P^F, microwave transitions must occur between these mixed states and T_{+1} and T_{-1}. This requires that a substantial H_1 field be present during the lifetime of P^F. In Figure 2 magnetic resonance spectra of P^F are presented. The signal 200 ns after the laser pulse results from monitoring the ^3P population, which increases upon application of 1-kW microwaves at resonance. However, 5 ns after the laser pulse we directly observe the resonance signal of P^F. This signal shows that the P^F population decreases upon application of resonant microwaves. Since resonant microwaves increase the amount of $^3[P^+I^-]$ at the expense of $^1[P^+I^-]$, the observed decrease in P^F yield (the sum of $^1[P^+I^-]$ and $^3[P^+I^-]$ concentrations) at resonance shows that the decay rate of $^1[P^+I^-]$ to ground state, k_S, is significantly slower than that of $^3[P^+I^-]$, k_T, to ^3P. If $k_S > k_T$, then the P^F yield would increase at resonance. Moreover, if $k_S = k_T$, no P^F resonance would appear. It is important to note that the resonance observed by monitoring ^3P 200 ns after the laser flash would appear regardless of whether $k_S > k_T$, $k_T > k_S$, or $k_S = k_T$. Appearance of this signal only requires that resonant microwaves increase the amount of $^3[P^+I^-]$ leading to ^3P.

Earlier experiments concerning magnetic field effects alone have concluded that k_S is probably smaller than k_T.[3,7] In addition, several quantum mechanical models of magnetic field effects on the yield of ^3P have examined a wide variety of k_S and k_T values and have generally supported the notion that $k_S < k_T$.[8] Within the constraints of the radical pair model our data demonstrate directly that $k_S < k_T$. In conclusion, the ability both to monitor and to control the dynamics of radical pair populations directly should prove very useful in determining structure and mechanism in electron-transfer reactions especially in important biological systems such as photosynthesis.

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Asymmetric Synthesis via Acetal Templates. 4. Reactions with Silylacetylenic Compounds. Formation of Chiral Propargylic Alcohols

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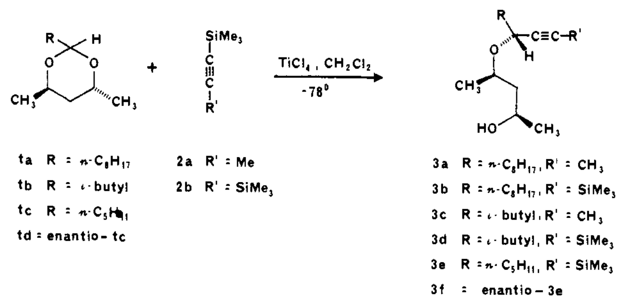
Recently we disclosed[1] the titanium tetrachloride catalyzed coupling of some chiral acetals, e.g., **1a**, with allyltrimethylsilane.[2] The products were formed diastereoselectively, and removal of the chiral auxiliary afforded optically active homoallylic alcohols, ee 65–74%. The coupling results (diastereomeric ratios up to 88:12) are at least qualitatively consistent with the Bartlett model[1] for the transition state of a related, but more selective (ratio 92:8), intramolecular reaction.[3]

As part of a program aimed at exploring the acetal reaction with various nucleophiles, we now report on the coupling with (trimethylsilyl)acetylenic compounds.[4] From these experiments a methodology has emerged for the highly enantioselective production of secondary propargylic alcohols. In addition, this study promised to shed some light on whether the diastereoselectivity of the process is enhanced by the presence of a substituent (the trimethylsilyl group, in the present instance) located at the reacting site of the nucleophilic partner.[5]

Scheme I

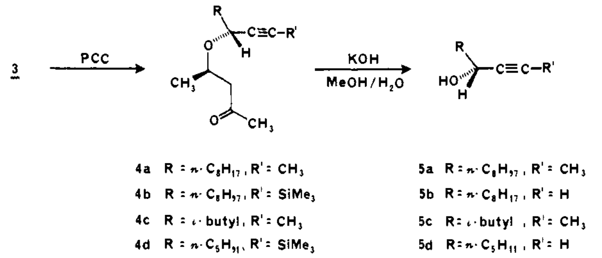


1a R = n-C_8H_{17}
1b R = i-butyl
1c R = n-C_5H_{11}
1d = enantio-1c

2a R' = Me
2b R' = $SiMe_3$

3a R = n-C_8H_{17}, R' = CH_3
3b R = n-C_8H_{17}, R' = $SiMe_3$
3c R = i-butyl, R' = CH_3
3d R = i-butyl, R' = $SiMe_3$
3e R = n-C_5H_{11}, R' = $SiMe_3$
3f = enantio-3e

Scheme II



4a R = n-C_8H_{17}, R' = CH_3
4b R = n-C_8H_{17}, R' = $SiMe_3$
4c R = i-butyl, R' = CH_3
4d R = n-C_5H_{11}, R' = $SiMe_3$
4e = enantio-4d

5a R = n-C_8H_{17}, R' = CH_3
5b R = n-C_8H_{17}, R' = H
5c R = i-butyl, R' = CH_3
5d R = n-C_5H_{11}, R' = H
5e = enantio-5d

Table I. Results of the Transformation Shown in Scheme I

	1			3[8b,9]		
entry	acetal[7,8b,9]	% yield	2, silylacetylene	coupled product	% yield	diastereomeric ratio[10]
1	1a	96	2a	3a	81	93:7
2	1a	96	2b	3b	98	96.5:3.5
3	1b	91	2a	3c	94	86:14
4	1b	91	2b	3d	85	94:6
5	1c	95	2b	3e	91	96.5:3.5
6	1d	96	2b	3f	90	96:4

Table II. Results of the Transformation Shown in Scheme II

		4[8a,9]		5[8b,9a]			
entry	3, coupled product	ketone	% yield	propargylic alcohol	% yield	$[\alpha]^{23}_D$ (c, solvent), deg	% ee[11]
1	3a	4a	99	5a	95[9b]	+8.6 (1.0, CCl_4)	87
2	3b	4b	97	5b	92	+14.3 (1.0, Et_2O)	90
3	3c	4c	93	5c	90	+10.2 (4.9, $CHCl_3$)	70
4	3e	4d	97	5d	88	+19.3 (1.0, Et_2O)	90
5	3f	4e	98	5e	91	−20.3 (1.0, Et_2O)	92

The couplings of the acetal **1** with the silylacetylenes **2**[6] to give **3** (Scheme I, Table I) were performed as described for the reactions with allyltrimethylsilane,[1] except that with the (trimethylsilyl)propyne (**2a**) reactions (Table I, entries 1 and 3) a

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(1) Paper 3: Bartlett, P. A.; Johnson, W. S.; Elliott, J. D. *J. Am. Chem. Soc.*, in press.

(2) The first example of this type of condensation was reported by McNamara andKishi: McNamara, J. M.; Kishi, Y. *J. Am. Chem. Soc.* **1982**, *104*, 7371–7372.

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(4) Lewis acid catalyzed acylations and alkylations of silylacetylenes are well-known. See inter alia: Fleming, I. "Comprehensive Organic Chemistry", Barton, D. H. R., Ollis, W. D., Eds.; Pergamon Press: Oxford, 1979; Vol. 3, p 613. Birkofer, L.; Ritter, A.; Uhlenbrauck, H. *Chem. Ber.* **1963**, *96*, 3280–3288.

(5) Such a substituent was originally suggested as being responsible for the asymmetric induction observed on cyclization of the (2*R*,3*R*)-butanediol acetal of 5,9-dimethyldeca-(5*E*)-9-dienal, the proposed effect being due to nonbonded interactions between the C-7 group and one of the chiral centers.[3]

(6) Available from Aldrich Chemical Co.

(7) Prepared by the conditions described in ref 1.

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larger excess (2.5 mol equiv) of titanium tetrachloride was used in order to minimize formation of an as yet unidentified nonpolar byproduct. The conversions of the coupled products **3**, via **4**, into the propargylic alcohols **5** (Scheme II, Table II) were also performed by the previously described procedures.[1] In the case of ketones **4b**, **4d**, and **4e** the base treatment to effect β-elimination resulted in concomitant desilylation giving **5b**, **5d**, and **5e**, respectively.

It is particularly noteworthy that the diastereomeric forms of the coupled products **3** were readily separated by rapid low-pressure column chromatography,[8b] thus providing a route to propargylic alcohols **5** of 100% optical purity.

The constitution of the propargylic alcohols **5**, which can be presumed to have the *R* configuration on the basis of previous precendents,[1,3] was confirmed as follows. The optical rotation of alcohol **5b** (Table II, entry 2) is in close agreement with the $[\alpha]_D^{23}$ +14.8° reported for a specimen of (*R*)-(+)-**5b** of approximately 90% optical purity, obtained by classical resolution of racemic material.[12] It is noteworthy that **5b**, which is available optically pure by our method (see above), is an intermediate in the synthesis of methyl (*E*)-2,4,5-tetradecatrienoate, a pheromone of the male dried bean beetle.[12]

The rotation of alcohol **5c** (Table II, entry 3), which has been used for the synthesis of (2*R*,4′*R*,8′*R*)-α-tocopherol,[13] is in excellent agreement with that calculated[13] for a sample of 70% ee, namely $[\alpha]_D^{23}$ +10.15° (*c* 4.9, $CHCl_3$).

The rotations of alcohols **5d** and **5e** (Table II) entries 4 and 5 are in good agreement with those reported[14] for the respective *R* and *S* antipodes, which have been used as intermediates in the synthesis of the ω side chain of prostaglandins (15*R*)- and (15*S*)-PGB_1.[15]

The results presented here indicate that the Lewis acid catalyzed reaction of chiral acetals **1a**–**1e** with silylacetylenes **2a** and **2b** is considerably more diastereoselective than the corresponding reaction with allyltrimethylsilane.[1] Considering that (a) chiral acetals of type **1** are readily available in both enantiomeric forms[16] and (b) removal of the chiral auxiliary in the coupled products **2** is highly efficient, the methodology disclosed here represents an extremely attractive alternative to existing asymmetric syntheses of secondary propargylic alcohols.[17] Numerous examples may be cited that attest to the synthetic versatility of these compounds. In particular alkylation of hydroxyl-protected chiral secondary propargylic alcohols possessing a terminal acetylenic function, i.e., **5** (R = alkyl, R′ = H) has been shown to proceed without noticeable racemization.[18] Equally noteworthy is that compounds of type **5** (R = R′ = alkyl), in which the acetylenic function is nonterminal, are progenitors of the corresponding *E*[13,19] and *Z*[13,20] allylic alcohols, as well as of optically active allenes.[21]

Acknowledgment. We are indebted to the National Institutes of Health and the National Science Foundation for support of this research. We also express our appreciation to Professor P. A. Bartlett for helpful discussions and to Dr. A. Tai of the Institute of Protein Research, Osaka University, for the gift of generous samples of (2*R*,4*R*)- and of (2*S*,4*S*)-pentanediol.

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(8) (a) The crude product was homogeneous with respect to GC and TLC. (b) The product was purified by low-pressure column chromatography using Merck silica gel 60 H for thin-layer chromatography.

(9) (a) The ^1H NMR, IR, and mass spectra were consistent with the assigned structure. (b) A satisfactory combustion analysis was obtained for an appropriately purified specimen of this compound.

(10) The diastereomeric ratio was determined by GC on a 12-m SE-54 capillary column, which showed a base-line separation of the two peaks.

(11) Determined by GC analysis (base-line separation) of (*R*)-(+)-MTPA esters. See: Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543–2549.

(12) Mori, K.; Nukada, T.; Ebata, T. *Tetrahedron* **1981**, *37*, 1343–1347.

(13) Lit. $[\alpha]_D^{25}$ +13.48° (*c* 4.9, $CHCl_3$), optical purity 93% by MTPA-ester method.[11] See: Chan, K. K.; Cohen, N.; De Noble, J. P.; Specian, A. C., Jr.; Saucy, G. *J. Org. Chem.* **1976**, *41*, 3497–3505.

(14) Lit. $[\alpha]_D^{25}$ +19.8°, optical purity 100% by MTPA-ester method.[11] See: Fried, J.; Lin, C.; Mehra, M.; Kao, W.; Dalven, P. *Ann. N.Y. Acad. Sci.* **1971**, *180*, 38–63.

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(16) Ito, K.; Harada, T.; Tai, A. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3367–3368.

(17) See inter alia: Mukaiyama, T.; Suzuki, K.; Soai, K.; Sato, T. *Chem. Lett.* **1979**, 447–448. Midland, M. M.; Kazubski, A. *J. Org. Chem.* **1982**, *47*, 2495–2496; 2814–2816.

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(19) See inter alia: Djerassi, C.; Grant, B. *J. Org. Chem.* **1974**, *39*, 968–970. Johnson, W. S.; Escher, S.; Metcalf, B. W. *J. Am. Chem. Soc.* **1976**, *98*, 1039–1041.

(20) See inter alia: Gutmann, H.; Lindlar, H. "Chemistry of Acetylenes", Viehe, H. G., Ed.; Marcel Dekker: New York, 1969; p 360.

(21) For an example see ref 13.

μ-(η^5:η^5-Cyclooctatetraene)bis[(η^5-cyclopentadienyl)vanadium]: Preparation, Structure, and ESR Characterization of Its Radical Anion

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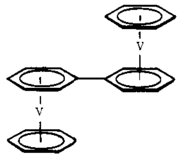
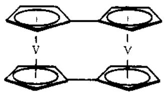
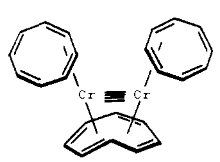
Electron spin–spin interaction in dinuclear complexes of vanadium, which may be looked at as built from paramagnetic units, ranges from slight—μ(η^6:η^6-biphenyl)bis[(η^6-benzene)vanadium], I, is a diradical with a triplet ground state[1]—to extensive—bis(fulvalene)divanadium, II, is diamagnetic.[2] However, very few molecules have been synthesized and characterized structurally, in which genuine vanadium–vanadium bonds pertain.[3] This is in stark contrast to the coordination chemistry of chromium, where species with multiple metal–metal bonds are legion.[4] As an example, the complex μ-(η^5:η^5-cyclooctatetraene)bis[(η^4-cyclooctatetraene)chromium],[5] III, may be cited. The short metal–metal distance, *d*(Cr–Cr) = 221.4 pm, in this species was rationalized in terms of a quadruple Cr–Cr bond, which leads to 18 valence electron shells for the chromium atoms.



I



II



III

An isoelectronic complex with vanadium replacing chromium would demand terminal rings donating five electrons rather than the four electrons furnished by η^4-cyclooctatetraene. We therefore

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