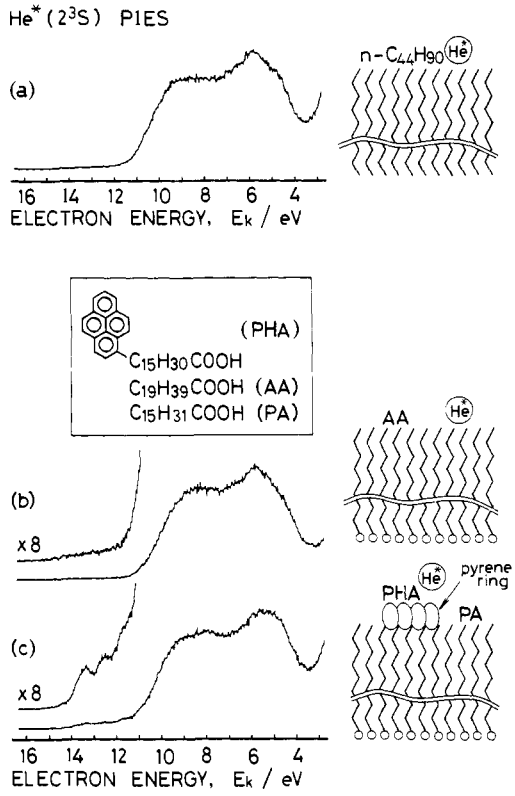

Figure 1. He* (2 ^{3}S, 19.82 eV) PIES of three films: (a) an evaporated film of tetratetracontane (n-$C_{44}H_{90}$); (b) an LB monolayer film of arachidic acid (AA); (c) a mixed LB monolayer film of palmitic acid (PA) and 16-(1-pyrenyl)hexadecanoic acid (PHA) (33 mol % PHA). The schematic diagram of surface molecules in each film is also shown on the right of the corresponding spectrum.

to study the orientation of molecules in the outermost surface layer.[9-11] We have already shown that films prepared with the same molecules but having different orientations provide completely different PIES.[10] We intend in this paper, however, to indicate that films prepared with different molecules but exposing the same part outside the surface give almost the same PIES.

Figure 1a shows He* (2 ^{3}S, 19.82 eV) PIES of a n-alkane (n-$C_{44}H_{90}$, tetratetracontane) film prepared in situ by vacuum deposition onto a copper substrate at room temperature. This film was studied as a model for an alkyl end surface of the LB film. The PIES of monolayer LB films are shown in Figure 1b,c. Curve b is for a film of arachidic acid (AA; eicosanoic acid) and curve c for a mixed film of palmitic acid (PA; hexadecanoic acid) and 16-(1-pyrenyl)hexadecanoic acid (PHA) (33 mol % PHA). AA was spread on an aqueous subphase[12] and transferred onto a stainless steel substrate[13] at 35 mN/m by the Langmuir-Blodgett technique. The mixed monolayer was prepared under the same conditions, except that the surface pressure for deposition was 25 mN/m. All the spectra in Figure 1 were measured with an ultrahigh vacuum electron spectrometer.[11]

The PIES of the AA monolayer has a very similar appearance to that of the n-alkane evaporated film in spite of the lack of the hydrophilic group in the n-alkane and also the different length of the hydrocarbon chain between the two compounds. Upon evaporation, long-chain n-alkanes form polycrystalline films with the c axis, which is parallel to the chain direction, perpendicular to the substrate surface[14] (see the right of Figure 1a). Since a methyl end of the molecule is exposed to the film surface, σ orbitals with large distribution at the methyl end are predominantly attacked by metastables to form the features of the PIES in Figure 1a. Therefore, the close resemblance between the PIES of the n-alkane film and that of the AA monolayer indicates that AA is oriented with its *methyl* end toward the outside (see the right of Figure 1b.[15] Thus, molecules having different structures as a whole but common parts exposed outside give almost the same PIES, which leads to the identification of the molecular end at the film surface.

In the PIES of the mixed-monolayer LB film (Figure 1c), three bands are observed in the high electron energy region. The corresponding bands are not found in Figure 1b. With the ultraviolet photoelectron spectrum (UPS) of pyrene[16] as a reference, these bands are assigned to four π orbitals of the pyrene ring (two orbitals are responsible for the third band). This observation clearly indicates that PHA is oriented with its pyrene ring exposed to the film surface (see the right of Figure 1c). In addition, since the pyrene ring can be regarded as a model for the functional part of the amphiphile, the above results demonstrate the usefulness of PIES in the study of functionalized film surfaces.

In conclusion, PIES provides direct information about the end of molecules exposed outside the LB film surface. It should be noted that the analysis of the PIES is straightforward; we can determine the exposed molecular end of an LB film, comparing its PIES with that of a model compound having the same molecular end. In addition to the study of functionalized film surfaces, the observation of the change in PIES dependent on the number of layers enables us to discriminate among the types (X, Y, or Z) of the LB films. Furthermore, the rearrangement of molecules during film preparation as well as the character of the inhomogeneity at the film surface[17] can be sensitively detected by PIES.

Acknowledgment. We thank Professor Kazuhiko Seki, Hiroshima University, for his helpful discussion.

(12) The subphase contains 0.3 mM $CaCl_2$ and 0.05 mM $NaHCO_3$. Therefore, it may be more appropriate to consider this film as a calcium arachidate film.

(13) The substrate was smoothed with alumina to obtain a mirror surface and cleaned ultrasonically with organic solvents.

(14) Seki, K.; Inokuchi, H. *Chem. Phys. Lett.* **1982**, *89*, 268-272. Hashimoto, S.; Seki, K.; Sato, N.; Inokuchi, H. *J. Chem. Phys.* **1982**, *76*, 163-172.

(15) We have also obtained n-alkane films in which surface molecules lie exposing their "sides" (methylene groups) outside. Though the surfaces are hydrophobic in these cases as well, their PIES are entirely different from those of the "methyl surfaces" shown in Figure 1 (Ozaki, H.; Harada, Y., unpublished results).

(16) Boschi, R.; Schmidt, W. *Tetrahedron Lett.* **1972**, *25*, 2577-2580.

(17) Nishiyama, K.; Fujihira, M.; Ozaki, H.; Harada, Y., unpublished results.

(*E*)-Selective Olefination of Aldehydes by means of *gem*-Dichromium Reagents Derived by Reduction of *gem*-Diiodoalkanes with Chromium(II) Chloride

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The geminal dimetallic reagent **1** is expected to add to a carbonyl carbon to form a β-oxymetal-substituted organometallic compound **2** which can then eliminate to give an olefin (Scheme I).[1] This approach provides useful methods for the methylenation (**1**, R^2 = H) of aldehydes or ketones by means of CH_2I_2-Zn-Me_3Al[2] or CH_2X_2 (X = I, Br)-Zn-$TiCl_4$.[2,3] These methods have some advantages compared to the Wittig reaction.

However, the geminal dimetallic reagents have not been widely utilized for the preparation of a 1,2-disubstituted olefin[4] from an

(1) Bertini, F.; Grasselli, P.; Zubiani, G.; Cainelli, G. *Tetrahedron* **1970**, *26*, 1281.

(2) Takai, K.; Hotta, Y.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1978**, 2417; *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1698.

(3) (a) Hibino, J.; Okazoe, T.; Takai, K.; Nozaki, H. *Tetrahedron Lett.* **1985**, *26*, 5579, 5581. (b) Lombardo, L. *Ibid.* **1982**, *23*, 4293.

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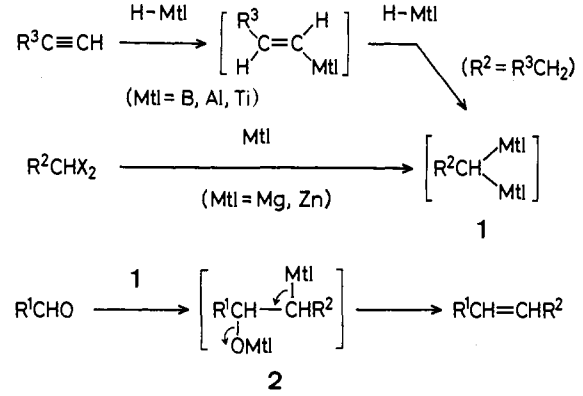
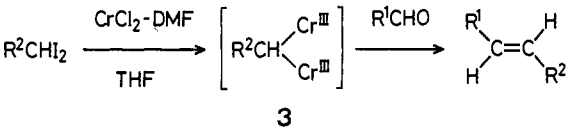
Scheme I



Scheme II



aldehyde because of the following limitations: (i) low reactivity of the geminal dimetallic compounds (MtI = B[5] or Al[6]); (ii) lack of stereoselectivity of the products;[5b,6c] (iii) side reactions such as the reduction of a carbonyl group[1] or reductive coupling of an aldehyde to a 1,2-diol.[7] Recently, Knochel and Normant reported that 1-magnesium 1-zinc compounds add to aldehydes with the assistance of BF_3·OEt_2 to give olefins with good *E* selectivity.[8] However, the reagents are limited to 2-allyl-substituted 1-magnesium 1-zinc compounds, since the reagents are prepared by allylzincation of alkenylmagnesium compounds. We describe herein a simple and general method for the conversion of an aldehyde to an (*E*)-alkene by means of a geminal dichromium reagent,[9-11] prepared by direct reduction of a *gem*-diiodoalkane[13] with chromium(II) chloride in THF, which overcomes the weak points of the nonstabilized phosphorus ylides[14,15] (Scheme II).

The results shown in Table I disclose the wide applicability of the geminal dichromium procedure. The salient features of the process are as follows.

(1) High *E* selectivity is seen in all cases, especially with aliphatic aldehydes. The *E*/*Z* ratios increase with increasing bulkiness of the substituent on the aldehyde (R^1). Reaction with pivalaldehyde (run 10) is worth noting, because it is difficult to obtain *E*-alkylidenation products from this aldehyde even by Schlosser's β-oxidoylide method.[15,16]

(2) Reduction of 1,1-diiodoethane with $CrCl_2$ in tetrahydrofuran (THF) proceeds smoothly to give the 1,1-dichromioethane reagent, which reacts with aldehydes to furnish ethylidenation products

Table I. Alkylidenation of Aldehydes by means of Geminal Dichromium Reagents

run	R^1	R^2	method[a]	time, h	yield,[b] %	*E*/*Z*[c]
1	*n*-C_5H_{11}	Me	A	4.5	94[d]	96/4
2	*n*-$C_{11}H_{23}$		A	5	81	95/5
3	$Ph(CH_2)_2$		A	10	85	97/3
4	Et_2CH		A	2	99[d]	98/2
5	4-(*i*-Pr)C_6H_4		A	10	97	84/16
6			C	5	84	78/22
7	$(CH_2)_5C{=}CH$		A	7.5	93	89/11
8	*n*-C_8H_{17}	Pr	A	24	38	95/5[e]
9			B	1.5	85	96/4[e]
10	*t*-Bu		B	1	96[d]	99/1
11	Ph		B	1	87	88/12
12			C	0.5	60	51/49
13	*n*-C_5H_{11}	*i*-Pr	A	24	12[d]	72/28
14			B[f]	1	74[d]	93/7
15	Ph		B[f]	2	79	88/12
16	Pr	*t*-Bu	B	0.5	90[d]	94/6
17	Ph		B	2	80	96/4
18	Ph	H	A[g]	24	70[d]	
19			B	3	92[d]	
20	*n*-$C_{11}H_{23}$		B	3	73	

[a] Method A: An aldehyde (1.0 mmol) was treated with 1,1-diiodoethane (2.0 mmol) and $CrCl_2$ (8.0 mmol) in THF. See ref 17a. Method B: An aldehyde (1.0 mmol) was treated with 1,1-diiodoalkane (2.0 mmol) and a $CrCl_2$ (8.0 mmol)–DMF (8.0 mmol) complex in THF. See ref 17b. Method C: A combination of $CrCl_3$ (4.0 mmol) and zinc (6.0 mmol) was employed instead of $CrCl_2$ (8.0 mmol). [b] Isolated yields unless otherwise noted. [c] The *E*/*Z* ratios of products were determined by capirally GLPC and/or NMR analysis. [d] GLPC yields. [e] The *E*/*Z* ratios were determined by GLPC of the corresponding epoxides. [f] Fourfold excess of the geminal dichromium reagent was employed. [g] The reaction was conducted at 35 °C.

in excellent yields (method A).[17a] In contrast, reactions with the other *gem*-diiodoalkanes by method A gave the desired olefins in 10–50% yields (runs 8 and 13). The reduction power of chromium(II) can be enhanced significantly by complex formation with donor ligands, such as ethylene diamine[9] or TMEDA.[18] Dimethylformamide (DMF) was found to be the most effective of these ligands.[19] Thus the reaction was conducted by using the chromium(II) complex pretreated with 1 equiv of DMF (method B).[17b] Diiodomethane was reduced smoothly under condition B (runs 19 and 20).[2,3]

(3) The reactivity of organic halides to chromium(II) chloride falls in the order I > Br > Cl.[9,10d] Reaction of 4-isopropylbenzaldehyde with 1,1-dibromo- and 1,1-dichloroethane at 25 °C for 24 h afforded a 14% yield and none of the ethylidenation

(4) Reaction between a metal alkylidene complex and an aldehyde affords a 1,2-disubstituted olefin. However, the reported *E*/*Z* ratios of the olefins are not high. (a) Ta: Schrock, R. R. *J. Am. Chem. Soc.* **1976**, *98*, 5399. Zr: Clift, S. M.; Schwartz, J. *Ibid.* **1984**, *106*, 8300. (b) W: Aguero, A.; Kress, J.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1986**, 531.

(5) (a) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1961**, *83*, 3834. (b) Cainelli, G.; Bello, G. D.; Zubiani, G. *Tetrahedron Lett.* **1966**, 4315.

(6) (a) Wilke, G.; Mueller, H. *Justus Liebigs Ann. Chem.* **1960**, *629*, 222. (b) Zweifel, G.; Steele, R. B. *Tetrahedron Lett.* **1966**, 6021. (c) Cainelli, G.; Bertini, F.; Grasselli, P.; Zubiani, G. *Ibid.* **1967**, 1581.

(7) Alkylidenation of ketones leading to trisubstituted olefins proceeds smoothly with a reagent prepared by zinc reduction of $RCHX_2$ (X = I, Br) in the presence of $TiCl_4$ (Okazoe, T.; Takai, K.; Utimoto, K., unpublished results). However, treatment of an aldehyde with this system affords a considerable amount of a pinacol-type 1,2-diol derived from the low-valent titanium.

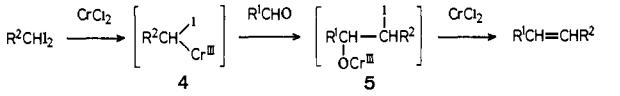
(8) Knochel, P.; Normant, J. F. *Tetrahedron Lett.* **1986**, *27*, 1039.

(9) For reduction of alkyl halides with chromium(II) complexes, see: (a) Kochi, J. K.; Mocadlo, P. E. *J. Am. Chem. Soc.* **1966**, *88*, 4094. (b) Kochi, J. K.; Powers, J. W. *Ibid.* **1970**, *92*, 137.

(10) For reduction of polyhalogen compounds with chromium(II) complexes, see: (a) Castro, C. E.; Kray, W. C., Jr. *J. Am. Chem. Soc.* **1966**, *88*, 4447. (b) Dodd, D.; Johnson, M. D. *J. Chem. Soc. A* **1968**, 34. (c) Nohr, R. S.; Spreer, L. O. *Inorg. Chem.* **1974**, *13*, 1239. (d) Takai, K.; Nitta, K.; Utimoto, K. *J. Am. Chem. Soc.* **1986**, *108*, 7408.

(11) There is a possibility of an alternative sequence involving the attack of an (α-haloalkyl)chromium reagent **4** on an aldehyde followed by chromium-induced elimination reaction (Scheme III). However, we are tempted

Scheme III



to reject the above pathway for the following reasons. (i) None of the monoiodide nor halohydrin, which would derive from hydrolysis of **4** and **5**, respectively, was detected during the reaction process. (ii) Cyclopropane compounds, which are produced by electrophilic addition of chromium carbenoid to the desired olefins, were not isolated.[10a] (iii) Deoxygenation of both *trans*- and *cis*-2-butene oxides with chromium(II) complexes is reported to give 2-butene in a ratio of *E*/*Z* ≃ 55/45.[12] These results suggest that the third step in Scheme III is not a stereospecific process, as one-electron reduction of **5** would give the same intermediates.

(12) Kochi, J. K.; Singleton, D. M. *J. Am. Chem. Soc.* **1968**, *90*, 1582.

(13) (a) Letsinger, R. L.; Kammeyer, C. W. *J. Am. Chem. Soc.* **1951**, *73*, 4476. (b) Pross, A.; Sternhell, S. *Aust. J. Chem.* **1970**, *23*, 989.

(14) (a) Maercker, A. *Org. React.* **1965**, *14*, 270. (b) Schlosser, M. *Top. Stereochem.* **1970**, *5*, 1.

(15) Schlosser, M.; Christmann, K. F. *Angew. Chem.* **1966**, *78*, 115.

(16) Coates, R. M.; Johnson, M. W. *J. Org. Chem.* **1980**, *45*, 2685.

product, respectively. Thus *gem*-diiodo compounds are essential for the reaction (run 5).

(4) A combination of $CrCl_3$ and zinc can be employed instead of $CrCl_2$ (method C, runs 6 and 12). However, the E/Z ratios of the olefins resulting from method C are low compared to that of those from method A or B.[20]

(5) To obtain trisubstituted olefins, two pathways were examined. One is the reaction of **3** with ketones.[7,21] The reactive 1,1-dichromioethane afforded the ethylidenation products of ketones, even of easily enolizable ones, in good yields.[22] However, yields of the olefination product of ketones with the other 1,1-dichromium reagents are rather low.[23] Another approach is the reaction of aldehyde and geminal dichromium reagent, prepared by $CrCl_2$ reduction of $RR'CI_2$. Reaction between benzaldehyde and 2,2-diiodopentane with $CrCl_2$–DMF in THF at 25 °C gave a complex mixture containing only 7% of the desired trisubstituted olefin (E/Z = 63/37).

Although the controlling mechanism for E/Z selectivity is still obscure, the mild conditions[24] and high E selectivity characterize the method as a useful alternative to the Wittig olefination.

Registry No. (*E*)-$C_5H_{11}CH$=CHMe, 13389-42-9; (*E*)-$C_{11}H_{23}CH$=CHMe, 35953-54-9; (*E*)-$Ph(CH_2)_2CH$=CHMe, 16091-23-9; (*E*)-Et_2CHCH=CHMe, 19781-63-6; (*E*)-4-(*i*-Pr)C_6H_4CH=CHMe, 27250-21-1; (*Z*)-4-(*i*-Pr)C_6H_4CH=CHMe, 27250-20-0; (*E*)-$(CH_2)_5C$=CHCH=CHMe, 1551-68-4; (*Z*)-$(CH_2)_5C$=CHCH=CHMe, 1551-67-3; (*E*)-$C_8H_{17}CH$=CHPr, 41446-55-3; (*E*)-*t*-BuCH=CHPr, 19550-75-5; (*E*)-PhCH=CHPr, 16002-93-0; (*Z*)-PhCH=CHPr, 7642-18-4; (*E*)-$C_5H_{11}CH$=CHPr-*i*, 51090-06-3; (*Z*)-$C_5H_{11}CH$=CHPr-*i*, 51090-07-4; (*E*)-PhCH=CHPr-*i*, 15325-61-8; (*Z*)-PhCH=CHPr-*i*, 15325-56-1; $PhCH=CH_2$, 100-42-5; $C_{11}H_{23}CH=CH_2$, 2437-56-1; $C_5H_{11}CHO$, 66-25-1; $C_{11}H_{23}CHO$, 112-54-9; $Ph(CH_2)_2CHO$, 104-53-0; Et_2CHCHO, 97-96-1; 4-(*i*-Pr)C_6H_4CHO, 122-03-2; $(CH_2)_5$-C=CHCHO, 1713-63-9; $C_8H_{17}CHO$, 124-19-6; *t*-BuCHO, 630-19-3; PhCHO, 100-52-7; PrCHO, 123-72-8; $MeCHI_2$, 594-02-5; $PrCHI_2$, 66587-65-3; *i*-$PrCHI_2$, 10250-55-2; *t*-$BuCHI_2$, 2443-89-2; CH_2I_2, 75-11-6; $CrCl_2$, 10049-05-5; $CrCl_3$, 10025-73-7; Zn, 7440-66-6; $(PhCH_2)_2CO$, 102-04-5; $(PhCH_2)_2C$=$CHCH_3$, 40558-71-2; $H_3C(C-H_2)_2CH$=$CH(CH_2)_4CH_3$, 19689-18-0; cyclododecanone, 830-13-7; ethylidenecyclododecane, 106161-78-8; 1-tetralone, 529-34-0; (*E*)-1-ethylidenetetralone, 106161-79-9; (*Z*)-1-ethylidenetetralone, 106161-80-2; butylidenecyclododecane, 106161-81-3.

(17) Typical procedures are as follows. (a) Method A: Anhydrous $CrCl_2$ (purchased from Aldrich Co., 0.98 g, 8.0 mmol) is suspended in THF (20 mL) under an argon atmosphere. A solution of an aldehyde (1.0 mmol) and 1,1-diiodoethane[13a] (0.56 g, 2.0 mmol) in THF (3 mL) is added at 25 °C to the suspension. After it was stirred at 25 °C for the number of hours shown in Table I, the mixture is diluted with pentane (15 mL), poured into water (40 mL), and extracted with pentane (3 × 15 mL). The organic extracts are washed with brine, dried (Na_2SO_4), and concentrated. Purification by short-column chromatography on silica gel (pentane) affords the ethylidenation product. (b) Method B: To a stirring suspension of anhydrous $CrCl_2$ (0.98 g, 8.0 mmol) in THF (20 mL) is added DMF (0.62 mL, 8.0 mmol) at 25 °C under an argon atmosphere. After 30 min of stirring, a solution of an aldehyde (1.0 mmol) and 1,1-diiodoalkane[13b] (2.0 mmol) in THF (3 mL) is added at 25 °C. The pale green suspension turns to dark green and then to a dark brown solution. (When a lump of the $CrCl_2$ complex remains at this stage, ultrasonic irradiation is effective to get a homogeneous solution.) The resulting mixture is stirred at 25 °C for an appropriate time, described in Table I. The mixture is subjected to aqueous workup (vide infra). Purification by short-column chromatography (pentane) gives the desired olefin.

(18) Nakatsukasa, S.; Takai, K.; Utimoto, K. *J. Org. Chem.* **1986**, *51*, 5045.

(19) The yields of the olefinic products were about 20% in DMF solvent, since *gem*-diiodo compounds were consumed very fast in this solvent.

(20) During the reaction in method C, 1-iodobutane, which was not observed in method A and B, was detected by GLPC.

(21) Yoshida, T. *Chem. Lett.* **1982**, 429.

(22) Reaction of cyclododecanone with 1,1-diiodoethane (2.0 equiv) and $CrCl_2$ (8.0 equiv) in THF proceeded at 25 °C for 27 h to afford ethylidenecyclododecane in 96% yield. Easily enolizable ketones, dibenzyl ketone and 1-tetralone, were converted to the corresponding ethylidenation products in 88% and 85% yield (E/Z = 16/84), respectively, after stirring at 25 °C for 8 h (ultrasonic irradiation for 4 h).

(23) Treatment of cyclododecanone with 1,1-diiodobutane and $CrCl_2$–DMF (method B) at 25 °C for 18 h gave the desired butylidenation product in 15% yield along with a 75% recovery of the unchanged ketone.

(24) Under the conditions of method B (preparation of 4-decene from hexanal and 1,1-diiodobutane in 80–90%), compounds were recovered in the following order: ethyl octanoate (97% recovery); nonanal diethylene acetal (97%); nonanenitrile (99%); 1-dodecyne (100%); 1-iodooctane (93%).

Applications of Tartrate Ester Modified Allylic Boronates in Organic Synthesis: An Efficient, Highly Stereoselective Synthesis of the C(19)–C(29) Segment of Rifamycin S†

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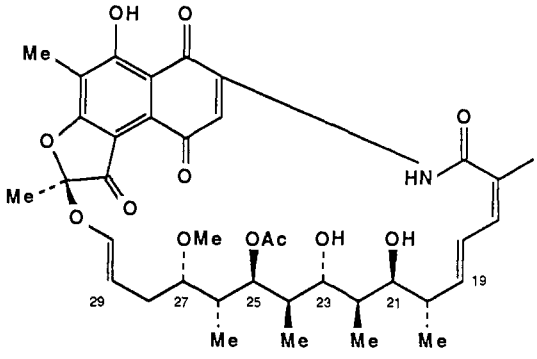
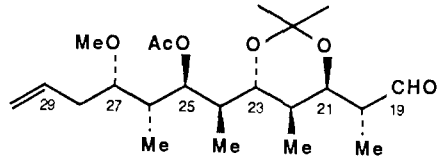
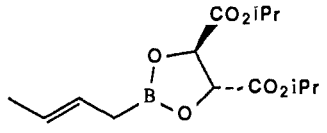
Rifamycin S (**1**) is a well-known member of the ansamycin antibiotic group.[3] We became interested in undertaking a synthesis of the stereochemically rich ansa chain (C(19)–C(29) segment, c.f., compound **2**)[4] in order to explore the applicability of tartrate ester modified allylic boronates **3** and **4**[5] as chiral E(O) propionate and acetate enolate equivalents in complex synthetic problems. We are pleased to report herein, therefore, that **2** has been synthesized by a 16-step synthesis that proceeds in 15% yield and with 75% overall stereoselectiviy.[6] The brevity, efficiency and selectivity of this synthesis rivals alternative acyclic approaches,[4a,e,f,h] a clear testimony to the potential of **3** and **4** as reagents for organic synthesis.



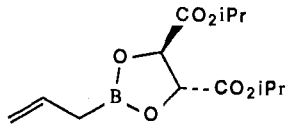
1



2



(R,R) - **3**



(R,R) - **4**

The synthesis of **2** (Scheme I) commenced with the reaction of (*S,S*)-**3** and chiral aldehyde (*S*)-**5**. This transformation, described in detail elsewhere,[7] is a mismatched double asymmetric reaction[8] and provides **6** as the major component of an 88:11:1 mixture. Compound **6**, isolated in 75% yield, was smoothly transformed into aldehyde **7**[9] which served as the substrate for the second crotylboronate addition reaction.[10] The combination

† This manuscript is dedicated to Professor George H. Büchi on the occasion of his 65th birthday.

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