sponding 1,4-dienes virtually upon mixing.[12] A portion of our results are summarized in Table I. Yields in all cases are good to excellent. Several noteworthy features of these couplings are apparent; firstly, stereochemical integrity about the olefinic center of the educt is completely maintained. Equally impressive is the range of functionality which is tolerated. Hence, branched chain sugars are readily prepared (entry 4), sulfur-containing substrates do not interfere (entry 5), and highly reactive centers of electrophilicity, as with an ethyl ester (entry 6)[13] or a fully functionalized cephem (entry 7), are compatable.

Although regiochemical issues in the allyl and methallyl cases do not apply, it is important to note that prenyl couplings occur with >99% α-attack, which is completely opposite to what is expected in Lewis acid promoted couplings with electrophiles.[14] Crotyl cuprates, which give quite efficient displacements under these conditions, unfortunately appear to react both regio- and stereorandomly, as 2-3:1 mixtures of *Z*:*E* products result, along with ca. 1-2:1 ratios of α:γ attack.

In summary, an extremely facile route to 1,4-dienes has been uncovered utilizing allylic cyanocuprate technology together with both relatively simple and complex vinyl triflate reaction partners.

Acknowledgment. Financial support provided by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the NSF (Grant CHE 87-03757) is gratefully acknowledged. We warmly express our gratitude to the 3M Company (St. Paul, MN) for a generous sample of trifluoromethanesulfonic acid.

Registry No. (*Z*)-$\mathrm{PhCH_2CH{=}C(CH_3)OTF}$, 123994-43-4; (*E*)-$\mathrm{PhCH_2CH{=}CH(OTF)}$, 123994-45-6; (*Z*)-$\mathrm{PhCH_2CH{=}CH(OTF)}$, 123994-46-7; $\mathrm{(CH_2{=}C(CH_3)CH_2)_2Cu(CN)Li_2}$, 122700-72-5; $\mathrm{[(CH_3)_2C{=}CHCH_2]_2Cu(CN)Li_2}$, 122700-73-6; $\mathrm{(CH_2{=}CHCH_2)_2Cu(CN)Li_2}$, 91328-60-8; $\mathrm{(CH_3)_2C{=}CHCH_2Cu(Th)(CN)Li_2}$, 124020-71-9; (*E*)-$\mathrm{(CH_3CH{=}CHCH_2)_2Cu(CN)Li_2}$, 124020-72-0; (Th)Cu(CN)Li, 112426-02-5; 5,5-diphenyl-2-[[(trifluoromethyl)sulfonyl]oxy]-1,3-cyclohexadiene, 123994-44-5; methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-[[(trifluoromethyl)sulfonyl]oxy]-α-D-*erythro*-hex-2-enopyranoside, 123994-47-8; (*E*)-3-(1,3-dithian-2-yl)-1-phenyl-2-[[(trifluoromethyl)sulfonyl]oxy]-1-propene, 123994-48-9; ethyl 2-[[(trifluoromethyl)sulfonyl]oxy]-1-cyclopentanecarboxylate, 122539-74-6; diphenyl 7-(*tert*-butylcarbonylamino)-3-[[(trifluoromethyl)sulfonyl]oxy]-3-cepham-4-carboxylate, 123054-32-0; 1-[[(trifluoromethyl)sulfonyl]oxy]-3,4-dihydronaphthalene, 123994-49-0; ((*Z*)-3,5-dimethyl-2,5-hexadienyl)benzene, 123994-50-3; 5,5-diphenyl-2-(2-methylpropenyl)-1,3-cyclohexadiene, 123994-51-4; (*E*)-(6-methyl-2,5-heptadienyl)benzene, 123994-52-5; (*Z*)-(6-methyl-2,5-heptadienyl)benzene, 123994-53-6; methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-(2-propenyl)-α-D-*erythro*-hex-2-enopyranoside, 123994-54-7; (*E*)-2-[methyl(1,3-dithianyl)]-1,4-pentadienylbenzene, 123994-55-8; ethyl $\Delta^{1,2}$-2-(3-methyl-2-butenyl)cyclopentenecarboxylate, 123994-56-9; diphenyl 7-(*tert*-butylcarbonylamino)-3-(3-methyl-2-butenyl)-3-cepham-4-carboxylate, 123994-57-0; (*E*)-1-(2-butenyl)-3,4-dihydronaphthalene, 123994-58-1; (*Z*)-1-(2-butenyl)-3,4-dihydronaphthalene, 123994-59-2; 1-(1-methyl-2-propen-1-yl)-3,4-dihydronaphthalene, 57256-49-2; tributyl(3-methyl-2-butenyl)stannane, 53911-92-5; methyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside, 65530-27-0.

Supplementary Material Available: Experimental data and spectra for all products in Table I (14 pages). Ordering information is given on any current masthead page.

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[12] A representative procedure (Table I, entry 3) is as follows: To a −78 °C solution of 705 mg (1.87 mmol) of tributyl(3-methyl-2-butenyl)stannane[11] in 2.0 mL of anhydrous tetrahydrofuran (THF) was added 1.20 mL of methyllithium (1.55 M in diethyl ether, 1.86 mmol) via syringe. The resulting golden solution was stirred 15 min at −78 °C. Independently, a 10-mL two-necked flask was charged with 84 mg (0.93 mmol) of CuCN and 40 mg (0.93 mmol) of LiCl, gently flame-dried in vacuo, and then purged three times with Ar. Anhydrous THF (1.20 mL) was introduced via syringe, and the solubilized Cu(I) salt was cooled to −78 °C, whereupon, the solution of prenyllithium was immediately and rapidly charged into the two-necked flask via cannula, and the resulting pale yellow solution was stirred 10 min at −78 °C. The reagent was treated with 165 mg (0.62 mmol, as an 8:1 mixture of *E*:*Z* isomers, respectively) of 3-phenyl-1-(((trifluoromethyl)sulfonyl)oxy)propene dissolved in 0.5 mL of dry THF. A reddish color ensued and persisted for 15 min, at which time the reaction was quenched with 2 mL of 10% $\mathrm{NH_3}$/saturated $\mathrm{NH_4Cl}$ aqueous solution, diluted with 10 mL of hexanes, and allowed to warm to ambient temperature. Following ethereal extraction, the organic extract was washed with brine and dried over $\mathrm{Na_2SO_4}$. The volatiles were removed with a rotary evaporator and purification by flash chromatography (ICN Silica 32-63, 60A, eluting with petroleum ether boiling range 38–50 °C) afforded 91 mg (79%) of (6-methyl-2,5-heptadienyl)benzene as an 8:1 mixture of *E*:*Z* isomers.

[13] Attempts to effect this coupling with prenyltributylstannane under the influence of $\mathrm{Pd(PPh_3)_4/LiCl}$ in refluxing THF[6a,b] afforded ca. 10–20% yields of the desired material after 3 days. Considerable amounts of starting material were recovered (ca. 55%), with only trace quantities of the β-chloro enoate being detected by capillary GC analyses (comparison with an authentic sample).

[14] See, for examples: Yamamoto, Y.; Maruyama, K.; Matsumoto, K. *J. Chem. Soc., Chem. Commun.* **1984**, 548. Trost, B. M.; Keinan, E. *Tetrahedron Lett.* **1980**, *21*, 2595.

An Efficient Screen for Determining Solid-State Hydrogen-Bonding Patterns in Carboxylic Acids

Peggy A. Vanderhoff, Roger A. Lalancette,* and Hugh W. Thompson

Carl A. Olson Memorial Laboratories, Department of Chemistry, Rutgers University, Newark, New Jersey 07102

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Summary: Simple crystalline keto carboxylic acids adopt hydrogen-bonding modes that are either intra- or intermolecular, with the latter, far larger, class including carboxyl dimers and carboxyl-to-ketone catemers; it is demonstrated that symmetry-based differences between solid-state infrared and Raman spectra may be reliably used to differentiate those with dimeric H-bonding from those with noncentrosymmetric H-bonding patterns.

With few exceptions, simple carboxylic acids in their pure condensed phases exist as mutually hydrogen-bonded pairs.[1] However, when other functional groups capable

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[1] Leiserowitz, L. *Acta Crystallogr.* **1976**, *B32*, 775–802.

0022-3263/90/1955-1696\$02.50/0

Table I. Solid-State (KBr) Infrared and Raman Carbonyl Stretching Frequencies for Dimerically vs Catemerically Hydrogen-Bonded Keto Carboxylic Acids

compound	infrared (cm^{-1}) acid	infrared (cm^{-1}) ketone	Raman (cm^{-1}) acid	Raman (cm^{-1}) ketone	Δ (cm^{-1}) for acid
Dimeric Keto Acids					
(±)-9-oxobicyclo[3.3.1]nonane-1-carboxylic acid[a]	1692	1721	1651	1722	41
(±)-2-benzoylbenzoic acid[b]	1690	1676	1624	1672	66
(±)-2-benzoylbenzoic acid·H_2O[b]	1684	1663	1654	1667	30
(+)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptane-1-carboxylic acid[a]	1692	1750	1641	1749	51
(±)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptane-1-carboxylic acid[a]	1696	1750	1650	1744	46
(±)-3-benzoylpropionic acid[a]	1709	1684	1627	1679	82
(±)-6-oxobicyclo[2.2.1]heptane-*endo*-2-carboxylic acid[a,c]	1703	1747	1662	1749	41
Catemeric Keto Acids					
(±)-*cis*-3-acetyl-2,2-dimethylcyclobutaneacetic acid[d]	1733	1683	1732	1684	1
(±)-10-carboxy-Δ^1-octal-2-one[a,e]	1723	1637	1720	1630	3
(+)-4,7,7-trimethyl-3-oxobicyclo[2.2.1]heptane-*endo*-2-carboxylic acid[f]	1757, 1733	1709	1758, 1732	1704	1
(±)-4,7,7-trimethyl-3-oxobicyclo[2.2.1]heptane-*endo*-2-carboxylic acid[f]	1760, 1737	1710	1763, 1727	1704	10

[a] Reference 5. [b] Reference 9. [c] Reference 8. [d] Reference 3j. [e] Reference 10. [f] Reference 3k.

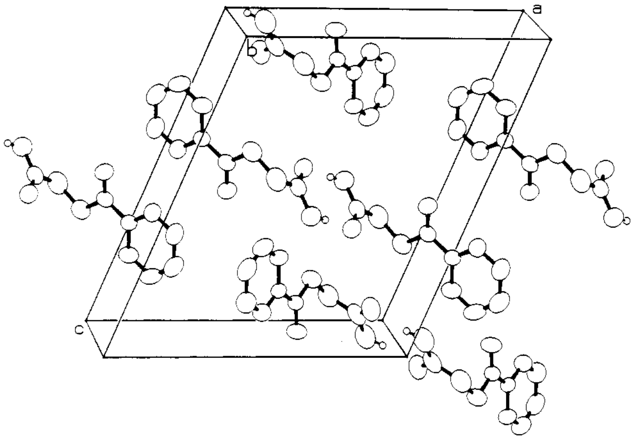

Figure 1. Partial packing diagram for (±)-3-benzoylpropionic acid (Table I), with molecules of opposite conformational chirality forming centrosymmetric hydrogen-bonded carboxyl dimers of two types, centered on cell edges (shown at lower right with an extracellular molecule) and on faces. Dimer centered on the front face has a translational companion, omitted for clarity, centered on the rear face.

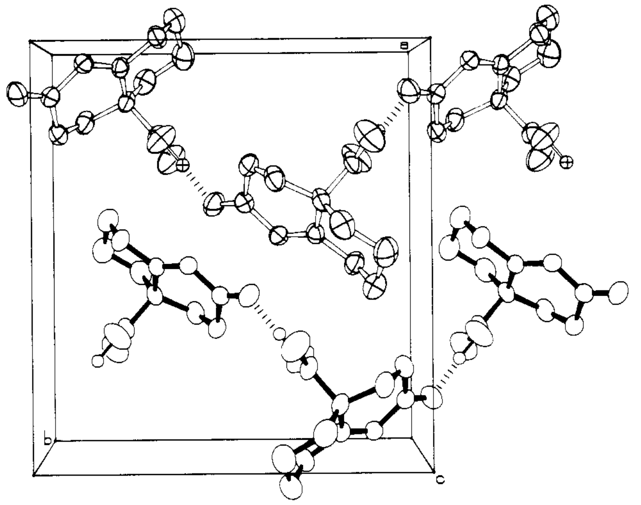

Figure 2. View of (±)-10-carboxy-Δ^1-octal-2-one (Table I) showing the helices generated by catemeric carboxyl-to-ketone hydrogen bonding along a screw axis. Each helix contains molecules of only one chirality, indicated by differential shading of the bonds and atoms.

of participating in hydrogen bonding are present within the same molecule, formation of rings or chains may compete with dimeric pairing.[1,2]

Keto carboxylic acids have received little attention in this regard but are known from published X-ray studies to exist in at least three associational forms in the crystalline state. By far the most common is carboxylic acid pairing that leaves the ketone uninvolved; however a number of instances are now known of chains formed by intermolecular acid-to-ketone hydrogen bonding.[3] Figures 1 and 2 show representative examples of these two hydrogen-bonding patterns. In addition, a few cases have been reported of intramolecular hydrogen bonding in simple crystalline keto acids.[4]

In pursuing less common solid-state H-bonding patterns in keto carboxylic acids, we have determined the associational behavior of several such compounds by single-crystal X-ray analysis.[3j,k,5] However this method suffers from several weaknesses. It sometimes fails due to inability to obtain usable crystals and is, in any event, somewhat complex and time-consuming. Moreover, without screening of some sort, it was quite inefficient for our purpose, as the great majority of keto acids adopt the carboxyl-dimer H-bonding pattern.

As a diagnostic of H-bonding mode we considered solid-state infrared spectroscopy; besides other less consistent changes,[3f,5a] hydrogen bonding produces frequency shifts in the carbonyl stretching vibrations of both ketones and carboxylic acids.[2,6] These shifts are tantalizing as determinants of solid-state hydrogen bonding; however their use is likewise not ideal, in part because they are similar

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[2] For leading references, see: March, J. *Advanced Organic Chemistry*, 2nd ed.; Wiley: New York, 1985; pp 71–74.

[3] (a) Amagaya, S.; Takai, M.; Ogihara, Y.; Iitaka, Y. *Acta Crystallogr.* **1977**, *B33*, 261–263. (b) Precigoux, G.; Busetta, B.; Hospital, M. *Ibid.* **1977**, *B33*, 563–565, 566–568. Lalancette, R. A.; Slifer, P. B.; Thompson, H. W. *Ibid.* **1989**, *B45*, 596–597. (c) Chadwick, D. J.; Dunitz, J. D. *J. Chem. Soc., Perkin Trans. 2* **1979**, 276–284. (d) Fortier, S.; DeTitta, G. T.; Fronckowiak, M.; Smith, G. D.; Hauptman, H. A. *Acta Crystallogr.* **1979**, *B35*, 2062–2066. (e) Carpy, A.; Goursolle, M.; Leger, J. M. *Ibid.* **1980**, *B36*, 1706–1708. (f) Jefferies, P. R.; Payne, T. G.; Ralston, C. L.; White, A. H. *Aust. J. Chem.* **1981**, *34*, 1001–1007. (g) Bertolasi, V.; Ferretti, V.; Gilli, G. *Cryst. Struct. Commun.* **1982**, *11*, 1459–1465. (h) Peeters, O. M.; Blaton, N. M.; De Ranter, C. J. *Bull. Soc. Chim. Belg.* **1983**, *92*, 191–192. (i) Preut, H.; Kreiser, W.; Mueller, T.; Jones, P. G. *Acta Crystallogr.* **1985**, *C41*, 1480–1482. (j) Vanderhoff, P. A.; Thompson, H. W.; Lalancette, R. A. *Ibid.* **1986**, *C42*, 1766–1769. (k) Lalancette, R. A.; Vanderhoff, P. A.; Thompson, H. W. *Ibid.* Submitted for publication.

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[5] (a) Vanderhoff, P. A. M. S. Thesis, Rutgers University, Newark, 1985. (b) Vanderhoff, P. A. Ph.D. Dissertation, Rutgers University, Newark, 1988.

[6] Avram, M.; Mateescu, G. D. *Infrared Spectroscopy*; Wiley: New York, 1972; pp 377–379, 388–393, 412–413.

in magnitude to shifts produced by other factors that may be present, such as conjugation and strain. In addition, there are always at least two carbonyl bands present, and a shift must be defined relative to some standard, whose selection may present difficulties. Solid-state vs solution IR spectra of such compounds often differ in the carbonyl region, but using those differences diagnostically is problematic because a variety of complications arise and the H-bonding patterns in solution can frequently only be guessed at.[6,7]

The most common H-bonding pattern for simple keto acids, acid pairing, involves an eight-membered dimeric ring structure, which permits strong coupling of the stretching vibrations for the two acid carbonyls. Because of the local centrosymmetry, the symmetric stretching mode produces no change in dipole moment and is IR-inactive but does create changes in polarizability and is Raman-active. The reverse is true for the unsymmetrical stretch, with an appreciable energy difference anticipated between the two coupled modes. Because no other observed pattern of hydrogen bonding in keto acids presents this combination of symmetry and strong vibrational coupling, we anticipated that the coordinated use of infrared and Raman spectroscopies might specify unambiguously the presence or absence of paired-carboxyl hydrogen bonding and thus serve as a screen for alternative H-bonding patterns.

We have tested this prediction with the eleven keto acids shown in Table I, whose single-crystal X-ray structures are also available.[3j,k,5,8a] The carbonyl vibrational modes for arrangements of low symmetry are active in both the IR and Raman spectra, at nearly identical frequencies. Only the carboxyl dimers exhibit IR and Raman bands at appreciably different frequencies, the average difference between the asymmetric and symmetric stretching modes being ca. 50 cm^{-1}.[9b]

This method appears ideal for efficient differentiation of solid-state carboxylic acids that are dimerically hydrogen-bonded from those with other H-bonding patterns.[11] It should be applicable not only to keto acids but to acids containing a variety of other additional H-bonding functions.

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(7) (a) Valtes, R. E.; Flitsch, W. *Ring-Chain Tautomerism*; Plenum: New York, 1985; pp 19 ff. (b) Grande, K. D.; Rosenfeld, S. M. *J. Org. Chem.* **1980**, *45*, 1626-1628.

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(9) (a) Lalancette, R. A.; Vanderhoff, P. A.; Thompson, H. W. *Acta Crystallogr.* In press. (b) The 30 cm^{-1} value presumably reflects diminished vibrational coupling due to insertion of water; without this entry the average $\Delta\nu$ is 54.5 cm^{-1}.

(10) Thompson, H. W.; Shah, N. V. *J. Org. Chem.* **1983**, *48*, 1325-1328.

(11) For recent work on the use of solid-state NMR spectroscopy in determining H-bonding patterns, see: Etter, M. C.; Hoye, R. C.; Vojta, G. M. *Crystallogr. Rev.* **1988**, *1*, 281.

Stereoselective Osmylation of 1,1-Disubstituted Olefins: Effect of Allylic Substituents on Reaction Diastereoselectivity

David A. Evans* and Stephen W. Kaldor

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

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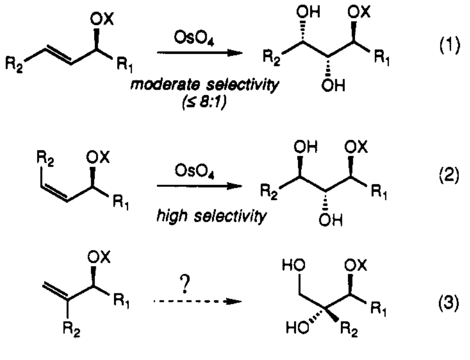
Summary: The osmylation of 1,1-disubstituted olefins possessing an allylic, oxygen-bearing stereocenter proceeds in a stereoregular fashion with high diastereoselectivity.

The reaction of osmium tetraoxide with 1,2-disubstituted olefins containing an allylic, oxygen-bearing stereocenter affords diols with a stereochemically predictable outcome (eqs 1-2).[1,2] A sufficient number of examples have now been studied to provide good precedent for projecting both the sense and degree of asymmetric induction in these reactions. On the other hand, documentation of the influence of structure on the stereoselective osmylation of 1,1-disubstituted allylic alcohol derivatives (eq 3) is limited to several cases which do not provide a sufficient body of information for confident extrapolation.



Scolastico has documented an example of a diastereoselective osmylation of an α,β-unsaturated ester which was found to afford one diastereomer (eq 4).[3] A highly stereoselective example was also described by Stork and Kahn for an *E* trisubstituted unsaturated ester as both the alcohol and the ethoxyethyl ether derivatives (eq 5).[4] In this study it was concluded that the electronic effect of the carbomethoxyl substituent in enhancing reaction diastereoselection was "considerable" based on the qualitative

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(1) Cha, J. K.; Christ, W. J.; Kishi, Y. *Tetrahedron Lett.* **1983**, *24*, 3943-3496 and 3947-3950; *Tetrahedron* **1984**, *40*, 2247-2255.

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