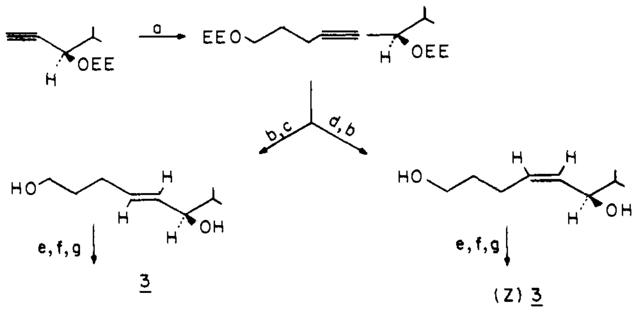
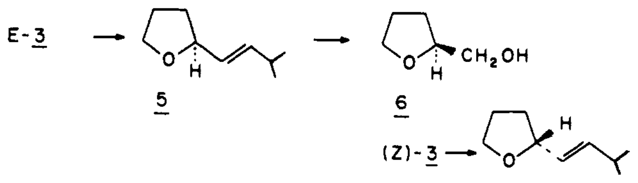
Scheme I[a,b]



[a] In the above formulas, EE = α-ethoyethyl. [b] Key: (a) 1 equiv of LiBu, 8:1 THF:HMPT, −78 °C; $Br(CH_2)_3OCH(CH_3)OC_2H_5$ (1 equiv), 2 days, room temperature (70%). (b) 2:1 acetic acid: water, THF; room temperature overnight. (c) Lithium aluminum hydride, NaOMe, THF; reflux 3 h. (d) 5% $Pd\text{-}BaSO_4$ (quinoline); methanol. (e) *tert*-Butyldimethylchlorosilane, 4-(dimethylamino)pyridine (0.1 equiv), triethylamine (1 equiv); methylene chloride overnight, room temperature (86%). (f) LiBu, 5:1 THF:HMPT, 2,6-dichlorobenzoyl chloride, 1 h, −78 °C → room temperature (83%). (g) $(Bu)_4N^+F^-$ (1.1 equiv); room temperature, 3 h (92%); $[\alpha]_D$ −28°, CH_2Cl_2).

point of concern is that alkoxide ions are hard nucleophiles, as are amino groups, and it is known that the latter can displace to some extent syn as well as anti to the transition metal in the allylic complex.[6] The result is loss of specificity in the transfer of asymmetry. Indeed, under the conditions we used (see below), palladium-mediated cyclization to pyrrolidines gave poor transfer (overall syn) of chirality.

We can report, however, that, at least with an (*E*)-allylic alcohol system such as **3**, Pd^0 gives very efficient chirality transfer: treatment of **3** with tetrakis(triphenylphosphine)palladium (0.05 equiv) in the presence of 2 equiv of triethylamine in acetonitrile solution[7] gave (30–45 min at 35–37 °C) a 95% yield of (*S*)-2-(3-methyl-1-(*E*)-butenyl)tetrahydrofuran (**5**), $[\alpha]_D$ −10.7° (*c* 2.79, CH_2Cl_2). The absolute stereochemistry and the optical purity were conveniently determined by conversion (ozone in methylene chloride, lithium aluminum hydride in ether) to the known tetrahydro-2-furylcarbinol (**6**), which had $[\alpha]_D$ +13.9° (*c* 0.88, nitromethane). The pure *S* compound has[8] $[\alpha]_D$ +17.6°. The optical purity of the carbinol derived via cyclization was thus ~80%, implying complete transfer of chirality in the overall syn sense (ester of an (*R*)-(*E*)-alkenylcarbinol leads to an (*S*)-2-tetrahydrofurfuryl carbinol).



The same sequence, starting with the alkenyl carbinol of the same *R* absolute configuration as (*E*)-**3** but with a *Z* double bond, should lead to a tetrahydrofuran of the opposite absolute stereochemistry, correlating now with the (*R*)-2-tetrahydrofurfuryl carbinol. We have verified that that is the case, although the transfer in chirality is slightly less efficient (90–95%) with the *Z* starting material. It is not unlikely that a small amount of isomerization of the π-allyl intermediate from *Z* to *E* is responsible for the slight loss of efficiency.

It should be noted that the clean transfer of chirality from alkenylcarbinol to tetrahydrofuran is not simply the result of an overall syn process in the palladium-catalyzed reaction, since an overall syn process leading to a cis double bond in the product would have resulted in the generation of the opposite chirality at the 2-position of the tetrahydrofuran ring. The efficient chirality transfer we observed is thus a consequence not only of a syn displacement process but also of the fact that the transition state involving the formation of a trans-alkenyl substituent at the 2-position of the incipient tetrahydrofuran is decisively favored.

We outline in Scheme I the synthesis of the *Z*-olefinic glycol **3** and of its *E* isomer, starting with the readily available[9] (*R*)-4-methyl-1-pentyn-3-ol.

Since ethynyl carbinols of known absolute stereochemistry are readily obtainable, we believe that the efficient transfer of chirality we have demonstrated should prove a very efficient general route to either *R* and *S* 2-substituted tetrahydrofurans.

Acknowledgment. We thank the National Science Foundation for partial support of this work and also NATO and the French Ministère des Affaires Etrangères for Fellowship support to J.M.P.

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(6) (a) Trost, B. M.; Keinan, E. *J. Org. Chem.* **1979**, *44*, 3451. (b) In an earlier paper the same authors point out (*J. Am. Chem. Soc.* **1978**, *100*, 7779) that a polymer-bound palladium catalyst can overcome the poor stereocontrol observed with amines and the homogeneous catalysts. This approach may or may not be a general one (cf. ref 6a).

(7) For the use of this particular Pd^0 catalyst and solvent system, cf.: Trost, B.; Genet, J. P. *J. Am. Chem. Soc.* **1976**, *98*, 8516.

(8) Hartman, F. C.; Barker, R. *J. Org. Chem.* **1964**, *29*, 873. Gagnaire, D.; Butt, A. *Bull. Soc. Chim. Fr.* **1961**, 312.

(9) Vigneron, J. P.; Bloy, V. *Tetrahedron Lett.* **1979**, *20*, 2683.

Additions and Corrections

Tetraphenylarsonium 1,2,3,4,5-Pentakis(methylmercapto)cyclopentadienide [*J. Am. Chem. Soc.* **1981**, *103*, 5885]. F. WUDL,* D. NALEWAJEK, F. J. ROTELLA, and E. GEBERT.

Page 5888, Table III, first column: The C13–C14 bond length should be 1.40 (1) Å; all other entries in the table are correct.

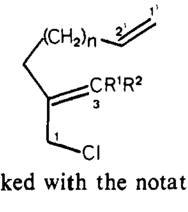
An Electron-Diffraction Investigation of the Molecular Structure of Gaseous 2,3-Butanedione (Biacetyl) at 228 and 525 °C [*J. Am. Chem. Soc.* **1979**, *101*, 3730]. DONALD D. DANIELSON and KENNETH HEDBERG.*

Page 3730, abstract, line 6: The parameter $r(C\text{–}C)_{conj} - r(C\text{–}C)_{Me}$ should have the subscripts interchanged to read $r(C\text{–}C)_{Me} - r(C\text{–}C)_{conj}$.

Intramolecular Type II "Metallo-Ene" Reactions of (2-Alkenylallyl)magnesium Chlorides: Regio- and Stereochemical Studies [*J. Am. Chem. Soc.* **1982**, *104*, 6476–6477]. WOLFGANG OPPOLZER,* RITA PITTELOUD, and HEINRICH F. STRAUSS.

Page 6476, Table I, entry a: The temperature should be corrected to 130 °C.

Page 6476, eq 2: The formula



in eq 2 should be marked with the notation **1**.