Elemental analyses were performed in our laboratory.

3-*O*-Benzyl-5,6-dideoxy-1,2-*O*-isopropylidene-6-*C*-nitro-α-D-*xylo*-hex-5-enofuranose (4). Dehydration of the nitro alcohol was improved as follows. To a cooled (0 °C) solution of 3-*O*-benzyl-6-deoxy-1,2-*O*-isopropylidene-6-*C*-nitro-α-L-idofuranose (4.0 g, 11.8 mmol) and Et_3N (4.93 mL, 35.4 mmol) in ether (30 mL) was added dropwise $MeSO_2Cl$ (1.46 mL, 18.9 mmol). After being stirred at 0 °C for 30 min and at room temperature for 5 h, the mixture was poured into cold 5% HCl and extracted with AcOEt. The extracts were washed with brine and dried (Na_2SO_4). Evaporation of the solvents followed by column chromatography (SiO_2, hexane/AcOEt, 3:1) of the residue afforded the nitroolefin 4 (3.71 g, 98%) as an oil: bp 135–140 °C (0.04 mm); $[\alpha]^{23}_D$ −30.46° (*c* 1.50) (lit.[5] −29.1°); IR (neat) 3090, 3040, 3021, 1655 (C=C), 1527 (NO_2), 1449, 1350 (NO_2), 1327, 1157, 1075, 1025, 785, 760, 692 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 1.31, 1.47 (s, 6, CH_3), 3.99 (d, *J* = 3.6 Hz, 1, CHO), 4.40–4.90 (m, 5, CH_2Ph, C=$CHNO_2$, CHO), 5.93 (d, *J* = 3.6 Hz, 1, CHO), 7.10–7.35 (m, 6, PhH, CH=CNO_2); ^{13}C NMR ($CDCl_3$) δ 26.1 (q), 26.8 (q), 72.2 (t), 77.0 (d), 82.4 (d, 2C), 105.1 (d), 112.3 (s), 127.8 (d), 128.3 (d), 128.6 (d), 136.0 (d), 136.7 (s), 140.9 (d).

3-*O*-Benzyl-5,6-dideoxy-1,2-*O*-isopropylidene-6-*C*-nitro-α-D-*xylo*-hexanofuranose (5). To a cooled (0 °C) solution of nitroolefin 4 (3.5 g, 10.9 mmol) in MeOH (30 mL) was added dropwise a solution of $NaBH_4$ (0.62 g, 16.4 mmol) in H_2O (6 mL) over a period of 30 min. The mixture was stirred at room temperature for 5 h and then treated with cold 5% HCl. The products were taken up in benzene/AcOEt (1:1), and extracts were washed with brine, dried (Na_2SO_4), and concentrated. The residue was purified by column chromatography (SiO_2, hexane/AcOEt, 3:1) to give **5** (3.35 g, 95%) as an oil: bp 130–135 °C (0.02 mm); $[\alpha]^{22}_D$ −44.28° (*c* 1.57); IR (neat) 3042, 3017, 1554 (NO_2), 1490, 1448, 1426, 1372 (NO_2), 1347, 1252, 1210, 1160, 1072, 1071, 885, 852, 785, 757, 732, 692 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 1.32, 1.48 (s, 6, CH_3), 2.36 (m, 2, CH_2), 3.86 (d, *J* = 4 Hz, 1, CHO), 4.18–4.80 (m, 6, CH_2Ph, CH_2NO_2, CHO), 5.94 (d, *J* = 4 Hz, 1, OCHO), 7.40 (s, 5, PhH); ^{13}C NMR ($CDCl_3$) δ 26.1, 26.3, 71.7, 72.4, 76.6, 82.0, 82.1, 104.7, 111.7, 127.8, 128.1, 128.6, 137.1. Anal. Calcd for $C_{16}H_{21}NO_6$: C, 59.43; H, 6.55. Found: C, 59.34; H, 6.63.

3-*O*-Benzyl-5,6-dideoxy-6-*C*-nitro-α-D-*xylo*-hexanofuranose (6). A solution of **5** (668 mg, 2.07 mmol) in THF (1 mL) and 6 M HCl (4 mL) was stirred at room temperature for 10 h. The mixture was extracted with AcOEt, and the extracts were washed with brine and dried (Na_2SO_4). Evaporation of the solvents followed by column chromatography (SiO_2, hexane/AcOEt, 1:1) gave **6** (539 mg, 92%) as an oil: $[\alpha]^{16}_D$ +11.23° (*c* 4.12); IR (neat) 3380 (OH), 3068, 3035, 1555 (NO_2), 1500, 1455, 1432, 1380 (NO_2), 1350, 1209, 1116, 1062, 739, 700 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 2.24 (m, 2, CH_2), 3.49–4.67 (m, 8, CH_2Ph, CHO, OH), 4.93 (d, *J* = 16.1 Hz, 1, CHO), 5.34 (d, *J* = 3.8 Hz, 1, OCHO), 7.27 (s, 5, PhH). Anal. Calcd for $C_{13}H_{17}NO_6$: C, 55.12; H, 6.05. Found: C, 55.05; H, 6.16.

(2*S*,3*R*)-2-(Benzyloxy)-3-(formyloxy)-5-nitropentanal (2). To a cooled (0 °C) solution of diol **6** (500 mg, 1.77 mmol) in MeOH (1 mL) was added a solution of $NaIO_4$ (492 mg, 2.30 mmol) in H_2O (6 mL). The mixture was stirred at room temperature for 5 h and then partitioned with saturated $NaHCO_3$ and toluene/AcOEt (1:1). The organic layer was washed with brine, dried (Na_2SO_4), and concentrated. The crude product was purified by column chromatography (SiO_2, hexane/AcOEt, 1:1) to afford **2** (482 mg, 97% as an oil: bp 140–145 °C (0.02 mm); $[\alpha]^{17}_D$ −24.91° (*c* 5.00); IR (neat) 3041, 3020, 2710 (CHO), 1725 (CHO), 1555 (NO_2), 1495, 1452, 1431, 1376 (NO_2), 1156, 1068, 916, 878, 751, 699 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 2.38 (m, 2, CH_2), 3.92 (d, *J* = 3.6 Hz, 1, CHO), 4.35 (t, *J* = 6.4 Hz, 2, CH_2NO_2), 4.67 (AB_q, *J* = 11 Hz, 2, CH_2Ph), 5.38 (m, 1, CHOCO), 7.33 (s, 5, PhH), 7.97 (s, 1, OCHO), 9.61 (s, 1, CHO); ^{13}C NMR ($CDCl_3$) δ 28.0 (t), 68.9 (d), 71.7 (t), 73.5 (t), 82.7 (d), 128.4 (d), 128.6 (d), 128.7 (d), 136.2 (s), 160.1 (d), 200.0 (d). Anal. Calcd for $C_{13}H_{15}NO_6$: C, 55.51; H, 5.38. Found: C, 55.63; H, 5.46.

(1*R*,2*R*)-2-(Benzyloxy)-3-hydroxy-4-nitrocyclopentan-1-ol Formate (7). To a cooled (0 °C) solution of nitro aldehyde **2** (290 mg, 1.03 mmol) in DMF (3 mL) Et_3N was added dropwise (0.03 mL, 0.21 mmol). The mixture was stirred at room temperature for 5 h, and the reaction was quenched with cold 5% HCl. The mixture was extracted with AcOEt, and the extracts were washed with brine, dried (Na_2SO_4), and concentrated. The crude product was purified by column chromatography (SiO_2, hexane/AcOEt, 2:1) to give **7** (276 mg, 95%) as an oil: $[\alpha]^{18}_D$ −5.62° (*c* 2.75); IR (neat) 3400 (OH), 3045, 3020, 1722 (CHO), 1555 (NO_2), 1498, 1454, 1372 (NO_2), 1170, 1121, 782, 760, 697 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$), δ 2.00–3.50 (m, 4, CH_2, $CHNO_2$, OH), 3.70–4.25 (m, 1, CHO), 4.30–4.90 (m, 1, CHO), 4.67 (s, 2, CH_2Ph), 5.18 (m, 1, CHOCO), 7.32 (s, 5, PhH), 7.97 (br s, 1, OCHO). Anal. Calcd for $C_{13}H_{15}NO_6$: C, 55.51; H, 5.38. Found: C, 55.40; H, 5.29.

(3*R*,4*R*)-3-(Benzyloxy)-4-(formyloxy)-1-nitro-1-cyclopentene (1). To a cooled (0 °C) solution of nitro alcohol **7** (120 mg, 0.43 mmol) and Et_3N (0.24 mL, 1.72 mmol) in ether (8 mL) was added dropwise $MeSO_2Cl$ (0.053 mL, 0.69 mmol). The mixture was stirred at 0 °C for 30 min and at reflux for 5 h, and then the reaction was quenched with cold 5% HCl. The mixture was extracted with AcOEt, and the extracts were washed with brine and dried (Na_2SO_4). Evaporation of the solvent followed by column chromatography (SiO_2, hexane/AcOEt, 3:1) gave the cyclopentene **1** (103 mg, 92%) as an oil: $[\alpha]^{20}_D$ −118.79° (*c* 1.45); IR (neat) 3038, 3018, 1720 (C=O), 1643 (C=C), 1523 (NO_2), 1451, 1360 (NO_2), 1164, 1095, 1064, 739, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.76 (d, *J* = 17.6 Hz, 1, $CHCNO_2$), 3.52 (dd, *J* = 17.6, 7.3 Hz, 1, $CHCNO_2$), 4.69 (AB_q, *J* = 17.6 Hz, Δ_{AB} = 27.6 Hz, 2, CH_2Ph), 4.71 (m, 1, CHOBn), 5.43 (dt, *J* = 7.3, 3.3 Hz, 1, CHOC=O), 6.85 (d, *J* = 1.8 Hz, 1, CH=CNO_2), 7.35 (m, 5, PhH), 8.05 (s, 1, CHO); ^{13}C NMR ($CDCl_3$) δ 35.3 (t), 72.4 (t), 76.5 (d), 85.1 (d), 128.0 (d), 128.3 (d), 128.7 (d), 132.3 (d), 136.9 (s), 151.9 (s), 159.9 (d). Anal. Calcd for $C_{13}H_{13}NO_5$: C, 59.31; H, 4.98. Found: C, 59.18; H, 4.81.

Dehydration of 7 with 1,3-Dicyclohexylcarbodiimide (DCC). A solution of **7** (150 mg, 0.535 mmol), DCC (221 mg, 1.07 mmol), and $CuCl_2 \cdot 2H_2O$ (5.0 mg, 0.03 mmol) in ether (5 mL) was heated at reflux for 24 h. Evaporation of the solvent followed by column chromatography (SiO_2, hexane/AcOEt, 5:1) of the residue afforded **1** (120 mg, 86%) as an oil.

Stereospecific Synthesis of the Important Retinoid Synthon Ethyl *trans*-3-Formyl-2-butenoate via Direct Two-Stage Oxidation of Ethyl 3-Methyl-2-butenoate

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all-trans-Retinoic acid is a metabolite of vitamin A (retinol) capable of supporting the functions of vitamin A in the maintenance of normal growth and epithelial cell differentiation.[1] Retinoic acid and some of its analogues (retinoids) have recently generated much interest as agents useful for the treatment of skin disorders[2] and as potential cancer chemopreventive or chemotherapeutic compounds.[3,4] At present, it remains unclear whether retinoic acid or further metabolites of retinoic acid represent biologically active forms of the vitamin.

Recently we have been engaged in programs directed toward the preparation of retinoic acid metabolites and their analogs.[5,6] Our present interests require the synthesis of quantities of the ethyl ester of *trans*-3-formyl-2-bute-

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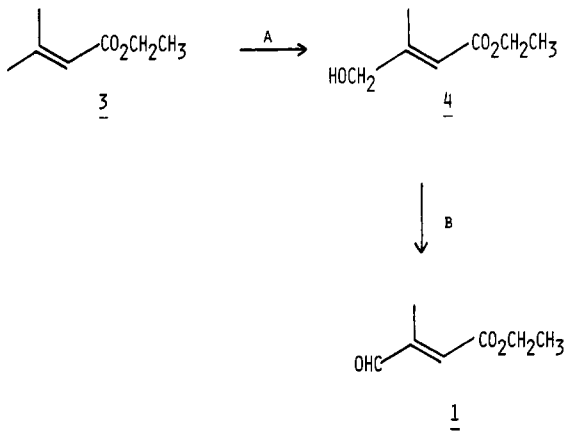
Scheme I[a]



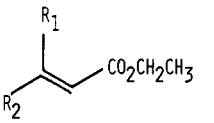
[a] (A) $2SeO_2$, 95% EtOH, reflux; 90%; (B) $5MnO_2$, CH_2Cl_2, 0 → 25 °C; 88%.

noate (1). This synthon has been an important component of many syntheses of retinoic acids[7] including Rosenberger's recent preparation of our current target, the retinoic acid metabolite 4-hydroxyretinoic acid.[8]

This relatively simple aldehyde 1 is generally obtained by the multistep synthesis of Sisido and co-workers[9] reported in the late 1950's. The method is based upon Krohnke's procedure[10] for the acid-catalyzed hydrolysis of a relatively inaccessible aryl nitrone to the aldehyde. Overall, this route yields only modest quantities of 1, due, no doubt, to its acid lability as well as its high volatility and thermal instability which causes difficulties during purification by vacuum distillation. In addition, utilizing now routine ^1H NMR techniques, we find that the first step in this procedure, bromination of ethyl 3-methyl-2-butenoate via *N*-bromosuccinimide in $CHCl_3$, does not produce the trans bromo compound stereospecifically as originally believed[9] but a 45:55 cis/trans mixture of the 3-(bromomethyl)-2-butenoates 2. Therefore, we felt that more efficient methods of preparation of the important synthon 1 would be useful.

In 1971, Bhalerao and Rapoport reported the stereospecific oxidation of trisubstituted 2-methyl 2-enes to trans aldehydes using 2 equiv of SeO_2 in refluxing EtOH.[11] We therefore anticipated that SeO_2 oxidation of ethyl 3-methyl-2-butenoate (3) would yield 1 directly. However, even under more forcing conditions, we find that SeO_2 oxidation of 3 stereospecifically produces the trans-hydroxymethyl compound 4 in high yields (Scheme I). That this unexpected result is due to the proximity of the polar carbethoxy moiety is suggested by our ability to repeat Rapoport's oxidation of 2-methyl-2-heptene to the trans aldehyde under these conditions.[11] In addition, Rapoport has also shown that the more remote α,β-unsaturated carbethoxy group present in a synthetic precursor to *dl*-sirenin does not hinder this methyl-to-aldehyde oxidation.[12] As might be expected, however, oxidation of hydroxymethyl compound 4 with excess MnO_2 rapidly produces the desired aldehyde 1 in excellent crude yield (Scheme I). Purification of this volatile, labile aldehyde by distillation generally results in poor overall yield.[9] Therefore, silica gel column chromatography (40% EtOAc/hexane) was attempted as a means of purification. This method also proved unsatisfactory, causing extensive polymerization and isolation of 1 in only 45% yields. Fortunately, rapid, argon-driven silica gel flash column chromatography using purified 80% CH_2Cl_2/hexane for elution permitted isolation of pure 1 in 72% yield. This aldehyde is assumed to be greater than 98% *trans*-1 since no resonances assignable to the cis isomer were observed in the 270-MHz ^1H NMR spectrum.

Product stereochemistry assignments have been based principally on ^1H NMR analysis. Thus, the assignment of configurations have been aided by comparison of the resonance frequencies of the methyl and methylene groups in 1 and 4 with the isomer mixture 2 prepared by nonstereospecific bromination of 3 (see above). More importantly, 1 has been assigned the trans configuration on the basis of comparisons of its aldehyde proton resonance (δ 9.54) with that of the cis isomer (δ 10.12) prepared by nonstereospecific methods (R. W. Curley, Jr., and C. J. Ticoras, unpublished results). Our earlier work[5,14] as well as the NMR studies of Rapoport's group,[15] have shown that, as expected, the cis aldehyde proton resonance appears downfield relative to the resonance frequency of the trans isomer in these types of molecules.



1, $R_1 = CH_3$; $R_2 = CHO$
2, R_1 or $R_2 = BrCH_2$; R_2 or $R_1 = CH_3$
3, $R_1 = R_2 = CH_3$

In summary, we have prepared the important retinoid synthon 1 by an extremely efficient route. This route should permit ready preparation of synthetic scale quantities of 1 for further studies on retinoic acid chemistry.

Experimental Section

All melting points, determined with a Thomas-Hoover capillary apparatus, are uncorrected. ^1H NMR spectra were recorded on a Bruker WP-80 or IBM NR/270 spectrometer with Me_4Si as an internal standard at 0 ppm. IR spectra were determined with a Beckman IR 4320 infrared spectrophotometer as liquid films. UV spectra were recorded with a Beckman DU-40 spectrophotometer. Gas chromatography–mass spectra were obtained on a Finnigan 4021 instrument and a DB1, 30 m × 0.25 mm fused silica column at 200 °C. Electron impact high resolution mass spectra were obtained with a Kratos MS-30 spectrometer. TLC was performed on silica gel 60 F_{254} precoated aluminum-backed plates from EM Reagents. Flash chromatography[13] was done on silica gel 60, 230–400 mesh, from EM Reagents using Ar to provide elution pressure.

Most manipulations of these air-sensitive materials were performed under an Ar atmosphere. Commercial Ar was dried by being bubbled through concentrated H_2SO_4 and then through $CaSO_4$/NaOH. CH_2Cl_2 was dried over anhydrous K_2CO_3, distilled, and stored over 3A molecular sieve. This solvent was then passed through basic alumina, Brockman activity grade I, immediately prior to use. All other organic solvents were appropriately purified and/or dried prior to use.

Ethyl *trans*-3-(Hydroxymethyl)-2-butenoate (4). In a round-bottomed flask equipped with an Ar inlet, reflux condenser, and magnetic stirrer were mixed 256 mg (2 mmol) of ethyl 3-methyl-2-butenoate (3) and 444 mg (4 mmol) of SeO_2 in 30 mL of 95% EtOH. The reaction mixture was stirred at reflux for 24

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h and then the solution was concentrated under reduced pressure to a volume of 5 mL. This solution was diluted with 50% EtOAc/hexane and washed with saturated $NaHCO_3$. The aqueous layer was washed with additional EtOAc/hexane and the combined organic extracts were washed with saturated NaCl and dried (Na_2SO_4). Drying agent was removed by vacuum filtration, and the solution was concentrated under reduced pressure to afford 260 mg (90%) of **4** as a light yellow oil: IR 3483, 1740, 1665 cm^{-1}; NMR ($CDCl_3$) δ 1.29 (t, 3, CH_2CH_3, J = 7.5 Hz), 1.60 (br s, 1, OH), 2.10 (d, 2, $=CCH_3$, J = 1 Hz), 4.16 (br s, 2, CH_2OH), 4.17 (q, 2, CH_2CH_3, J = 7.5 Hz), 5.99 (m, 1, =CH).

Ethyl *trans*-3-Formyl-2-butenoate (1). To an oven-dried, round-bottomed flask equipped with a magnetic stirrer, Ar inlet, and $CaSO_4$ drying tube was added a solution of 195 mg (1.4 mmol) of **4** in 10 mL of CH_2Cl_2. The solution was cooled in an ice bath and 587 mg (6.8 mmol) of MnO_2 was added. The suspension was stirred for 1 h while being warmed to ambient temperature. The reaction mixture was vacuum filtered through diatomaceous earth and the CH_2Cl_2 was removed under reduced pressure at 23 °C to afford 152 mg (88%) of **1** as a light yellow oil. Flash chromatography of this oil (80% CH_2Cl_2/hexane) afforded 124 mg (72%) of **1**: TLC (EtOAc/hexane, 1:3) R_f 0.41; IR 1710, 1625 cm^{-1}; UV (hexane) λ_{max} 228 nm (ϵ 2250); NMR ($CDCl_3$) δ 1.34 (t, 3, CH_2CH_3, J = 7 Hz), 2.16 (d, 3, $=CCH_3$, J = 1.5 Hz), 4.28 (q, 2, CH_2CH_3, J = 7 Hz), 6.49 (d, 1, =CH, J = 1.5 Hz), 9.54 (s, 1, CHO); GC/MS, m/e (relative intensity) $(M)^+$ 142 (2), $(M - CH_3CH_2OH)$ 96 (100).

The 2,4-dinitrophenylhydrazone derivative of **1** was prepared by standard procedures: mp 197–199 °C (lit.[16] mp 199–200 °C); HRMS, m/e required for $C_{13}H_{14}N_4O_6$ 332.0914, observed 322.0923.

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Model Studies for the Synthesis of Trichothecenes. Synthesis of *rac*-Trichodiene and *rac*-Bazzanene

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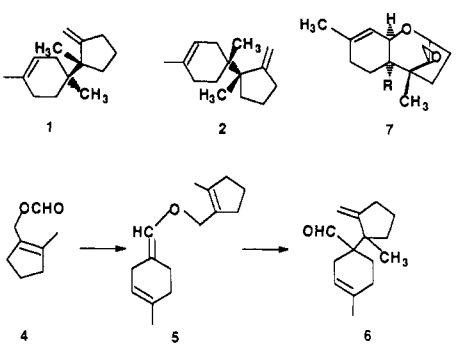
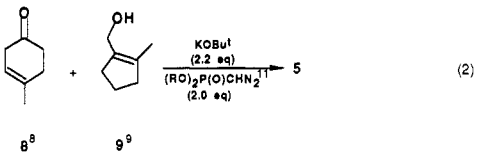
The recent publication by Suda of a novel, albeit stereorandom, approach to the synthesis of *rac*-trichodiene (**1**) and *rac*-bazzanene (**2**)[1] and the difficulties encountered by other workers in repeating the Wittig reaction that constitutes the first step in the sequence (eq 1)[2] prompt the present report of our closely related synthetic approach to these hydrocarbons.

A critical step in the aforementioned synthesis is the Claisen rearrangement of the allyl vinyl ethers **5**, intermediates obtained from the Wittig reaction between **3** and **4** and characterized spectroscopically (eq 1); the resulting



50–50 mixture of the aldehydes **6** was reduced to **1** and **2** by use of the Wolff–Kishner reaction.[1] We have also prepared the ethers **5**,[3] in 50% isolated yield based on ketone **8**, by application of our previously reported methodology that involves generation and trapping of alkylidenecarbenes (eq 2),[4] and have converted them to



1 and **2**[5] by the same sequence of reactions as that used by Suda.[1] However, the present synthesis of **5** is conceptually significant because its success augurs well for the eventual development of a diastereoselective approach to *rac*-trichodiene (**1**)[6] and of a convergent preparation of its biosynthetic descendants,[7] the trichothecenes **7**.

Prediction of the stereochemical outcome of any synthetic sequence involving formation and subsequent rearrangement of **5** requires knowledge of the conformation preferred for the latter step. As shown in Figure 1, if a chair-like conformation is adopted, it is the *E* isomer of **5** that provides an aldehyde, **6T**, having the stereochemistry appropriate for generation of **1**; should isomerization occur by way of a boat-like conformation, this same isomer leads to the diastereomeric aldehyde **6B** that would serve as a precursor of **2**. The converse is true for (*Z*)-**5**, of course.

That the chair-like geometry is preferred was demonstrated in the following way. Application of the methodology of eq 2 provided a 60:40 mixture of the isomeric ethers **5**, the major component of which was shown to be (*Z*)-**5** by dissection of the ^1H NMR spectrum. Most diagnostic for assignment of relative stereochemistry to the isomers were the multiplets centered at δ 2.54 and 2.79 that are ascribable to the bis-allylic methylene groups at C-2 of the cyclohexene ring; the lower field resonance is assigned to the *Z* isomer by analogy to data drawn from ^1H NMR spectra of *acyclic* enol ethers.[12] Mixtures containing

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(2) Prof. D. Cane (Brown University) has informed us that his research group has been unable to repeat the preparation of an allyl vinyl ether from an allyl formate, as reported in ref 1 (personal communication with permission to cite).

(3) The mixture of **5** has a ^1H NMR spectrum consonant with that reported by Suda.[1]. Moreover, its ^{13}C NMR spectrum and exact mass are consistent with those expected (see Experimental Section).

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(5) Identified by comparison of mass and ^1H NMR spectra with those of authentic **1** and **2**; the latter spectra were kindly provided by Prof. S. C. Welch (University of Houston).

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(9) Prepared in 53% overall yield from 1-acetyl-2-methylcyclopentene[10a] by oxidation with KOCl,[10bc] followed by reduction of the resulting acid with LAH.[10d]

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