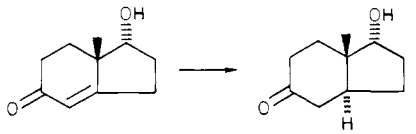
= α-hydroxyl) the result of heterogeneous hydrogenation (5% palladium on charcoal) was still the almost exclusive formation of the *cis*-indanone **2**, R = α-hydroxyl.

We are pleased to report, however, that the homogeneous iridium reduction in methylene chloride now gave very largely the *trans*-indanone **4** (ratio of trans to cis ~96:4).[7] This rather



3 4

dramatic result of stereochemical control by an appositely placed hydroxyl led us to examine a considerable number of other unsaturated alcohol systems. The results are shown in Table I.

It is apparent that cyclohexenols with allylic or homoallylic double bonds are reduced with high selectivity (~97:3) for secondary alcohols and more than 99:1 for the tertiary analogues. It is interesting that the primary cyclohexenylcarbinols give only fair (entries 2 and 3) or no selectivity (entry 1). Whether this results from less favorable equilibria with unsaturated primary alcohols, or from a certain ambiguity regarding the preferred stereochemistry of these particular hydroxy olefin complexes, or yet some other cause, is at present unknown.

It is worth noting that all these reductions are catalytic and usually proceed rapidly and in high yield. The previously mentioned deactivation of the catalyst by alcohols[6] could easily have led to the conclusion that any successful hydrogenation of an olefinic alcohol would be noncatalytic, but it is clear that rapid ligand equilibration on the catalyst must take place between the initially formed saturated alcohol and its unsaturated precursor.

In all the above cases, essentially no stereoselectivity was observed under heterogeneous conditions, with 5% palladium on charcoal. Similarly, and in keeping with the directing influence of the hydroxyl group, the acetates that were examined (from entries 1 through 6) gave essentially no selectivity under the homogeneous iridium conditions.

It is too early to tell the range of reactions of olefins that might be controlled, stereochemistry and regiochemically, by the coordination of homogeneous transition-metal catalysts with hydroxyls or other ligating functions. It is already clear, however, that hydroxyl-directed hydrogenation is a reaction of considerable generality.

Acknowledgment. We thank the National Institutes of Health and the National Science Foundation for their support of this work.

Registry No. 3, 84367-54-4; *trans*-**4**, 84367-55-5; *cis*-**4**, 84367-56-6; $[Ir(cod)Py(PCy_3)]PF_6$, 64536-78-3; 2-methylenecyclohexylmethanol, 78426-32-1; 3-methylcyclohex-2-en-1-ylmethanol, 80729-05-1; 1,3-dimethylcyclohex-2-en-1-ylmethanol, 84281-25-4; 3-methylcyclohex-2-en-1-ol, 21378-21-2; 4-methylcyclohex-3-en-1-ol, 51422-70-9; 3-methylcyclohex-3-en-1-ol, 53783-91-8; 1,3-dimethylcyclohex-2-en-1-ol, 29481-98-9; 1,4-dimethylcyclohex-3-en-1-ol, 70837-28-4; 1,3-dimethylcyclohex-3-en-1-ol, 71933-07-8; *trans*-2-methylcyclohexylmethanol, 3937-46-0; *cis*-2-methylcyclohexylmethanol, 3937-45-9; *trans*-3-methylcyclohexylmethanol, 84281-26-5; *cis*-3-methylcyclohexylmethanol, 24453-33-6; *trans*-1,3-dimethylcyclohexylmethanol, 84281-27-6; *cis*-1,3-dimethylcyclohexylmethanol, 84281-28-7; *trans*-3-methylcyclohexanol, 7443-55-2; *cis*-3-methylcyclohexanol, 5454-79-5; *trans*-4-methylcyclohexanol, 7731-29-5; *cis*-4-methylcyclohexanol, 7731-28-4; *trans*-1,4-dimethylcyclohexanol, 16980-60-2; *cis*-1,4-dimethylcyclohexanol, 16980-61-3; *trans*-1,3-dimethylcyclohexanol, 15466-93-0; *cis*-1,3-dimethylcyclohexanol, 15466-94-1.

(10) The stereochemistry was established by comparison (NMR, GC) with authentic substances made by hydride reduction of the related ketones: Brown, H. C.; Krishnamurthy, S. *J. Am. Chem. Soc.* **1972**, *94*, 7159. Dauben, W. G.; Fonken, G. J.; Noyce, D. S. *Ibid.* **1956**, *78*, 2579.

(11) The stereochemistry was established by use of the ^1H and ^{13}C NMR data reported in the following: Grenier-Coustalot, M. F.; Zahidi, A.; Bonastre, J.; Grenier, P. *Bull. Soc. Chim. Fr.* **1979**, 229. Rei, M.-H. *J. Org. Chem.* **1979**, *44*, 2760.

2-Substituted Tetrahydrofurans of Known Absolute Stereochemistry by S_cN' Chirality Transfer

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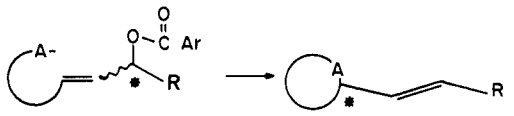
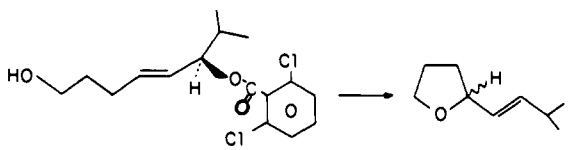
To the extent that it leads to a predictable stereochemical result, the SN_2-like cyclization of esters of optically active allylic alcohols (**1** → **2**) holds considerable interest since such a process results



1 2

in the transfer of the carbon–oxygen chirality to that of a carbon atom of the newly formed ring. We have previously shown that when A in **1** above is either a sulfur[1] or a carbon atom,[2] the S_cN' reaction takes place with a high degree of concertedness to give entry of the A group anti to the departing ester, thus leading to tetrahydrothiophene and cyclopentane systems of known absolute stereochemistry.

The poor nucleophilic properties of an alkoxide ion did not augur well for the possibility of extending the process to the synthesis of optically active tetrahydrofurans or pyrrolidines (cf. **1**, A = O or N). The problem, of course, is that hard anions like alkoxide ions are not very suitable for the S_cN' reaction involving departing benzoates. In fact, clean cyclization to the 2-alkenylfuran **4** could



E-3 4

be achieved by starting with the 2,6-dichlorobenzoate of the (*R*)-*trans*-diol **3** (80% optical purity; for preparation, see below) in the polar solvent 2,2,2-trifluoroethanol (2 h reflux with 2.2 equiv of potassium *tert*-butoxide; 69% yield), but under these conditions the product (**4**) was almost entirely racemized.[3]

This type of cyclization also did not prove useful as a route to chiral pyrrolidines. When in **3** above the cyclizing hydroxyl was replaced by a methylamino group, cyclization in refluxing trifluoroethanol, in the presence of triethylamine, gave very considerable racemization. It is worthy of note, however, that to the very small extent that chirality was transferred, the same anti relationship of the entering and departing groups was found that we had previously demonstrated for thio and carbon anions.

The difficulty attending simple base-catalyzed formation of a tetrahydrofuran ring led us to consider the applicability of the Pd-assisted SN′ reaction.[4] In considering this possibility, we were conscious of two problems. Intermolecular alkylations to form ethers have been shown to be quite efficient with aryl ethers of allylic alcohols[5] but are often poor with their esters. A second

(1) Stork, G.; Kreft, A. F. *J. Am. Chem. Soc.* **1977**, *99*, 3851.
(2) Stork, G.; Schoofs, A. R. *J. Am. Chem. Soc.* **1979**, *101*, 5081.
(3) All compounds were purified by "flash" chromatography on silica, generally with a pentane–ether elution. Satisfactory spectral data were obtained for all compounds.
(4) For a recent review, see: Trost, B. *Acc. Chem. Res.* **1980**, *13*, 385. The pioneering work of Trost in establishing the stereochemistry of palladium-mediated displacement by carbanions in allylic systems is reviewed in that reference. See also: Trost, B.; Runge, T. A. *J. Am. Chem. Soc.* **1981**, *103*, 7559.
(5) The formation of ethers by palladium-assisted intermolecular displacement, starting with allylic alcohol derivatives, was first demonstrated by Hata et al.: Hata, G.; Takahashi, K.; Miyake, A. *J. Chem. Soc., Chem. Commun.* **1970**, 1392. Cf.: Takahashi, K.; Miyake, A.; Hata, G. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 230. A referee has brought to our attention an unpublished paper reporting the formation, with fair to good stereoselectivity, of spirotetrahydrofurans by palladium-catalyzed S_cN' processes (Stanton, S. A.; Felman, S. W.; Parkhurst, C. S.; Godleski, S. A. *J. Am. Chem. Soc.*, in press.

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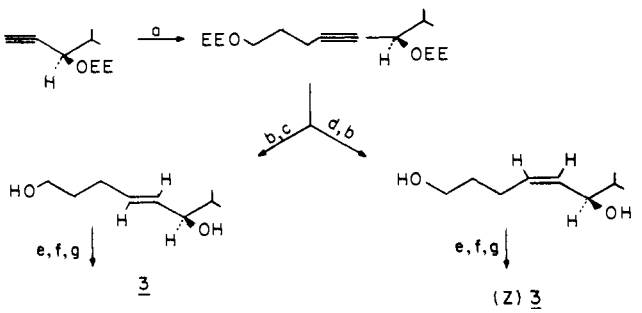
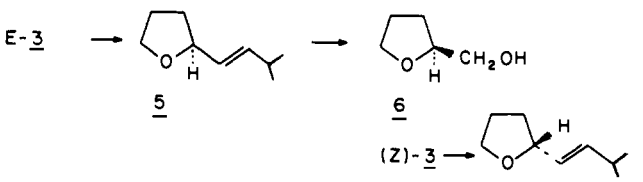
Scheme I[a,b]



[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–$BaSO_4$ (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.

(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.

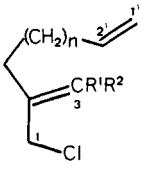
An Electron-Diffraction Investigation of the Molecular Structure of Gaseous 2,3-Butanedione (Biacetyl) at 228 and 525 °C [*J. Am. Chem. Soc.* **1979**, *101*, 3730]. DONALD D. DANIELSON and KENNETH HEDBERG.*

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

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**.