in hexane) followed by warming the reaction to 0 °C for 1 h. The resulting anomeric mixture of lactols (1.0 equiv) dissolved in benzene (0.1 M) was then converted into the lactolide **11** (90% yield from **10**, greater than 95% anomerically pure, axial) by treatment at 22 °C with a mixture of isopropyl alcohol (10.0 equiv) and PPTSA (0.2 equiv).[12] Hydrogenation of **11** (1.0 equiv) in THF solution (0.3 M) using 15% by weight of Rh·Al_2O_3 at 1900 psi for 22 h afforded the saturated lactolide greater than 95% stereochemically pure.[13] The conversion of this material into the target lactonic acid **1** was accomplished by sequential treatment of it (1.0 equiv) with 75% acetic acid (0.1 M, stirring for 18 h at 22 °C), sodium metaperiodate (6.5 equiv, stirring for 1 h at 0 °C), and then chromium trioxide (0.2 equiv, stirring for 3 h at 0 °C). Standard workup followed by chromatography and crystallization gave pure Prelog Djerassi lactonic acid, mp 115–115.5 °C, in 65% yield from **11**. This material proved identical with a sample of racemic **1**.[14]

In addition to employing the enolate **2** as a four-carbon unit, we were interested in its utility as a two-carbon synthon: to this end, we examined degradation reactions of the adduct **3**. Treatment of **3** (1.0 equiv) in a 5:1 mixture of THF and water (0.1 M) containing H_5IO_6 (5.5 equiv) for 48 h at 22 °C gave an excellent yield of the hydroxy acid **12**, thereby suggesting new avenues of use for this type of enolate system. The possibility of realizing enantioselective aldol reactions using chiral amine derivatives of **2** is currently under investigation.

Acknowledgment. M.A.P. gratefully acknowledges receipt of a Sherman-Clarke fellowship from the University of Rochester.

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[12] For a discussion of the anomeric effect, see: (a) Lemieux, R. U. *Pure Appl. Chem.* **1971**, *27*, 527. (b) Zefirov, N. S.; Shekhtman, N. M. *Russ. Chem. Rev.* **1971**, *40*, 315.

[13] Hydrogenation of a methoxy analogue of this type of lactolide has been reported in ref 3d. We thank Professor Danishefsky for suggesting the isopropyl residue at the anomeric center since its greater axial population enhances the stereochemical outcome of lactolide reduction.

[14] We thank Professor S. Masamune for a generous sample of racemic **1**.

Lewis Acid Catalyzed Cyclocondensations of Functionalized Dienes with Aldehydes

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The reactions of highly "nucleophilic" derivatives of 1,3-butadiene with "electrophilic" olefins and acetylenes have been helpful in the total synthesis of a wide variety of natural products.[1] We now report on the cyclocondensations of such dienes with aldehydes. It is already clear that the potentialities of this reaction are substantial and far-reaching.

Our orienting goal in this investigation was a projected total synthesis of the important hypocholestemic natural product compactin (**1**).[2] The viability of the retrosynthetic dissection implied in Figure 1 remains to be demonstrated. However, the analysis has already had heuristic value in stimulating new synthetic strategies directed toward the potential subunits **2**[3] and **3**. Herein thought focus on the latter system. The though was that **3** might be derived from **4**. Compound **4** was envisioned as arising from precursor **4′** which was seen to be the formal cycloadduct of **5** and **6**.

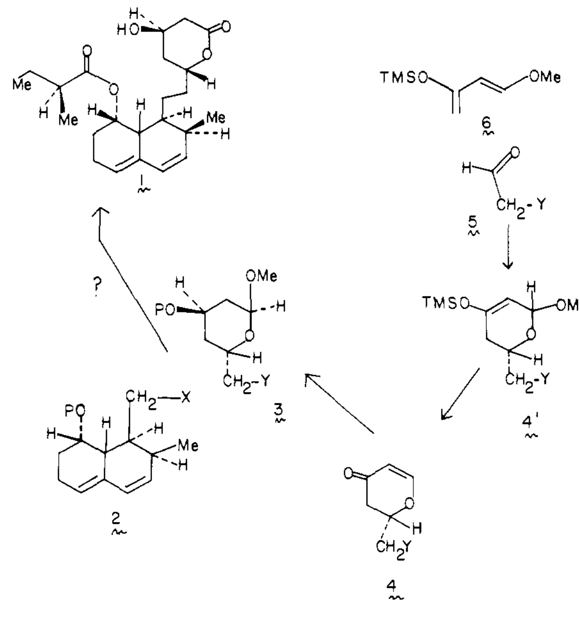
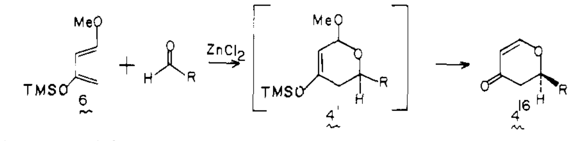


Figure 1.

Table I



entry[17]	*R*	yield of **4**, %
a	CH_2OCH_2Ph	87
b	CH_2SPh	70
c	CHNHCbz	80
d	Ph[18]	65
e	*p*-NO_2Ph	58
f	*o*-OCH_3Ph	58
g	CH_3[19]	17
h	CH_2CH_3[18]	48
i	$CH(CH_3)_2$	43
j	$CH_2CH(CH_3)_2$	37

In this communication we describe (i) the "cycloaddition"[4] of siloxy dienes with aldehydes via Lewis acid catalysis, (ii) the use of this process in the stereoslective synthesis of the pyranone portion of compactin, and (iii) the development of a fully synthetic general route to hexose systems and modified hexose systems. The latter are important components in a variety of antibiotics[5] and antitumor agents.[6]

The ability of a carbonyl group, in principle, to function as a "heterodienophile" in an apparent[4] Diels–Alder reaction with conjugated dienes has been previously recognized. The bulk of these reports have involved particularly reactive carbonyl groups such as glyoxalate[7,8] or mesoxalate.[9] More recently, there have

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[1] Danishefsky, S. *Acc. Chem. Res.* submitted for publication.

[2] Brown, A. G.; Smale, T. C.; King, T. J.; Hasenkamp, R.; Thompson, R. H. *J. Chem. Soc., Perkin trans. 1* **1976**, 1165. For a recent synthesis of (+)-compactin: Wang, Nai-Y.; Hsu, Chi-Tung; Shih, Charles J. *J. Am. Chem. Soc.* **1981**, *103*, 6538.

[3] For new chemistry directed toward systems of the type **2**, see: Danishefsky, S.; Funk, R. L.; Kerwin, J. F., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 6889.

[4] We emphasize that at this juncture the term cycloaddition has structural rather than mechanistic implications. The issue of mechanism will be dealt with separately. For the moment we note that in the cases involving zinc chloride catalysis, no intermediates on the way to type **4** products have been detected. In the boron trifluoride cases, possible intermediates have been detected.

[5] Rinehard, K. L., Jr.; Suami, T. "Aminocyclitol Antibiotics"; American Chemical Society: Washington, DC, 1980; Am. Chem. Soc. Sym. Ser. No. 125.

[6] Remers, W. A. "The Chemistry of Antitumor Antibiotics"; Wiley: New Yok, 1979; Vol. 1.

[7] Shavrygina, O. A.; Makin, S. M. *Khim-Farm. Zh.* **1969**, *3*, 17.

[8] Jurczak, J.; Zamojski, A. *Tetrahedron* **1972**, *28*, 1505. David, S.; Eustache, J. *J. Chem. Soc. Perkin Trans. 1* **1979**, 2230.

[9] Konowal, A.; Jurczak, J.; Zamojski, A. *Rocz. Chem.* **1968**, *42*, 2045.

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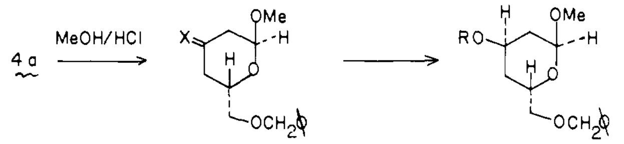
been described two instances involving the use of nonconjugated aldehydes with dienes with recourse to very high pressures.[10] *It is the substance of our finding that Lewis acids such as zinc chloride[11] or boron trifluoride promote the cyclocondensations[4] of highly functionalized dienes with a broad spectrum of aldehydes under very mild conditions.* There are thus obtained 2-substituted 2,3-dihydro-γ-pyrones.[12,13] These systems lend themselves to a variety of useful elaborations, some of which we enumerate below.

The reactions shown in Table I were conducted with 1.1:1.0 ratio of aldehyde/diene in benzene containing 0.5 equiv of anhydrous zinc chloride[14] at room temperature for 1–2 days. Yields refer to homogeneous material after chromatography. It must be emphasized that these yields have not been optimized. Our early efforts have been largely devoted to applications of the type **4** products to various synthetic problem (vide infra). However, even at this early stage, several trends appear to be emerging. The reaction seems to be more effective with aldehydes bearing α heterosubstitution (see entries a–c). In the simple case of acetaldehyde (entry g), the yield using zinc chloride catalysis is very poor (17%). However, improvement (37%) can be realized by carrying out the reaction thermally (3 equiv of aldehyde in benzene in a sealed tube) in the absence of catalyst. The scope of this strictly thermal cycloaddition remains to be determined.

Fortunately, it appears that the catalyzed reaction will tolerate branching at the α and β carbons reasonably well (see entries h–j). The stereochemical consequence of carrying out this cyclocondensation with aldehydes containing a chiral center α to the carbonyl group will be the subject of the communication which follows this one.[15]

The conversion of compound **4a** to the differentiated pyran derivative **8a** was accomplished in three steps. In the first step, **4a** reacts with methanolic HCl to afford a 69% yield of **7a**.[20] The latter undergoes deketalization with acetone containing a trace of HCl. The conformation of the resultant **7b** is apparently controlled by the anomeric effect.[21] Not surprisingly then, **7b** reacts with L-Selectride with clean equatorial delivery of "hydride" to afford an 88% yield of an alcohol, **8a**. The stereochemistry of this product was defined by NMR analysis of its derived acetate, **8b**.[16,22]



7a X = dimethylketal

7b X = O

8a R = H

8b R = Ac

We now describe the utilization of the dihydropyrones (type **4** system) in the synthesis of the 4-deoxyhexoses, which are difficultly accessable. Treatment of dihydropyranone **4a** with diisobutylaluminum hydride in benzene afforded, in 86% yield, the glycal **9a**.[16,23] Hydroxylation of the glycal double bond was achieved through reaction of **9a** with molybdinium oxide–hydrogen peroxide by using well-established precedents.[24] The resultant triol **10a** was best characterized as its triacetate, **10b**,[16,25] which is seen to be a *dl*-4-deoxymannose[26] derivative.

Prior acetylation of **9a** afforded the glycal acetate **9b** which upon hydroxylation with osmium tetroxide provided the diol **11**. Acetylation of **11** with pyridine in acetic anhydride afforded the anomeric acetate mixture **12** in which both anomers are in the 4-deoxyglucose series.[27] Also, Ferrier rearrangement[28] of glycal **9a** with methanolic hydrogen chloride affords the $\Delta^{2,3}$-4-deoxy derivative **13**.

At this writing, we have only carried forward the 6-benzyloxy system **4a**. It seems not unlikely that through similarly simple manipulations, the other adducts in Table I could be elaborated into hexose, branched hexose, and deoxyhexose targets.

The full scope of functional group and steric hindrance tolerance of this cyclocondensation[4] reaction has not been defined. However, the total synthesis of the racemate of the rare hexose, talose, as its 1β,-2,3,4,6-pentaacetate derivative, **20**, is illustrative of some promising possibilities in this connection. For this purpose, the trioxygenated diene, **15**,[29] was employed. Compound **15** was

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(10) Jurczak, J.; Chmielewski, M.; Filipek, S. *Synthesis* **1979**, 41. Chmielewski, M.; Jurczak, J. *J. Org. Chem.* **1981**, *46*, 2230.

(11) Aben, R. W.; Scheeren, H. W. *J. Chem. Soc. Perkin Trans. 1* **1979**, 3132. In this paper, the possibility of using zinc chloride catalysis was raised. However, no examples were provided.

(12) For previous syntheses of 2,3-dihydro-2-alkylpyran-4-ones: Vinick, F. J.; Gschwend, H. W. *Tetrahedron Lett.* **1978**, *4*, 315. Duperrier, A.; Moreau, M.; Gelin, S.; Dreux, J. *Bull. Soc. Chim. Fr.* **1974**, 2207 and references cited therein.

(13) For related pyrones, see: Koreeda, M.; Akagi, H. *Tetrahedron Lett.* **1980**, *21*, 1197. Morgan, T. A.; Ganem, B. *Ibid.* **1980**, *21*, 2773. Ross, W. J.; Todd, A., Clark, B. P.; Morgan, S. E.; Baldwin, J. E. *Ibid.* **1981**, *22*, 2207.

(14) The results using other Lewis acids will be the subject of future communications.

(15) Danishefsky, S.; Kato, N., Askin, D.; Kerwin, J. F., Jr., submitted for publication.

(16) Satisfactory IR, NMR, and mass spectra were obtained for all new compounds, representative NMR data follow. **4a**: ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.28 (br s, 6 H), 5.23 (d, *J*. = 6 Hz, 1 H), 4.51 (m, 3 H), 3.52 (d, J = 4.5 Hz, 2 H), 2.75 (dd, *J* = 12.5, 16 Hz, 1 H), 2.4 (dd, *J* = 4.5, 16 Hz, 1 H). **4b** ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.3 (m, 6 H), 5.32 (d, *J* = 6 Hz, 1 H), 4.45 (m, 1 H), 3.2 (2 dd, *J* = 5, 15 Hz, 2 H), 2.52 (m, 2 H). **4d**: ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.2 (br s, 6 H), 5.4 (dd, *J* = 1, 6 Hz, 1 H), 5.3 (dd, *J* = 4.5, 12 Hz, 1 H), 2.3–3.0 (m, 2 H). **4i**: ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.4 (d, *J* = 6 Hz, 1 H), 5.35 (d, *J* = 6 Hz, 1 H), 4.35 (m, 1 H), 2.45 (m, 2 H), 2.0 (m, 1 H,) 1.0 (2 d, *J* = 7 Hz, 6 H). **8b**: ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.33 (s, 5 H), 5.1 (m, 1 H), 4.85 (m, 1 H), 4.6 (s, 2 H), 4.25 (m, 1 H), 3.53 (m, 2 H), 3.35 (s, 3 H) 2.05 (s, 3 H), 1.6–1.95 (m, 4 H). **9a**: ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.4 (s, 5 H) 6.38 (d. *J* = 6 Hz, 1 H), 4.72 (ddd, *J* = 1.5, 6 Hz, 1 H), 4.55 (s, 2 H), 4.0–4.5 (br m, 2 H), 3.55 (m, 2H), 2.5 (br s, 1 H), 2.15 (dddd, *J* = 1.5, 6, 14 Hz, 1 H), 1.7 (ddd, *J* = 8, 10, 14 Hz, 1 H). **10b**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.38 (s, 5 H), 5.76 (d, *J* = 1 Hz, 1 H), 5.38 (dd, *J* = 1, 3 Hz, 1 H), 5.08 (ddd, *J* = 5.5, 7 Hz, 1 H), 4.57 (s, 2 H), 3.85 (m, 1 H), 3.65 (dd, *J* = 5.0, 10 Hz, 1 H), 3.55 (dd, *J* = 4.8, 10 Hz, 1 H), 2.18 (s, 3 H), 2.0–2.15 (m, 7 H including singlets at 2.08 and 2.01), 1.87 (apparent dt, *J* = 3 Hz, 7 Hz, 1 H). **16**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.26–7.38 (m, 6 H), 5.42 (d, *J* = 6 Hz, 1 H), 4.84 (ddd, *J* = 3.0, 6.0, 6.6 Hz, 1 H), 4.54 (s, 2 H), 4.50 (d, *J* = 6.0 Hz, 1 H), 3.87 (dd, *J* = 6.6, 11.4 Hz, 1 H), 3.77 (dd, *J* = 3.0, 11.4 Hz, 1 H). **17**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.29–7.37 (m, 5 H), 6.39 (dd, *J* = 6.25, 1.47, 1 H_1), 4.70 (ddd, *J* = 6.25, 2.2, 1.2 Hz, 1 H_2), 4.59 (s, 2 H), 4.33 (m, 1 H), 4.00–4.04 (m, 2 H) 3.79 (d, *J* = 4.78 Hz, 2 H). **18**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.25–7.37 (m, 5 H), 5.82 (d, *J* = 1.47, 1 H), 5.39 (br d, *J* = 3.68 Hz, 2 H), 5.13 (t, *J* = 3.68 Hz, 1 H), 4.57, (d. *J* = 11.9 Hz, 1 H), 4.40 (d, *J* = 11.9 Hz, 1 H), 4.00 (ddd, *J* = 1, 5.88, 6.99, 1 H), 3.54–3.67 (2 dd, *J* = 5.88, 6.99, 9.56 Hz, 2 H), 2.17, 2.10, 2.04, 2.00 (4OAc, 4s, 12 H).

(17) (a) **5a**: Arndt, H. C.; Carroll, S. A. *Synthesis* **1979**, 202. (b) **5b**: Toyoshima, K.; Okuyama, T.; Fueno, T. *J. Org. Chem.* **1978**, *43*, 2789. For other syntheses of α-(thioalkyl)acetaldehydes refer to: Wick, E.; Yamanishi, T.; Wertheimer, L. C.; Hoff, J. E.; Proctor, B. E.; Goldblith, S. *J. Agric. Food Chem.* **1961**, *9*, 289.

(18) Sher, F.; Isidor, J. L; Taneja, H. R.; Carlson, R. M. *Tetrahedron Lett.* **1973**, *14*, 577.

(19) Nakanishi, K.; Nagao, M.; Okada, K. *J. Pharm. Soc. Jpn.* **1968**, *88*, 1044.

(20) A minor product obtained in 18% yield was corresponding *cis*-glycoside whose NMR spectral properties are δ (90 MHz, $CDCl_3$) 7.3 (s, 5 H), 4.54 (s, 2 H), 4.45 (dd, *J* = 2, 9 Hz, 1 H), 3.45–3.95 (m, 6 H), 3.13 (s, 3 H), 3.10 (s, 3 H), 1.85–2.35 (m, 2 H), 1.15–150 (m, 2 H), (9 Hz, 1 H), 3.45–3.95 (m, 6 H), 3.13 (s, 3 H), 3.10 (s, 3H), 1.85–2.35 (m, 2 H), 1.15–150 (m, 2 H).

(21) Wolfe, S.; Whangbo, M.-H.; Mitchell, D. J. *Carbohydr. Res.* **1979**, *69*, 1 and references cited therein.

(22) Reduction with DIBAL gave a mixture of both alcohols which were characterized as their acetates.

(23) Chalmers, A. A.; Hall, R. H. *J. Chem. Soc. Perkin Trans. 2* **1974**, 728. Guthrie, R. D.; Irvine, R. W. *Aust. J. Chem.* **1980**, *33*, 1037.

(24) Bilik, V.; Kučār, S. *Carbohydr. Res.* **1970**, *13*, 311.

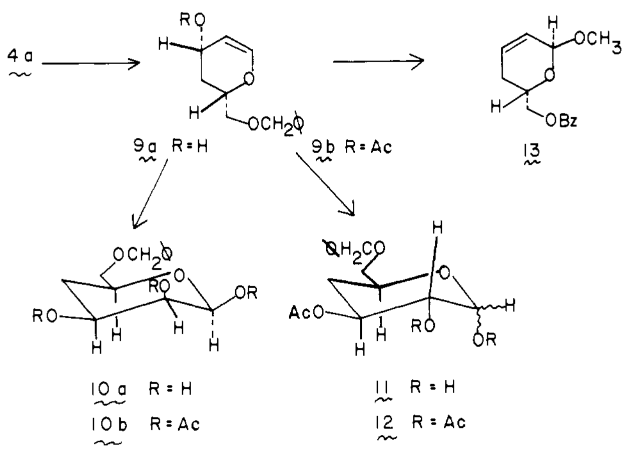
(25) A minor amount of the α anomer is also isolated as its triacetate.

(26) Rasmussen, J. R. *J. Org. Chem.* **1980**, *45*, 2725. Čerñy, M.; Stañek, J., Jr.; Pacāk, *J. Collect. Czech. Chem. Commun.* **1969**, *34*, 1750. Lichtenthaler, F. W.; Kraska, U.; Ogawa, S. *Tetrahedron Lett.* **1978**, 1323.

(27) Cf: Barton, D. H. R.; Subramanian, R. *J. Chem. Soc. Perkin Trans. 1* **1977**, 1718. Hedgley, E. J.; Overend, W. G.; Rennie, R. A. C. *J. Chem. Soc.* **1963**, 4701.

(28) Ferrier, R. J. *J. Chem. Soc.* **1964**, 5443.

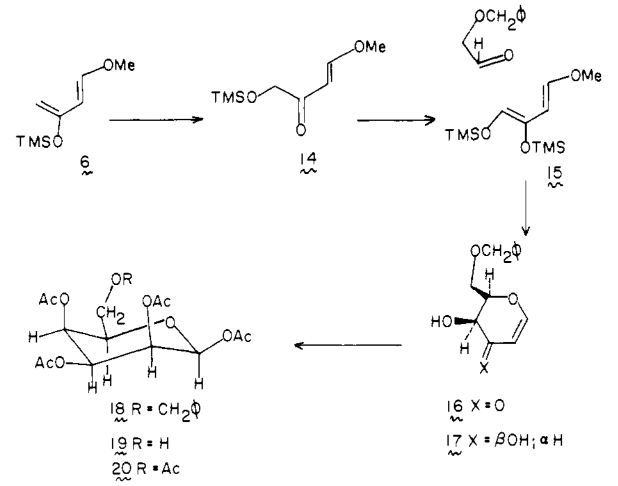
(29) Diene **15** was obtained in only ca. 70% purity. The enone **14** is the most predominant and obvious of several contaminants. The nature of the other impurities is not understood. The NMR (90 MHz, $CDCl_3$) spectral properties of **15** measured in this context are δ 6.59 (d, *J* = 12 Hz, 1 H), 5.69 (s, 1 H), 5.20 (d, *J* = 12 Hz, 1 H), 3.53 (s, 3 H), 0.20 (s, 18 H).



prepared by the enol silylation of **14** under our standard conditions ($Me_3SiCl-Et_3N-ZnCl_2$). Compound **14** was, in turn, obtained from a Rubottom reaction[30] on diene **6**. At this stage, the stereochemistry of the diene is not known.

Reaction of **15** with benzyloxyacetaldehyde[17a] was carried out in methylene chloride in the presence of boron trifluoride etherate at −78 °C. The resultant product[31] was treated with trifluoroacetic acid[4] in tetrahydrofuran at room temperature to afford a 42% yield of the hydroxy enone **16**.[16] Reduction of **16** with DIBAL afforded the glycal **17**[16] which upon hydroxylation and peracetylation by known methods[24] afforded the racemic β-talose derivative **18**.[32]

The structure and stereochemistry of **18** was proven by its conversion, upon hydrogenolysis to **19** which, upon acetylation afforded **20**. An authentic sample of **20** was obtained by separation of a 1:3 mixture of β-:α-talose pentaacetates, in turn available by acetylation of talose.[33]



Given the chemical versatility of the dihydro-γ-pyrones and the stereochemical control, which can be exercised over their transformation products by exploiting well-known principles of carbohydrate chemistry, this cyclocondensation reaction of nucleophilic dienes and aldehydes, under extremely mild conditions, will find broad usage in the synthesis of a variety of natural products. Such studies are in progress in our laboratory, and early results are most encouraging.

Acknowledgment. This research was supported by P.H.S. Grant HL48136-02. NMR spectra were obtained through the auspices of the Northeast Regional N.S.F./N.M.R. Facility at Yale University which was supported by the N.S.F. Chemistry Division Grant C.H.E. 7916210.

Registry No. (±)-**4a**, 80127-39-5; (±)-**4b**, 80127-40-8; (±)-**4c**, 80127-41-9; (±)-**4d**, 80127-42-0; (±)-**4e**, 80127-43-1; (±)-**4f**, 80127-44-2; (±)-**4g**, 80127-45-3; (±)-**4h**, 80127-46-4; (±)-**4i**, 80127-47-5; (±)-**4j**, 80127-48-6; **6**, 59414-23-2; (±)-*trans*-**7a**, 80127-49-7; (±)-*cis*-**7a**, 80127-50-0; (±)-*trans*-**7b**, 80127-51-1; (±)-**8a**, 80127-52-2; (±)-**8b**, 80127-53-3; (±)-**9a**, 80127-54-4; (±)-**9b**, 80127-55-5; (±)-**10a**, 80127-56-6; (±)-**10b**, 80127-57-7; (±)-**11** isomer 1, 80127-58-8; (±)-**12** isomer 1, 80127-60-2; (±)-**12** isomer 2, 80127-61-3; (±)-**13**, 80127-62-4; **14**, 80127-63-5; **15**, 80127-64-6; (±)-**16**, 80127-65-7; (±)-**17**, 80127-66-8; (±)-**18**, 80127-67-9; (±)-**19**, 80184-00-5; (±)-**20**, 80184-01-6; (phenylmethoxy)acetaldehyde, 60656-87-3; phenylthioacetaldehyde, 66303-55-7; (benzyloxycarbonylamino)acetaldehyde, 67561-03-9; benzaldehyde, 100-52-7; 4-nitrobenzaldehyde, 555-16-8; 2-methoxybenzaldehyde, 135-02-4; acetaldehyde, 75-07-0; propanal, 123-38-6; 2-methylpropanal, 78-84-2; 3-methylbutanal, 590-86-3; (±)-**11** isomer 2, 80127-59-9.

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[30] Rubottom, G. M.; Vazquez, M. A.; Pelegrina, D. R. *Tetrahedron Lett.* **1974**, 4319.

[31] In this instance, no dihydropyrone is isolated prior to treatment with trifluoroacetic acid.

[32] The NMR data are given[16] for the kinetically produced β-acetoxy anomer **18**. In another run in the totally synthetic series, the thermodynamically more stable α-acetate version of **20** was isolated as the major product. Hence, at present we do not have a reliable procedure for controlling the anomeric state of the final talose derivative.

[33] Cf: Streefkerk, D. G.; de Bie, M. J. A.; Vliengenthart, J. F. G. *Carbohydr. Res.* **1974**, *38*, 47.

Stereochemical Consequences of the Lewis Acid Catalyzed Cyclocondensation of Oxygenated Dienes with Aldehydes. A Rapid and Stereoselective Entry to Various Natural Products Derived from Propionate

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Received August 24, 1981

In the preceding communication, we described the Lewis acid catalyzed cyclocondensation of 1,3-dioxygenated dienes with representative aldehydes. This process gives rise to 2,3-dihydro-γ-pyrones.[1a] Applications of such dihydropyrones to the synthesis of hexose related targets were described.

The cyclocondensation of **1** with aldehyde **2**, bearing a chiral center α to the formyl group, would give rise to **3**. The relative stereochemistry at C_2 and C_3[1b] in product **3** can be related to the Cram rules[2,3] which deal with the diastereofacial[4] sense of addition of nucleophiles to carbonyl groups.[5] The relationship between C_3 and C_4[1b] might be similarly related in the erythro–threo dichotomy in aldol condensations.[6,7] Alternatively, from the perspective of a cycloaddition process,[8] the C_3–C_4 relationship in product **3** might be perceived in terms of the issue of endo vs. exo alignments. It is noted that insofar as a cis silyl ether such as **1** is viewed as a cis enolate equivalent,[9] the "aldol" product of

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[1] (a) Danishefsky, S.; Kerwin, J. F., Jr.; Kobayashi, S. *J. Am. Chem. Soc.*, preceding paper in this issue. (b) The numbering system used in discussing adduct **3** anticipates its conversion to **11** and is based on that used by Bartlett.[11g]

[2] Cram, D. J.; Elhafez, F. *J. Am. Chem. Soc.* **1952**, *74*, 5828. Cram, D. J.; Kopecky, K. R. *Ibid.* **1959**, *81*, 2748.

[3] For a very recent paper on this subject, see: Yamamoto, Y.; Maruyama, K. *Tetrahedron Lett.* **1981**, 2895.

[4] Heathcock, C. H.; Young, S. D.; Hagen, J. P.; Pirrung, M. C.; White, C. T.; Van Der Veer, D. *J. Org. Chem.* **1980**, *45*, 3846.

[5] Cf.: Cherest, M.; Felkin, H.; Prudent, N. *Tetrahedron Lett.* **1968**, 2199.

[6] Cf.: Heathcock, C. H.; Buse, C. T.; Kleschick, W. A.; Pirrung, M. C.; Sohn, J. E.; Lampe, J. *J. Org. Chem.* **1980**, *45*, 1066.

[7] Dubois, J. E.; Fellmann, P. *Tetrahedron Lett.* **1975**, 1225.

[8] The term cycloaddition as we use it here has no implication with respect to degree of concertedness.

[9] Compound **4** may be viewed as a vinylogous silylketene acetal. The stereochemistry of "Mukaiyama" type aldols of silylketene acetals was reported by: Chan, T. H.; Aida, T.; Lau, P. W. K.; Gorys, V.; Harpp, D. N. *Tetrahedron Lett.* **1979**, 4029.

0002-7863/82/1504-0360$01.25/0