In summary, our results as well as those of other workers[2-5,8] demonstrate that a wide variety of spiro, bridged, and fused polycyclic systems can be assembled by intramolecular palladium-catalyzed alkene arylations. The studies reported here specifically illustrate the ease with which quaternary centers can be formed by intramolecular Heck reactions and demonstrate that intramolecularity can overcome the usual reluctance of highly substituted alkenes to participate in palladium-catalyzed reactions. Our results also show that competing palladium-catalyzed isomerization of the alkene product can be greatly reduced by conducting the cyclization at room temperature in the presence of a silver salt. Since the cyclization substrates are typically available in just a few steps from commercial materials, we anticipate that intramolecular alkene arylations will prove useful for preparing a variety of complex aromatic heterocyclic as well as carbocyclic natural products. Studies in these areas are currently underway in our laboratories.

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Registry No. **1**, 509-15-9; **2b** (X = Br), 102804-51-3; **2b** (X = I), 109686-67-1; **2c** (X = Br), 109686-65-9; **2d** (X = Br), 109686-66-0; **3b**, 109686-68-2; **3b** (regioisomer), 109686-71-7; **3c**, 109686-69-3; **3d**, 109686-70-6; **4a**, 109686-42-2; **4b**, 109686-43-3; **5** (regioisomer 1), 109686-57-9; **5** (regioisomer 2), 109686-58-0; **6**, 109686-44-4; **7** (regioisomer 1), 109719-20-2; **7** (regioisomer 2), 109719-21-3; **8**, 109270-63-5; **9**, 109241-05-6; **10**, 109686-45-5; **10** (deiodinated), 109686-61-5; **11** (regioisomer 1), 109686-63-7; **11** (regioisomer 2), 109686-62-6; 1′,2′-dihydrospiro[cyclohexane-1,3′-(3*H*)indole], 4740-63-0; 2,2′-bis[[2-(1-cyclohexenyl)ethyl]-methylaminocarbonyl]-1,1′-biphenyl, 109686-64-8; 1-bromo-2-[(4-*tert*-butyl-1-cyclohexenylcarbonyl)methylamino]benzene, 109686-35-3; 1-bromo-2-[(6-methyl-1-cyclohexenylcarbonyl)-methylamino]benzene, 109686-36-4; 1-bromo-2-[(2-methyl-1-cyclohexenylcarbonylmethyl amino]benzene, 109686-37-5; 2-bromo-*N*-(1-cyclopentenylcarbonyl)-*N*-methylaniline, 109686-38-6; 2-bromo-*N*-(1-cycloheptenylcarbonyl)-*N*-methylaniline, 109686-39-7; 1-(2-iodobenzyl)-1-(methoxycarbonyl)-2-hexene, 109686-40-0; 1-iodo-2-(1-cyclohexenylmethyloxy)benzene, 109686-41-1; 1-iodo-*N*-(1-cyclohexen-4-ylmethyl)-*N*-(methoxycarbonyl)aniline, 109719-18-8; *cis*-1′,2′-dihydro-1′-methyl-2′-oxo-4-*tert*-butylspiro-[cyclohex-2-ene-1,3′-[3*H*]indole], 109686-46-6; *trans*-1′,2′-dihydro-1′-methyl-2′-oxo-4-*tert*-butylspiro[cyclohex-2-ene-1,3′-[3*H*]indole], 109686-47-7; 1′,2′-dihydro-1′,2-dimethyl-2′-oxospiro[cyclohex-2-ene-1,3′-[3*H*]indole, 109686-48-8; 1′,2′-dihydro-1′,2-dimethyl-2′-oxospiro[cyclohex-3-ene-1,3′-[3*H*]indole, 109686-49-9; 1′,2′-dihydro-1′-methyl-2-methylenyl-2′-oxospiro-[cyclohexane-1,3′-[3*H*]indole, 109686-50-2; 1′,2′-dihydro-1′,2-dimethyl-2′-oxospiro[cyclohex-2-ene-1,3′-[3*H*]indole, 109719-19-9; 1′,2′-dihydro-1′-methyl-2′-oxospiro[cyclopent-2-ene-1,3′-[3*H*]-indole], 109686-51-3; 1′,2′-dihydro-1′-methyl-2′-oxospiro[cyclopent-3-ene-1,3′-[3*H*]indole), 109686-52-4; *cis*-2,4a,9,9a-tetrahydro-9a-(methoxycarbonyl)-1*H*-fluorene, 109686-53-5; *cis*-4,4a,9,9a-tetrahydro-9a-(methoxycarbonyl)-1*H*-fluorene, 109686-54-6; spiro[benzofuran-3(2*H*),1′-cyclohex-2-ene], 109686-55-7; spiro[benzofuran-3(2*H*),1′-cyclohex-3-ene], 109686-56-8; 5,8,9,10,11a-pentahydro-11-(methoxycarbonyl)-11-aza-5,9-methanobenzocyclononene, 109686-59-1; 5,6,9,10,11a-pentahydro-11-(methoxycarbonyl)-11-aza-5,9-methanobenzocyclononene, 109686-60-4; *cis*-1′,2′-dihydro-1′,2-dimethyl-2′-oxospiro-[cyclohex-2-ene-1,3′-[3*H*]indole], 109719-12-2; *trans*-1′,2′-dihydro-1′,2-dimethyl-2′-oxospiro[cyclohex-2-ene-1,3′-[3*H*]indole], 109686-72-8; 1′,2′-dihydro-1′-methyl-2′-oxospiro[cyclohept-2-ene-1,3′-[3*H*]indole], 109686-73-9; 1′,2′-dihydro-1′-methyl-2′-oxospiro[cyclohept-3-ene-1,3′-[3*H*]indole], 109686-74-0.

Supplementary Material Available: Copies of the ^{1}H NMR spectra for **3c**, **3d**, and the cyclization products reported in Table I, entries 3, 4, 5, 6 (dihydro), 7 (dihydro), 10, 11, and 13 (12 pages). Ordering information is given on any current masthead page.

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Lewis Acid Induced Nucleophilic Substitution Reactions of β-Nitro Sulfides via Episulfonium Ions[1]

Summary: The nitro group of β-nitro sulfides is replaced by a cyano or allyl group via episulfonium intermediates on treatment with Me_3SiY (Y = CN or allyl) in the presence of an appropriate Lewis acid.

Sir: Recently nucleophilic substitution reactions of aliphatic nitro compounds have drawn much attention as a new synthetic method, for the nitro group serves as an excellent activating group for carbon–carbon bond-forming reactions. The following nucleophilic substitution reactions of aliphatic nitro compounds have been documented; nucleophilic substitution reaction via one-electron-transfer processes,[2] palladium-catalyzed substitution reactions of allylic nitro compounds,[3] palladium-uncatalyzed substitution reactions of allylic nitro compounds,[4] and Lewis acid induced substitution reactions of tertiary, benzylic, or allylic nitro compounds.[5] Thus, nitro groups can be replaced by nucleophiles in all of these reactions. However, primary or secondary nitro groups are not replaced by nucleophiles except for benzylic or allylic cases. Here we report a new type of nucleophilic substitution reaction of nitro compounds, namely, the replacement of the nitro group of β-nitro sulfides by nucleophiles in the presence of an appropriate Lewis acid.

β-Nitro sulfides are readily prepared by the condensation reaction of aldehydes or ketones with nitro compounds followed by the Michael addition of thiols. This two-step reaction can also be done in a one-pot procedure by mixing carbonyl compounds, nitro compounds, and thiols in the presence of amines.[6] Treatment of thus obtained β-nitro sulfides **1** with Me_3SiY (Y = CN, $CH_2CH{=}CH_2$) in the presence of an appropriate Lewis acid gave the substitution product (**2** and **3**), where the nitro group was cleanly replaced by CN or $CH_2CH{=}CH_2$, respectively: the results are summarized in Table I. This is the first general case of replacement of primary or secondary nitro groups by nucleophiles. Assistance by the β-phenylthio function is crucial for the present Lewis acid induced substitution

(1) This paper is dedicated to the late professor Ryozo Goto, Kyoto University.

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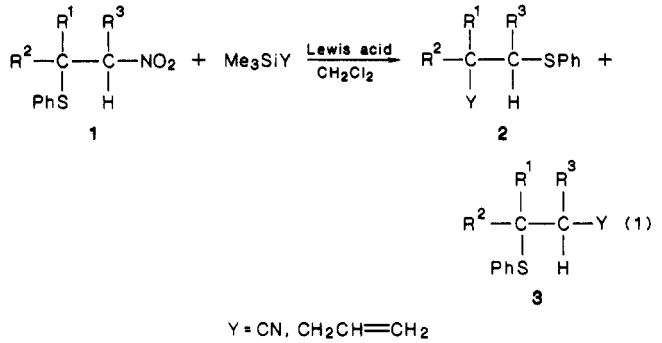
Table I. Nucleophilic Displacement of Nitro Group of 1 by Y[a]

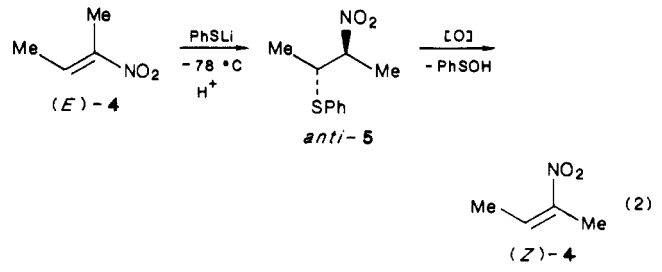
entry	R^1	R^2	R^3	Y	Lewis acid (equiv)	time, h	yield (%) of 2 + 3	ratio of 2/3[b]
1	Me	Me	H	CN	$SnCl_4$ (2)	24	64	73/27
2	Me	Me	H	$CH_2CH{=}CH_2$	$AlCl_3$ (2)	1	72	93/7
3	Me	Et	H	CN	$SnCl_4$ (2)	12	61	86/14
4	Me	Et	H	$CH_2CH{=}CH_2$	$AlCl_3$ (2)	1	63	84/16
5	Me	n-C_6H_{13}	H	CN	$SnCl_4$ (2)	6	72	82/18
6	Ph	H	H	$CH_2CH{=}CH_2$	$AlCl_3$ (2)	1	79	94/6
7		$-(CH_2)_4-$	H	CN	$SnCl_4$ (2)	14	69	95/5
8[c]	Me	H	Me	CN	$SnCl_4$ (2)	18	60	
9[c]	Me	H	Me	$CH_2CH{=}CH_2$	$TiCl_4$ (2)	6	60	
10[c]	Me	H	Et	$CH_2CN{=}CH_2$	$TiCl_4$ (2)	6	55	75/25
11[c]	Et	H	Me	$CH_2CH{=}CH_2$	$TiCl_4$ (2)	6	55	25/75
12	H	H	Et	$CH_2CH{=}CH_2$	$TiCl_4$ (2)	6	52	43/57

[a] The reaction was carried out by stirring a mixture of β-nitro sulfides (1 mmol), Me_3SiY (5 mmol), and Lewis acid (1–2 mmol) in CH_2Cl_2 (5 mL) under Ar at 20 °C. The product was purified by distillation or column chromatography after the usual workup. [b] The ratio was determined by GLC and NMR. [c] A mixture of anti and syn nitro sulfides was used and the product consisted of two stereoisomers.

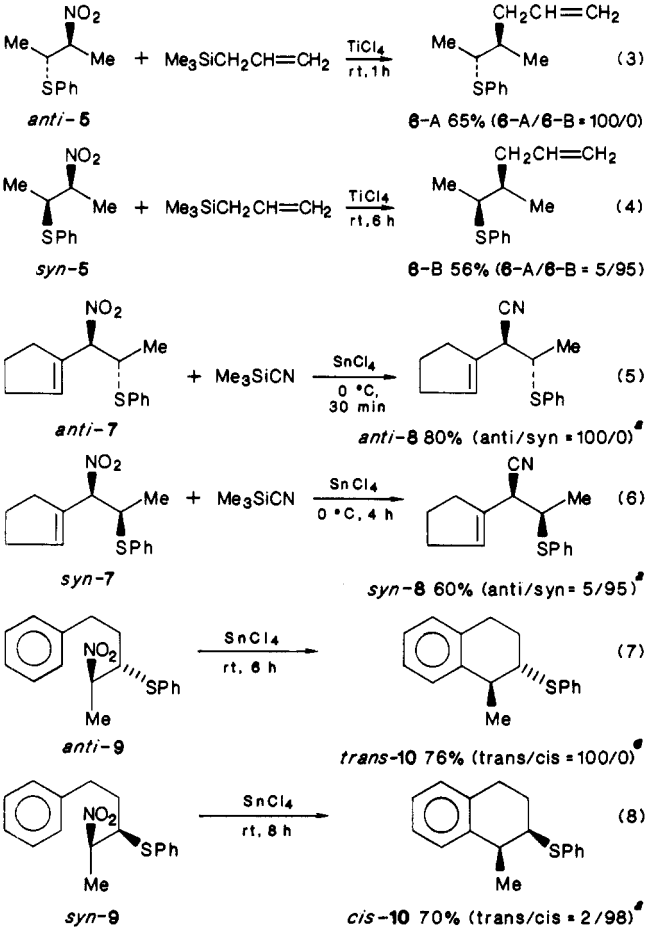
reaction, for treatment of 2-nitrobutane with Me_3SiY in the presence of a Lewis acid such as $AlCl_3$, $SnCl_4$, or $TiCl_4$ gave no substitution products and 2-nitrobutane was recovered. The reaction appears to proceed via episulfonium ions, since the reaction between 2-nitro-3-(phenylthio)pentane and 3-nitro-2-(phenylthio)pentane gives the same product spread. The regiochemistry of the attack of the nucleophiles is also rationalized by assuming episulfonium intermediates. When the nitro group is primary, migration of the phenylthio group predominates. In other cases, a mixture of **2** and **3** was obtained. The ratio of **2**/**3** depends on the nature of R^1, R^2, and Y. It appears that the predominant product formed is that from the most positive carbon of the episulfonium ion intermediate.



The stereochemistry of the present substitution reaction was studied to confirm the existence of episulfonium ion intermediates. Anti β-nitro sulfides were prepared by the addition of PhSLi to (*E*)-nitroolefins at −78 °C. For example, (*E*)-2-nitro-2-butene (**4**) was converted into *anti*-**5** by this method. The anti structure was confirmed by transformation of this compound into (*Z*)-**4** by oxidation and subsequent syn elimination.[7] The conventional



Scheme I[a]



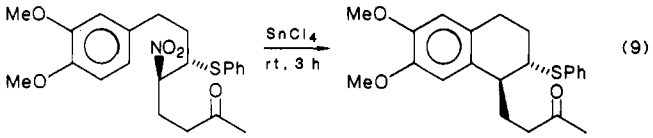
[a] The isomer ratio was determined by GLC.

Michael addition of thiophenol to nitroolefins proceeds nonstereoselectively. For example, the reaction of **4** with thiophenol in the presence of triethylamine (0.1 equiv) gives a mixture of *syn*-**5** and *anti*-**5**, whose ratio was 60:40. Pure *syn*-**5** was isolated by column chromatography after treatment of the mixture with Et_3SiH.[8] Thus, pure anti and syn β-nitro sulfides are now readily obtained.[9] These

(7) (*E*)-**4** and (*Z*)-**4** were readily determined by NMR; the vinylic proton of the *Z* isomer appears at higher field than that of the *E* isomer due to strong anisotrope effect of the nitro group. Hayama, T.; Tomoda, S.; Takeuch, Y.; Nomura, Y. *Tetrahedron Lett.* **1982**, *23*, 4733. NMR ($CDCl_3$) of C=CH in (*E*)-**4** δ 7.20, (*Z*)-**4** δ 5.87. The present transformation provides a general method for the conversion of (*E*)-nitroolefins to (*Z*)-nitroolefins.

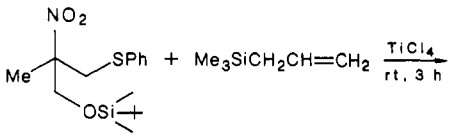
(8) The nitro group of β-nitro sulfides is replaced by hydrogen on treatment with triethylsilane in the presence of $SnCl_4$, see: Ono, N.; Hashimoto, T.; Jun, T. X.; Kaji, A. *Tetrahedron Lett.* **1987**, *28*, 2277. The nitro group of anti β-nitro sulfides is more rapidly replaced by hydrogen than that of syn isomer. The separation of syn β-nitro sulfides is very easy by column chromatography after the treatment of the anti and syn mixture with Et_3SiH.

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]

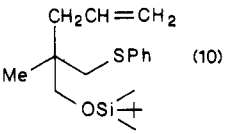


(9)

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.

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(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

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