m, 2 H), 3.03 (s, 3 H), 3.61 (dd, J = 8.8 and 5.9 Hz, H), 3.9 (m, H), 3.99 (dd, J = 8.8 and 1.3 Hz, H), 4.25 (m, H), 4.64 (dd, J = 4.7 and 1.4 Hz, H); MS, calcd for $C_{16}H_{28}NO_6$ (M + 1) 330.1916, found 330.1880.

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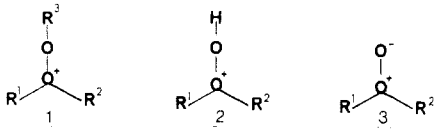
Registry No. **2**, 102308-32-7; **3a**, 54125-02-9; **3b**, 102308-33-8; **4a**, 102308-34-9; 4b, 102308-35-0; **5a**, 102308-36-1; **5b**, 102308-37-2; **6a**, 102308-38-3; **6b**, 102308-39-4; **8** (isomer 1), 102308-40-7; **8** (isomer 2), 102308-42-9; **9**, 102308-41-8; 4-methoxy-3-buten-2-one, 51731-17-0.

Communications

Oxygen Transfer by Dialkylperoxonium Ions

Summary: Oxygen-transfer from dialkylperoxonium ions R_2O^+OH has been demonstrated for three such species, where R_2 is a hydrocarbon chain or ring, by oxidation of several dialkyl sulfoxides, methyl phenyl sulfide, and the succinimide anion, with concurrent formation of the corresponding cyclic or bicyclic ether R_2O.

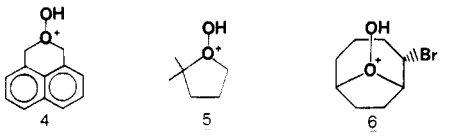
Sir: The formation of trialkylperoxonium ions **1** has been proposed in the Lewis acid induced ring closure of alkylperoxy bromides[1-3] and in the reaction of electrophiles with alkylperoxy alkenes.[4] Subsequent transformations of these intermediates has resulted in peroxy migration[1,3] or Baeyer–Villiger type O–O cleavage.[2,4]



Product studies of parallel reactions with hydroperoxy bromides and alkenes suggest the intermediacy of the corresponding dialkylperoxonium ions **2**.[3,4] However, further evidence is required to substantiate the existence of these ions and to confirm their suggested potential as oxygen-transfer reagents.[4]

The species **2** are structurally related not only to $H_3O_2^+$ but also to dioxygen ylides **3**, such as carbonyl oxides[5,6] and perepoxides,[7] and we anticipated that they might show oxygen-transfer chemistry of an intermediate nature.

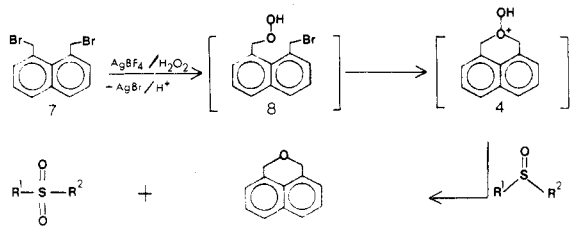
We now wish to report our preliminary findings on the oxygen-transfer capabilities of the three dialkylperoxonium ions, **4–6**.



Reaction of 1,8-bis(bromomethyl)naphthalene (**7**) with an excess of 85% hydrogen peroxide in diethyl ether, dried with $MgSO_4$, and silver tetrafluoroborate at 0 °C resulted in complete consumption of the dibromide and production of naphthopyran but in yields *no* greater than 45%. Upon incorporation of dialkyl sulfoxides, yields of naphthopyran could be increased up to 71%, with concurrent oxidation of the sulfoxide to sulfone (Scheme I). Although sulfone could arise from oxidation by $H_3O_2^+$, which can be present since acid is liberated during the formation of hydroperoxy bromide **8**, the *accompanying* increase in the yield of naphthopyran is consistent with the intermediacy of **4**. However, we sought stronger evidence for **4** through a *correlation* of sulfone and naphthopyran yields.

Thus, the reaction was carried out at room temperature for 90 s with 1, 2, or 3 mol equiv of benzyl methyl sulfoxide present and then quenched with triphenylphosphine to destroy excess hydrogen peroxide. The resultant products

Scheme I



$R^1 = R^2 = Me$; $R^1 = Me$, $R^2 = Ph$; $R^1 = Me$, $R^2 = CH_2Ph$; $R^1 = R^2 = Ph$

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