extension is indeed a fundamental process in the synthesis of acetate-derived natural products for which general methodologies have been sought, e.g., aldol reaction[14d] and the epoxidation-reductive ring cleavage sequence.[24] After extensive reactions including reagent **20** with R′ = SMe, SPh, SeMe, Se-*c*-C_6H_{11}, and SePh,[14d] we find that the aldehyde **19** behaves in a manner totally unexpected from model experiments. Therefore, we conclude at this time that the following aldol reaction of **19** serves as the best solution, in terms of yield, stereoselectivity, and operational simplicity, all considered. Thus, with the chiral boron enolate **20** (R = trimethylsilyl, instead of *tert*-butyldimethylsilyl; R′ = H) in our standard boron-mediated aldol reaction with 9-BBN(OTf),[15] **19** provides a 4:1 mixture of aldol products **21** and **22** in 88% yield. The stereochemical assignments to these compounds are based on spectral comparison with similar racemic aldol products obtained earlier.[11] While both the substrate **19** and reagent **20** exhibit small but apparently "matched"[8b] diastereofacial selectivities,[14e] thus bringing about the above modest ratio, this selectivity certainly falls short of the standards originally set for this project. Further efforts to enhance this ratio continue.

Compound **21** is subjected to the following functional group transformations: (1) removal of the chiral auxiliary (100%),[15] (2) catalytic hydrogenolysis [5% Pd/C in aqueous ethanol (100%)], (3) stepwise silylation [*t*-$BuMe_2SiCl$[14f]], (4) hydrolysis of the silyl ester (80%) to give **23**, (5) conversion (78%) into the thioester ($ClCO_2Et$, TlS-*t*-Bu); (6) selective hydrolysis of the primary silyl ether to provide **24** (87%) $[\alpha]^{23}_D = +74.4°$ (*c* 1.35, $CHCl_3$), $[\alpha]^{25}_D = +78.3°$ (*c* 0.47, $CHCl_3$). Comparison of **24** with material derived from tylonolide[14g] establishes the identity of these compounds.

Conversion of **24** into **4** involves an intriguing ring "switching". Collins-Ratcliffe oxidation of **24** proceeds smoothly to provide the corresponding aldehyde (**25**), which upon treatment with 70% aqueous acetic acid and THF (1:1) at 50 °C, forms exclusively a γ-lactol, liberating the C(9) carboxylic acid. Subsequent methylation of the lactol with trimethyl orthoformate and methanol in THF containing *p*-toluenesulfonic acid completes the synthesis of **4** (84%, 3 steps), which is an approximately 3:2 mixture of two compounds epimeric at the C(6″) position. The synthetic material is identical with that obtained from natural **2** except for a slight difference in the epimeric ratio.[14g] This varying ratio is of no consequence to the remaining sequence of the tylonolide synthesis that follows.

Synthesis of 2 from 4. This last sequence leading to **2** patterns after that adopted in the synthesis of narbonolide.[9] Thus, treatment with 2,2′-dipyridyl disulfide (1.5 equiv) and triphenylphosphine (1.5 equiv)[14h] converts **4** to its 2-pyridine thioester **26** (75%), which is in turn reacted in ether with lithium bis-[(trimethylsilyl)methyl]cuprate to provide the α-(trimethylsilyl)methyl ketone **27** (80%).[9] The corresponding anion generated with lithium hexamethyldisilazide in tetrahydrofuran at −78 °C is highly nucleophilic and undergoes a Peterson condensation with the left-hand fragment **3** to give rise to a seco acid derivative (**28**) in 60% yield. The base-sensitive C(3) silyloxyl group remains virtually intact. So that the phosphoric acid mixed anhydride procedure[9] for lactonization could be used, the thioester of **28** is hydrolyzed with mercuric trifluoroacetate followed by aqueous $NaHCO_3$ (100%),[25] and then the C(3) and C(15) *tert*-butyldimethylsilyl groups are removed with pyridine hydrofluoride[26] to give **29** (83%). Treatment of **29** (0.1 mM) in 1 mL of tetrahydrofuran with triethylamine (0.1 mM) and diphenyl phosphorochloridate (0.1 mM) at 0 °C produces the mixed anhydride, which after dilution with 40 mL of benzene, is added over a period of 8 h to 60 mL of warm (80 °C) benzene containing 4-(dimethylamino)pyridine (0.6 mM). The solution is refluxed for 10 h and then worked up in the usual manner. The yield of **30** is 32%.[14h] Regeneration of the C(6″) and C(14′) hydroxyl groups from **30** (70% aqueous AcOH) (100%) completes the synthesis of tylonolide (**2**), the intact and unmodified aglycone of tylosin.[27]

Acknowledgment. We thank Dr. M. Gorman, Eli Lilly Co., for a generous gift of tylosin and Professor S. Ōmura, Kitasato University and Dr. Y. Ito, Tanabe Seiyaku Co. Ltd., through whose courtesy a sample of the antibiotic M-4365 G_2 was made available to us. We also thank the National Institutes of Health (Grant AI 15403) for financial support. T.K. is on leave from Mitsui Toatsu Chemicals Inc., Japan. High-resolution mass spectra were provided by the facility, supported by the National Institutes of Health (Grant RR 00317; principal investigator Professor K. Biemann), from the Biotechnology Resources Branch, Division of Research Resources.

Supplementary Material Available: Listing of optical rotations and spectral data and additional comments on several reactions (11 pages). Ordering information is given on any current masthead page.

(24) (a) Ma, P.; Martin, V. S.; Masamune, S.; Sharpless, K. B.; Viti, S. M. *J. Org. Chem.* **1982**, *47*, 1378. (b) Minami, N.; Ko, S. S.; Kishi, Y. *J. Am. Chem. Soc.* **1982**, *104*, 1109.

(25) Masamune, S. *Aldrichimica* **1978**, *11*, 23.

(26) (a) Trost, B. M.; Caldwell, C. G. *Tetrahedron Lett.* **1981**, *22*, 4999. (b) Nicolaou, K. C.; Seitz, S. P.; Pavia, M. R.; Petasis, N. A. *J. Org. Chem.* **1979**, *44*, 4011.

(27) Antibiotic M-4365 G_2 (Kinumaki, A.; et al. *J. Antibiot.* **1977**, *30*, 443) is converted to its intact aglycone, which has been shown to be 14′-deoxytylonolide by synthesis (see ref 14i).

Aldol Strategy: Coordination of the Lithium Cation with an Alkoxy Substituent

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Lithium and magnesium enolates used in aldol reactions, in contrast to boron enolates, exhibit distinctive propensities for coordination with oxygenated functional groups present in either the enolate itself or the reacting aldehyde.[1] This rather general observation is also encountered in many other reactions, including those involving organolithium and Grignard reagents. The profound stereochemical consequences resulting from this coordination have beenm delineated by Cram's cyclic (coordination) model,[2] and its validity has been amply demonstrated in the literature.[3] Although until quite recently only a modest stereoselectivity (apparently) due to this effect had been attained in the aldol reaction,[4] we observed that the lithium enolate derived from **1** (Scheme I) reacted with aldehyde **2** to provide **3** with a 17:1 diastereoselectivity.[5] This result has led us to search for the factors necessary to achieve this high and synthetically significant selection. This communication discloses new findings encountered in this pursuit, which culminates in a remarkably simplified synthesis of the ansa chain of the antibiotic rifamycin S, as described in the last of this series.[6]

(1) Masamune, S. In "Organic Synthesis Today and Tomorrow"; Trost, B. M., Hutchinson, C. R., Eds.; Pergamon Press: New York, 1981; pp 199-215.

(2) (a) Cram, D. J.; Abd Elhafez, F. A. *J. Am. Chem. Soc.* **1952**, *74*, 5828. (b) Cram, D. J.; Kopecky, K. R. *Ibid.* **1959**, *81*, 2748. (c) Cram, D. J.; Wilson, D. R. *Ibid*, **1963**, *85*, 1245.

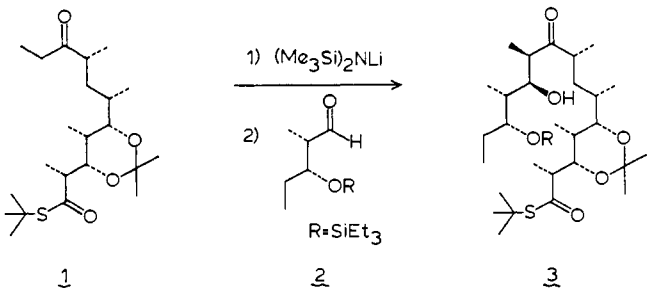
(3) For instance, see: (a) Morrison, J. D.; Mosher, H. S. In "Asymmetric Organic Reactions"; American Chemical Society; Washington, D.C., 1976; Chapt 3. (b) Boyd, D. R.; McKervey, M. A. *Q. Rev. Chem. Soc.* **1968**, *22*, 95. (c) Inch, T. D. *Synthesis* **1970**, *2*, 466. For recent dramatic examples, see: (d) Still, W. C.; McDonald, J. H., III *Tetrahedron Lett.* **1980**, *21*, 1031. (e) Still, W. C.; Schneider, J. A. *Ibid.* **1980**, *21*, 1035.

(4) Collum, D. B.; McDonald, J. H., III; Still, W. C. *J. Am. Chem. Soc.* **1980**, *102*, 2118.

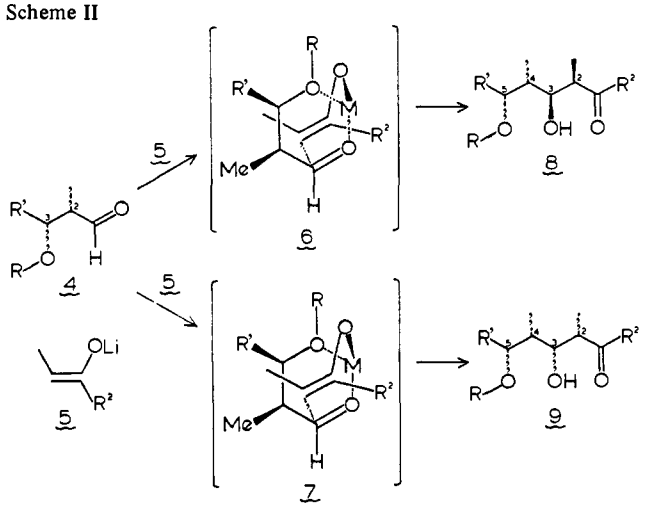
(5) Masamune, S.; Hirama, M.; Mori, S.; Ali, Sk. A.; Garvey, D. S. *J. Am. Chem. Soc.* **1981**, *103*, 1568.

0002-7863/82/1504-5526$01.25/0

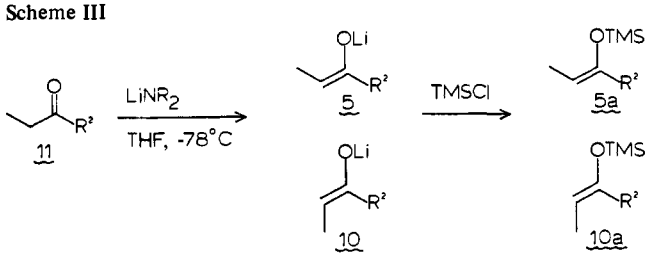
Scheme I



Scheme II



Scheme III



Assume that reaction of a *syn*-3-alkoxy-2-methylcarboxaldehyde **4** (Scheme II) with a *Z*(*O*)-enolate (**5**)[7] proceeds through a Cram-type[2] transition state (**6**) [with **5** approaching **4** from the $\alpha(re)$ face of **4**] or (**7**) [with **5** approaching **4** from the $\beta(si)$ face of **4**].[8] Transition states **6** and **7** should provide the 2,3-*syn*,3,4-*anti*,4,5-*syn*-3,5-dihydroxy-2,4-dimethylcarbonyl derivative **8** and the corresponding 2,3-*syn*,3,4-*syn*,4,5-*syn* derivative **9**,[7] respectively. As the lithium cation coordinates more tightly with both aldehydic and ethereal oxygen atoms of **4**, the interaction between the enolate **5** (carrying the substituent R^2) and the two substituents at the 3- and 2-positions of the aldehyde **4** will increase in **7**, but not in **6**. Thus, the selective construction of the system **8** is now reduced to two problems: (1) how to achieve the exclusive formation of the *Z*(*O*)-enolate and (2) what R^1 and R^2 do we select to attain a sufficiently high diastereofacial selectivity[9] of aldehyde **4**.

(6) Masamune, S.; Imperiali, B.; Garvey, D. S. *J. Am. Chem. Soc.*, following communication in this issue.

(7) For the stereochemical descriptors, syn and anti, and *Z*(O), see: Masamune, S.; Kaiho, T.; Garvey, D. S. *J. Am. Chem. Soc.*, preceding communication in this issue.

(8) Lithium enolates normally exist in cubic, tetrameric form as demonstrated by X-ray analysis as well as by solution NMR spectroscopy. The lithium is tetracoordinate: (a) Amstutz, R.; Schweizer, W. B.; Seebach, D.; Dunitz, J. D. *Helv. Chim. Acta* **1981**, *64*, 2617. (b) Seebach, D.; Amstutz, R.; Dunitz, J. D. *Ibid.* **1981**, *64*, 2622. Obviously the actual reaction course of the aldol reaction is extremely complex. Therefore, the model used here simply shows a process of rationalizing the experimental results.

(9) For the definition of this word, see: Masamune, S.; Lu, L. D.-L.; Jackson, W. P.; Kaiho, T.; Toyoda, T. *J. Am. Chem. Soc.*, preceding communication in this issue.

Table I. *Z*:*E* Ratio of the Enolates Derived from Ethyl Ketones

R^2 in 11	base	*Z*:*E* ratio[a]	combined yield of 5a and 10a, %
Et (11a)	*i*-Pr_2NLi	30:70[b]	78
Et (11a)	$(Me_3Si)_2NLi$	70:30[b]	75
Et (11a)	$(Me_2PhSi)_2NLi$ (12)	100:0	78
Et (11a)	$(Et_3Si)_2NLi$	99:1	80
Cy[c] (11b)	*i*-Pr_2NLi	61:39	82
Cy (11b)	$(Me_3Si)_2NLi$	85:15	84
Cy (11b)	$(Me_2PhSi)_2NLi$ (12)	>99:1	90
Cy (11b)	$(Et_3Si)_2NLi$	94:6	89

[a] The enolates were converted into the corresponding trimethylsilyl ethers (5a and 10a), the ratios of which were determined by both GLP chromatography and ^1H NMR spectroscopy (250 MHz). The two analytical methods provided the same results within experimental errors. The ratios of the enolates are assumed to be the same as those of the silyl ether. [b] These two values are in agreement with those reported earlier.[10a] [c] Cy = cyclohexyl.

Table II. Aldol Reaction of 3-Alkoxy-2-methylcarboxaldehydes (4, R = CH_2OCH_2Ph) with the Lithium *Z*(*O*)-Enolate (5, R^2 = Et or Cyclohexyl): 4 + 5 → 8 + 9

entry	R^1 in 4	R^2 in 5	8:9[a]	combined yield of 8 and 9, %
1	H (4a)[b]	Et	4:1	87
2	H (4a)	Cy[c]	3.6:1	79
3	Et (4b)[d]	Et	5:1	81
4	Et (4b)	Cy	9:1	79
5	$PhCD_2$ (4c)[d]	Et	5.5:1	71
6	$PhCD_2$ (4c)	Cy	9:1	70
7	*i*-Pr (4d)[e]	Et	6.9:1	75
8	*i*-Pr (4d)	Cy	11.5:1	68
9	*t*-$BuMe_2SiOCH_2CH_2$ (4e)[e]	Et	13:1	82
10	*t*-$BuMe_2SiOCH_2CH_2$ (4e)	Cy	19:1	79

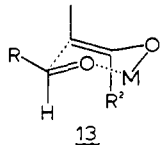
[a] The ratios were determined by ^1H NMR spectroscopy (250 or 270 MHz) and high-pressure liquid chromatography, both of which provide mutually consistent results. [b] 4a [(+)-enantiomer]: (a) Goodhue, G. T.; Schaeffer, J. R. *Biotechnol. Bioeng.* 1971, *13*, 203. (b) Cohen, N.; Eichel, W. F.; Lopresti, R. J.; Neukom, C.; Saucy, G. *J. Org. Chem.* 1976, *41*, 3505. (c) Choy, W.; Ma, P.; Masamune, S. *Tetrahedron Lett.* 1981, *22*, 3555. [c] Cy = cyclohexyl. [d] 4b-d (racemic mixture): Hirama, M.; Garvey, D. S.; Lu, L. D.-L.; Masamune, S. *Tetrahedron Lett.* 1979, 3937. [e] 4e [(+)-enantiomer]: Masamune, S.; Choy, W.; Kerdesky, F. A. J.; Imperiali, B. *J. Am. Chem. Soc.* 1981, *103*, 1566.

Exclusive Formation of the *Z*-Enolates from Ethyl Ketones. In general the *Z*:*E* ratio of the two geometrically differing enolates **5** and **10** generated from an ethyl ketone (**11**, Scheme III) with a lithium amide depends largely on the size of the R^2 group in **11** as well as the basicity and steric bulk of the base used.[10a] Thus, while treatment of 2,2-dimethylpentan-3-one (**11** with a bulky R^2) with lithium diisopropylamide provides its *Z*-enolate (**5**, R^2 = *t*-Bu) quantitatively, the *direct* exclusive generation of the *Z*-lithium enolate from a ketone with a less bulky substituent R^2 such as ethyl has not been realized.[10a] Of the numerous bases examined, we now find one that achieves this task. In the case of pentan-3-one (**11a**) and of ethyl cyclohexyl ketone (**11b**), chosen as representative ethyl ketones having a small and a medium R^2 group, respectively, reaction with a few of the bases provides the *Z*:*E* ratios shown in Table I, as analyzed by the corresponding trimethylsilyl ethers (**5a** and **10a**) obtained from their lithium enolates.[10b] Clearly, in both cases, **11a** and **11b**, the ratio is significantly enhanced as the size of the substituents of the disilazide increases, and in particular, the use of lithium 1,1,3,3-tetramethyl-1,3-diphenyldisilazide (**12**)[11] leads to the exclusive

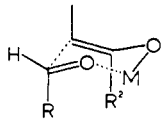
(10) For comments on this subject, see the supplementary material; "a" of "10a" indicates section a of this attachment.

formation of Z-enolates. This last finding is general for a variety of simple ketones and obviously has great synthetic utility.

Aldol Reaction of 4 with a Lithium Z-Enolate. The 3-hydroxy-2-methylcarboxylic acid esters corresponding to **4a-e** (see Scheme II) are prepared according to known procedures (Table II) in either optically active or racemic form and then are converted to the aldehydes **4a-e** in the usual fashion. The aldol reaction with the Z-enolate generated with **12** proceeds efficiently (<5 min) at -78 °C to provide two major products, **8** and **9**,[10c] in 70-90% yield in addition to minor 2,3-anti stereoisomers corresponding to **8** and **9**. The amounts of these 2,3-anti isomers are significantly smaller[10d] than those observed in the aldol reaction with an aldehyde carrying no alkoxy substituent. In the latter general case, the reaction proceeds rather nonselectively even with the pure Z-enolate of pentan-3-one.[10e] The two enolate approaches to this aldehyde are shown in **13** and **14**, which lead to the 2,3-syn



13



14

and 2,3-anti product, respectively. The selection between the two approaches depends *largely* on the steric bulk of R^2, and thus only enolates with an extremely large R^2 (e.g., *t*-Bu) proceed exclusively through the transition-state **13**.[10b,e] While the size of R^2 is still important in the reaction with **4**, the β-alkoxy substituent in the transition state organizes a rigid framework (with the lithium cation) which would steer the reaction to create the 2,3-syn stereochemistry. More importantly the interaction between the enolate with R^2 and the two groups, methyl and in particular R^1, of the aldehyde causes the energy difference between **6** and **7**, which is translated into the ratio of **8** and **9**. With a small interaction (entries 1-3 in Table II) the ratio ranges between 3.5:1 to 5:1 and increases to approximately 10:1 with R^1 = primary or secondary alkyl and R^2 = secondary alkyl (entries 4, 6, 8). Most significantly, when R^1 carries an additional ethereal substituent, thus creating yet another ligand to coordinate the lithium cation, the observed selectivities (entries 9, 10) now exceed 10:1.[12] The synthetic significance of the above findings will be clearly demonstrated in the following communication.

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Registry No. (±)-**4a**, 79027-30-8; (±)-**4b**, 82892-19-1; (±)-**4c**, 82892-20-4; (±)-**4d**, 82892-21-5; (+)-**4e**, 82892-22-6; **5** (R^2 = Et), 74016-27-6; **5** (R^2 = Cy), 82892-23-7; **5a**, 51425-54-8; **5b**, 76436-98-1; (±)-**8** (R = CH_2OCH_2Ph; R^1 = H; R^2 = Et), 82892-24-8; (±)-**8** (R = CH_2OCH_2Ph; R^1 = H; R^2 = Cy), 82892-25-9; (±)-**8** (R = CH_2OCH_2Ph; R^1 = Et; R^2 = Et), 82892-26-0; (±)-**8** (R = CH_2OCH_2Ph; R^1 = Et; R^2 = Cy), 82892-27-1; (±)-**8** (R = CH_2OCH_2Ph; R^1 = CD_2Ph; R^2 = Et), 82892-28-2; (±)-**8** (R = CH_2OCH_2Ph; R^1 = CD_2Ph; R^2 = Cy), 82892-29-3; (±)-**8** (R = CH_2OCH_2Ph; R^1 = *i*-Pr; R^2 = Et), 82892-30-6; (±)-**8** (R = CH_2OCH_2Ph; R^1 = *i*-Pr; R^2 = Cy), 82892-31-7; **8** (R = CH_2OCH_2Ph; R^1 = $CH_2CH_2DSiMe_2Bu$-*t*; R^2 = Et), 82892-32-8; **8** (R = CH_2OCH_2Ph; R^1 = $CH_2CH_2OSiMe_2Bu$-*t*; R^2 = Cy), 82892-33-9; (±)-**9** (R = CH_2OCH_2Ph; R^1 = H; R^2 = Et), 82916-75-4; (±)-**9** (R = CH_2OCH_2Ph; R^1 = H; R^2 = Cy), 82916-76-5; (±)-**9** (R = CH_2OCH_2Ph; R^1 = Et; R^2 = Et), 82916-77-6; (±)-**9** (R = CH_2OCH_2Ph; R^1 = Et; R^2 = Cy), 82916-78-7; (±)-**9** (R = CH_2OCH_2Ph; R^1 = CD_2Ph; R^2 = Et), 82916-79-8; (±)-**9** (R = CH_2OCH_2Ph; R^1 = CD_2Ph; R^2 = Cy), 82916-80-1; (±)-**9** (R = CH_2OCH_2Ph; R^1 = *i*-Pr; R^2 = Et), 82916-81-2; (±)-**9** (R = CH_2OCH_2Ph; R^1 = *i*-Pr; R^2 = Cy), 82916-82-3; **9** (R = CH_2OCH_2Ph; R^1 = $CH_2CH_2OSiMeBu$-*t*; R^2 = Et), 82916-83-4; **9** (R = CH_2OCH_2Ph; R^1 = $CH_2CH_2OSiMeBu$-*t*; R^2 = Cy), 82916-84-5; **10a**, 51425-53-7; **10b**, 76437-07-5; **11a**, 96-22-0; **11b**, 1123-86-0; **12**, 82892-34-0; $(i\text{-Pr})_2NLi$, 4111-54-0; $(Me_3Si)_2NLi$, 4039-32-1; $(Et_3Si)_2NLi$, 82892-35-1; $(PhMe_2Si)_2NH$, 3449-26-1; $(Et_3Si)_2NH$, 2117-18-2.

Supplementary Material Available: Listing of spectral data and comments (6 pages). Ordering information is given on any current masthead page.

(11) Zhinkin, D. Y.; Mal'nova, G. N.; Gorislavskaya, Zh. V. *Zh. Obshch. Khim.* **1968**, *38*, 2800.

(12) It should be cautioned that when the lithium or magnesium enolate is generated from a methyl or ethyl ketone with an R^2 carrying an alkoxy group in **11**, the cation definitely coordinates *intramolecularly* with this ethereal substituent, unless it is protected with a bulky group.[6] In the aldol reaction of such an enolate with **4**, the *intermolecular* coordination of the cation with the alkoxyl substituent of **4** is lessened significantly and is perhaps nearly nonexistent in some cases. The stereochemical outcome of this reaction should be different from that described in the text. Examples are found in the last aldol reaction used to combine two major fragments of monensin. Monensin: (a) Collum, D. B.; McDonald, J. H., III; Still, W. C. *J. Am. Chem. Soc.* **1980**, *102*, 2120. (b) Fukuyama, T.; Akasaka, K.; Karanewsky, D. S.; Wang, C.-L. J.; Schmid, G.; Kishi, Y. *Ibid.* **1979**, *101*, 262. Other examples: (c) Masamune, S., to be submitted for publication.

Synthesis of Ansamycins: The Ansa Chain of Rifamycin S

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The antibiotic rifamycin S (**1**)[1] is a well-known representative member of the ansamycin family.[2] The unique structure of this compound[3] is characterized by the naphthoquinone moiety bridged at the 2- and 12-positions by the "ansa" chain (**2**, Scheme I), which is rich in chirality. Our synthetic interest in this chain arises from the presence of a symmetry element that becomes all the more evident with two retrosynthetic operations: (1) oxidation of the C(23)-hydroxyl group to the ketone and (2) hydration of the C(18)-C(19) double bond (see **3**). The C(18)-C(28) fragment, incorporating all the chiral centers in **3**, now has C_s symmetry (if R^2 = Me). Dissection of **3** leads to a set of four units, A, B, A′, C (retrosynthesis I), or another set, A, B, C, D (retrosynthesis II), the former (I) being more symmetrical than the latter. Note that (1) units A and A′ are enantiomeric and are readily available in >99% optically pure form through a diastereoselective aldol reaction[4] and that (2) each half [C(18)-C(23) and C(23)-C(28)] of the fragment **3** constitutes a 2,3-*syn*,3,4-*anti*,4,5-*syn*-2,4-dihydroxy-3,5-dimethylcarbonyl system (numbering starts with the carbonyl group)[5] whose stereoselective synthesis can now be achieved again by a single aldol reaction.[6] Thus full recognition and *utilization* of this symmetry will simplify, to a great extent,

(1) For the isolation of **1** from the fermentation broths of *Nocardia mediterranei* (formerly known as *Streptomyces mediterranei*), see: Sensi, P.; Greco, A. M.; Ballotta, R. *Antibiot. Ann.* **1960**, 262.

(2) For reviews of the ansamycins: (a) Brufani, M. In "Topics in Antibiotic Chemistry"; Sammes P., Ed.; Ellis Horwood: Sussex, 1977; Vol. 1, Part B. (b) Rinehart, K. L., Jr.; Shield, L. S. In "Progress in the Chemistry of Organic Natural Products"; Herz, W., Grisebach, H., Kirby, G. W., Eds.; Springer-Verlag: New York, 1976; Vol. 33, pp 231-307.

(3) For the classical chemical degradation work, see: (a) Prelog, V. *Pure Appl. Chem.* **1963**, *7*, 551. (b) Oppolzer, W.; Prelog, V. *Helv. Chim. Acta* **1973**, *56*, 287. For the crystallographic analysis of rifamycin B *p*-iodoanilide, see: (c) Brufani, M.; Fedeli, W.; Giacomello, G.; Vaciago, A. *Atti Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Nat., Rend.* **1964**, *36*, 113; *Experientia* **1964**, *20*, 339.

(4) Masamune, S.; Choy, W.; Kerdesky, F. A. J.; Imperiali, B. *J. Am. Chem. Soc.* **1981**, *103*, 1566.

(5) For the definition of syn and anti, see: Masamune, S.; Kaiho, T.; Garvey, D. S. *J. Am. Chem. Soc.*, preceding communication in this issue.

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