$$\frac{D_{CH_2}}{D_{CH_3}} = \frac{(n-1)k_H/k_D}{(n-1)k_H/k_D + 1} \quad (1)$$

where D equals the normalized integration value and n equals the number of protons available for abstraction. Thus k_H/k_D is found to be 3.35.[16] All of the data are consistent with the loss of a proton from C-9 of **3** and with the intermediacy of the α-terpinyl cation in limonene biosynthesis. The use of this spectral technique provides great simplicity in determining the regiospecificity of proton abstraction as well as in calculating the KIE without the use of labeled substrates or enzyme isolation.

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(16) Melander, L.; Saunders, W. H. *Reaction Rates of Isotopic Molecules*; John Wiley & Sons: New York, 1980; pp 91-111.

Acyclic Stereocontrol via an Electron-Transfer Process. Remarkable Stereochemical Difference between One- and Two-Electron Events

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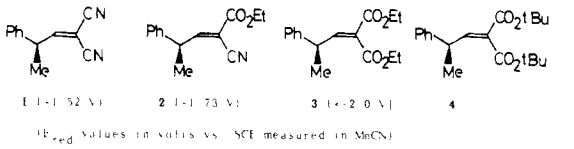
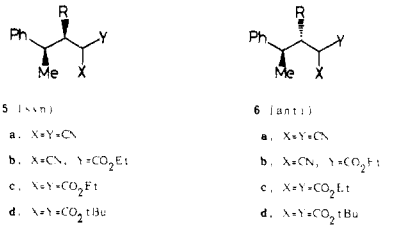
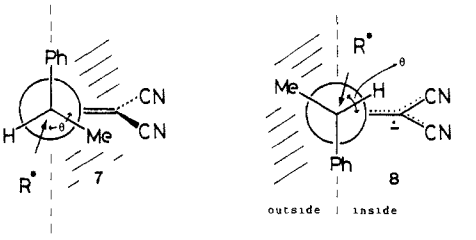
Acyclic stereocontrol is of current importance in practical and theoretical organic chemistry.[1] Stereochemistries of nucleophilic and electrophilic reactions have been widely investigated,[1] and their theoretical studies have also been carried out recently.[2] However, stereochemical study of a radical process in acyclic systems is very rare, although the theoretical prediction has been made.[2] Furthermore, the acyclic stereochemistry via an electron-transfer process has not yet been investigated systematically.[3] We report, for the first time, a surprising stereochemical difference between a nucleophilic process and an electron-transfer process in an acyclic system.

The nucleophilic addition with organometallic compounds, the free-radical addition, and the allylation via photoinduced electron transfer were investigated by using the Michael acceptors (**1-4**) bearing a chiral center at the γ-position.[4] The diastereoselectivities are summarized in Table I. Organocopper addition to **1** gave the syn isomer **5a** predominantly regardless of the reagent (entries 1-4). On the other hand, other organometallic reagents such as the allyltin and the aluminum ate complex afforded the anti isomer **6a** predominantly (entries 5 and 6). The stereochemistries of **5** and **6** were determined unambiguously by comparison with an authentic material (Supplementary Material).[5]







The cuprate addition to **2** again gave the syn adduct **5b** predominantly (entries 10 and 12). Quite interestingly, however, the alkylcopper addition to **2** produced the anti adduct **6b** predominantly (entries 9 and 11). The same tendency was observed for the organocopper addition to **3** and **4** (entries 13-20).

We anticipated that the marked stereochemical contrast between the organocoppers and other organometallic reagents in the addition to **1** and between the cuprates and alkylcoppers in the addition to **2-4** would be a reflection of the electron-transfer process.[6] Actually, the photoinduced electron-transfer allylation[7] of **1** with allyltin gave **5a** predominantly (entry 7), although the desired adduct was obtained in very low yield. The radical addition[8] of BuI to **1** produced **6a** preferentially (entry 8), and the similar radical allylation[8] of **1** with allyl iodide also gave the anti isomer predominantly.

The addition of ordinary organometallics such as allyltin-$TiCl_4$ and allylsilane-$TiCl_4$ to **3** gives the anti isomer **6c** predominantly,[1] and this stereoselectivity is in good agreement with the selectivity predicted by a modified Felkin or Cram rule. Therefore, the diastereoselection exhibited in the alkylcopper addition to **2-4** as well as the stereoselectivity in entries 5 and 6 fall under the category of the normal selectivity predictable from nucleophilic additions.

The diastereoselectivities of the organocopper addition in the presence of *p*-dinitrobenzene (pDNB),[9] which possesses a strong electron acceptor ability, are summarized in Table II. *The syn selectivity was changed to the anti selectivity.* pDNB presumably accepts an electron from RCu[10] and thus prevents formation of the radical anion of **1** (entries 1 and 3). In these cases, both the anti preference and low conversion were observed. The R_2CuLi-pDNB system also exhibited the anti preference, while the *conversion was enhanced* (entries 2, 5-7). The reason of this enhancement is not clear,[11] but it seems that pDNB again prevents

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(1) For example, see: Yamamoto, Y. *Acc. Chem. Res.* **1987**, *20*, 243 and references cited therein.
(2) Houk, K. N.; Paddon-Row, M. N.; Rondan, N. G.; Wu, Y. D.; Brown, F. K.; Spellmeyer, D. C.; Metz, J. T.; Li, Y.; Loncharich, R. J. *Science (Washington, D.C.)* **1986**, *231*, 1108.
(3) Yamamoto, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1985**, *107*, 6411.
(4) The asymmetric induction in **1** was studied previously. Kruger, D.; Sopchik, A. E.; Kingsbury, C. A. *J. Org. Chem.* **1984**, *49*, 778.
(5) The stereochemistry determined by us was in agreement with the previous assignment[4] and made by ^1H NMR. However, the isomer ratio in the addition of Me_2CuLi did not agree (entry 2 vs Table I of ref 4).
(6) (a) House, H. O. *Acc. Chem. Res.* **1976**, *9*, 59. (b) Posner, G. H. *An Introduction to Synthesis using Organocopper Reagents*; John Wiley: 1980. See, also: (c) Corey, E. J.; Boaz, N. W. *Tetrahedron Lett.* **1985**, *26*, 6015.
(7) For example, Mizuno, K.; Toda, S.; Otsuji, Y. *Chem. Lett.* **1987**, 203.
(8) Giese, B.; G-Gomez, J. A.; Witzel, T. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 69.
(9) Yang, D.; Tanner, D. D. *J. Org. Chem.* **1986**, *51*, 2267.
(10) When pDNB was added to a colorless ether solution of Me_2CuLi, the color immediately changed to dark brown.
(11) This interesting observation may be rationalized as follows. $(R_2CuLi)^{\bullet+}$ produced by an electron transfer may react more rapidly and more cleanly with the Michael acceptors than R_2CuLi itself. $(RCu)^{\bullet+}$ might easily decompose to R• and thus lose capability of the conjugate addition. Further aspects are now under active investigation.

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Table I. Diastereoselectivity in the Reaction in **1-4**[a]

entry	substrate	reagent, RM	reacn condn[d]	syn/anti (**5**/**6**)	total isold yield, %
1	**1**	MeCu	-78 → -20, 1.5	77/23	72
2	**1**	Me_2CuLi	-78 → -20, 1.5	87/13	73
3	**1**	BuCu	-78 → -20, 1.5	77/23	89
4	**1**	Bu_2CuLi	-78 → -20, 1.5	91/9	79
5	**1**	Me_4AlLi	-78 → 0, 2	37/63	75
6	**1**	$CH_2{=}CHCH_2SnBu_3$, $TiCl_4$	-78 → -20, 1.5	29/71	52
7	**1**	$CH_2{=}CHCH_2SnBu_3$, phenanthrene	hν, rt,[e] 1	70/30	4[b]
8	**1**	BuI, Bu_3SnH, AIBN	toluene, 110, 1	18/82	13[c]
9	**2**	MeCu	-78 → -20, 1.5	38/62	92
10	**2**	Me_2CuLi	-78 → -20, 1.5	62/38	91
11	**2**	BuCu	-78 → -20, 1.5	25/75	79
12	**2**	Bu_2CuLi	-78 → -20, 1.5	75/25	68
13	**3**	MeCu	-78 → -20, 1.5	25/75	93
14	**3**	Me_2CuLi	-78 → -20, 1.5	68/32	87
15	**3**	BuCu	-78 → -20, 1.5	31/69	83
16	**3**	Bu_2CuLi	-78 → -20, 1.5	67/33	90
17	**4**	MeCu	-78 → -20, 1.5	16/84	62
18	**4**	$Me_2CuLi{\cdot}MeLi$	-78 → -20, 1.5	60/40	87
19	**4**	BuCu	-78 → -20, 1.5	14/86	91
20	**4**	Bu_2CuLi	-78 → -20, 1.5	78/22	83

[a] All reactions were carried out on 1-mmol scale. The product was isolated through a column of silica gel. The isomer ratio was determined by capillary GLC (SE-30, 25 m) and/or ^1H NMR analyses. Three equivalents of the organocopper reagents were used. In entries 5 and 6, a slight excess of RM was added. In entries 7 and 8, 2 equiv of allyltin and BuI were utilized. [b] The regioisomer of **5a**, $PhCHMeCH_2CRXY$, was obtained as a major product (see ref 7). [c] The reaction was not clean, and many unidentified products were obtained along with the desired adduct. [d] Temperatures are given in °C, and time is measured in hours. [e] Room temperature.

Table II. Diastereoselectivity in the Presence of pDNB[a]

entry	substrate	organocopper	pDNB (equiv)	syn/anti (**5**/**6**)	total yield,[b] %
1	**1**	MeCu	3	33/67	30
2	**1**	Me_2CuLi	3	33/67	99
3	**1**	BuCu	3	28/72	21
4	**1**	Bu_2CuLi	3	32/68	79
5	**2**	Me_2CuLi	1	39/61	99
6	**2**	Bu_2CuLi	1[c]	39/61	99
7	**3**	Me_2CuLi	1	42/58	99
8	**3**	Bu_2CuLi	3	34/66	82

[a] To an ether solution of organocoppers (3 mmol) was added pDNB in THF at -78 °C, and then substrates (1 mmol) were added. [b] By GLC. The starting substrate was recovered when the reaction resulted in low yield. [c] pDNB in ether was used.

an electron transfer to the Michael acceptors and the copper species[11] reacts with **1-3** instead of their anion radicals.

The difference between RCu and R_2CuLi in **2-4** and the similarity between RCu and R_2CuLi in **1** are in good agreement with the E_{red} values. Both reagents must produce the radical anion of **1**, since **1** possesses high ability to accept an electron. When the ability of substrates **2-4** is not so high, only R_2CuLi which possesses higher electron-donating capability must produce the radical anions. Taken together, the syn selectivity can be explained by the intermediacy of the radical anions of Michael acceptors.[12]

The attack angle, θ, of nucleophiles and radicals is greater than 90°,[2] and thus the steric factor of the outside region becomes important in controlling the selectivity. Therefore, the anti isomer is produced via **7** (a modified Felkin model). On the other hand, in the radical anion intermediate the interaction between the HOMO of substrate and R* group dictates the stereoselectivity.[2] The electrophilic attack occurs with acute θ, and the inside region of **8** is stereodetermining. In conclusion, the stereochemical results taken as a whole not only provide the first example of acyclic stereocontrol via an electron-transfer process but also demonstrate a delicate balance of the mechanisms of the organometallic conjugate additions.

Acknowledgment. We thank Professor T. Miyashi of our department for measurement of E_{red} values.

Supplementary Material Available: Experimental details of the structure determination of **5** and **6** (2 pages). Ordering information is given on any current masthead page.

(12) The syn selectivity of organocopper addition to **1** may be ascribed to participation of the d-orbital.[13] However, the difference in **2-4** and the effect of pDNB cannot be explained by this concept.

(13) Corey, E. J.; Boaz, N. W. *Tetrahedron Lett.* **1984**, 3063.

Inorganic Analogues of Langmuir-Blodgett Films: Adsorption of Ordered Zirconium 1,10-Decanebisphosphonate Multilayers on Silicon Surfaces

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The preparation of organized monolayer and multilayer molecular assemblies at interfaces continues to be an area of great current interest.[1-5] Studies of these assemblies have been motivated by their relevance to a variety of heterogeneous phenomena including solid-state microelectronics,[6] electrochemistry,[4,7] and catalysis.[8] One route to the preparation of such structures is via the classical Langmuir-Blodgett monolayer transfer technique;[9] this powerful approach unfortunately suffers from several drawbacks, most notably the requirement for planar substrates and a sensitivity to environmental contaminants. Sagiv and coworkers[10] have demonstrated the feasibilty of multilayer synthesis via sequential adsorption and chemical activation of chlorosilanes. Their synthetic method is conceptually novel because it does not involve monolayer transfer steps; however, it has failed to yield organized surface structures more than two or three layers thick because of imperfect ordering of alkyl chains within the layers.

We report here a multilayer synthesis based on the sequential adsorption of components of zirconium 1,10-decanebisphosphonate (ZDBP), $Zr(O_3PC_{10}H_{20}PO_3)$. This is a water-insoluble salt which contains alternating polar Zr-O-P and nonpolar alkyl layers, with a 17.3-Å crystallographic layer spacing.[11] We selected this compound as a basis for surface multilayer synthesis because it (like many transition-metal phosphonates) spontaneously crystallizes as a layered compound when solutions of the appropriate metal salt and phosphonic acid are mixed. The process of growing ZDBP surface multilayers is shown in Scheme I. In the first step,

(1) Allara, D. L.; Nuzzo, R. G. *Langmuir* **1985**, *1*, 45; **1985**, *1*, 52.
(2) (a) Maoz, R.; Sagiv, J. *J. Colloid Interface Sci.* **1984**, *100*, 465. (b) Gun, J.; Iscovici, R.; Sagiv, J. *J. Colloid Interface Sci.* **1984**, *101*, 201.
(3) Sabatani, E.; Rubinstein, I.; Maoz, R.; Sagiv, J. *J. Electroanal. Chem.* **1987**, *219*, 365.
(4) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559.
(5) Nuzzo, R. G.; Fusco, F. A.; Allara, D. L. *J. Am. Chem. Soc.* **1987**, *109*, 2358.
(6) (a) Roberts, G. G. *Adv. Phys.* **1985**, *34*, 475. (b) Broers, A. N.; Pomerantz, M. *Thin Solid Films* **1983**, *99*, 323. (c) Fariss, G; Lando, J.; Rickert, S. *Thin Solid Films* **1983**, *99*, 305.
(7) (a) Finklea, H. O.; Avery, S.; Lynch, M. *Langmuir* **1987**, *3*, 409. (b) Finklea, H. O.; Robinson, L. P.; Blackburn, A.; Richter, B.; Allara, D.; Bright, T. *Langmuir* **1986**, *2*, 239. (c) Li, T. T.-T.; Weaver, M. J. *J. Am. Chem. Soc.* **1984**, *106*, 6107.
(8) Somorjai, G. A. *Chemistry in Two Dimensions: Surfaces*; Cornell University Press: Ithaca, NY, 1981.
(9) (a) Blodgett, K. B. *J. Am. Chem. Soc.* **1935**, *57*, 1007. (b) Blodgett, K. B.; Langmuir, I. *Phys. Rev.* **1937**, *51*, 964.
(10) Netzer, L.; Sagiv, J. *J. Am. Chem. Soc.* **1983**, *105*, 674.
(11) Dines, M. B.; DiGiacomo, P. M. *Inorg. Chem.* **1981**, *20*, 92.

0002-7863/88/1510-0618$01.50/0