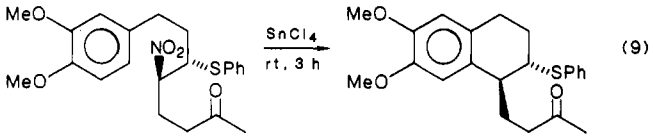
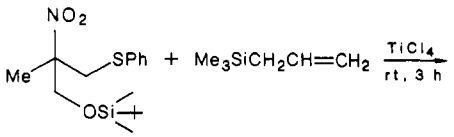
β-nitro sulfides underwent the highly stereoselective formation of carbon–carbon bonds by nitro displacement as shown in eq 3–8 (Scheme I). In every case, the anti isomer reacted with nucleophiles more rapidly than the corresponding syn isomer. When the 1:1 mixture of *anti*-**7** and *syn*-**7** was allowed to react with cyanotrimethylsilane at 0 °C, only *anti*-**7** was consumed for 5 min to give *anti*-**8** and *syn*-**7** was recovered. Exposure of β-nitro sulfide (**9**) to $SnCl_4$ in CH_2Cl_2 gave cyclic products, where the reaction proceeded stereoselectively. As *anti*-**9** and *syn*-**9** gave *trans*-**10** and *cis*-**10**,[10] the reaction proceeds with retention of configuration which supports the intermediacy of episulfonium ions.[11] Considering the retention of configuration, the products of the reaction of eq 3–6 should be as shown. The nitro group can be replaced by nucleophiles after it has served as an activating group for carbon–carbon bond formation. For example, the Michael addition or nitro aldol condensation of β-nitro sulfides and subsequent substitution reactions such as those of eq 9 and 10 provides a useful synthetic method, where nitro compounds serve as 1,1-dipole synthons.[12]

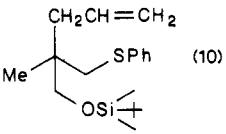


(9)

anti-**11** *trans*-**12** 86%



13



(10)

14 50%

Registry No. 1 (R^1 = Me, R^2 = Me, R^3 = H), 52265-30-2; 1 (R^1 = Me, R^2 = Et, R^3 = H), 109585-25-3; 1 (R^1 = Me, R^2 = C_6H_{13}, R^3 = H), 109585-26-4; 1 (R^1 = Ph, R^2 = H, R^3 = H), 4231-84-9; 1 (R^1 = $(CH_2)_4$ = R^2, R^3 = H), 109585-27-5; *anti*-1 (R^1 = Me, R^2 = H, R^3 = Me), 109585-28-6; *anti*-1 (R^1 = Me, R^2 = H, R^3 = Et), 109585-29-7; *syn*-1 (R^1 = Me, R^2 = H, R^3 = Et), 109585-60-6; *anti*-1 (R^1 = Et, R^2 = H, R^3 = Me), 109585-30-0; *syn*-1 (R^1 = Et, R^2 = H, R^3 = Me), 109585-61-7; 1 (R^1 = H, R^2 = H, R^3 = Et), 109585-31-1; **2** (R^1 = R^2 = Me, R^3 = H, Y = CN), 109585-32-2; **2** (R^1 = R^2 = Me, R^3 = H, Y = CH_2CH =CH_2), 89113-74-6; **2** (R^1 = Me, R^2 = Et, R^3 = H, Y = CN), 109585-35-5; **2** (R^1 = Me, R^2 = Et, R^3 = H, Y = CH_2CH = CH_2), 109585-37-7; **2** (R^1 = Me, R^2 = C_6H_{13}, R^3 = H, Y = CN), 109585-39-9; **2** (R^1 = Ph, R^2 = R^3 = H, Y = CH_2CH = CH_2), 89113-73-5; **2** (R^1 = R^2 = $(CH_2)_4$, R^3 = H, Y = CN), 109585-42-4; **2** (R^1 = Me, R^2 = H, R^3 = Et, Y = CH_2CH=CH_2), 109585-44-6; **2** (R^1 = R^2 = H, R^3 = Et, Y = CH_2CH = CH_2), 109585-46-8; **3** (R^1 = R^2 = Me, R^3 = H, Y = CN), 109585-33-3; **3** (R^1 = R^2 = Me, R^3 = H, Y = CH_2CH=CH_2), 109585-34-4; **3** (R^1 = Me, R^2 = Et, R^3 = H, Y = CN), 109585-36-6; **3** (R^1 = Me, R^2 = Et, R^3 = H, Y = CH_2CH=CH_2), 109585-38-8; **3** (R^1 = Me, R^2 = C_6H_{13}, R^3 = H, Y = CN), 109585-40-2; **3** (R^1 = Ph, R^2 = R^3 = H, Y = CH_2CH=CH_2), 109585-41-3; **3** (R^1 = R^2 = $(CH_2)_4$, R^3 = H, Y = CN), 109585-43-5; **3** (R^1 = Me, R^2 = H, R^3 = Et, Y = CH_2CH=CH_2), 109585-45-7; **3** (R^1 = R^2 = H, R^3 = Et, Y = CH_2CH = CH_2), 109585-47-9; (*E*)-**4**, 27748-48-7; *syn*-**5**, 109585-48-0; **6**-A, 89127-69-5; **6**-B, 89113-70-2; *anti*-**F**, 109585-49-1; *syn*-**F**, 109636-86-4; *anti*-**8**, 109585-50-4; *syn*-**8**, 109585-51-5; *anti*-**9**, 109585-52-6; *syn*-**9**, 109585-54-8; *trans*-**10**, 109585-53-7; *cis*-**10**, 109585-55-9; *anti*-**11**, 109585-56-0; *trans*-**12**, 109585-57-1; **13**, 109585-58-2; **14**, 109585-59-3; Me_3SiCN, 7677-24-9; Me_3SiCH_2CH=CH_2, 762-72-1; PhSLi, 2973-86-6.

(9) NMR data of β-nitro sulfides. *anti*-**5**: δ 1.33 (d, 3 H, *J* = 7 Hz), 1.66 (d, 3 H, *J* = 7 Hz), 3.52 (q, d, *J* = 7, 7 Hz, 1 H) 4.40 (q, d, *J* = 7, 7 Hz, 1 H), 7.2–7.5 (m, 5 H). *syn*-**5**: δ 1.27 (d, 3 H, *J* = 7 Hz), 1.55 (d, 3 H, *J* = 7 Hz), 3.80 (q, d, 1 H, *J* = 7, 7 Hz), 4.40 (q, d, 1 H, *J* = 7, 7 Hz), 7.2–7.5 (m, 5 H). *anti*-**7**: mp 47 °C; δ 1.31 (d, 3 H, *J* = 7 Hz), 1.60–2.40 (m, 6 H), 3.71 (q, d, 1 H, *J* = 7, 7 Hz), 5.03 (m, 1 H), 5.93 (m, 1 H), 7.1–7.6 (m, 5 H). *syn*-**7**: mp 58 °C, δ 1.62–2.04 (m, 6 H), 3.80 (q, d, 1 H, *J* = 7, 7 Hz), 5.03 (m, 1 H), 5.50 (m, 1 H), 7.1–7.6 (m, 5 H). *anti*-**9**: δ 1.60 (d, 3 H, *J* = 7 Hz), 1.84 (m, 2 H), 2.78 (t, 2 H, *J* = 7 Hz), 3.36 (t, d, 2 H, *J* = 7, 7 Hz), 4.55 (q, d, 1 H, *J* = 7, 7 Hz), 7.1–7.5 (m, 5 H). *syn*-**9**: δ 1.56 (d, 3 H, *J* = 7 Hz), 1.84 (m, 2 H), 2.80 (t, 2 H, *J* = 7 Hz), 3.56 (q, d, 1 H, *J* = 7, 7 Hz), 4.50 (q, d, 1 H, *J* = 7, 7 Hz), 7.1–7.5 (m, 5 H).

(10) Spectral data of these compounds. *trans*-**10**: NMR ($CDCl_3$) δ 1.40 (d, 3 H, *J* = 7 Hz), 1.60–2.25 (m, 2 H), 2.50–3.20 (m, 3 H), 3.36 (m, 1 H), 7.0–7.6 (m, 9 H); MS (M^+) calcd for $C_{17}H_{18}OS$ 254.1139, obsd 254.1152. *cis*-**10**: NMR ($CDCl_3$) δ 1.27 (d, 3 H, *J* = 7 Hz), 1.70–2.43 (m, 2 H), 2.55–3.30 (m, 3 H), 3.70 (m, 1 H), 7.2–7.6 (m, 9 H); MS (M^+) obsd 254.1148. As the quasi-equatrial methyl of *trans*-**10** is deshielded relative to the quasi-axial methyl of *cis*-**10**, they are readily assigned. *trans*-**12**: 1.90–2.20 (m, 2 H), 2.08 (s, 3 H), 2.20–3.03 (m, 8 H), 3.84 (s, 3 H), 3.99 (s, 3 H), 6.84 (s, 1 H), 7.02 (s, 1 H), 7.2–7.5 (m, 5 H); MS (M^+) calcd for $C_{22}H_{26}SO_3$ 370.1602, obsd 370.1601. All other compounds have been fully charactilized by IR, NMR, and MS spectral data as appropriate. Satisfactory elemental analyses have been obtained on all new compounds.

(11) Smit, W. A.; Zefitrov, N. S.; Bodtokov, I. V.; Krimer, N. A. *Acc. Chem. Res.* **1979**, *12*, 282.

(12) Sulfones as 1,1-dipoles, see: Trost, B. M.; Ghadiri, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 7260.

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Synthesis of the Upper Spirotetronic Acid Fragment of Kijanolide

Summary: Two approaches to the upper fragment of kijanolide (**1**), which involve Diels–Alder reactions of functionalized triene **8** with propynal and of triene **20** with methyl 5-methylenetetronate (**22**), are reported.

Sir: Kijanolide (**1**) and tetronolide (**2**), the aglycons of macrocyclic antibiotics kijanimicin[1] and tetrocarcin,[2] have attracted considerable synthetic interest since elucidation of the structures in 1980. Marshall et al.[3] recently reported a stereoselective synthesis of the lower octalin fragment, common between **1** and **2**, by Lewis acid catalyzed intramolecular Diels–Alder cyclization of an (*all-E*)-2,8,10,12-tetradecatetraenal intermediate; the novel technique initially developed in their synthetic study on the analogous subunit of chlorothricolide (**3**).[4] More recently, our group

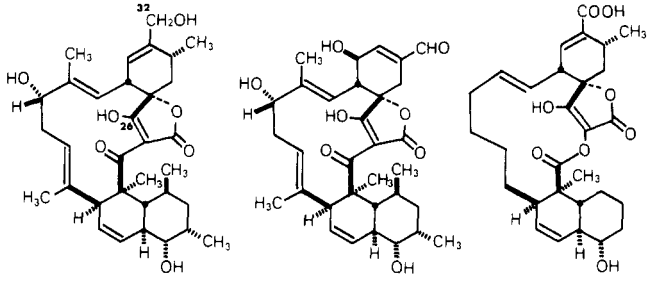
(1) (a) Mallams, A. K.; Puar, M. S.; Rossman, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 3938–3940. (b) Mallams, A. K.; Puar, M. S.; Rossman, R. R.; McPhail, A. T.; Macfarlane, R. D. *Ibid.* **1981**, *103*, 3940–3943. (c) Mallams, A. K.; Puar, M. S.; Rossman, R. R.; McPhail, A. T.; Macfarlane, R. D.; Stephens, R. L. *J. Chem. Soc., Perkin Trans. 1* **1983**, 1497–1534.

(2) (a) Hirayama, N.; Kasai, M.; Shirahata, K.; Ohashi, Y.; Sasada, Y. *Tetrahedron Lett.* **1980**, *21*, 2559–2560. (b) Tomita, F.; Tamaoki, T.; Shirahata, K.; Kasai, M.; Morimoto, M.; Ohkubo, S.; Mineura, K.; Ishii, S. *J. Antibiot.* **1980**, *33*, 668–670. (c) Tomita, F.; Tamaoki, T. *Ibid.* **1980**, *33*, 940–945. (d) Tamaoki, T.; Kasai, M.; Shirahata, K.; Ohkubo, S.; Morimoto, M.; Mineura, K.; Ishii, S.; Tomita, F. *Ibid.* **1980**, *33*, 946–950. (e) Tamaoki, T.; Kasai, M.; Shirahata, K.; Tomita, F. *Ibid.* **1982**, *35*, 979–984.

(3) Marshall, J. A.; Grote, J.; Shearer, B. *J. Org. Chem.* **1986**, *51*, 1633–1635.

0022-3263/87/1952-4135$01.50/0

described the first synthesis[5] of the upper spirotetronic acid fragment of **2** and also introduced a methodology[6] for the construction of the macrocyclic nucleus which involves assemblage of two upper and lower subunits. Described here is the first synthesis of the upper fragment of **1** by utilizing Diels–Alder reaction for placing the cis side chains on the cyclohexene ring.[7]



1 **2** **3**

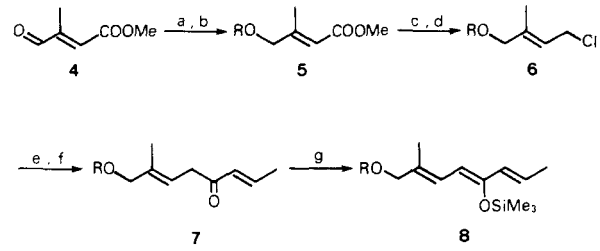
The (trimethylsilyl)oxy triene **8** (a 9:1 mixture of 4*Z* and 4*E* isomers), prepared from methyl γ-oxosenecioate (**4**) as outlined in Scheme I, was allowed to react with excess propargyl aldehyde in refluxing toluene to afford, in ca. 60% yield, a mixture of regioisomeric cycloadducts **9** and **10** (ratio, 1:1.4)[9] which was separable by silica gel chromatography (Scheme II). The structures were assigned by decoupling experiments in the ^{1}H NMR. The desired adduct **9** was reduced with *i*-Bu_2AlH to the corresponding alcohol, which was led to *O*-*tert*-butyldimethylsilyl derivative **11**. This cyclohexadienol silyl ether was subjected to selective desilylation under carefully controlled conditions (HF_x–pyridine[10] in acetonitrile at room temperature,

Table I. ^{1}H NMR Comparison of 16 with Kijanolide

	16	26,32-di-*O*-methyl-kijanolide[a]
H-6	3.49 (dm, 11.5)	3.42 (d, 9.7)
H-7	5.43 (br s)	5.47 (s)
H-9	2.62 (dqd, 7.3, 7.3, 1.5)	2.61 (dq, 7.0, 7.5)
H-10	1.71 (dd, 14.2, 1.5)	1.76 (d, 14.1)
	2.28 (dd, 14.2, 7.3)	2.33 (dd, 14.1, 7.0)
Me-9	1.26 (d, 7.3)	1.28 (d, 7.5)

[a] Kijanolide numbering as indicated in structure 1.

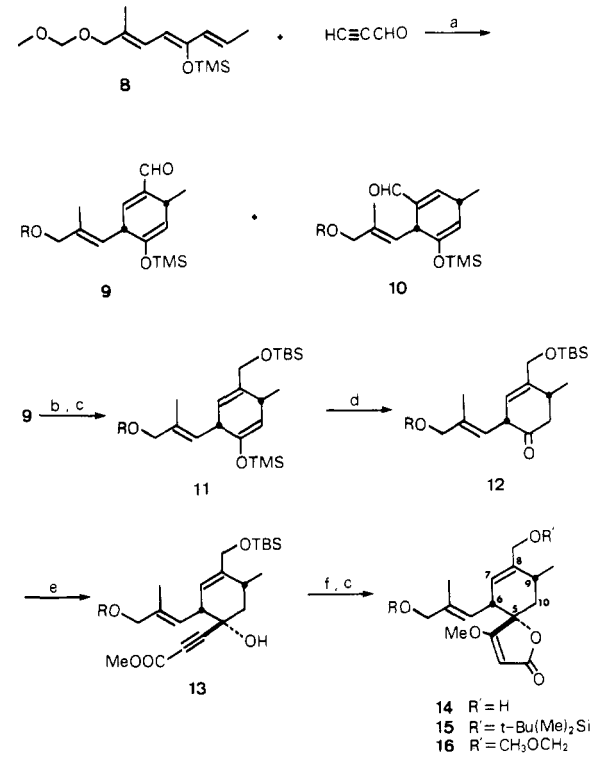
Scheme I[a,8]



4 **5** **6** **7** **8**

[a] R = CH_3OCH_2; (a) $NaBH_4$, $CeCl_3$, MeOH, 0 °C (92%); (b) CH_3OCH_2Cl, *i*-Pr_2NEt, CH_2Cl_2, room temperature (90%); (c) *i*-Bu_2AlH, Et_2O, 0 °C (81%); (d) NCS, Me_2S, CH_2Cl_2, −20 °C to 10 °C (88%); (e) (*E*)-CH_3CH=$CHCH(CN)OSiMe_3$, LDA, THF, −78 °C, then **6**, to −50 °C (90%); (f) HF, MeCN, room temperature, then aqueous $NaHCO_3$, 40 °C (94%); (g) LDA, HMPA, THF, −78 °C, then Me_3SiCl, to −40 °C (81%).

Scheme II[a,8]



8 **9** **10** **11** **12** **13**

14 R′ = H
15 R′ = t-Bu(Me)$_2$Si
16 R′ = CH_3OCH_2

[a] R = CH_3OCH_2; (a) PhMe, reflux, 20 h (59%, 9/10 = 1:1.4∼1.7); (b) *i*-Bu_2AlH, Et_2O, 0 °C; (c) *t*-Bu(Me)$_2$SiCl, imidazole, DMF, room temperature; (d) HF_x–pyridine, MeCN, room temperature (52% from **9**); (e) Cl_2CeC≡$CCOOMe$, THF, −100 °C to −35 °C (63%); (f) MeOK, MeOH, reflux (57%).

few minutes) to give β,γ-unsaturated cyclohexenone **12** in 52% yield from **9**. Prolonged reaction or use of *n*-Bu_4NF for the desilylation resulted in extensive epimerization of the side chain and/or elimination of *tert*-butyldimethylsilanol to give conjugated trienes and further decomposition products.

Treatment of the ketone **12** with 6 equiv of Cl_2CeC≡$CCOOMe$[11] (generated from LiC≡$CCOOMe$ and $CeCl_3$)[12]

(4) Synthetic work on chlorothricolide. (a) Marshall, J. A.; Shearer, B. G.; Crooks, S. L. *J. Org. Chem.* **1987**, *52*, 1236–1245. (b) Marshall, J. A.; Grote, J.; Audia, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1186–1194. (c) Marshall, J. A.; Audia, J. E.; Grote, J.; Shearer, B. G. *Tetrahedron* **1986**, *42*, 2893–2902. (d) Marshall, J. A.; Audia, J. E.; Shearer, B. G. *J. Org. Chem.* **1986**, *51*, 1730–1735. (e) Marshall, J. A.; Audia, J. E.; Grote, J. *J. Org. Chem.* **1986**, *51*, 1155–1157. (f) Ireland, R. E.; Varney, M. D. *J. Org. Chem.* **1986**, *51*, 635–648. (g) Boeckman, R. K., Jr.; Barta, T. E. *J. Org. Chem.* **1985**, *50*, 3421–3423. (h) Roush, W. R.; Kageyama, M. *Tetrahedron Lett.* **1985**, *26*, 4327–4330. (i) Marshall, J. A.; Audia, J. E.; Grote, J. *J. Org. Chem.* **1984**, *49*, 5277–5279. (j) Schmidt, R. R.; Hirsenkorn, R. *Tetrahedron Lett.* **1984**, *25*, 4357–4360. (k) Snider, B. B.; Burbaum, B. W. *J. Org. Chem.* **1983**, *48*, 4370–4374. (l) Roush, W. R.; Gillis, H. R. *J. Org. Chem.* **1982**, *47*, 4825–4829. (m) Hall, S. E.; Roush, W. R. *J. Org. Chem.* **1982**, *47*, 4611–4621. (n) Takeda, K.; Shinagawa, M.; Koizumi, T.; Yoshii, E. *Chem. Pharm. Bull.* **1982**, *30*, 4000–4005. (o) Roush, W. R.; Hall, S. E. *J. Am. Chem. Soc.* **1981**, *103*, 5200–5211. (p) Ireland, R. E.; Thompson, W. J.; Srouji, G. H.; Etter, R. *J. Org. Chem.* **1981**, *46*, 4863–4873. (q) Ireland, R. E.; Thompson, W. J. *J. Org. Chem.* **1979**, *44*, 3041–3052.

(5) Takeda, K.; Kato, H.; Sasahara, H.; Yoshii, E. *J. Chem. Soc., Chem. Commun.* **1986**, 1197–1198.

(6) (a) Takeda, K.; Urahata, M.; Yoshii, E.; Takayanagi, H.; Ogura, H. *J. Org. Chem.* **1986**, *51*, 4735–4737. (b) Takeda, K.; Shibata, Y.; Sagawa, Y.; Urahata, M.; Funaki, K.; Hori, K.; Sasahara, H.; Yoshii, E. *J. Org. Chem.* **1985**, *50*, 4673–4681.

(7) An attempt to utilize the same strategy for the synthesis of the upper fragment of **3** has been reported (ref 4j).

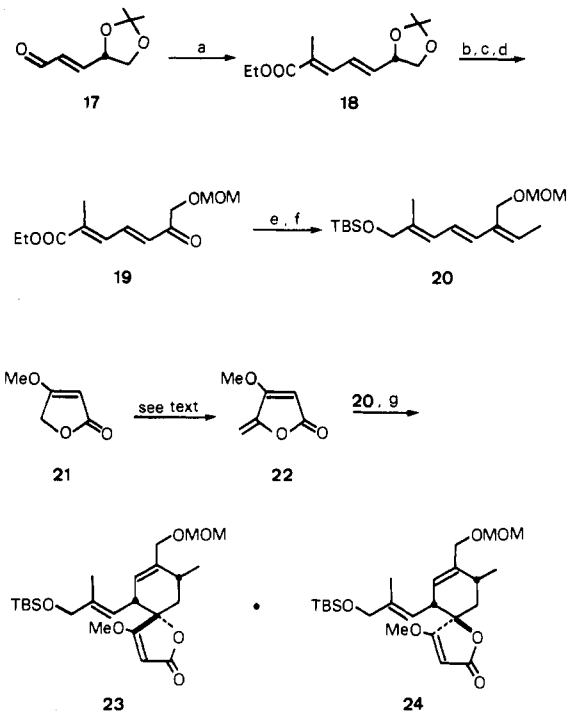
(8) All compounds containing chiral centers are racemic. One enantiomer corresponding to **1** is depicted for graphic simplicity.

(9) A similar regioisomeric ratio was obtained with methyl propiolate.

(10) Trost, B. M.; Caldwell, C. G.; Murayama, E.; Heissler, D. *J. Org. Chem.* **1983**, *48*, 3252–3265. For the selective desilylation of **11**, the presence of excess pyridine was detrimental causing extensive epimerization of the product ketone **12**.

(11) Ethynylation of highly enolizable 2-tetralones with TMSC≡$CCeCl_2$ was introduced by S. Terashima. (a) Suzuki, M.; Kimura, Y.; Terashima, S. *Chem. Lett.* **1984**, 1543–1546. (b) Tamura, Y.; Sasho, M.; Akai, S.; Kishimoto, H.; Sekihachi, J.-I.; Kita, Y. *Tetrahedron Lett.* **1986**, *27*, 195–198.

Scheme III[a,8]



[a] (a) $Ph_3P{=}C(Me)COOEt$, PhH, room temperature (96%, 2E/2Z = ca. 7:3); (b) p-TsOH, MeCN, H_2O, reflux (92%); (c) CH_3OCH_2Cl, i-Pr_2NEt, CH_2Cl_2, -50 °C to -20 °C (52%); (d) Swern oxidation (77%, 2E/2Z = ca. 9:1); (e) $Ph_3P{=}CHCH_3$, THF, -70 °C to room temperature (70%); (f) i-Bu_2AlH, Et_2O, 0 °C, then t-Bu(Me)$_2$SiCl, imidazole, DMF, room temperature (98%, ca. 90% purity); (g) o-$C_6H_4(Cl)_2$, 180 °C, (43%).

produced the acetylenic carbinol **13** as a single adduct in 63% yield. The stereochemistry at the carbinol center was determined at the next stage. The equatorial attack of the acetylide presumably derives from the nonbonded interaction associated with the pseudoaxial methyl substituent[13] and, to some extent, from the bulkiness of the Ce metal.[14] Transformation of **13** into spirotetronate **15** was cleanly achieved in 57% yield by heating with methanolic MeOK,[15] followed by O-silylation. The stereostructure of **15** was determined on the basis of ^1H NMR spectral analysis of the derived di-MOM ether **16**. As shown in Table I, compound **16** and di-*O*-methylkijanolide[1c] are very similar in the chemical shifts and coupling constants for the protons on the cyclohexene rings.

The second route to the upper fragment of **1** we envisaged was direct construction of the functionalized spiro ring by Diels-Alder cyclization of 5-methylenetetronate **22** with an appropriate triene. The dienophile **22** was prepared from methyl tetronate (**21**) by three steps: (1) (dimethylamino)methylenation at C(5) with $(Me_2N)_2CHOMe$;[16] (2) $NaBH_3CN$ reduction; (3) quaternization of the resulting 5-[(dimethylamino)methyl]tetronate with MeI followed by treatment with aqueous $NaHCO_3$ (72% overall yield, without purification of intermediates). The requisite triene **20** was prepared by the route shown in Scheme III.

Cycloaddition of **20** and **22** proceeded sluggishly, in contrast to a facile intramolecular version that we had employed in the total synthesis[17] of (±)-ircinianin, a marine sponge sesterterpene. After heating in *o*-dichlorobenzene at 180 °C for 7 h, there was obtained a mixture of diastereomeric adducts **23** and **24** (ratio, 1:3; separable by HPLC) in a combined yield of 43%. The ^1H NMR spectrum of the minor isomer **23** was quite similar to that of **16** in terms of chemical shifts and coupling constants. On the other hand, the major isomer **24** was significantly different from **23** in H-6$_\beta$ and H-10$_\beta$ resonances, upfield shifts of 0.31 and 0.44 ppm, respectively, which could be attributable to a shielding effect of the tetronate carbonyl in vicinity. The stereostructure of **23** was confirmed by the identity of the derived di-MOM ether with **16** in ^1H NMR.

In conclusion, of the two approaches described above, the first one (Scheme II) is evidently advantageous in terms of selectivity and yield in the crucial Diels-Alder cyclization. Synthesis of the top-half of **3** using the same strategy is in progress in this laboratory.

Note Added in Proof. The unfavorable product ratio of **9**/**10** (1:1.4-1.7) (Scheme II) could have been greatly improved to 7.2:1 (48% yield) by conducting the Diels-Alder reaction in trichloroethylene (ca. 80 °C, 14 h) and in the presence of Yb(fod)$_3$ (4 mol %).

Supplementary Material Available: Experimental details and spectral data of compounds used (12 pages). Ordering information is given on any current masthead page.

(12) (a) Imamoto, T.; Kusumoto, T.; Tawarayama, Y.; Sugiura, Y.; Mita, T.; Hatanaka, Y.; Yokoyama, M. *J. Org. Chem.* **1984**, *49*, 3904-3912. (b) Imamoto, T.; Sugiura, Y.; Takiyama, N. *Tetrahedron Lett.* **1984**, *25*, 4233-4236.

(13) For preferential axial attack of lithiopropiolate to unhindered cyclohexanone systems, see: Caine, D.; Smith, T. L., Jr. *Synth. Commun.* **1980**, *10*, 751-759; *J. Am. Chem. Soc.* **1980**, *102*, 7568-7570.

(14) With 2-methylcyclohexanone we observed the following ratios of axial to equatorial attack in THF: LiC≡CCOOMe, 67/33; $Cl_2CeC{\equiv}$CCOOMe, 43/57.

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Received May 18, 1987

Seeking the Ideal Dehydrating Reagent

Summary: A set of "phosphonium anhydride" reagents is shown to have virtually ideal properties as selective oxygen extractors for net dehydration reactions in a series of illustrative examples.

Sir: A reaction central to synthesis is the bonding of an electrophile to oxygen to activate its release as a leaving group via elimination or substitution reactions, the overall result a net loss of water. Many electrophiles have been used for this purpose,[1] and all have drawbacks. In a project calling for formation of 2-arylbenzimidazoles from an aryl carboxylic acid and a substituted *o*-phenylenediamine, we found that the standard procedures were quite inadequate, as were many common phosphorus reagents. We focused on phosphorus electrophiles because of the unusual strength of the P-O bond. This implies avid first attack on oxygen and a very favorable second step releasing the oxygen as a phosphoryl group, the net effect an overall dehydration. We sought a reagent easy to prepare, se-

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