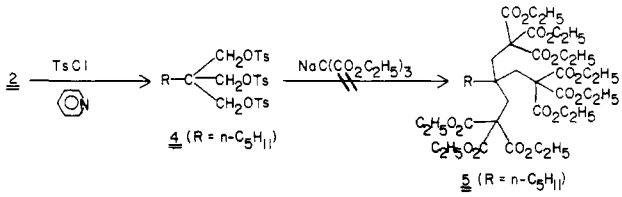
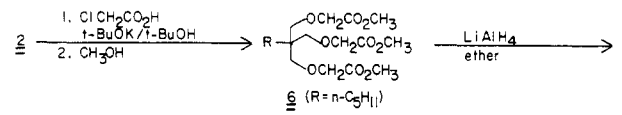
cross-Cannizzaro reaction[18] of heptanal with formaldehyde cleanly gave (60%) the desired **2**.

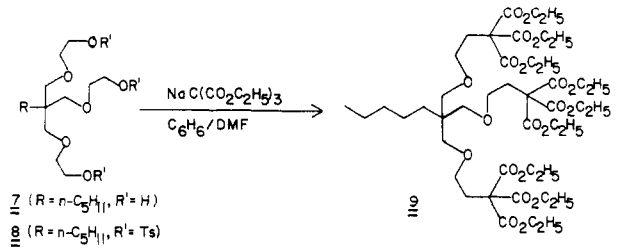
Growth of the second tier by repetition of the above sequence was envisioned, thus **2** was transformed (70%) to the tris-tosylate **4** [mp 122–123 °C; ^{13}C NMR δ 41.8



(C^4°), 67.9 (CH_2O)] by standard conditions[9] using anhydrous pyridine at 0 °C. Treatment of **4** with triethyl sodiomethanetricarboxylate under diverse conditions did not generate the anticipated **5**; simple nucleophilic attack in triplicate failed probably due to the steric crowding at one or more of the terminal carbons. Circumvention of this problem in the triplication sequence utilizes an extender group.

Elongation of triol **2** with chloroacetic acid in the presence of *t*-BuOK/*t*-BuOH and subsequent esterification of the intermediate triacid with MeOH afforded (95%) **6**

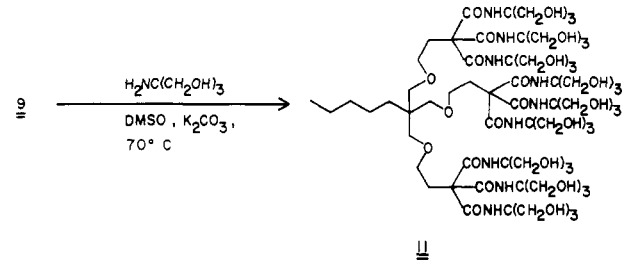




[oil; bp 180 °C (0.8 mm)]. Reduction of **6** with $LiAlH_4$ in ether gave (80%) the extended triol **7** [oil; bp 180 °C (1 mm); ^{13}C NMR δ 43.2 (C^4°), 78.7 (CCH_2O), 74.1 (CH_2CH_2OH), 61.6 (CH_2OH)], which was tosylated as above to give (90%) *tritosylate* **8** [oil; ^{13}C NMR δ 43.2 (C^4°), 78.6 (CCH_2O)]. Without further purification **8** was treated with $NaC(CO_2Et)_3$ in C_6H_6–DMF (1:1) at 110 °C to afford (70%) the desired nonaester **9** [oil; bp 200–210 °C (2 mm); ^{13}C NMR δ 43.3 (C^4°), 78.8 (CCH_2), 67.6 (CH_2OCH_2), 34.1 (CH_2CCO), 74.0 (*C*CO), 166.8 (CO)]. Even though ^1H NMR is rather worthless in structural analyses of these dense cascades, ^{13}C NMR is an ideal diagnostic tool due to their inherent symmetry.

A third tier construction utilizes amide formation. Treatment of **9** with tris(hydroxymethyl)aminomethane (**10**) at 70 °C in Me_2SO generates (90%) the [27]-arborol **11** [oil; ^{13}C NMR δ 44.5 (CH_2CCH_2), 62.5 (HNC), 65.1 (CH_2OH), 75.2 (*C*CO), 171.6 (CO)], which is infinitely water soluble even though the molecular weight is >1600.

This communication describes only the preliminary methodology and work is currently in progress in our laboratories to delineate the synthetic as well as the physical properties of these novel cascade molecules.



Acknowledgment. We thank the LSU Center for Energy Studies and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

Registry No. **1**, 20484-14-4; **2**, 20762-79-2; **3**, 64251-19-0; **4**, 96150-67-3; **5**, 96150-68-4; **6**, 96150-69-5; **7**, 96150-70-8; **8**, 96150-71-9; **9**, 96150-72-0; **10**, 77-86-1; **11**, 96150-73-1; $BrCH_2(CH_2)_3CH_3$, 110-53-2; $NaC(CO_2Et)_3$, 68922-87-2; $CH_3(CH_2)_5CHO$, 111-71-7; HCHO, 50-00-0; $ClCH_2CO_2H$, 79-11-8.

Supplementary Material Available: Experimental details of synthesis and characterization (7 pages). Ordering information is given on any current masthead page.

George R. Newkome,* Zhong-qi Yao[1c]
Gregory R. Baker, Vinod K. Gupta
Department of Chemistry
Louisiana State University
Baton Rouge, Louisiana 70803-1804
Received November 19, 1984

Stereoselective Syntheses of Alkenyl-Substituted 1,3-Dioxolanes or 4,7-Dihydro-1,3-dioxepins or an (*E*)-α,β-Unsaturated Aldehyde from (*Z*)-2-Butene-1,4-diols

Summary: Treatment of (*Z*)-2-butene-1,4-diols with boron trifluoride etherate in acetone solvent affords stereodefined alkenyl-substituted 1,3-dioxolanes or 4,7-dihydro-1,3-dioxepins or an (*E*)-α,β-unsaturated aldehyde, depending on the reaction temperature and time.

Sir: In connection with ongoing work, our need for ready access to isopropylidene derivatives of (*Z*)-2-butene-1,4-diols prompted us to explore methods for their preparation. In the course of these investigations we observed that treatment of the diol **1a** in acetone with boron trifluoride etherate at 50 °C did not afford the anticipated acetal **4a** but instead produced the (*E*)-α,β-unsaturated aldehyde **2a**. To delineate the scope of this interesting stereoselective transformation as well as to find conditions for the formation of the acetal **4a**, the reactions of a variety of (*Z*)-2-butene-1,4-diols **1a–d** with boron trifluoride etherate in acetone solvent were investigated.

We now report that the natures of the products derived from (*Z*)-2-butene-1,4-diols and boron trifluoride etherate in acetone are remarkably dependent upon the conditions under which the reaction is carried out. Thus, treatment of **1a**[1] (1 mmol) in acetone (2 mL) at 0 °C with BF_3·OEt_2 (1 equiv) followed by warming the reaction mixture at 50 °C for 1 h furnished, by GLC analysis, a 77% yield of the *E* aldehyde **2a**.[2-4] On the other hand, when the reaction was performed at 25 °C for 1 h, the GLC chromatogram

(17) (a) Grob, C. A.; Schiess, P. W. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 1. (b) Grob, C. A. *Ibid.* **1969**, *8*, 535.
(18) (a) Vogel, A. I. "A Text Book of Practical Organic Chemistry", 3rd ed.; Longmans: London, 1973; p 811. (b) Weibull, B.; Matell, M. *Acta Chem. Scand.* **1962**, *16*, 1062.

(1) Zweifel, G.; Backlund, S. J.; Leung, T. *J. Am. Chem. Soc.* **1977**, *99*, 5192.

0022-3263/85/1950-2004$01.50/0

Table I. Yields of Products Derived from Reactions of (*Z*)-2-Butene-1,4-diols in Acetone with $BF_3 \cdot OEt_2$

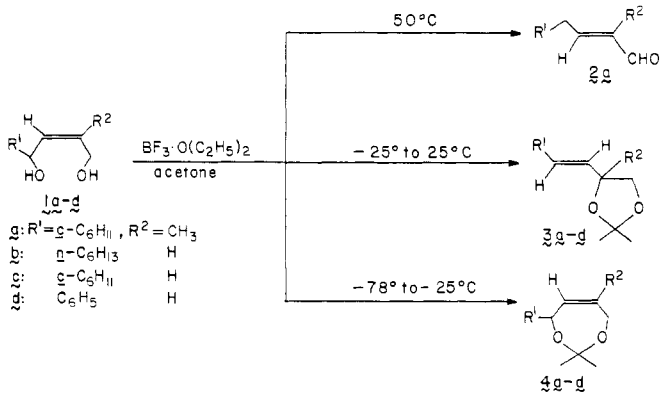
	1		reactn conditns		yield (isolated), %		
	R^1 =	R^2 =	temp, °C	time, h	aldehyde[a] **2**	1,3-dioxolane[b] **3**	4,7-dihydro-1,3-dioxepin[b] **4**
a	c-C_6H_{11}	CH_3	50	1	69		
			−25	4		85	
			−78	4			87
b	*n*-C_6H_{13}	H	25	0.25		69	
			−78	1			86
c	c-C_6H_{11}	H	25	0.25		64	
			−78	1			90
d	C_6H_5	H	0	1		78	
			−78	1			85

[a] The diol (10 mmol) in acetone (20 mL) was treated with $BF_3 \cdot OEt$, (10 mmol). [b] The diols (5 mmol) in acetone (10 mL) were treated with $BF_3 \cdot OEt_2$ (5 mmol).

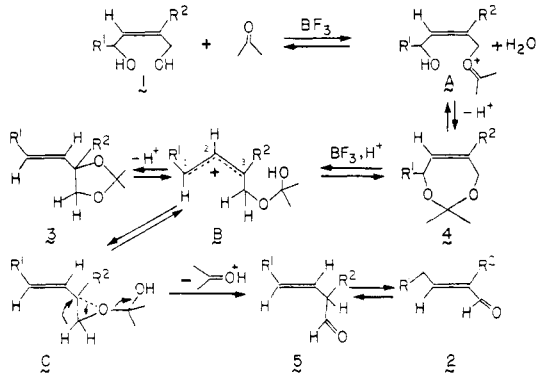
of the mixture revealed, in addition to **2a**, the corresponding β,γ-unsaturated aldehyde and the (*E*)-1,3-dioxolane **3a**. Lowering the reaction temperature from 25 °C to −25 °C resulted after 4 h in the nearly exclusive formation of **3a**. Finally, when the diol **1a** in acetone was reacted for 4 h at −78 °C with $BF_3 \cdot OEt_2$ in an attempt to increase the yield of the rearranged acetal **3a**, GLC analysis of the worked up product mixture showed the presence of still another compound, the unrearranged acetal **4a**.[5]

The successful preparations of the α,β-unsaturated aldehyde **2a**, the rearranged acetal **3a**, and the unrearranged acetal **4a** from a single precursor (**1a**) led us to include the readily accessible 1-alkyl- or phenyl-substituted (*Z*)-2-butene-1,4-diols **1b–d** in our study.[6] Unfortunately, under the optimal reaction conditions for conversion of the diol **1a** into the aldehyde **2a** (vide supra), the diols **1b–d** furnished the corresponding α,β-unsaturated aldehydes in only small amounts.[7] However, their reactions with $BF_3 \cdot OEt_2$ in acetone could be controlled to afford either the corresponding five-membered ring acetal.[8] **3b–d** or the seven-membered ring acetals[9] **4b–d** simply by varying the reaction temperature (Table I).

Although our primary aims in the present work were synthetic, the results obtained are also of considerable mechanistic interest. A possible mechanistic pathway for the formation of compounds **2**, **3**, and **4** is depicted below.



According to this proposal the seven-membered ring acetal **4**, formed by way of the oxonium ion **A**, is the product of kinetic control and thus the major product at low temperature. Under more vigorous conditions **4**, in the presence of BF_3-etherate or H^+, may undergo ring opening to **B**. This allylic cation can suffer attack by the hydroxyl group of the hemiacetal moiety either at its C_1 position to reform **4** or at its C_3 position to provide the five-membered ring acetal **3**. As **3** is thermodynamically more stable than **4**,[10] the major product formed at −25 °C to 25 °C is **3**. Finally, in the case of the dialkyl-substituted 2-butene-1,4-diol **1a**, under more vigorous conditions transformation of B to the oxonium species C by attack of the hemiacetal ether oxygen at C_3 becomes important. Subsequent irreversible 1,2-hydride shift produces the β,γ-unsaturated aldehyde **5**, which then isomerizes to the observed α,β-unsaturated aldehyde **2a**.



In summary, the boron trifluoride mediated conversion of the (*Z*)-2-butene-1,4-diol **1a** into the (*E*)-α,β-unsaturated

(2) The assignment of trans stereochemistry to the aldehyde **2a** is based on analogous published ^1H NMR data. Chan, K. C.; Jewell, R. A.; Nutting, W. H.; Rapoport, H. *J. Org. Chem.* **1968**, *33*, 3382.

(3) It should be noted that **2a** was also the major product when the reaction was carried out in methylene chloride instead of acetone. Moreover, **2a** was obtained in good yield when $BF_3 \cdot OEt_2$ was replaced by either $HClO_4$ (70%, 0.6 equiv) or by $TsOH \cdot H_2O$ (1 equiv).

(4) For alternative syntheses of α-substituted enals, see: Corey, E. J.; Enders, D.; Bock, M. G. *Tetrahedron Lett.* **1976**, 7. Chuit, C.; Corriu, R. J. P.; Reyé, C. *Synthesis* **1983**, 294.

(5) Interestingly, treatment of 3-butene-1,2-diols such as 1-phenyl-2-methyl-3-butene-1,2-diol with dilute H_2SO_4 furnished, depending on the reaction conditions, either the 2,5-dihydrofuran derivatives or the 1-butene-3,4-diols as main products. Gharbi-Benarous, J.; Morales-Rios, M. S.; Dana, G. *J. Org. Chem.* **1984**, *49*, 2039 and references cited therein.

(6) The (*Z*)-2-butene-1,4-diols **1b–d** were obtained by semihydrogenation of the corresponding 2-butyne-1,4-diols. Boeckman, R. K., Jr.; Thomas, E. W. *J. Am. Chem. Soc.* **1979**, *101*, 987.

(7) It has been reported that refluxing (*Z*)-2-butene-1,4-diols **1b** (R^1 = CH_3, *n*-C_3H_7, *n*-C_6H_{13}) and **1d** with dilute H_2SO_4 produces mixtures of α,β- and β,γ-unsaturated aldehydes along with dihydrofuran derivatives. Gauge, M. *Ann. Chim.* (*Paris*) **1951**, *6*, 648.

(8) For an alternative preparation of unsaturated 1,3-dioxolanes, see: Dumont, D.; Pfander, H. *Helv. Chim. Acta* **1983**, *66*, 815. Mulzer, J.; Kappert, M.; Huttner, G.; Jibril, I. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 704.

(9) For an alternative preparation of 4,7-dihydro-1,3-dioxepins, see: Scharf, H. D.; Frauenrath, H. *Chem. Ber.* **1980**, *113*, 1472.

(10) We have shown that **4b** in acetone at 25 °C in the presence of $BF_3 \cdot OEt_2$ is readily converted into **3b**.

aldehyde **2a** represents a new synthetic route to stereodefined trisubstituted olefins. Hydrolysis of the synthetically valuable (*E*)-1,3-dioxolanes **3**[11] should lead to the corresponding (*E*)-3-ene-1,2-diols. These are useful as intermediates for the synthesis of 1,3-dienes, 2,5-dihydrofurans[5] and various natural products.[12] Finally, 4,7-dihydro-1,3-dioxepins **4** are of value as precursors for a variety of chemical transformations[13] and as flavoring agents for food[14] and odorants for perfumes.[14]

(11) Johnson, F.; Paul, K. G.; Favana, D.; Ciabatti, R.; Guzzi, U. *J. Am. Chem. Soc.* **1982**, *104*, 2190. Mori, K. *Tetrahedron Lett.* **1976**, 1609.
(12) Yasuda, A.; Tanaka, S.; Yamamoto, H.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1752.
(13) Corey, E. J.; Bock, M. G. *Tetrahedron Lett.* **1975**, 2643. Elliot, W. J.; Fried, T. *J. Org. Chem.* **1976**, *41*, 2469. Suzuki, H.; Yashima, H.; Hirose, T.; Takahashi, M.; Moro-oka, Y.; Ikawa, T. *Tetrahedron Lett.* **1980**, *21*, 4927.
(14) Tavares, R. F.; Agran, J.; Easter, W. H.; Blau, L. *Chem. Abstr.* **1974**, *81*, 152294j. Tavares, R. F.; Agran, J.; Easter, W. M. *Chem. Abstr.* **1976**, *84*, 135736z.

Acknowledgment. We thank the National Science Foundation (CHE 82-05934) for financial support of this investigation.

Registry No. **1a**, 31551-96-9; **1b**, 96227-88-2; **1c**, 96227-90-6; **1d**, 62499-97-2; **2a**, 96227-85-9; **3a**, 96227-86-0; **3b**, 96227-87-1; **3c**, 96227-89-3; **3d**, 96227-91-7; **4a**, 96227-92-8; **4b**, 96227-93-9; **4c**, 96227-94-0; **4d**, 96227-95-1; acetone, 67-64-1.

Supplementary Material Available: Full experimental and spectral details for compounds **2a**, **3a–d**, and **4a–d** (4 pages). Ordering information is given on any current masthead page.

George Zweifel,* Teresa Leung
M. Ramin Najafi, Samir Najdi

Department of Chemistry
University of California
Davis, California 95616

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Additions and Corrections

Vol. 49, 1984

Louis S. Hegedus* and Robert J. Perry. Cobalt-Mediated Synthesis of Nitro Enones from 1,3-Dienes and Alkylnitronates.

Page 2572, column 1. Reference 9 should read: Herz, J. E.; González, E.; Mandel, B. *Aust. J. Chem.* **1970**, *23*, 857.

George A. Olah,* Lena Ohannesian, and Massoud Arvanaghi. Synthetic Methods and Reactions. 119. *N*-Formylmorpholine: A New and Effective Formylating Agent for the Preparation of Aldehydes and Dialkyl (1-Formylalkyl)-phosphonates from Grignard or Organolithium Reagents.

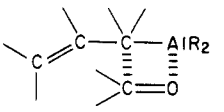
Page 3856, column 2. Reference 6 should be Aboujaoude, E. E.; Collignon, N.; Savignac, P. *Synthesis* **1983**, 634 and references cited therein.

Kevin T. Potts* and Eileen B. Walsh. Furfural Dimethylhydrazone: A Versatile Diene for Arene Cycloaromatization.

Page 4100. Table I: H_5 for compound **5** should read 7.54, not 4.54.

John J. Eisch* and Kenneth C. Fichter. Kinetic Control and Locoselectivity in the Electrophilic Cleavage of Allylic Aluminum Compounds: Reactions of Acenaphthenylaluminum Reagents with Carbonyl Substrates.

Page 4635. Structure **49** is incorrectly drawn; the proper structure is the following:



49

John W. Huffman,* Fred J. Matthews, and William H. Balke. Chair–Twist Equilibria in Some *tert*-Butyl Octalones.

Page 4946, column 2. After line 9, the following was omitted: "chair conformer (Figure 2), which was in turn 1.0 kcal/mol less than that of the ...".