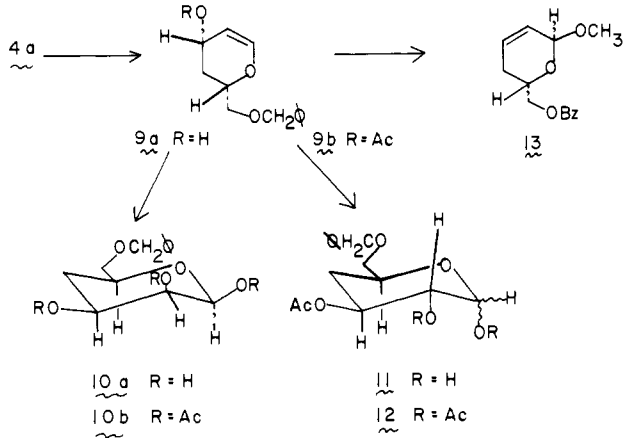
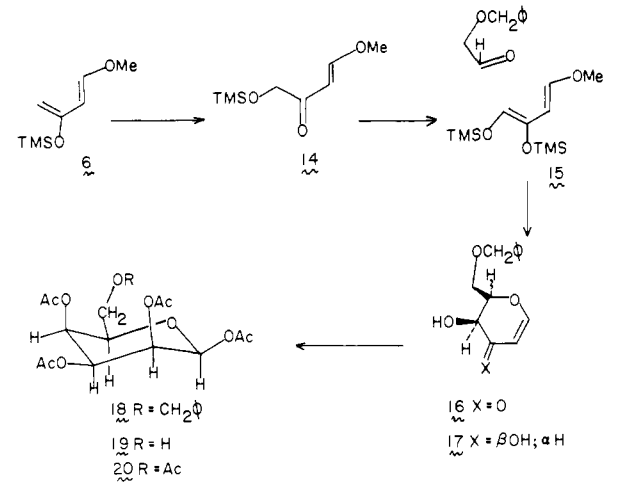


prepared by the enol silylation of **14** under our standard conditions (Me_3SiCl-Et_3N-$ZnCl_2$). Compound **14** was, in turn, obtained from a Rubottom reaction[30] on diene **6**. At this stage, the stereochemistry of the diene is not known.

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.

(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.

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.

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

Samuel Danishefsky,* Nobuo Kato, David Askin, and James F. Kerwin, Jr.

Department of Chemistry, Yale University
New Haven, Connecticut 06511

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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

(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.

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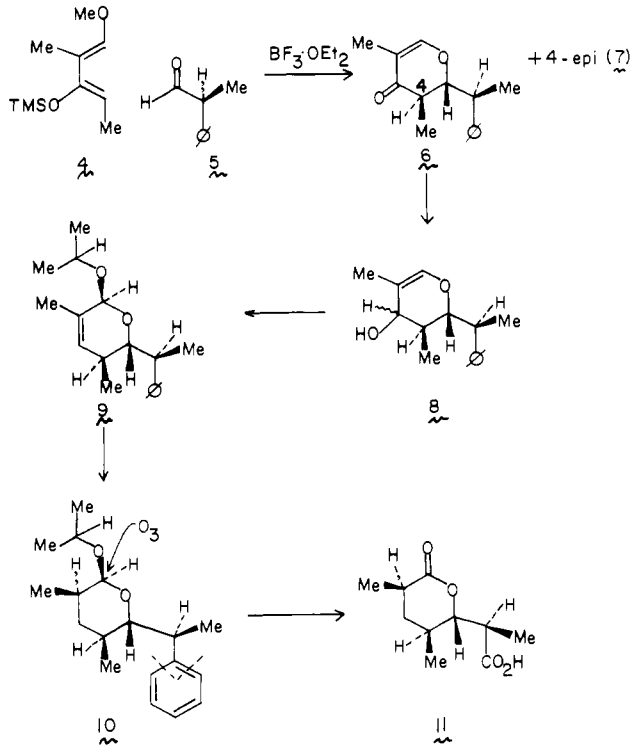
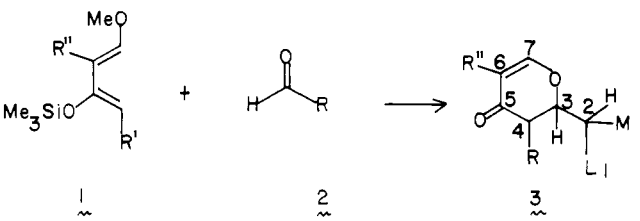
Scheme I



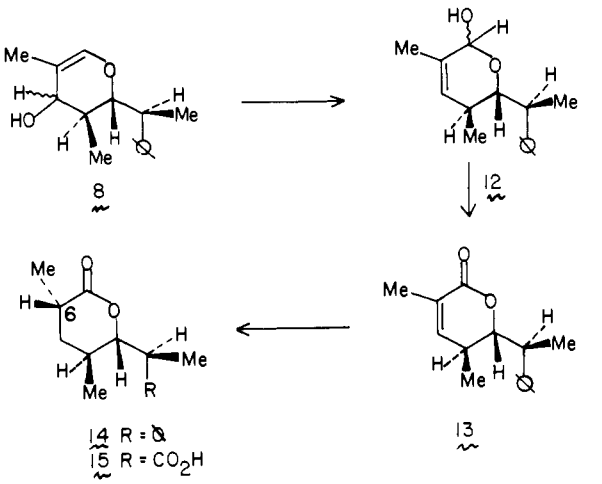
kinetic control should have an erythro relationship between C_3 and C_4.[6,7] This corresponds, on cyclization, to a cis disposition of R′ and R. When viewed as a cycloaddition process, the cis products would arise from an *endo alignment of R of the aldehyde with the diene system.*

In product **3**, there are access points for introducing additional functionality and chirality at carbons 5, 6, and 7. Thus, if the chirality about C_2, C_3, and C_4 can be controlled, the opportunity for extensive stereochemical development presents itself. In this communication, we show by example how this logic fares in practice. Parenthetically, we report a short (five steps) synthesis of the Prelog–Djerassi lactone (**11**)[10,11] from readily available starting materials via uncomplicated experimental procedures. The simplicity of modifying the configurations at C_4 and C_6 in these systems (vide infra) is another feature of this approach, which is particularly attractive for the synthesis of various propionate related natural products.



The readily available (two steps from diethyl ketone) silyloxy diene **4**[12] reacts with the commercially available aldehyde **5** in

Scheme II



methylene chloride at −78 °C in the presence of boron trifluoride etherate. After 1 h, the reaction mixture was treated with trifluoroacetic acid in tetrahydrofuran at room temperature for 2.5 h[13] to afford a 95% yield of a 4.3:1 mixture of compound **6**[14] and its C_4 epimer **7**.[14] Only traces of what we suspect to be the "anti-Cram" variation of either **6** or **7** could be analytically detected. Remarkably, purification of this mixture was achieved by *fractional crystallization of the minor component* **7**, mp

(10) (a) Djerassi, C.; Halpern, O. *J. Am. Chem. Soc.* **1957**, *79*, 3926. (b) Anlika, R.; Dvornik, D.; Gulber, K.; Heusser, H.; Prelog, V. *Helv. Chim. Acta* **1956**, *39*, 1785.

(11) For previous syntheses in this series, see: (a) Masamune, S.; Kim, C. U.; Wilson, K. E.; Spessaro, G. O.; Georghiou, P. E.; Bates, G. S. *J. Am. Chem. Soc.* **1975**, *97*, 3512. (b) White, J. D.; Fukuyama, Y. *Ibid.* **1979**, *101*, 226. (c) Stork, G.; Nair, V. *Ibid.* **1979**, *101*, 1315. (d) Narano, A.; Takimoto, S.; Inanaga, J.; Katsuki, T.; Ouchida, S.; Inoue, K.; Aiga, M.; Okukado, N.; Yamaguchi, M. *Chem. Lett.* **1979**, 1019. (e) Grieco, P. A.; Ohfune, Y.; Yokoyama, Y.; Owens, W. *J. Am. Chem. Soc.* **1979**, *101*, 4749. (f) Hirama, M.; Garvey, D. S.; Lu, L. D.-L.; Masamune, S. *Tetrahedron Lett.* **1979**, 3937. (g) Bartlett, P. A.; Adams, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 337. (h) Ireland, R. E.; Daub, J. P. *J. Org. Chem.* **1981**, *46*, 479. (i) Jarosz, S.; Fraser-Reid, B. *Tetrahedron Lett.* **1981**, 2533.

(12) Danishefsky, S.; Yan, C. F.; Singh, R. K.; Gammill, R.; McCurry, P.; Fritsch, N.; Clardy, J. *J. Am. Chem. Soc.* **1979**, *101*, 7001.

(13) Examination of the NMR spectrum prior to the treatment with trifluoroacetic acid indicated that the cyclocondensation products **6** and **7** were substantially produced. There was, however, some indication of an intermediate product, possibly involving formation of the "aldol" bond and transfer of the silyl group. The TFA treatment seems to convert this product or mixture to the dihydropyrones as reflected by NMR analysis. We emphasize that at this stage the intermediate has not been characterized nor has its yield been determined.

(14) Satisfactory IR, NMR, and mass spectral data were obtained for the following compounds. **6**: IR ν ($CHCl_3$) 1658, 1620 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.34–7.14 (m, 6 H), 4.10 (dd, J = 4.5, 9 Hz, 1 H), 3.09 (dq, J = 4.5, 7 Hz, 1 H), 2.48 (qd, J = 7, 9 Hz, 1 H), 1.63 (s, 3 H), 1.38 (d, J = 7 Hz, 3 H), 1.17 (d, J = 7 Hz, 3 H); m/e 230 (M^+). **7**: IR ν ($CHCl_3$) 1665, 1623 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.35–7.20 (m, 4 H), 7.18–7.13 (m, 2 H), 4.29 (dd, J = 2.7, 11 Hz, 1 H), 3.10 (qd, J = 6.7, 11 Hz, 1 H), 2.00 (dq, J = 2.7, 7.4 Hz, 1 H), 1.67 (d, J = 1 Hz, 3 H), 1.41 (d, J = 6.7 Hz, 3 H), 1.01 (d, J = 7.4 Hz, 3 H); m/e 230 (M^+), 125. **8α** (equatorial hydroxy isomer): mp 92–94 C; IR ν ($CHCl_3$) 1665 cm^{-1}; ^1H NMR (270, MHz, $CDCl_3$) δ 7.32–7.16 (m, 5 H), 6.16 (s, 1 H), 3.72 (m, 2 H), 3.22 (dq, J = 5, 7 Hz, 1 H), 1.81 (m, 1 H), 1.61 (s, 3 H), 1.50 (br d, J = 8 Hz, 1 H, exchangeable with D_2O), 1.27 (d, J = 7 Hz, 3 H), 1.04 (d, J = 7 Hz, 3 H); m/e 232 (M^+), 109. **8β** (axial hydroxy isomer): mp 96–97.5 °C, IR ν ($CHCl_3$) 1665 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.38–7.17 (m, 5 H), 6.21 (br s, 1 H), 3.77 (m, 1 H), 3.71 (dd, J = 2.5, 10 Hz, 1 H), 3.00 (dq, J = 2.5, 7 Hz, 1 H), 1.86 (m, 1 H), 1.65 (s, 3 H), 1.52 (br s, 1 H, exchangeable with D_2O), 1.27 (d, J = 7 Hz, 3 H), 1.10 (d, J = 7 Hz, 3 H); m/e 232 (M^+), 127. **9**: ^1H NMR (90 MHz, $CDCl_3$) δ 7.41–7.10 (m, 5 H), 5.36 (s, 1 H), 4.71 (s, 1 H), 3.56 (dd, J = 3, 9 Hz, 1 H), 3.52 (septet, J = 6 Hz, 1 H), 3.04 (dq, J = 3, 6 Hz, 1 H), 2.32 (m, 1 H), 1.63 (s, 3 H), 1.30 (d, J = 6 Hz, 3 H), 1.00 (d, J = 3 Hz, 3 H), 0.94 (d, J = 3 Hz, 3 H), 0.54 (d, J = 6 Hz, 3 H); m/e 274 (M^+), 98. **10**: ^1H NMR (270 MHz, $CDCl_3$) δ 7.31–7.10 (m, 5 H), 4.55 (d, J = 2 Hz, 1 H), 3.46 (dd, J = 2, 10 Hz, 1 H), 3.10 (septet, J = 6 Hz, 1 H), 3.00 (dq, J = 2, 7 Hz, 1 H), 1.85–1.59 (m, 2 H), 1.44 (m, 1 H), 1.26 (d, J = 7 Hz, 3 H), 1.22 (m, 1 H), 0.91 (d, J = 6.5 Hz, 3 H), 0.86 (d, J = 6 Hz, 3 H), 0.78 (d, J = 6.5 Hz, 3 H), 0.57 (d, J = 6 Hz, 3 H); m/e 276 (M^+), 83. **11**: IR ν ($CHCl_3$) 3600–2400, 1725, 1718 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 8.80 (br s, 1 H, exchangeable with D_2O), 4.59 (dd, J = 2.3, 10 Hz, 1 H), 2.76 (dq, J = 2.3, 7 Hz, 1 H), 2.52 (m, 1 H), 2.02–1.81 (m, 2 H), 1.46 (m, 1 H), 1.29 (d, J = 7 Hz, 3 H), 1.20 (d, J = 7 Hz, 3 H), 1.02 (d, J = 6.5 Hz, 3 H); m/e 200 (M^+), 56. **13**: IR ν ($CHCl_3$) 1700 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 7.37–7.17 (m, 5 H), 6.30 (m, 1 H), 4.17 (t, J = 6 Hz, 1 H), 3.02 (quintet-like, $J \sim 6$ Hz, 1 H), 2.39 (m, 1 H), 1.88 (s, 3 H), 1.36 (d, J = 7 Hz, 3 H), 1.06 (d, J = 7 Hz, 3 H); m/e 230 $M^{(+)}$, 125. **14**: IR ν ($CHCl_3$) 1725 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 7.38–7.13 (m, 5 H), 4.07 (dd, J = 4 Hz, 9 Hz, 1 H), 2.96 (dq, J = 4, 7 Hz, 1 H), 2.53 (m, 1 H), 2.2–1.4 (m, 3 H), 1.36 (d, J = 7 Hz, 3 H), 1.20 (d, J = 7 Hz, 3 H), 1.03 (d, J = 6 Hz, 3 H); m/e 232 (M^+), 127. **15**: IR ν ($CHCl_3$) 3600–2400, 1735, 1710 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 8.35 (br s, 1 H, exchangeable with D_2O), 4.52 (dd, J = 3, 10 Hz, 1 H), 2.71 (m, 2 H), 2.2–1.4 (m, 3 H), 1.24 (d, J = 6 Hz, 6 H), 1.03 (d, J = 6 Hz, 3 H); m/e 200 (M^+), 56.

135-137 °C. There is thus obtained the desired **6** in 80% yield at a purity level of 94%. That **6** and **7** have the same relative stereochemistry at carbons 2 and 3, but differ only in the C_3-C_4 relationship, is strongly suggested by their partial equilibration with alumina.[15]

Reduction of **6** with DIBAL in benzene-toluene afforded the isomers **8**. Although readily accomplished, there is no need to separate these hydroxy epimers.[14] Each compound undergoes a Ferrier-type rearrangement[16] (isopropyl alcohol, *p*-TsOH, 0 °C) to give (96%) the β-disposed *anomer* **9**. The tendency of the Ferrier rearrangement to produce an axial glycoside is undoubtedly responsible for the stereospecific formation of **9**.[14]

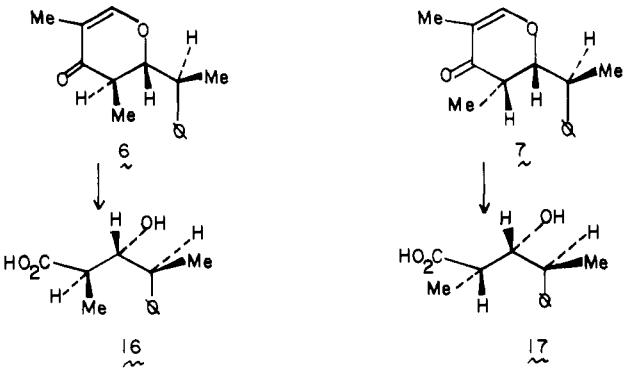
Flanked as it is by two β functions, the double bond in **9** suffers catalytic reduction (H_2/Pd-Al_2O_3; EtOAc) from its α face to afford **10**.[14] Compound **10**, mp 34-38 °C, was subjected to the action of ozone in aqueous acetic acid containing a trace of trifluoroacetic acid (4 h, room temperature). This was followed by reaction with hydrogen peroxide in aqueous acetic acid. There was thus obtained a 56% yield of **11**, mp 116-117 °C.[14] *Thus, in the ozonolysis process, the acetal linkage in* ***10*** *had suffered a Deslongchamps type of degradation,*[17] *concurrently with the more classical oxidative cleavage of its phenyl ring.*[18] The overall yield for this straightforward synthesis of **11** is currently 29% (unoptimized).

The C_6 epimer of **11**, i.e., compound **15**, can also be obtained in a stereospecific fashion from **8**. Toward this end, **8** is subjected to Ferrier rearrangement[16] by using aqueous HCl in dioxane. The resultant hemiacetal **12** on Jones oxidation gives the unsaturated lactone **13**.[14] Catalytic reduction of **13** (H_2/Pd/C; EtOH) affords, stereospecifically, the compound **6** epi system, **14**,[14] mp 66-69 °C. Thus, either the *cis*- or *trans*-4,6-dimethyl systems are available stereospecifically from a common intermediate. The structure of **14** was supported by its transformation (ozone, aqueous acetic acid, room temperature, 4 h, followed by hydrogen peroxide) to lactone **15**.[14]

We have also discovered a surprising medium effect on the stereochemistry of the cyclocondensation reaction. As noted above, when the reaction was carried out in methylene chloride at -78 °C, the ratio **6**/**7** was 4.3:1. However, when the reaction is conducted in carbon tetrachloride at room temperature, the ratio **6**/**7** becomes 1:4. Again, we could observe no loss in Cram's rule specificity.

The effect seems to arise primarily from the change in solvents since, in methylene chloride at -10 °C, the trans compound **6** still predominates. Obviously a great deal of experimentation awaits us in seeking to improve upon the cis:trans specificities and in determining the origin of this medium effect. The possibility that it reflects a change of mechanism in the cyclocondensation reaction will be explored.

Finally, we note the possibility of using the dihydropyrones as masked and manageable equivalents of β-aldols. This dimension of the new methodology was demonstrated. Ozonolysis of **6** or **7** in methanol at -78 °C followed by reaction with alkaline hydrogen peroxide resulted in the smooth formation of the known[19,20] **16** (mp 106.5-107.5 °C) and **17** (mp 136-138 °C), respectively. There is no erosion in stereochemical homogeneity in this simple unveiling procedure. Plans to exploit the synthetic equivalency between the now readily available dihydro-γ-pyrones and β-hydroxycarbonyl systems of defined stereochemistry abound, and their implementation is currently being pursued.



Acknowledgment. We would like to thank Professor R. Schlessinger for disclosure of his excellent synthesis of the Prelog-Djerassi lactone prior to publication. 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.

(15) Of course, the equilibration of **6** and **7** per se does not establish the identity of their configurations at C_3 since the mechanism of equilibration might, in principle, involve β elimination of the oxygen from position 3 and recyclization. However, preliminary results in our laboratory (N. Kato) indicate that the recyclization process of the 1-hydroxypenta-1,4-dien-3-one (produced under different conditions) does not smoothly occur under our reaction conditions.

(16) Ferrier, R. J. *J. Chem. Soc.* **1964**, 5443.
(17) Deslongchamps, P.; Moreau, C. *Can. J. Chem.* **1971**, *49*, 2465.
(18) Criegee, R.; Höver, H. *Chem. Ber.* **1960**, *93*, 2521.
(19) Pirrung, M. C.; Heathcock, C. H. *J. Org. Chem.* **1980**, *45*, 1727.
(20) Heathcock, C. H.; Pirrung, M. C.; Buse, C. T.; Hagen, J. P.; Young, D. S.; Sohn, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 7077. Heathcock, C. H.; Pirrung, M. C.; Lampe, J.; Buse, C. T.; Young, S. D. *J. Org. Chem.* **1981**, *46*, 2290.

Two-Dimensional NMR Investigation of Amide Proton Exchange in H_2O Solution

J. D. Cutnell

Department of Physics, Southern Illinois University Carbondale, Illinois 62901

Received September 21, 1981

This communication demonstrates the feasibility of using the Redfield[1] technique for H_2O suppression in a two-dimensional NMR study[2] of exchanging amide protons. The basic 2-D technique for studying exchange has been described in detail and applied to systems other than those which involve amide protons exchanging with an H_2O solvent.[2-4] The Redfield technique for suppressing the H_2O resonance and enhancing dynamic range has been widely used in one-dimensional NMR studies, including saturation-transfer experiments designed to elucidate exchange mechanisms.[5] Combination of the 2-D and Redfield techniques significantly extends NMR capability for studies of an important class of chemical exchange kinetics.

The Redfield excitation operates by stimulating the resonances of interest while leaving the intense H_2O resonance relatively unexcited.[1] However, in the 2-D experiment ($-90°_x$-evolution-$90°_x$-mixing-$90°_x$-detection-preparation-)$_n$ it is crucial that both resonances of the exchanging pair be excited by the first two 90° pulses of the sequence.[2,3] This is so, because for each resonance, frequency labeling (which gives the second chemical shift dimension) and kinetic development of the spin system (which allows the exchange process to be observed) must occur before observation of the free induction decay. Thus, only the third or acquisition pulse in the sequence can be a Redfield pulse. In terms of technical difficulty it may be thought that this situation is analogous to that encountered in Redfield under-water decoupling, where the

(1) Redfield, A. G.; Kunz, S. D.; Ralph, E. K. *J. Magn. Reson.* **1975**, *19*, 116-117.
(2) Jeener, J.; Meier, B. H.; Bachmann; Ernst, R. R. *J. Chem. Phys.* **1979**, *71*, 4546-4553.
(3) Macura, S.; Ernst, R. R. *Mol. Phys.* **1980**, *41*, 95-117.
(4) Kumar, A.; Ernst, R. R.; Wüthrich, K. *Biochem. Biophys. Res. Commun.* **1980**, *95*, 1-6.
(5) Cutnell, J. D.; LaMar, G. N.; Kong, S. B. *J. Am. Chem. Soc.* **1981**, *103*, 3567-3572.

0002-7863/82/1504-0362$01.25/0